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The Essential Oils

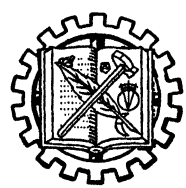
BY

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VOLUME THREE

INDIVIDUAL ESSENTIAL OILS
OF THE PLANT FAMILIES
RUTACEAE AND *LABIATAE*



1949

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Dedicated
to Mr. Frederick H. Leonhardt,
President of
Fritzsche Brothers, Inc.,
whose vision and generosity made this
work possible

PREFACE

The third and the succeeding volumes of the series "The Essential Oils" will consist of monographs on individual oils, describing their botanical and geographical origin, methods of cultivation of the plants from which they are derived, techniques of distillation and yield of oil, their physicochemical properties, chemical composition, total production, and uses in the industry.

The individual oils are grouped within the families to which the respective aromatic plants belong, but in the sequence of the plant families no botanical system is followed. This arrangement has been chosen for the practical purpose of giving first place to those families the essential oils of which are technically and commercially most important. Thus, the present volume will describe the oils of the plant families *Rutaceae* (with special emphasis on the very important citrus oils) and *Labiatae*. The policy of arranging the families according to commercial and practical utility will be adhered to throughout the following volumes, but at the end of the last volume there will be a table or key showing the classification of the essential oils according to a modern botanical system. This policy will permit greater flexibility and ease in the sequence of the various oils than could be achieved by following a rigid system of plant taxonomy.

The literature on essential oils accumulated during the last hundred years contains references to thousands of oils that have been produced in various countries on a purely experimental basis. However, much of the data on these experimental oils, particularly their plant origin, are badly confused, if not outright contradictory. No real purpose would be served by including these unimportant oils in a work intended for practical use, and whose scope must be limited of necessity. The author has, therefore, decided to describe only those oils that are of technical importance and actually used in our industry, or offer at least commercial possibilities, or incite particular scientific interest. It appears preferable to describe these oils from every angle and on good authority, rather than to indulge in a futile discussion on countless experimental oils about which many factors, particularly their botanical origin, are highly questionable.

In the discussion of each individual oil the author has depended not only upon his own experience accumulated during many years of work in the essential oil-producing regions all over the world, but also upon the experience of Fritzsche Brothers, Inc., New York, in producing and handling

essential oils for almost eighty years. Moreover, the voluminous literature on the subject, representing the result of research by hundreds of prominent scientists, has been carefully screened and edited, with a view to excluding data that might appear dubious. Wherever this was not possible, the original findings have been cited with reserve and as questionable.

The collection of the author's own data would, of course, have been impossible without the wholehearted and splendid cooperation of hundreds of planters, essential oil producers and dealers in every part of the world.

ERNEST GUENTHER

New York, N. Y.
October, 1949

NOTE

All temperatures given in this work are expressed in degrees Centigrade unless otherwise specified in the text.

ACKNOWLEDGMENT

The writing of the present and following volumes has been rendered particularly difficult by the course of world events during the past decade. Something in the nature of a revolution in the essential oil industry was effected by the Second World War and its aftermath, with the elimination of certain traditional sources of supply and the development of new ones. For more than ten years the industry has, in effect, been in a stage of transition.

To keep abreast of the constant changes within the field, in both hemispheres, would have proved impossible for the author had he not been able to count upon the interest and generous cooperation of numerous experts, producers and planters all over the world, who have supplied him with exact and up-to-date information, otherwise unobtainable.

Any complete enumeration of all those to whom an acknowledgment of gratitude is due would unfortunately be out of the question, but the author wishes especially to thank the following among his many collaborators:

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The Editors of *The Perfumery and Essential Oil Record,* London, generously gave permission to quote freely from the article on "Extraction of Citrus Oils," by F. K. Donovan, which appeared in the Special Issue of that magazine for 1937.

The author is, as usual, deeply indebted to a number of his associates at Fritzsche Brothers, Inc., New York. He would like to mention particularly Mr. B. F. Zimmer who was of great help in compiling data on the physicochemical properties of essential oils examined in the laboratories of Fritzsche Brothers, Inc., over a long period of years. Thanks are due also to Dr. Darrell Althausen, Mr. Edward E. Langenau, Mr. W. P. Leidy and Mr. A. H. Hansen, Jr., of the same Company, for their constant advice and help with many phases of the work. And, of course, his deepest gratitude goes to the author's secretarial staff—Mrs. Ann Blake Hencken, Miss Catherine McGuire, Mrs. Agnes Clancy Melody, and Mrs. Elizabeth Adelmann, who shouldered much of the responsibility for the preparation of a difficult manuscript.

ERNEST GUENTHER

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CHAPTER I

ESSENTIAL OILS OF THE PLANT FAMILY *RUTACEAE*

A. ESSENTIAL OILS OF THE GENUS *CITRUS*

INTRODUCTION

Swingle,[1] the eminent authority on citrus plants, believes that the genus *Citrus*, comprising sixteen species and eight varieties, may have originated in the New Guinea-Melanesia region; its subsequent evolution into many different species, however, took place chiefly on the mainland of southeastern Asia. In fact, it is only there that the most highly developed species of citrus can be considered as indigenous. A few of these species reached the Asiatic mainland, and these sour and bitter, indeed almost inedible, species doubtless developed into the fragrant, delicious species of the subgenus *Eucitrus*, in many ways the finest fruit known to man.

It seems highly probable that in China, Japan, India, and other oriental countries accidental hybridization has resulted, among assorted citrus fruit trees, from the action of bees and other insects seeking the abundant honey of citrus flowers. In Swingle's opinion it is only reasonable to suppose that if, after such hybridization, chance seedlings reached fruition, they would be propagated by the villagers when such trees bore fruit of superior quality.

The members of the subgenus *Eucitrus*, including all the commonly cultivated species of citrus, extended their range from eastern Asia to India and ultimately reached the countries bordering the Mediterranean basin. From southern Europe they were finally brought to the New World, and to all other countries in which conditions are favorable for their growth.

Under normal conditions most citrus varieties grow prolifically, developing a great abundance of leaves, flowers and fruit, especially when favored by a rich soil and by a warm, humid climate, such as the tropics offer. In more temperate zones, citrus trees grow more slowly and less prolifically, due to occasional spells of cool weather, which retard the plant's biological activities. It appears that, for this reason, the perfume and flavor (or in other words the essential oil contained in the leaves, blossoms and fruit) are more abundant and more pronounced in trees growing in temperate regions than those growing in the tropics. The cooler highlands of tropical countries offer similar conditions, but in many cases rainfalls are frequent, and the moisture content is high, which favors scab and other diseases.

The essential oils expressed from the rinds of the citrus fruit, or distilled from their flowers or leaves, have attained great importance as flavoring

[1] H. J. Webber and L. D. Batchelor, "The Citrus Industry," Univ. Calif. Press, Vol. I, 1943, 137, 387.

agents for all kinds of beverages—alcoholic and nonalcoholic—baked goods, candies, puddings, gelatin desserts, chewing gums, and pharmaceuticals. They are also used in perfumes, toilet waters, cosmetics, and for the scenting of soaps. There is hardly a product in the food, beverage, soap, cosmetic, and perfume industries which does not contain at least a small quantity of the delightfully scented, refreshing citrus oils. The production and consumption of these oils have, therefore, reached a large volume.

THE EXPRESSION OF CITRUS OILS

The Occurrence of Essential Oils [1] in the Peels of Citrus Fruit

The essential oil of the citrus fruit is contained in numerous oval, balloon-shaped oil sacs, glands or vesicles, the diameter of which varies from 0.4 to 0.6 mm. Ductless, and without communication with surrounding cells or the exterior, they have no proper walls, but are simply bounded by the debris of degraded tissue.

These oil sacs or glands are distributed irregularly in the outer, colored ("flavedo") portion of the peel of maturing or mature fruit, more specifically in the outer mesocarp, beneath epicarp and hypoderm, and above the inner mesocarp, which is the light colored portion ("albedo") of the peel. This albedo consists of cellulose, hemicellulose, lignin, pectins, pentosans, sugars, glycosides, bitter substances, and mineral matter. The glycoside in oranges, lemons, and tangerines is hesperidin; that in the grapefruit, naringin. On maturation of the fruit, the cells of the albedo become much elongated and branched, forming an intricate network of cells and large intracellular spaces, which give the ripe peel its spongy texture. This spongy layer plays an important role in the expression of the oil, since it easily absorbs the oil ejected from the sacs, and thus causes some mechanical difficulties.

Donovan [2] has given an excellent description of what happens when the oil sacs are ruptured by pressure from outside. In the words of Donovan, the "walls" of the oil cells are not readily broken. For example, if a peel is subjected to reduced pressure, or immersed in boiling water or brine, and

[1] The seeds of citrus fruits contain a fatty oil which is quite different from the volatile oil in the peel, and will not be considered in this discussion.

[2] *Perfumery Essential Oil Record,* Special Issue (1937), 4.

subjected to steam distillation at atmospheric or reduced pressure, only little oil escapes from the sacs. In order to recover all the oil, by distillation, it is necessary first to break up the tissues by mincing or trituration, with due precautions to prevent loss of oil by spurting. But if the walls of the oil glands are lacerated, or ruptured by bending, the oil contents are ejected with considerable force and to a relatively great distance, as can be seen by bending a piece of peel against a candle flame. This is important in the various processes of extraction. The force of ejection varies with the stage of maturity and the degree of freshness—being greater in fresher, immature fruit. As a matter of fact, the yield of oil by the usual industrial processes shows a marked falling off as the season advances and the fruit becomes riper. This is probably in considerable measure due to the above factor, because the results of investigations to that effect suggest that there is no corresponding decrease in the actual oil content of the peel.

Furthermore, rupture of the cell wall is easier, and spurting of the oil more forcible, in the presence of water. This may perhaps be partly explained as follows: the cells surrounding the oil sacs contain salts (and colloids) in aqueous solution, and in contact with water the higher osmotic pressure of the cell contents induces diffusion of water into them, increasing the turgor pressure, and subjecting the oil sacs to stress from every side. Any similar diffusion into the oil sacs themselves, which seems less likely, will increase this effect. Moreover, the flavedo in which the oil sacs lie, and more especially the adjacent albedo, are spongy and absorb liquids with great readiness. An average lemon weighs some 100 to 120 g., of which the peel forms about one-half, whereas the total oil content of the peel is only some 0.5 to 0.7 g. If the great volume of spongy tissue is not filled with water it tends to absorb the oil as the sacs are broken and holds it with great tenacity, so that pressure yields first aqueous fluid and only later oil. Therefore, in Sicily, peels are immersed in water for several hours before being subjected to the "sponge" process. Water, or a dilute aqueous solution of certain salts, is employed in many machines, although here there are other reasons, in some cases of greater importance, for its use—e.g., to prevent loss by spurting, to act as a carrier, etc.

The oil sacs are not all located equally deep below the cuticle, nor of the same size, and the yield of oil in any process based upon pressure on the peel depends upon the force applied; even with a strong pressure the smaller and deeper oil sacs tend to resist rupture. Only distillation of finely divided material yields the whole of the oil present.

When fruit is allowed to wither after plucking, the skin becomes increasingly tough and elastic, so that laceration of the oil sacs is more and more difficult and less oil spurts. The same change occurs, if more slowly, when

fruit is allowed to wither on the tree. The yield of oil from such fruit will be considerably lower than that obtained in the fresh state.

The walls bounding the oil sacs consist largely of cellulose and pectins, the latter typical colloids, exerting a strong influence in the phenomena mentioned. The sacs themselves contain not only oil, but tissue fluids rich in pectins and, by whatever method the oil is liberated, it will always be accompanied by these colloidal solutions. The product of expression, in which nothing but water has been used as a carrier, is thus never a simple mixture of oil and water, but a very thin emulsion which, if left to stand, gradually separates a supernatant layer of dense emulsion and cell detritus. The greater part of the essential oil liberated is contained in this floating layer, although none may be visible as an oily stratum. In general, not more than a few pools of oil separate spontaneously. The mechanism of formation of this upper layer, and the phenomena succeeding it on longer standing, are themselves of great interest, but must be omitted here.

The dense emulsion is exceedingly difficult to break, and this problem offers the chief obstacle in the production of good quality "machine" oils. Three processes have been used for the purpose: first, filtration through sponges or similar material such as wool, which adsorb the colloidal matter and yield an easily separable mixture of oil and water. This procedure has been applied with success in the "sponge" process of handpressing and in the older Calabrian bergamot machine; in both cases the proportion of colloidal substances brought into contact with the oil is relatively small. Second, distillation; this, however, always tends to cause deterioration of the oil, if (acid) juice is present. Third, centrifugation; the last process, in spite of great advantages, was first attended by difficulties as regards completeness of separation and yield, but these have now been surmounted to a large degree, so that the method has become invaluable for fully automatic recovery of expressed citrus peel oils.

Methods of Expressing Italian Citrus Oils

The Italian (Sicilian) citrus oil industry seems to be of considerable age, but little is known about its actual beginning. According to Bennett,[8] the first reference is contained in the "Lettere della Sicilia" of the Abbot Domenico Sestini, published at Florence in 1780. In two letters dated November 1776, the Abbot described the export of fruit, oranges, lemons, and citrons, the production of peel in brine, which he stated was initiated in that year, and of juice and essential oil. His account of the extraction of essential oils by the "sponge" process agrees in all material respects with the

[8] "Nuovi Processi dell'Industria Agrumaria," "Realtà," December (1936).

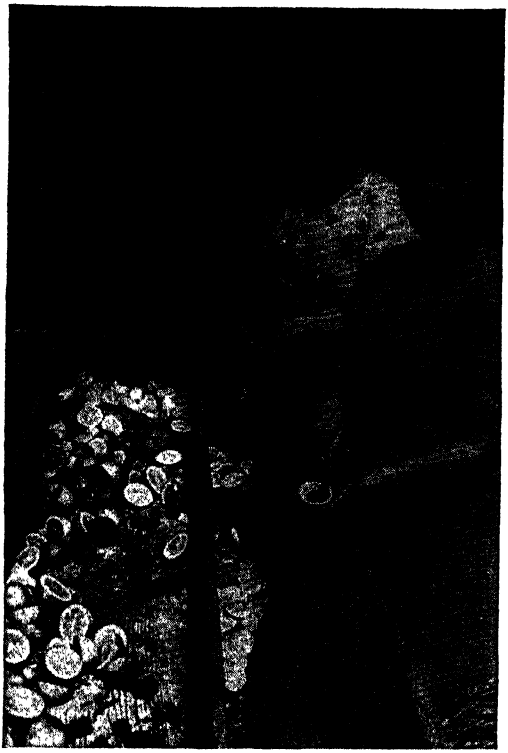
present-day technique. He added that another type of oil, less valued, was obtained by distillation. The Abbot estimated the annual production of "sponge" oil as about 4,000 lb., of distilled oil as 3,000 lb.

Much has been written in standard works and periodicals about the processes by which citrus oils are recovered in Sicily and Calabria. However, most of that material has become obsolete, as handpressing in Italy has been superseded by machine pressing in increasing measure, and new machine models have continued to appear on the market. Since the publication of a thorough study by Rodanò [4] important new advances have been made which have been described periodically by Bennett,[5] and by La Face,[6] both authorities in the field. An excellent and incidentally the most concise paper on the subject is that of Donovan,[7] much of which is included in the following pages.

I. Hand Processes

A. "Sponge" Process.—In this old and well-known process the work is done entirely by hand in cellars amidst heaps and baskets of citrus fruit and peels, illuminated by the dim light of candles. The work, in which all able members of the family participate, starts long before dawn and lasts until late in the afternoon. To the visitor it offers a picture of incredible drudgery. Women and children cut the freshly harvested fruit transversely into halves—*metodo della scorza in due*—(the older *scorzetta* method in which the fruit was cut into three longitudinal pieces has been abandoned for many years, although the name is still used mistakenly in textbooks for the current method). Standing along wooden troughs, other women and children quickly and skillfully remove the pulp from the halved fruit with a special sharp-edged spoon, *rastrello*. The peel is then immersed in water for several hours and finally pressed. The actual pressing of the peel requires skill and considerable, continued force, and hence is done by men. The contact with oil affects the fingernails. The men sit on low stools in front of earthen pots provided with a lip; across the pot a sturdy wooden bar or bamboo stick is laid. The worker holds, with the left hand, either one large or two smaller flat sponges on top of the wooden crossbar and, with the right hand, presses the fruit peel against the upper sponge. Thinner peels can be pressed from the inside, *a sparare*, whereas thicker peels must be pressed from the outside, *a mantice*. The emulsion ejected from the oil sacs and cells is soaked up by the sponge, which must be kept scrupulously clean;

[4] "Industria e Commercio dei Derivati Agrumari," Hoepli, Milan (1929).
[5] "Nuovi Processi dell'Industria Agrumaria," "Realtà," December (1936).
[6] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria,* **5** (1930), 180; and successive issues. *Chem. Abstracts* **25** (1931), 2240.
[7] *Perfumery Essential Oil Record,* Special Issue (1937).



Left: Removal of the pulp from the halved citrus fruit in Sicily, prior to sponge pressing.

Below: Sponge pressing of the oil from the peel of citrus fruit in Sicily.

Both photos courtesy of Fritzsche Brothers, Inc., New York.



it retains solid matter and adsorbs colloidal substances. By squeezing the contents of the sponge from time to time into the pot beneath, the presser obtains a mixture of oil and water, which separates easily in the pot; the oil is finally decanted and drawn off.

Where this method is employed, the oil ejected will be accompanied by a minimum of aqueous solution, for the hand pressure is controlled so as just to break the oil sacs. The colloidal substances are readily adsorbed by the sponge, and separated from the oil, the latter being kept in the pot only for a limited time, and without agitation, before complete separation. These circumstances are most favorable for recovery of oil, with a minimum tendency for any change to occur.

The oil recovered is said to amount to some 50 to 75 per cent of that originally present, but Rodanò [8] has pointed out that these figures are open to considerable doubt for several reasons: the weights of incoming fruit are not always carefully checked when the season is at its height; the weight of the peels changes after soaking in water; the presser rejects poor or damaged peels, etc.

As regards yield in general, the "sponge" process is far more susceptible than mechanical methods to such differences as the physical condition of the peel, the ability of the operator, and the prevailing temperatures.

The "sponge" process requires much labor and is, therefore, expensive. According to Donovan,[9] for an average thousand lemons weighing 120 kg., cutting into halves requires some 30 min. of a boy's labor; removal of pulp some 75 min. of a woman's; and expression of the oil from 2½ to 3 hr. of a skilled man's labor. A modern machine, *pellatrice,* treats ten times this quantity in 1 hr., with labor only for charging the fruit.

Even the removal of the pulp with the spoon-like *rastrello* requires skilled and low-priced labor, but it is the pressing operation which is most difficult and costly, and which has tended to place larger undertakings entirely in the hands of highly specialized workmen. In consequence, the industry in Sicily and Calabria is divided into a large number of very small units, each managed in many cases by the members of a single family. Another difficulty is that there exists no possibility of determining accurately the yield of oil to be expected; two skilled men, working side by side, may obtain different yields from the same batch of fruit. For these reasons, methods have long been sought which should be wholly or at least in part independent of these variables, particularly of hand expression.

Handpressing, by the very nature of the process, yields an oil closely approximating that which exists in the fruit; it was formerly responsible for practically the entire Italian production of lemon and orange oils. Rodanò,

[8] "Industria e Commercio dei Derivati Agrumari," Hoepli, Milan (1929).
[9] *Perfumery Essential Oil Record,* Special Issue (1937).

in 1930, estimated the "sponge" lemon oil to be some 80 per cent of the total production; La Face, in 1930, placed the figure at about 50 per cent. Orange oil was at that time entirely handpressed. The proportion has fallen steadily, and today handpressed oil constitutes only a fraction of the total production. At the end of 1939, Dr. F. La Face, Director of the Stazione Sperimentale in Reggio Calabria, told the author that only about 20 to 25 per cent of Sicily's lemon oil was then "sponge" made. Small units distant from producing centers, mountain families, and the like still extract limited quantities of lemon oil by this method, for the cost of transport of fruit makes it imperative to work on the spot and their small crop would not justify setting up machines. But larger enterprises mechanize at least the expression process. Most of the Sicilian orange oil is still handpressed, but small machines are being adapted also for oranges and mandarins. (For details see sections on "Oil of Sweet Orange," "Oil of Bitter Orange," and "Oil of Mandarin.")

Foreign markets still continue to demand "genuine Sicilian Handpressed Sponge Lemon Oil," apparently unaware of the changes that have taken place in the industry in the last years, and of the fact that oils made in some of the modern machines are almost indistinguishable from "sponge" oils by physical, chemical, or organoleptic tests.

B. Écuelle Process.—This process is said to have been developed in Nice (Southern France) many years ago, but is no longer used in Europe. It should be described here, however, since some of the present Italian machines are based upon the principle of *écuelling*. The *écuelle* is employed today in the West Indies, to which it was probably introduced by early French settlers for the making of handpressed (coldpressed) orange and lime oil.

The *écuelle* consists of a shallow bowl of copper with a hollow central tube with which it forms a sort of funnel. The bowl is equipped with large brass nails with blunt ends, across which the fruit is rolled, by hand, with some pressure, until the entire surface of the fruit has yielded up its oil. The latter dribbles down, together with the aqueous cell contents, into the central tube where it separates by decantation. Obviously, *écuelling* demands more labor even than hand sponging and is practical only where cheap labor abounds. *Écuelling*, however, is not efficient, since it yields only about 20 per cent of the oil contained in the fruit peel. Because of much contact of the fruit and the oil with the hands of the workers, while they roll the fruit, the process cannot be considered very hygienic.

The old *Calabrese* bergamot machine employed in Calabria (Southern Italy) is, in fact, the prototype of the mechanization of the *écuelle* process. Analyzing the principle of the *écuelle*, Rodanò [10] has shown its relationship

[10] "Industria e Commercio dei Derivati Agrumari," Hoepli, Milan (1929).



Écuelling of oranges in the West Indies. *Courtesy of Fritzsche Brothers, Inc., New York.*

to the "sponge" and other processes. He summarizes the action of the *écuelle* on the epidermis of the fruit as follows:

1. Laceration of the epidermis and oil sacs.
2. Creation of areas of compression in the peel, surrounded by areas of lower pressure, across which the oil flows to the exterior.
3. Part abrasion of the peel, with formation of finely divided detritus, or removal of small pieces.

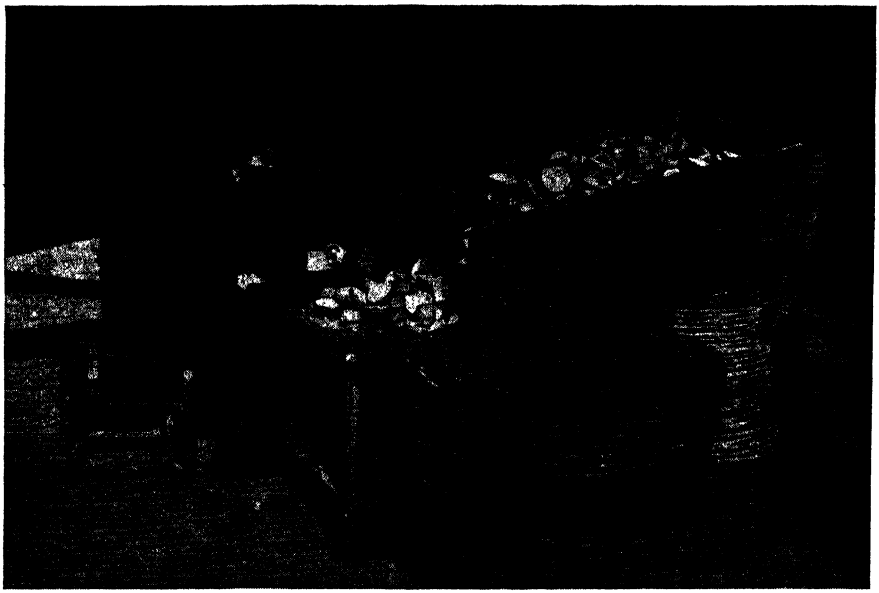
All these actions play their role in the *écuelle* process, whereas in the "sponge" method the effect is practically limited to 1 and 2; this represents the fundamental difference between the two processes. The apparently important difference, that in one case the whole fruit and in the other case the peel only is treated, is merely a concomitant and without special significance; in fact, many inventors have sought to subject the whole fruit to the actions 1 and 2 only. That they have failed so far has been due solely to the practical difficulties involved.

As will be seen later, the Italian machines which treat the *whole* fruit subject it to all the actions of the *écuelle*. In the *sfumatrici* which treat peel only (after separation from the pulp) the action 3 may be more or less eliminated, as will be recognized by an examination of the actual techniques of pressing employed. It may be well to emphasize again that no method gives only oil on expression; it is always attended by cell fluids containing pectins, which accompany the oil in the glands.

II. Machines Treating Separated Peels

A. Hand Machines.—In view of the special skill for hand expressing required in the "sponge" process and of the amount of energy expended, especially when the peels are thick and resistant, as is often the case in Eastern Sicily, early attempts were made to mechanize this part of the process only. Several simple machines were devised, based on the principle of the lever—the *macchinetta a leva,* of which the Lo Castro machine patented in 1909 is an example, as are also the so-called Zona machine and others. In all of these the preliminary processing—i.e., cutting the fruit into halves, removal of pulp, and immersion in water—is done exactly as in the hand process. For expression the peel is placed in a hollow sponge, attached above with other sponges to a plate actuated by the lever, and fixed below with additional sponges to the base; the sponge is fitted above a funnel through which oil and aqueous phase pass to a receiving vessel. The parts which come into contact with oil and water are usually of brass or bronze. The

lever is depressed, squeezing the peel within the sponge, then raised; the peel is turned over, and the process repeated until completed. The method constitutes a *sfumatura a mantice* and, because of the less vigorous effort required, can be worked by women or children. The oil, separated from the water in the usual way by decantation, resembles in all respects hand-pressed oil; the yield, too, is much the same.

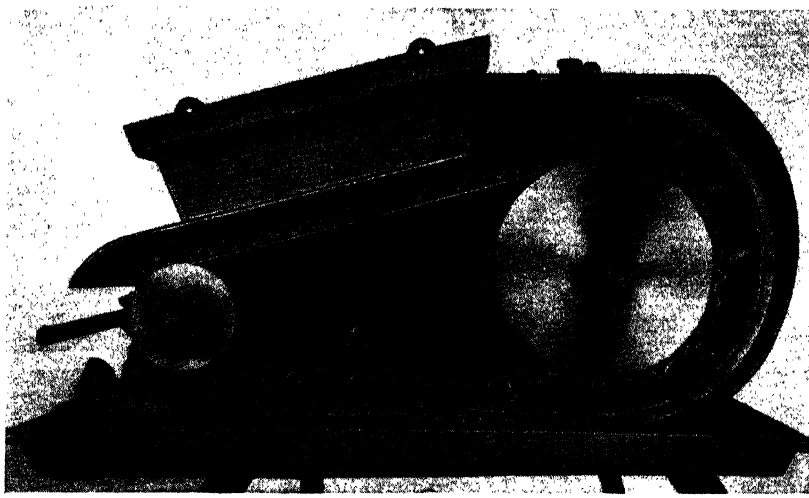


Courtesy of Fritzsche Brothers, Inc., New York.

Macchinetta a leva, used in Sicily for the expression of citrus oils.

B. Automatic Machines for Expressing the Oil—Sfumatrici.—Although the hand machines described above dispense with the arduous and specialized handpressing, they do not effect any saving of time or labor. The peels of the halved fruit must be treated singly, and the time taken for each is not less than in the purely manual method. A logical development of this type of machine was, therefore, to mechanize the process of pressing, so that peels could be fed into hoppers and discharged automatically. The machines which treat only the peels, after removal of the juice and pulp, are called *sfumatrici;* they must not be confused with those processing the whole fruit (*pellatrici*) which will be described later. This should be kept in mind since many manufacturers now produce both types—Avena, Cannavò, Speciale, and Vinci, for example. In Sicily, the term "machine" generally is applied to that which works the whole fruit, whereas a machine processing peels only is called a *sfumatrice.*

According to Donovan,[11] the principle of the *sfumatrici* consists in a thorough bending of each peel in order to expel the maximum quantity of oil. However, the peel must not be subjected to such high pressure that much of the fluid contents of the other cells, particularly of those in the albedo, is squeezed out at the same time. These other tissue fluids increase the colloidal contents of the aqueous phase and tend to promote emulsification and deterioration of the oil phase. It is further desirable that the peels should not be broken or badly damaged because, if sound, they may



Courtesy of Antonino Gallo, Messina, Italy.

Speciale Sfumatrice.

be marketed as peels in brine. This last proviso can usually be met only by sacrificing a certain proportion of the yield of oil since, as we have seen, fairly drastic treatment is necessary for maximum expression, and mechanical methods are not capable of the refinements of manual pressure.

The *sfumatrici* are for the most part simple and relatively inexpensive machines; they depend upon the same principle in having a moving member mounted within or against a stationary member. The peels are dragged round and turned and compressed against lugs, or in a narrower channel arranged for by eccentric mounting of the rotating member, or by other means. *Sfumatrici* are now widely used in Sicily, each district tending to use the machine of local design and construction. The oil is usually carried down to decantation vessels in a stream of water, the emulsion being collected and pressed in wool or sponges to yield oil and water, which are then separated. The yield is higher than in the "sponge" process, some 4–5 oz.

[11] *Perfumery Essential Oil Record,* Special Issue (1937), 4.

per quintal [12] fruit being commonly claimed. In general the oil approximates very closely "sponge" oil, apart from minor differences induced by contact with the water and substances dissolved in it.

The citral content, specific gravity, and nonvolatile residue of lemon oil extracted in a *sfumatrice* are usually slightly lower than those of a "sponge" oil pressed from the same type of fruit, but most often the figures are well within the range for normal "sponge" oils. In other respects, too—odor, flavor, and composition, for example—a good *sfumatrice* oil is almost indistinguishable from "sponge" oil. Some of the latest *sfumatrice* models are capable of processing up to 100,000 lemons per day.

If it were desired to correct the figures for specific gravity and residue, this could be accomplished by addition of an oil from a machine treating whole fruit (*pellatrice*), the properties of which are shifted in the opposite direction.

For a detailed description of the more important Italian *sfumatrici*, the reader is referred to the previously mentioned paper by Donovan.[13] Suffice it here to mention them only briefly.

(1) *Cianciolo Sfumatrice*

This machine was patented in 1927 by Luigi and Ettore Cianciolo. Since the peels had to be fed in singly and by hand, the *Cianciolo* machine has been superseded by later types.

(2) *Morasca Sfumatrice*

Patented in 1930 by Salvatore Morasca & Figlio in Messina.

The yield of oil appears to be higher than in the "sponge" process. The machine requires two operators and a 2 h.p. motor. It can treat about 20,000 peels of halved fruit, equivalent to 1 metric ton of whole fruit, per hour.

The oil is of very good quality, with only the minor differences from "sponge" oil mentioned; but the peels are broken on an average into three pieces and are useful, therefore, only for the preparation of pectin or cattle food. Some fifty of such machines were in operation in Sicily around 1937, batteries being used in several cases.

For oranges which have a softer peel, the distance between drum and cylinder, and the size of the slotted wedge, must be modified.

(3) *Andronaco Sfumatrice*

Of more recent design and now more popular, this machine resembles the Morasca in having a drum and cylinder action. In this case, however, the

[12] One quintal = one hundred kilograms.

[13] *Perfumery Essential Oil Record,* Special Issue (1937).

drum is mounted vertically, and the working parts are of hard wood. Invented and made in Acireale, the machine is now used largely in that district.

The oil is separated as usual; it is of very good quality and similar to "sponge"-pressed oil except for the usual slight difference in citral, specific gravity, and evaporation residue. Many of the Andronaco oils are practically indistinguishable from sponge oils.

The machine requires a ½ h.p. motor and treats the peels from about 1 metric ton of fruit per hour.

(*4*) *Speciale Sfumatrice*

Of still later construction, the machine was first patented in 1932 by Francesco Speciale in Giarre, but several improvements have been made since.

The yield of oil is said to be about 3 oz. higher per quintal (100 kg.) of fruit than that from any eccentric drum machine, and the action can be regulated so that few peels are broken.

The machine works entirely automatically and requires a 1 h.p. motor with a working capacity somewhat higher, perhaps, than that of the aforementioned machines. The home demand has increased and several machines have been exported.

(*5*) *Vinci Sfumatrice*

Also of latest design, the machine is constructed by Giuseppe Vinci in Contesse.

The oil has the general characteristics mentioned, but usually a large proportion of peels is broken.

(*6*) *Cannavò Sfumatrice*

Another recent type, invented by Paolo Cannavò in Giarre.

It treats the peels of 24 quintals of fruit per hour and gives a good yield of high quality oil, usually almost indistinguishable from "sponge" oils.

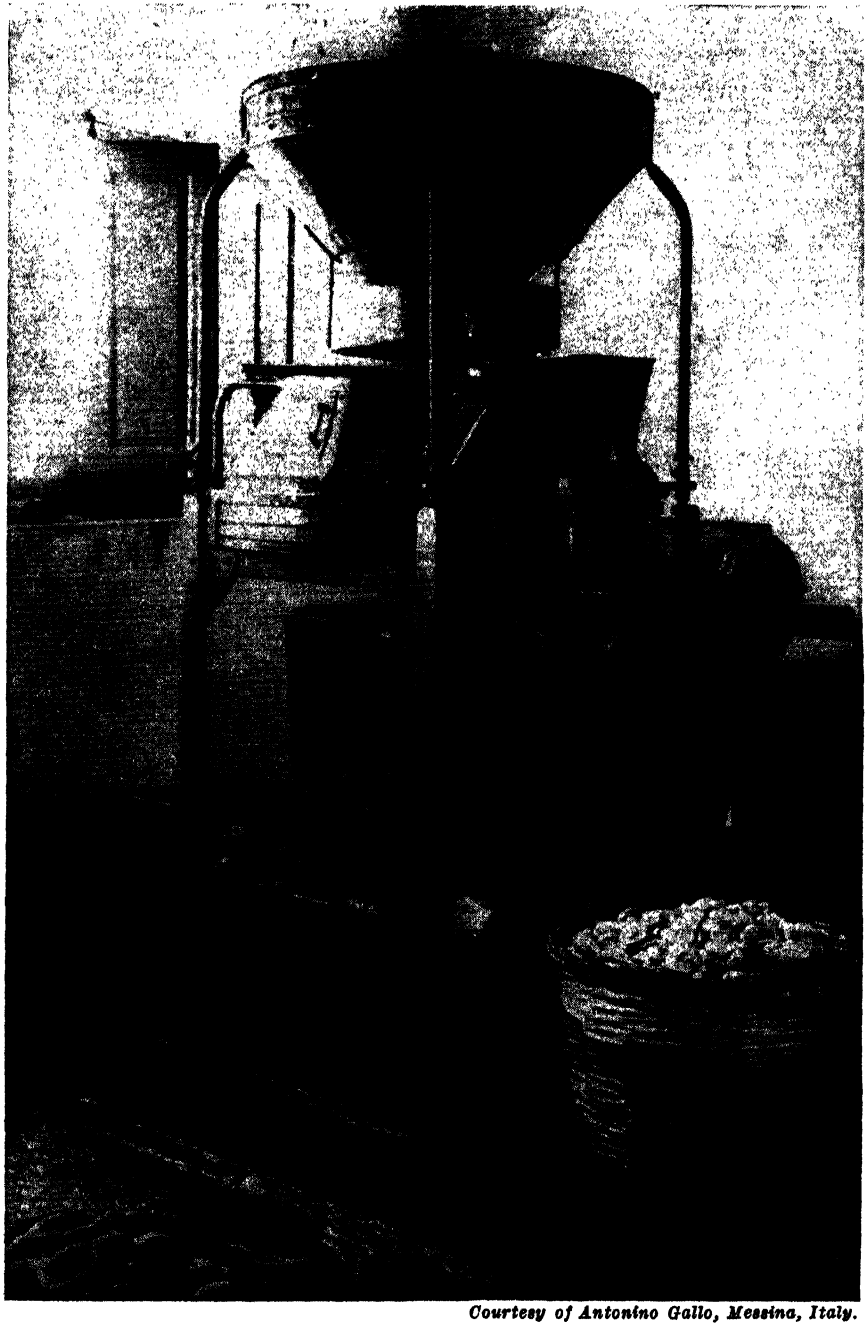
(*7*) *Ramino Sfumatrice*

Patented by G. Ramino in Palermo, and placed on the market about 1936, it depends upon the same general principle as do the above machines, but the translation of it into mechanical practice differs entirely from that of the machines described previously.

The machine works 20 to 24 quintals per hour and gives a good yield of high quality oil; the peels are pressed with practically no breakage.

(*8*) *Avena Sfumatrice*

The latest of its type, this machine was constructed and introduced in 1937 by G. and P. Avena in Pistunina.



Courtesy of Antonino Gallo, Messina, Italy.

Ramino Sfumatrice.

Externally, and in general design, it closely resembles the centrifugal machine (*pellatrice*) of the same firm, which processes whole fruit. G. and P. Avena had already acquired a high reputation with their *pellatrice* but the *sfumatrice,* of course, is much smaller.

The design of this low-priced machine is calculated to give a delicate action with a maximum turning and bending effect and with minimum tearing. The capacity is high, the peels of 1½ metric tons of fruit being worked per hour. The power required is very small; in fact the machine can be turned by hand, if necessary.

Summarizing, it can be said that the *sfumatrici* have, in late years, become quite popular in Sicily, as they give a good yield and quality of oil, and are adapted mainly to small-scale production. They present, however, only a partial solution of the problem of processing citrus fruit entirely by mechanical means, because the fruit still has to be cut into halves, and the pulp must be taken out by hand, with the *rastrello,* or by reaming. For this reason, only a few *sfumatrici* have been exported abroad and are being used today, chiefly in Spain and in South America (Brazil) for the treatment of oranges. Lately G. and P. Avena introduced a new fruit-halving machine which treats 500 to 550 fruits per minute, but efforts made in Sicily to devise mechanical methods for removing the pulp have remained only partly successful.* Complete mechanization of the whole process, however, has been achieved in the United States, where citrus fruit are processed on a very large scale, using the principle of the Italian *sfumatrici,* i.e., halving of the fruit, removing of the pulp, and expressing only the peel. A description of these machines employed in Florida and California will be given later.

III. Superficial Working of Whole Fruit by Rasping Machines

As Donovan [14] pointed out, it was only natural that attempts should have been made, at an early date, to extract the essential oil from whole citrus fruits by mechanical treatment of only the superficial layers, in which the oil is imbedded, rather than to mix the oil first with all the other constituents of the fruit, as is done in the crushing technique, which represents a later approach to the subject. However, when the whole fruit is crushed, the recovery of oil of good quality in good yield requires special attention.

* In 1948, two Sicilian companies, Officine Fratelli Indelicato, and Officine Francesco Speciale, both of Giarre, announced production of two new cutting and reaming machines of high capacity, which, if widely adopted, might go far towards solving this problem. (*Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **18** (1948), 21.)

[14] *Ibid.*

Another point of importance in the economics of the problem is the question of disposal of the juice. Apart from bergamot it can never be profitable to process citrus fruits for oil alone; in most cases it will be equally, if not more, important to find an outlet for the juice. Juice disposal is inseparably bound to the production of essential oils, which in the case of grapefruit, and of certain oranges, is of purely secondary importance. This statement holds true particularly of California and Florida, where the present citrus oil industry could never have been developed without utilization of the juice.

Citrus juices were once the starting material for the production of citric acid in Italy; the pulp was removed by hand in the "sponge" and *sfumatrice* processes, and for the most part expressed by large rapid action machines, or in small factories by more primitive presses, and used for the same purpose. The quantities reserved for beverage purposes were, relatively, quite small.

This situation is now completely changed; far from supplying foreign markets with citrate, the Italian production of citric acid has barely sufficed for domestic consumption, and the biological product has even been imported into Italy. The main outlet for juice in Italy today is in the ever-increasing demand for soft drinks. The market now insists upon juice of superior quality, such as can hardly be furnished if the whole fruit is crushed; even the pulp-cutting machines, which use knives and a shearing action, seldom, if ever, produce a juice of the requisite standard, for they invariably tend to introduce undesired tissue fluids into it, with a resulting bitter flavor among other effects. Furthermore, for beverage purposes, it is important that as little essential oil as possible should be left in the juice, for, on standing, oxidation of the terpenes produces an objectionable turpentine-like flavor. Lime juice is an exception in this respect, being employed with the oil present.

The common form of juice extraction in Italy is now by the use of rotating rosettes (reamers). This is by no means ideal, since it exposes the product to the air; an ideal extractor would work with the minimum of aeration in an entirely enclosed space.

The machine best adapted to the present requirements for production of oil and drinkable juice is the one which removes the essential oil as completely as possible, recovers it in good quality, and leaves the fruit in a sufficiently good condition to permit extraction of the juice. In Italy this is mostly done by hand reaming. The problem has been solved in California and Florida by the introduction of modern machines and processes. A modern machine of such type should be equally useful where the juice is destined for citrate production. In general a well-designed factory must be able to deal with juice in several ways, i.e., production of canned juice, concen-

trated juice, and citric acid. The exhausted peels can be utilized for extraction of pectin or as cattle food.

These considerations were not, of course, in the minds of those who, in Sicily, first aimed at the recovery of oil by superficial treatment of the whole fruit. To them the problem was simply that of reducing the necessary manual labor and of improving the yield. The early *macchinette* accomplished little saving in expense and required much skill; the *sfumatrici* represented a considerable saving in both, so that new machines have been introduced almost yearly up to the present. The *sfumatrici,* however, are employed only for expression of the oil from the peel, whereas treatment of the whole fruit further eliminates any preliminary cutting and scooping. The commonest of the machines treating whole fruit by rasping are listed below; for details the reader is referred to the paper by Donovan.[15] As has been stated, the action of these machines is fundamentally related to that of the *écuelle.*

Bergamot Machine ("Calabrese Macchina").—The working principles of this rather antiquated machine will be described under oil of bergamot, for the production of which it is still employed. The bergamot machine has been used occasionally also for lemon but, since it depends upon a uniform rolling movement, it works only part of the surface, and the yield of oil is very low. The oil produced is heavily colored, but has a fine odor and flavor.

The machine could be adapted for any spherical fruit, but it has a capacity of only about 1 quintal (100 kg.) per hour and is, therefore, cumbersome and relatively inefficient.

Lemon Machines.—On account of their ellipsoidal shape, lemons cannot be processed successfully in a machine like the *Calabrese,* for only the central portion will be worked as the fruit rolls about its longer axis. The mechanical treatment of lemons has progressed more slowly but, as often happens, resolution of the difficulties which delayed advance has resulted in the development of machines of high efficiency adaptable not only to lemons, but to other types of citrus fruits.

(*1*) *Perroni Paladini Machine*

This machine was patented in 1908, but the inventor died in the Messina earthquake before the machine had emerged from a purely experimental stage. It is of historical interest only.

(*2*) *Lo Verde Machine*

Patented in 1914 by Lorenzo Lo Verde in Palermo, it was the first machine to be used industrially for lemons in Sicily.

[15] *Ibid.*

The oil, usually deep green in color, was often lamentably low in citral content, high in nonvolatile residue and, as regards odor and flavor, generally inferior.

Today, the Lo Verde machine has been entirely superseded.

(3) *Vinci Machine*

Patented in 1917 by Giuseppe Vinci in Messina, this machine was based on the same principle as that of Lo Verde, but was of much better design.

The oil was usually deep green in color and tended toward the usual high fixed residue and other characteristics mentioned above. In spite of the large surface of metal in contact with oil and water it was, nevertheless, among the best machine oils of its period, as regards citral content and odor, up to 1930, particularly when early fruit was used.

The machine was used to a considerable extent in Eastern Sicily, but has now been almost completely superseded by the more rapid action, fully automatic types, in which its faults are eliminated.

Rotary Rasping Machines—Pellatrici.—The above-described machines were designed on the principle of working whole fruit singly, even if successive fruit might enter the machine while others were being worked, as could be done in the Vinci. They aimed at puncturing the oil sacs with a minimum of rasping; however, because of their design (apart from the bergamot machine) they were unable to give a prolonged and delicate action, but only a brisker and briefer one. It was seldom possible for the entire surface of a lemon to be worked uniformly, and not only rasping but also breakage occurred. However, when a quantity of fruit is charged at once into a rotary machine provided with abrasive surfaces and stationary abutments, which tear the rind and open the cells, the jostling of the fruit causes fresh portions to be presented constantly to the abrading surface, and the scraping becomes uniform. Projecting portions are removed, and the fruit is reduced to a more regular shape. At the same time the amount of detritus is increased relative to the methods previously described. This feature not only necessitates the elimination of detritus by the use of automatic presses, prior to the separation of oil and aqueous phase by centrifuging, but it has also a strong influence on the oil.

This principle has been used in the following machines, perfected now to a high degree of efficiency.

(4) *Cannavò Machine (Pellatrice)*

Patented in 1921 by Paolo Cannavò in Giarre.

The machine processes about 1 metric ton of fruit per hour, but in this, as well as in the other machines described later, the output always depends upon the time of working each batch; for lemons early in the season 4 min.

or more may be necessary, whereas in April as little as 2 min. suffices for soft, riper fruit. The output in oil per hour may not vary correspondingly, for recovery is greater from early fruit.

The Cannavò *pellatrice* gives a high yield of oil, which usually has a low citral content, high residue, pronounced color, and a flat "grassy" odor inferior to that of "sponge" oil. This, and the improved results now possible, will be discussed later.

The machine is sturdy, and simple in design. Its chief fault lies in the fact that not infrequently fruit is caught between the drums during discharge and smashed as they close. From 1925 onward it has enjoyed an increasing popularity, especially in Eastern Sicily.

(*5*) *Speciale Machine* (*Pellatrice*)

Patented in 1928, it is constructed by Lizzio & Speciale, in Giarre.

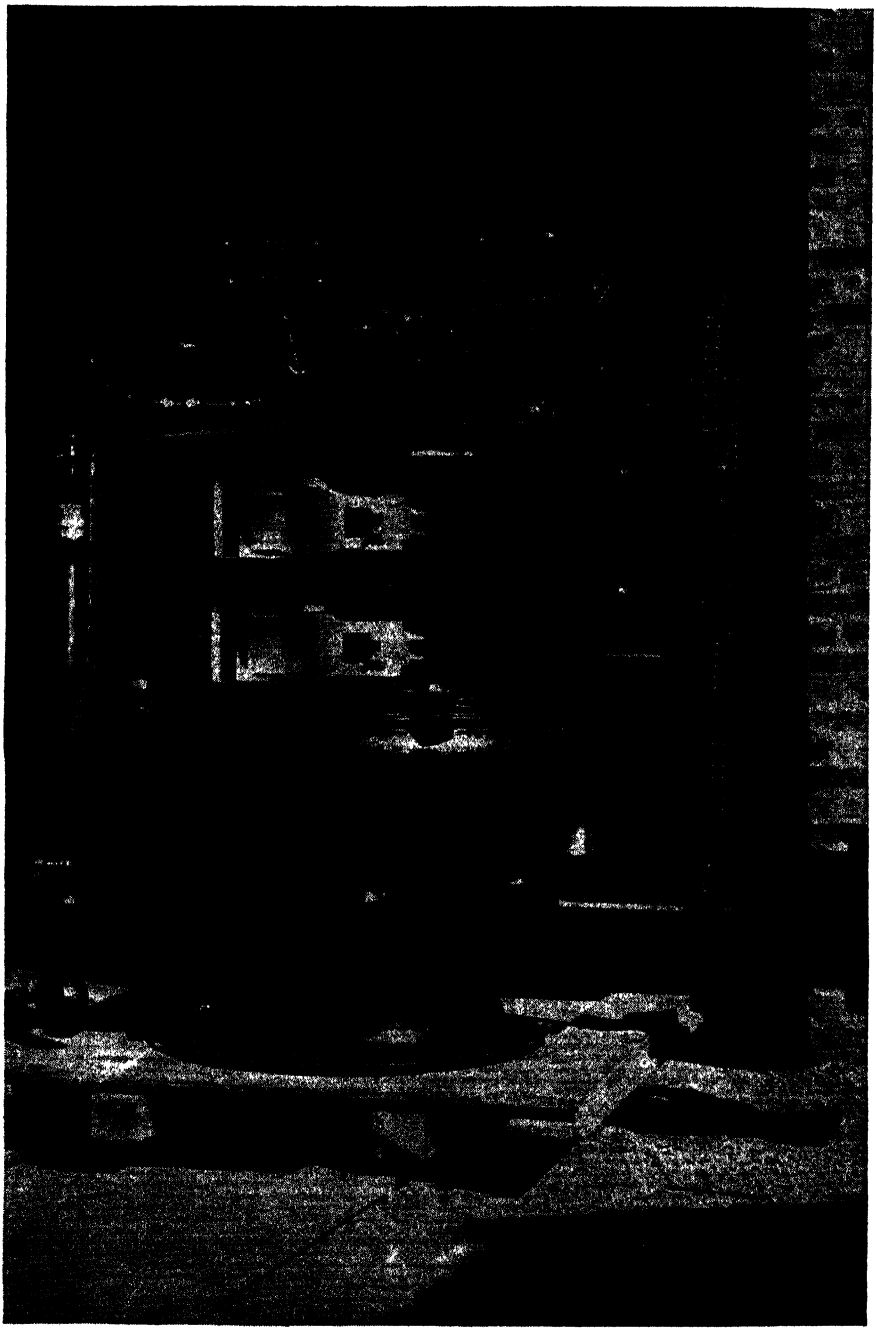
The Speciale *pellatrice* has a high capacity, the largest model processing about 2 metric tons of fruit per hour; other sizes are made down to 10 quintals per hour (1 quintal = 100 kg.). Up to 1937, more than fifty machines had been installed in Italy and abroad. With lemons it gives excellent results when modern methods of oil separation are used; with oranges it is less successful. The action seems to be too drastic, resulting in breakage of fruit; and oil separation becomes practically impossible. In the past the oil was separated in the manner described above, the remarks about quality made under the Cannavò machine applying also here. The yield of oil is very good.

(*6*) *Avena Machine* (*Pellatrice*)

In its original form this machine was patented in 1924 by Giuseppe and Placido Avena fu Carmelo, in Pistunina, but it has since been perfected in several details. It was rationally designed with attention to the particular conditions requisite for the recovery of essential oil from lemons and other citrus fruit and today represents a most efficient and attractive machine of general application.

The Avena *pellatrice* consists of a cast-iron body carrying a driving shaft, which rotates a vertical shaft, and two horizontal circular plates, the upper of which has a large central opening. The external diameter of the plates is 1.20 m.; they revolve at 55 to 60 turns per minute. The upper part of the machine, cylindrical in shape, is bolted to the casting; the walls surrounding the revolving plates are lined internally with interchangeable tough glass plates having superficial nonabrasive projections. The upper surfaces of the revolving plates are fitted with stainless steel segments having pyramidal abrasive points; these cover the whole of the peripheral area and are also interchangeable.

The fruit is charged into a hopper, which is divided into two parts by a fixed vertical diaphragm. The sliding bottom of the hopper is withdrawn, and the fruit



Courtesy of G. & P. Avena fu Carmelo, Pistunina-Messina, Italy.

Avena Pellatrice.

falls, half on to the upper plate, half through the central opening on to the lower plate. At the same time, water is admitted to spray tubes in both compartments; the disposition and form of these sprays being the result of much experimental work.

The fruits run round and, hurled against the walls and back to the plates, are mixed and uniformly rasped. The oil and detritus are carried down by the water into a circular canal, passing out through a port. After separation, the water is pumped back to the sprays.

In the old method the oil and detritus were carried with the water, through sieves, to the Florentine decantation vessels. The oil, separated as described, had the general character of oil of this type, the yield being very good.

In modern processing the mixture of oil, water and raspings passes through a continuous filter press, also made by Avena. The mixture is fed into the central opening and traverses a spiral path over a sieve, through which the liquid passes down through the body; the detritus is carried on to an Archimedean screw in the tube in front and is thoroughly pressed and discharged; the expressed fluids return to a central discharge in the rear.

The Avena *pellatrice* is small and compact, entirely enclosed in working position, all items of great importance for the recovery of oil. It is conspicuous for cleanliness of design, freedom from trouble in long use, and flexibility of action. The only attention needed consists in renewal of the lining plates and steel abrasing segments; the points of the latter, being small square pyramids, can be resharpened when worn, after, perhaps, three seasons' use, but they are thereby reduced in length and their lacerating action will be diminished. In general it is better to replace them by a new set when worn.

The larger model has a capacity of about 10,000 lemons (1 ton) per hour and requires a 1 h.p. motor; it uses 7 liters of water per minute. Smaller sizes, with one plate, are also made, with capacities of about 7 quintals per hour (1 quintal = 100 kg.).

By altering the speed of revolution and the time of working, the rasping effect can be brought to any desired intensity; consequently, the machine is very flexible in action and can deal with fruit at any stage of maturity and of any type. It has found a wider demand outside Italy than any other machine and is used equally for the production of orange and lime oils.

As Dr. F. La Face pointed out to the author during a visit to Sicily and Calabria in November, 1939, successful oil extraction in the Avena rotary rasping machine depends upon several factors:

1. Proper speed of rotation; if too fast, the resulting emulsion is hard to break.

2. Proper time of treating each batch of fruit; if too long, much emulsion will form; if too short, the yield of oil will be inferior.

3. As was explained, after rasping, the bulk of detritus is removed from the liquid phase in a continuous filter press; from there the emulsion of oil and aqueous phase flows into a high-speed centrifuge (usually an "Alpha De Laval"). The speed of this centrifuge must be carefully regulated; if too slow, the oil is not completely separated in the centrifuge and considerable amounts of oil remain suspended in the aqueous phase, flowing with it into the settling tanks.

Thus, there exist two types of oil, viz., the oil flowing directly from the centrifuge and the oil separating from the aqueous phase after a period of time in the settling tanks. The latter oil is inferior to the direct oil.

4. The water in the settling tanks should be renewed about every third day. If changed too frequently, considerable amounts of citral, other (somewhat water-soluble) aldehydes, and oxygenated constituents in general, would be lost; if not changed frequently enough, the water in the settling tanks becomes saturated with colloidal matter, enzymes, and ferments, which gravely affect the quality of the oil, as we shall see in the following pages.

The constructors of the Avena *pellatrice,* G. and P. Avena fu Carmelo, Pistunina, Sicily, claim the following advantages for their machine:

1. A single unit can be adapted to the processing of any kind of fruit, lemon, lime, orange, etc.

2. Fruit of any shape or size can be processed, without previous sorting by size.

3. If the abrasor plates (which are graded by size of point) are changed according to the condition of the fruit peel being processed, and if the number of the revolutions per minute is adjusted to the same condition, tearing of the skin will be greatly reduced, and even mature and soft fruit can be processed. Thus the machine may be used throughout the entire fruit-growing season.

4. The machine can be operated by steam, electric power, or by a combustion motor.

5. The yield and quality of the oil extracted with the Avena machine are good.

In general it can be said that the Avena *pellatrice* is a very efficient and well-constructed machine, adapted especially for moderate output and for fruit with a fairly hard peel.

(Florida oranges possess a thinner and softer skin than the Sicilian oranges, for which reason the Avena *pellatrice* would have to be modified by the insertion of stainless steel abrasor plates with very fine points which

act like a file. In this case the centrifugal speed of the machine has to be increased to obtain the desired effect of filing, rather than one of rough rasping. Large points on the abrasor plates have a tendency to tear hunks and pieces from soft-skinned fruit. After such a rough treatment, Florida oranges could no longer be used for the expression of juice, which is the most important product in the operation of the Florida canneries, the essential oil being a by-product only.)

Deterioration of Citrus Oils During Expression (Causes, Nature, and Prevention)

Years ago Bennett observed that the oxygenated constituents, to which lemon oil owes most of its odor and flavor, are the most soluble in water. When lemon oil is agitated vigorously with water, a gradual diminution in citral content occurs; the same is true also of the terpene alcohols and, to a lesser extent, of the esters. Furthermore, during agitation, air is thrashed into the liquid, thereby creating conditions favorable for hydrolysis, oxidation, and resinification. Colloidal substances always accompany the liberated citrus oils, tending to promote emulsification. In addition, when rasping machines are used, the emulsion is in contact with larger quantities of other soluble constituents, again assisting emulsification, and with much solid cell detritus, from which the oil phase dissolves coloring and resinous matter.

Ricevuto-Solina and Guzzardi [16] explained the loss of citral in the manufacture of lemon oil by the fact that during the process of recovery, pectin-containing water accumulates, which dissolves a certain quantity of citral. After a short time the pectin undergoes splitting with formation of methyl alcohol, which has a high solvent action upon citral. By rapidly centrifuging off the pectin water, the loss of citral can be decreased.

Bennett had noted that the emulsification tends to be more or less complete according to the degree of agitation to which the mixture has been subjected, the various machines differing considerably in this respect. In the old Vinci machine, for example, a large volume of water was almost stationary, the fruit running down through it and the liquid simply overflowing as the water entered from the wash sprays. In the rotary Sicilian machines the linear velocity at the periphery may be some four yards per second; a continuous shower of water is scattered over a large surface of rapidly rotating fruit, so that oil, aqueous solution of cell contents, air, and water are violently beaten together providing maximum possibilities for chemical action and solution of the undesirable coloring matter and resins.

[16] *Ann. chim. applicata* **31** (1941), 459. *Chem. Zentr.* I (1942), 2942.

Bennett considered that these factors were largely responsible for the changes in the oil which occurred, and for the probable formation of compounds of disagreeable odor, as was later shown to be the case.

Furthermore, in the old process of separation of the oil, the whole liquid was run, first through sieves, to remove coarser solids, and then into decantation vessels, where the dense emulsion usually rose to the surface of the first vessel. This dense emulsion was not removed as formed, but was left for a period sufficiently long, usually hours, to separate a sufficient quantity for soaking into sponges or other material, and for pressing in wool or hide. During all this time the oil remained in the most intimate mixture with the aqueous phase of the emulsion, smaller solid detritus, enzymes, and ferments, which abound in and on the surface of the fruit, and are carried down with the water. The degree of influence exerted by these factors upon the oil in the various machines, and the actual techniques employed when using these machines, account for the variation in the oils produced.

Bennett succeeded in showing that, by an effective method, in which the water sprays were modified and subsequent separation rendered more rapid, the quality of oil produced by machines could be greatly improved.

As was explained previously, in most machines the spraying water is used over and over again, machine pump and decantation tanks forming a closed cycle. The prime object of this procedure is to prevent mechanical loss of smaller globules of the oil emulsion, which fail to rise to the surface on first delivery to the decantation vessels; at the close of a working period the liquid is allowed to remain in repose for some hours before the oil emulsion is finally removed. The closed cycle possesses the additional advantage that the solution effect will be reduced to a minimum, the water becoming saturated with oxygenated constituents at the first running.

For the production of a good quality machine oil it seemed clear that, as in the "sponge" process, the oil should be separated from the aqueous phase as rapidly as possible—in ideal conditions immediately after liberation. With this in mind, Bennett suggested the use of centrifugal separation of the oil-water mixture delivered from the machines, but found that it was only moderately successful. Although the oil produced proved greatly superior to that separated by decantation, some difficulties persisted, particularly with machines of the rotary rasping type (*pellatrici*). Instead of a sharp separation of oil and aqueous phase, a dense emulsion tended to be built up in the centrifuge bowl, and only a proportion of the oil was completely separated, the remainder being simply concentrated into a buttery mass, of high oil content. More oil could be separated clear from this by redispersion in water and recentrifuging, but only in limited amount; and the total time in which the oil remained unseparated was still long.

A systematic study of the emulsification phenomena was, therefore, undertaken. Preliminary experiments showed that the substances taken up from the peel by the water played an important part in the formation of the persistent emulsion.

A small rotary rasping machine and a centrifuge of cream separator type were then installed; and aqueous phase and emulsion were examined, both directly and as regards the effect of various agents altering pH, electric charge, etc. In a normal run the highly colored aqueous phase contained some 1.35 g. of dissolved substances per liter; and it became clear that the plant resins and similar substances yielded from the rasped peel were the chief causes of the emulsification effect.

Examination of the action of various agents, particularly on the aqueous dispersions, showed eventually that separation of the oil from the mixture was promoted by the presence of small proportions of sodium bicarbonate, being further assisted in some cases by additions of sodium sulfate and similar salts. It was also found that such additions were without influence on the character of lemon oil, by shaking "sponge" oil with them for periods much longer than necessary in actual processing.

The method was then applied to the experimental separation of oil by making the indicated additions to the water used in the sprays and circulatory system. The tissue fluids are acid in reaction; and the circulatory water becomes acid from the moment of working, when water is used. Sodium bicarbonate neutralizes this and brings the pH to a little above 7. To make matters clear, bicarbonate is not added to neutralize the acid of broken fruits. Any such acid from juice must, of course, be neutralized, but the important point is that the epidermal tissue fluids are themselves acid. With a pH of about 8, the colloids have less emulsifying power; the addition of sodium sulfate or similar salts also tends to neutralize the electric charge of the colloidal micelles, although in most cases such additions are not necessary. It should be remembered that the enzymes and ferments act normally in acid medium, their activity being inhibited or impaired in the slightly alkaline bicarbonate medium.

The results of this investigation, which was carried out under the aegis of the Consiglio Nazionale della Ricerche, and with the collaboration of G. Cusmano, were published in 1930 and made available throughout Italy at no charge to the producers. Outside that country they are the subject of patents granted to A. H. Bennett.[17]

When a spray and carrier liquid consisting of a very dilute solution of sodium bicarbonate, with perhaps other salts, is used, the mixed liquid can be carried directly to a centrifuge and clear oil will be separated at

[17] U. S. Patent No. 1,814,888, July 14, 1931.

once. The time of contact with liquid and tissue solids is reduced to a negligible interval; and the effect of other objectionable influences will be eliminated by the nature of the solution.

It is not necessary to use fresh bicarbonate for the sprays; the usual closed system may be employed, bicarbonate solution being substituted for water. It gradually becomes charged with dissolved substances and should be rejected when these reach too heavy a proportion.

The analytical data of one of the first lemon oils produced by this method experimentally in 1930 were similar to those of "sponge" oils.

Specific Gravity at 15.5°	0.8595
Optical Rotation at 15.5°	+61° 30′
Citral Content	5.50%
Nonvolatile Residue	3.40%

The oil was of a golden color and had the odor and flavor of a "sponge" oil.

Bennett's process was adopted on a technical scale and it has been claimed that it gives even better results in the factory than in the laboratory. It may be applied in all cases where water is used in machines, whether *sfumatrici* or *pellatrici,* and whether the final oil separation is accomplished by centrifugation or, in the older manner, by decantation. For consistent recovery of a high-quality product, however, separation of oil as fast as liberated is advisable; in the case of rasping machines (*pellatrici*) it is absolutely necessary to use a centrifuge. This method constitutes the so-called Bennett-Cusmano, or "new Bennett process."

Lemon oils recovered by this method are claimed to be similar to "sponge" oils in citral content, possessing the same composition, odor, and flavor. Such lemon oils are, in general, of golden-yellow color and show a slightly higher nonvolatile residue than "sponge" oils, points of no material importance in the majority of uses to which lemon oil is put. They can easily and without damage be reduced in both respects by treatment with a small quantity of a decolorizing agent.

The nature of the deterioration suffered in varying degree by machine oils in the older processes was also studied by Bennett.[18]

On elimination of the terpenes it was found that "machine" lemon oils and "sponge" lemon oils gave about the same yield of concentrated oil, despite the citral deficiency in the "machine" oils. The explanation lies in the fact that the alcohol content of the latter was higher, compensating for their lower citral content. Although in "sponge" oils the ratio of alcohols to citral varied from 0.3 to 0.4, it was generally higher in "machine" oils, amounting to unity and more. In the oils produced by the Bennett-

[18] *Ann. chim. applicata* **22** (1932), 32.

Cusmano process, however, the ratio resembled that of the "sponge" oils, as shown in Table 1.1. The esters were not much affected in any case.

TABLE 1.1

Type	Citral in Original Oil (%)	Yield of Concentrate (%)	Composition of Concentrate			
			Citral (%)	Esters (%)	Alcohols (%)	Ratio Alcohol/Citral
Sponge, High Grade	5.05	6.70	53.90	13.70	14.15	0.264
Sponge, Low Grade	4.15	5.80	44.85	...	16.60	0.37
Sponge, April Oil	3.80	6.05	38.40	22.20	13.45	0.35
Machine 1	2.20	5.35	22.80 *	...	...	...
Machine 2	3.80	5.85	45.60	20.00	14.65	0.343
Machine 3	2.95	5.27	29.65	21.95	31.40	0.76
Machine 4	2.20	5.10	24.70	21.10	27.80	1.13
Machine 5	2.40	6.40	23.35	21.50	28.00	1.19
Machine 6	2.60	5.64	30.80	19.55	21.20	0.68
Machine 7	3.25	5.55	41.05	13.65	18.10	0.44
Machine, Bennett Process	4.45	6.15	52.05	16.90	13.00	0.25
* Sesquiterpeneless Oil Prepared			30.05	...	36.20	1.20

It will be seen that the "machine" oils show a variation from No. 2 to No. 5, where the deterioration is very high. The "Bennett" oil resembles "sponge" oil. It also appears that in the older machines alcohols tend to be formed, whether from terpenes or at the expense of citral, a point to be further investigated.

It might be mentioned that some oil remains as a dense emulsion in the centrifuge bowl. This is more pronounced when working in a small pilot plant; less so in actual manufacturing, where adjustments can be made more accurately and most of the oil in the emulsion can be separated in continuous operation. Any remaining oil may be recovered by distillation and has better qualities than the inferior distilled oils described later, for it is not recovered, as in that case, from contact with hot acid solution. In practice the direct yield of clear oil is so high that oil from the residual emulsion can often be neglected.

To summarize the working of rotary rasping machines in conjunction with the Bennett-Cusmano process: it is important that as much solid matter should be removed as possible. For this purpose the rotary rasping

machines are generally provided with a specially constructed continuous filter press (see Avena *pellatrice*). A wire sieve over the centrifuge inlet guards against escaped or smaller matter.

The centrifuge should be adjusted to the particular mixture which should be delivered from the rasping machine in a steady flow and of a composition as uniform as possible, without partial separation of the oil phase. The mixture of oil and bicarbonate solution must not be pumped, and the feed should be effected by gravity, either by lowering the centrifuges or, preferably, by raising the rasping machine.

The oil coming from the centrifuge should be received in a closed vessel, and the separated aqueous solution be discharged into a closed tank, so that any oil passing the centrifuge is not exposed. The tank should be connected in Florentine flask style with a second, and sometimes a third, tank (although this is hardly necessary); and the bicarbonate solution is pumped from the last vessel back to the sprays. It gradually becomes charged with dissolved substances, forming resin soaps and the like, some is lost on the surface of the discharged fruit; volume and strength of the bicarbonate solution must not fall below certain limits. Once adjusted correctly, the plant works with only supervisory attention, cleaning or swilling of the centrifuge after 4–5 hr., and thorough cleaning at night being sufficient. One appropriate separator is necessary for approximately 1,000 kg. fruit worked per hour.

Even green fruit can be processed to yield an oil of yellow color by a further small addition to the circulatory system, again with no effect upon the characteristic qualities of the oil.

Plants thus designed are of general application for citrus oils and are claimed to have proved successful outside of Italy for the recovery of orange and lime oils.

Keeping Qualities.—Oils made by the Bennett-Cusmano process have met a certain resistance and have occasionally been termed "alkali oils"; this, however, according to Donovan,[19] is a gratuitous and possibly misleading appellation, as it would be equally justifiable and reasonable to call "sponge" oils "acid oils." It has also been rumored that such oils do not keep as well as "sponge" oils. This Donovan parries with the claim that they have been in production for a long time. Donovan retained a sample made by him in the manner described above in June 1933, using Fiumefreddo lemons of a degree of ripeness never worked by older methods and giving an oil of low citral content. This was kept in a full, well-corked bottle in the dark; it was opened in February, 1937, and found to have a full fresh odor and flavor, quite unimpaired and free from oxidative or other

[19] *Perfumery Essential Oil Record,* Special Issue (1937).

foreign note. The analytical data, when first made and more than three and one-half years later, are given below:

	June 21, 1933	*February 16, 1937*
Specific Gravity at 15.5°	0.8570	0.8568
Optical Rotation at 15.5°	+60° 3′	+60° 6′
Citral Content	3.45%	3.40%
Nonvolatile Residue	4.12%	4.60%

Apart from the usual small rise in nonvolatile resinous matter, the properties were practically unaltered, after almost four years.

The Bennett-Cusmano process was soon adopted by several of the larger factories in Sicily using rotary rasping machines, and it proved successful both as regards yield and quality of oil. In one factory working some 120,000 lemons (about 12 metric tons) daily, the direct yield in the early season was at once one and one-half English pounds and more, per thousand fruit, and the citral content was consistently around 5 per cent. During ripening, the citral content, of course, diminishes in all lemon oils, and the yield also becomes lower as the season advances. It should, however, be noted that in a modern plant, with this process, it is practicable and economic to work fruit at a stage of maturity when no earlier method could be used. Donovan recovered lemon oil experimentally as late as mid-June, and witnessed the same process carried out at this advanced season in factories working primarily for beverage juice.

To close our discussion of the Bennett-Cusmano process, it will be interesting to learn whether it has proved its claims and merits by general adaptation in the Sicilian citrus oil industry. This question can only be answered by the statement that in the past ten years the Bennett-Cusmano process has been adopted by some processing plants using machines of the *pellatrice* type. In the meantime, however, the Italian lemon oil industry has displayed a decided tendency away from the *pellatrici* and toward the *sfumatrice* type; and in the case of *sfumatrici* the separation of oil and aqueous phase is so easy, especially when centrifugal separators are used, that the application of the Bennett-Cusmano process has become superfluous. Neither have the bergamot oil extraction plants using Avena *pellatrici* in conjunction with De Laval centrifugal separators experienced any difficulties in separating oil and aqueous phase; therefore, they did not have to resort to the Bennett-Cusmano process.

IV. Treatment of Citrus Fruit or Peel by High Pressure

A. Expression of Whole Fruit.—We have so far discussed methods of expressing the citrus peels with moderate pressure by hand ("sponge"

method) or by machines (*sfumatrici*), in both cases after halving of the fruit and after removal of the pulp; furthermore, we have reviewed the process of treating whole fruit by hand (*écuelling*) or by rotary rasping machines (*pellatrici*). Most of these methods are today employed in Southern Italy (Sicily and Calabria), and one method (*écuelling*) in the West Indies.

Another approach to this problem consists in the preliminary crushing of the whole fruit with subsequent separation of oil and aqueous phase (juice and cell liquid). This process has been used for many years in the West Indies for the production of lime juice as by-product; details will be found in the section on "Oil of Lime." Suffice it here to mention that in this process the whole fruit is crushed in mills as used for the crushing of sugar cane. Instead of sugar cane crushers, the lime producers in the West Indies and in Mexico now use also tapered screw presses. The juice is freed, by screening, from solid particles and detritus and distilled for the production of distilled lime oil, which has a peculiar, sharp flavor but enjoys great popularity for the flavoring of soft drinks, candies, confectioneries, etc. Or the juice and oil mixture is centrifuged for the production of coldpressed oil, which possesses a much more true-to-nature odor and flavor.

Bennett, in 1914, patented a similar method for large-scale production of lemon juice, citrate of lime, and citric acid, in Sicily. The principle of this so-called old Bennett process consists in crushing of the carefully washed fruit and in the *rapid* separation of oil and lemon juice in high-speed centrifuges. Since then, this process has been thoroughly studied in California and has been greatly improved in regard to machinery, yield, and quality of oil. Large quantities of lemon and orange oil have been produced in California according to this principle, the details of which will be described later. The most important feature in this process is to separate the oil from the juice as quickly as possible after pressing, as prolonged contact with the acid juice has a deleterious effect upon the oil. The rings in the bowl and the speed of the centrifuges must be so adjusted that clear oil is obtained, with a minimum possible portion left in the juice. Any clouding of the oil delivered indicates that the bowl in the centrifuge needs cleaning. For further clarification, the oil is then run through a second (clarifying) centrifuge of higher speed whereby traces of water and considerable waxy material are eliminated. Storing for several weeks at low temperature in a cold room will precipitate additional quantities of waxes and sediment, and after a final run through the high-speed centrifuge a clear oil will be obtained. When carefully conducted, this process yields an oil of good quality, comparable almost to "sponge" oil, although the

content of citral, other aldehydes and oxygenated compounds in general may be somewhat lower, due to part solution of these oil constituents in the large quantities of juice. The yield of oil, too, is somewhat lower than in other processes, principally for these reasons:

1. A fairly large proportion of oil remains in the press residues, especially if the fruit is pressed in screw presses, as the albedo of the peel acts as a kind of sponge, absorbing the oil expelled from the oil glands.
2. A small quantity remains in the material on the screens and in the dense buttery emulsion left in the bowl of the centrifuge.
3. A small quantity remains in the separated juice.

According to Donovan,[20] this loss of oil may amount in all to 30 per cent or more, whereas Bennett [21] speaks of 50 per cent of oil loss. However, an important part of this oil may be recovered, first, by distillation of the press residue, which in some parts of California and Florida is dehydrated for the making of cattle feed; second, by distillation of the residue in the centrifuge; and third, during flash pasteurization of the juice, or on concentration of the juice, or in the process of making citric acid.

B. Expression of Peel Only.—Another method aiming at modern production, in large quantities, of a very high-grade oil of orange and grapefruit has been developed successfully in the United States. The idea consists in the prevention of any contact or mixture of juice and essential oil, so that the chemical constitution of the oil is in no way affected by contact with the acid juice and, what is equally if not more important to the juice canners, the quality of the juice is not impaired by admixed traces of oil which readily oxidize and impart to the juice an objectionable off-flavor. For this purpose, the thoroughly washed fruit is cut into halves, from which the juice is reamed out or expressed by highly efficient juice-extracting machines, which will be described in ensuing sections.

The halved orange or grapefruit peels, which retain all their oil in the oil glands, are then expressed by passing through various types of specially designed oil presses, details of which will be found below. The resulting emulsion of spray water, detritus, cell liquid, and essential oil is separated by passing through a centrifuge (sludger) adjusted to a speed of 6,000–8,000 rpm and finally through a clarifying centrifuge (polisher) with a speed of 18,000 rpm. Some producers now use supercentrifuges rotating at 56,000 rpm, which yield very clear oils.

[20] *Ibid.*
[21] *Ibid.*, **35** (1944), 308.

V. Distillation of Citrus Fruit and Peel

The method of distillation for the recovery of citrus oil from its peel has evidently attracted the attention of the producers since early days, as distillation in general is a simple process for the isolation of essential oils from their plant materials in high yield.

In the case of citrus peel oils, however, distillation gives very unsatisfactory results in regard to quality, the steam distilled oil possessing an odor and flavor quite different from that of the original oil as it exists in the peel. The steam exerts a deleterious influence upon some of the constituents of the oil, especially if the oil is distilled from a mixture with the acid juice of the fruit, such as that obtained by crushing the whole fruit. The only exception is perhaps distilled lime oil, but in this case the trade during many years has simply become used to an oil with a peculiar, sharp odor. It does not exist naturally in the lime fruit, but was introduced by the lime growers in the West Indies some time ago when the oil was simply a by-product in the concentration of juice for citric acid. By distillation from the hot, acid juice, the citral content of the original lime oil will be reduced from about 6 per cent to about 1.5 per cent (for details see the section on "Oil of Lime"). Here, as well as in all other cases of citrus peel oils, the odor and flavor of the distilled oil are quite different from and inferior to the coldpressed oil.

Many attempts have, therefore, been undertaken with a view toward improvement of the distilled oil by modifying the process of distillation. Thus, Peratoner and Scarlata in Palermo (Sicily), before World War I, patented a process of distillation at reduced pressure. In this method, known as the "Peratoner Process," the whole fruit is minced and the mixture of juice and oil is immediately distilled at reduced pressure, the temperature being kept at about 50° to 60°. Any rise in temperature has a marked effect upon the resulting oil which will be deficient in aldehydes and inferior in regard to odor and flavor. If the mixture of juice and oil is allowed to stand, fermentation sets in and irreparably damages the oil.

Despite all precautions, the oils distilled by this process were of inferior quality, as compared with coldpressed oils; they seldom found their way abroad and were used mainly for cutting coldpressed oil to serve the cheaper market. In order to eliminate this practice, the Italian government, several years before World War II, prohibited the production of distilled oil by the Peratoner process. This process was revived in a modified form by Sardanovski,[22] who reported that an essential oil of good

[22] *Trudy Vsesoyuz. Inst. Efirno-Maslichnoĭ Prom., Ratsionalizatsiya Pererabotki Efirno-Maslichnogo Syr'ya* **8** (1940), 84. *Khim. Referat. Zhur.* **4**, 1 (1941), 145.

quality is obtained by distillation of mandarin peel under a pressure of 100 to 150 mm. The process is accelerated by using small pieces of the rind. The yield of oil may be increased by 20 per cent by keeping the peel in ethylene and by 29 per cent by keeping the whole fruit in ethylene. The content of oil in the rind, according to Sardanovski, does not change when the rind is kept in the frozen state for five days.

Large quantities of distilled lime oil, however, are still being produced in the West Indies and Mexico for the reason explained above. California and Florida have become heavy producers of distilled oil of orange, lemon, grapefruit, and tangerine—the oils often being offered as mixtures. These oils result as by-products in the various phases of treating the citrus fruit in the great canneries of Florida and California, as we shall see in the following pages.

MODERN, LARGE-SCALE CITRUS JUICE- AND OIL-PRESSING EQUIPMENT

North American Citrus Oils, a By-Product in the Canning of Citrus Juices

To understand the development and operation of the modern, highly efficient machinery at present employed for the recovery of citrus peel oils in North America, it is necessary to review the development of the California and Florida citrus industry, as well as the fundamental change that has occurred in this industry during the last few years. Prior to World War II, most of the California, and a good part of the Florida, citrus crop (orange, lemon, grapefruit, tangerine, and lime) was shipped in boxes, as edible fruit. The canned juices were not too popular, because their quality was not perfect, and the buying public complained of a stale or "cooked" off-flavor. At that time, the citrus peel oils were extracted largely from surplus fruit which could not be shipped to the fresh fruit market. This applied particularly to California, since Florida for many years has tried to dispose of much of its orange crop in the form of canned juice. Conditions varied from year to year, but in general it may be said that it was chiefly the surplus fruit only which was converted into canned juice, concentrated juice, canned fruit segments, essential oil, citric acid, pectins, cattle feed and molasses. Because of the high cost of labor prevailing in

the United States and the enormous quantities of fruit processed, none of the machines developed in Sicily for the expression of the oil could be used in California or Florida, and special machines of high capacity had to be evolved. The most important process of expressing citrus peel oil, used particularly in California on a very large scale, consisted of crushing the whole fruit, with subsequent centrifuging and separation of solids, juice, and oil.

In this process the fruit arriving at the factory is first washed, then mechanically conveyed from the washing tanks to slowly rotating heavy crusher rolls, made of stainless steel, where the whole fruit is crushed. Then the pulpy mass runs through a system of heavy, horizontally mounted cylinders, between which it is finely thinned out. The solid parts adhere to the stainless steel cylinders and are easily removed by scraper blades. The liquids, consisting of a thin emulsion of essential oil in citrus juice, run off the cylinders to be freed from solid particles (cell detritus) by screening, after which they are conveyed into a battery of high-speed centrifuges, where the oil is separated from the juice.

Instead of being crushed between rotating steel cylinders, the whole fruit can be run through presses built on the principle of the tapered screw and expeller. The crushing, pressing, and squeezing effect is similar to that obtained in the steel cylinders. An emulsion of juice, essential oil, and cell detritus results. This emulsion must be broken up by screening through successively finer screens (from 16 mesh to 60 mesh in the last screen) and by centrifuging.

As an important point it should be noted here that the emulsion of essential oil, juice, and cell detritus must not be left standing for any length of time, since such contact seriously impairs the flavor of the oil. For example, citral is quite easily converted into *p*-cymene by the action of citric acid in the presence of water (or acid juice). Enzymes will start to play their role, oxidation will set in, etc.

To prevent such changes in the oil, the oil-in-juice emulsion therefore must be broken up and separated by centrifuging immediately. The press residue of the crushed fruit retains considerable quantities of essential oil and is usually submitted to steam distillation, yielding distilled citrus peel oils.

In this connection it should be noted that the highest yield of citrus oil by any method is obtained by steam distillation of the finely ground citrus fruit. For this reason, steam distillation is used in the laboratories to determine analytically the amount of oil present in the fruit; it represents actually the most efficient method thus far evolved.

The essential oils obtained in California some years ago by the above-described process of crushing and coldpressing the entire fruit contained a

good amount of residual waxes, in fact more than are found in the Italian citrus oils, which are made by handpressing or in various small machines that merely puncture the skin of the fruit and wash out the oil. Because of their high wax content, the California oils sometimes separated and caused trouble in finished extracts, soft drinks, etc. In the last few years, however, California oils have been greatly improved by far superior methods of expression, by specially developed treatment, supercentrifuging, storing at low temperature, and clarifying, etc., so that most of the residual wax is eliminated. In fact such a degree of perfection has been attained in the course of the past years that extracts made with California lemon oils will remain perfectly clear for an indefinite period of time. In this respect the California lemon oils are superior to Italian oils. So far as California orange oils are concerned, a small trace of wax seems to impart a richer flavor; this small percentage is about the same as in today's imported oils. However, the above-described process possesses one advantage in that the oil will extract, from the juice, certain as yet unidentified flavoring substances, which give the oil a more delicate and richer flavor, genuinely recalling that of the fruit consumed in the United States, either in fresh fruit or juice form. The imported, and especially the Italian, oils have a more characteristic and sharper peel character, due largely to their higher content of citral, and other aldehydes and oxygenated compounds in general.

As has been pointed out, the old process just described has been largely superseded by more efficient methods which give a much better yield of oil and, incidentally, oils of better quality, containing a lesser percentage of waxes and a higher percentage of oxygenated constituents.

The old process, applied to oranges as well as lemons, was comparatively simple. It yielded large quantities of oil at relatively low cost. The juice remaining after the removal of the oil could be pasteurized and canned, or concentrated and canned; in the case of lemons it could be used for the making of citric acid. The crushed, residual peels served for the preparation of cattle feed and molasses. However, the old process suffered from several drawbacks. The yield of oil was usually low, since much of the oil, after pressing of the whole fruit, was absorbed by the spongy albedo from which it could no longer be recovered except by steam distillation, which yields an oil of inferior quality. Then too, the dispersion of small quantities of oil in the large volume of juice, even for a very short time, had a deleterious effect upon the quality of the oil, as well as of the juice. The juice dissolved some of the more water soluble constituents of the oil (aldehydes such as citral, alcohols, etc.) which are the most important and characteristic odor and flavor constituents of the citrus peel oils. Thus, citrus oils recovered by this process were usually somewhat low in aldehyde

content. On the other hand, the juice retained some of the essential oil, or at least certain constituents of it, and this retention has been found to be one of the main causes of the flavor spoilage of canned juice, particularly by oxidation of terpenes.[1] The juices, therefore, had to be most carefully de-oiled, also de-aerated, by vacuum distillation at 160° F. for 1½ to 2 min. Today, one of the fundamental rules in the canning of citrus juice is to keep the juice and oil entirely separate during the whole process of expressing juice and oil from the fruit. If this is done, the quality of both juice and oil will be greatly improved.

As has been said, the quantities of canned juice produced annually, prior to World War II, were limited at least in California; hence, the principle described above was largely neglected. In Florida, however, conditions were different because that state for many years has had a more or less prosperous canning industry, which has always strived toward improvement of quality in order to make canned juices more popular with the consuming public. It must not be forgotten that California oranges are excellent table fruit, whereas the Florida oranges lend themselves better to the expression of juice. Thus, Florida has developed a much more imporant canning industry than California,[2] and has sought constantly to increase the sale and appeal of juices by improvement of their quality. During the 1947–1948 season almost 50 million boxes of oranges, grapefruit, and tangerines were processed commercially in Florida for the canning of citrus juices (including concentrated juices) and citrus segments.

World War II accomplished another step in this direction. The demand for canned citrus juices on the part of the armed forces and lend-lease was enormous; and much money was spent on new, modern equipment and on research toward perfection of quality. The mechanical improvement effected may be attributed to three main factors: the introduction of modern equipment in general; the above-described elimination of any contact between essential oil and fruit juices during the actual process of expressing the fruit; and the introduction of flash pasteurization, which reduces the period of "cooking" of the juice to a minimum of time. Of late it has been found that rapidity of cooling is an equally important factor in the preparation of high quality juices. In modern operation, therefore, the juices are sterilized by heating to 240° F. for one second only, cooled immediately to 160°–170° F., and are then canned and again cooled to 80°–100° F. within

[1] Studying the disappearance of dissolved oxygen in canned orange juice, Henry and Clifcorn [*Canning Trade* **70**, No. 31 (1948), 7, 22. *Chem. Abstracts* **42** (1948), 2365] recently observed that *d*-limonene was associated with the flavor deterioration of the juice.

[2] California processes only 25–30% of its orange crop for juice and other by-products, *New York Times*, Nov. 2, 1947.

30 sec.[3] As a result of this entire development, canned citrus juices today are, if not perfect, at least greatly improved, and indeed approach the flavor of freshly pressed juices to such a degree that the general public is more willing than in the past to substitute canned juices for fresh juices. Consumption has been increased rapidly, and the entire citrus canning industry has lately undergone fundamental changes as regards methods of production. Old equipment and antiquated processes have been discarded; and the latest discoveries of chemistry and engineering have been applied.

It is not our intention to describe details pertaining to canning of juices, or to the extraction of by-products, such as citric acid, pectins, cattle feed, and molasses which a modern cannery must recover to operate on a competitive basis. We shall deal here exclusively with the expression of essential oils which, as explained above, are at present extracted in such a way that there is as little contact as possible between oil and juice. Let us thus describe briefly the working principles of the most popular machines and processes now used for this purpose in California and Florida. As has been pointed out, the industry is in a state of flux, new apparatus and processes being introduced constantly. As the citrus juice canning industry expands its activities into Mexico and other parts of Latin America, it can be expected that the quality of the citrus oils, and particularly of lime oil, produced in those countries will also be favorably affected. For all these reasons it is also very difficult, if not impossible, today to establish definite standards for the physicochemical properties of the citrus oils recovered in North and South America. Sufficient data on the properties of the oils made in these new machines are not readily available, and old-established standards may have to be revised from time to time and in the light of the latest developments.

Treatment of the Fruit Prior to Extraction of Juice and Oil.—Prior to the extraction of juice and oil, the fruit, after arrival in the packing houses, must be thoroughly washed, to remove soot, dirt, insects, and other foreign matter which would contaminate the juice during expression. For this purpose the fruit is first conveyed to large soaking tanks containing such detergents as inexpensive soap powder, quaternary ammonium compounds, trisodium phosphate, or sodium bicarbonate, and then sent through a washing machine equipped with scrubbing brushes. Instead of soaps or other surface reducing agents, some of the California packing houses use sodium hypochlorite solutions. Often, the washing (with soap, etc.) is carried out with hot water, almost steaming; this procedure obviously removes not only the dirt most efficiently, but also the protecting coat of natural waxes on the peel and a part of the essential oil embedded in the oil glands beneath

[3] In most canneries the juice is heated rapidly to 195°–205° F., canned at that temperature, and then cooled to 90° F. as rapidly as possible.

the wax coating. That some essential oil is lost by evaporation at least seems apparent from the odor emitted from these hot water tanks. The washed fruit then runs along a conveyer belt, to be carefully graded and inspected. After elimination of all rots, it finally reaches the juice presses.

It should be mentioned here that in the canneries on United States territory, the fruit is most strictly controlled. Government inspectors are on guard everywhere and see to it that no inferior fruit reaches the juice presses. Only sound fruit can be processed. The same strict control applies also to the packing houses of edible fruit for shipment. For this reason, aside from other factors, the juice extracted in our canneries is of prime quality, and the same holds true of the essential oils which today are mainly a by-product of canning operations.

One of the most important problems in the preparation of a good canned juice, possessing a natural flavor which will last during shelf life, and not spoil, is the elimination of all essential oil, which, by improper operation of the juice extraction process, might have gotten into the juice. Some types of juice extractors are in this respect much more efficient than others. To prevent any seepage of oil into the juice during expression of the juice from the fruit, some canners, i.e., those who are not interested in the recovery of the essential oil and simply discard it, submit the whole fruit, prior to expression, to a steam bath or a bath of hot water for a period of 30–60 sec., or in some cases for a longer period. What actually happens during this "steaming" does not seem quite clear. Some canners claim that by this process the essential oil is "sealed up" in the oil glands, others believe that a part of the essential oil simply will be vaporized and eliminated. Whatever the actual cause may be, juice from fruit thus treated contains less essential oil, and to a certain degree this applies also to peel similarly treated. At any rate it is very difficult to recover the oil by expression of steamed peel.

As a further precaution against the presence of essential oil in canned juice, the juice, after expression from the peel, is "de-oiled" in a continuous distillation process by flashing it in a de-oiler, operated under a vacuum ranging from 11 in. (190° F.) to 25.5 in. (130° F.). This process yields considerable quantities of distilled citrus oils which are of relatively good quality. Lately very novel and efficient juice presses have been introduced which eliminate any contact of juice with oil during the extraction process and, therefore, yield juices containing no trace of oil. Since de-oiling of the juice has become unnecessary with these machines, they are being increasingly applied in the canning industry.

Before concluding this section, it should be pointed out that much of the orchard fruit, although absolutely sound, is of inferior appearance, the skin being of a greenish color instead of a bright yellow or orange. This applies

to all oranges grown in the lower altitudes of tropical or very warm countries. As Camp [4] explains, such fruit contains the natural yellow in the rind; but the yellow is masked by an intense green color and does not dominate as a color until some cold weather has occurred. In Florida, for example, the fruit of some orange varieties becomes edible before there has been sufficient cold to eliminate the green. It has been found that treatment of green oranges with ethylene gas bleaches out the green color and the fruit shows as yellow. Therefore, the fruit, after arrival in the packing house, is stacked in the coloring or "de-greening" room, held there for 24–70 hr. at a temperature of about 85° F. and at a humidity of about 85 per cent. During that period ethylene gas is added in very low concentration. In some cases, however, the ethylene treatment does not suffice to bring out the natural orange color, and then the greenish fruit will have to be colored artificially. As a rule, fresh fruit packing houses hesitate to follow this latter procedure because by U. S. Government ruling fruit thus treated must bear a stamp "color added," and the public somewhat resents fruit thus labeled. The artificial coloring is carried out in the packing houses after washing of the fruit and prior to shipping. There are several methods, the details of which are irrelevant here. The fruit either passes through a bath consisting of an emulsion, or the dyes are administered with brushes, or the dye is sprayed on the fruit. For coloring purposes only certified food dyes may be used—for example, F. D. & C. Orange #2, or Orange SS, Red #32, and Oil Red XO. In general, it can be said that due to coloring of the fruit Florida oranges contain added colors more frequently than the California fruit, the latter possessing a much better natural color, due to the colder climate of California.

As far as the natural waxes of citrus fruit are concerned, they appear to offer some form of protection against loss of moisture. California fruit, for example, contains more natural wax than Florida fruit because of the drier climate in California. Now, all fruit, prior to packing, has to be washed thoroughly in soap solutions to remove soot, dust, earth, spray residue, scale, mold fungus, etc. In the course of this washing process a considerable amount of the natural waxes will be removed and must be replaced by the addition of synthetic wax coatings, to maintain the fruit in good condition. As Camp [5] pointed out, the function of these waxes is to increase the polish of the fruit and to reduce the amount of moisture lost in the period between packing and consumption of the fruit. Since about 80 per cent of the California orange crop goes to the fresh fruit market, most of the oranges in California are waxed prior to grading. The bulk of grapefruit is not waxed since total production in Texas, Florida, and California by far exceeds

[4] "Citrus Industry of Florida," *Florida State Dept. Agr.*, Tallahassee, Florida (1947), 145.
[5] *Ibid.*, 154.

consumption as fresh fruit, and much of the grapefruit crop is therefore converted into canned juice. As regards lemons: tree-ripened fruit does not withstand shipping very well, for which reason the fruit is picked green and cured in storage at a certain temperature and humidity until it can be shipped. Approximately half of the lemon crop is waxed for shipment as fresh fruit; the other half not waxed serves for processing purposes.

There exist on the market three principal types of wax mixture employed by the packing houses for the waxing of fresh citrus fruit:

Type I.—The so-called slab waxes, i.e., solid wax mixtures which are melted and mechanically brushed on the washed and warmed fruit. This process is most popular in California.

Type II.—The so-called liquid waxes, i.e., solutions of wax mixtures in low boiling petroleum solvents (such as used for dry-cleaning) which are sprayed on the washed fruit, the solvent then evaporating.

Type III.—The so-called liquid water-waxes, i.e., viscous wax mixtures which, on addition of water, form aqueous emulsions through which the fruit is conveyed. Emulsifying agents in this case are ordinary soaps, triethanolamine compounds, sulfonated higher fatty alcohols, and other surface reducing agents. An addition of as little as 0.1 per cent of these agents may be sufficient to create a satisfactory emulsion of the waxes in water.

The wax mixtures themselves consist usually of about 75 per cent of paraffin waxes and 25 per cent of polishing waxes. The former serve to render the peel of the fruit impermeable and to retain the natural moisture in the fruit. The polishing waxes (soluble on melting in paraffin waxes) give a smooth shine to the peel. Such waxes are carnauba, candelilla, tropical leaf waxes in general, beeswax, spermaceti; synthetic waxes made by various petroleum companies; synthetic resins (soluble in paraffin) which produce shine and polish; traces of shellac, etc.

One average orange, weighing approximately 200 g., is coated with about 0.02 g. of artificial wax. One U. S. ton of oranges (22 boxes) contains on the average 4,400 oranges, which would require about 88 g. of added wax. Calculating a yield of 5 lb. of coldpressed oil per ton of oranges, these 5 lb. of oil could therefore contain, at the most, 88 g. of artificial wax, provided the artificial waxes are completely and readily soluble in the essential oil. Fortunately, however, this is by no means the case; as a matter of fact most of the components used in the above-described artificial wax mixtures are only sparingly soluble in citrus oils; and it would appear that an oil properly dewaxed by storage at low temperature, clarifying, etc., would contain very little, if any, of these waxes. Due to the presence of emulsifying agents, the so-called "liquid water-waxes" (Type III) seem to

be taken up more easily by the essential oil, and traces of the coating may get into the oil on expression of the peel.

As has been pointed out, not all of the citrus crop goes to the fresh fruit packing houses to be waxed prior to shipping. In Florida, for example, more than 50 per cent of the orange harvest is hauled directly to the juice canneries, without being handled by the fresh fruit packing houses. In the very large canneries operating their own citrus groves, this percentage may be much higher than 50 per cent. As a matter of fact, modern canneries, intent on the production of high quality citrus oils, are careful to employ, for the recovery of citrus oil, only fruit taken directly from the orchards. Such "grove run" fruit obviously is not waxed. However, the fresh fruit packing houses always reject a certain quantity of "juice quality fruit" from the edible fruit pack, after it has been waxed and colored. It is for this reason that the analyst of an oil expressed from waxed fruit will occasionally be confronted with the presence of traces of strange waxes and colors which seem puzzling to him. When concentrating such lots of citrus oils for the preparation of terpeneless and sesquiterpeneless oils, the manufacturer may run into unexpected difficulties, due to the formation of heavy residues and disturbing emulsions.

It should also be mentioned here that the waxing of citrus fruit adds to the mechanical difficulties connected with the process of expressing the oil as the wax coating seems to seal up the oil in the glands.

Before discussing in more detail the highly efficient machines by which citrus peel oils are extracted today in the United States, we should briefly describe the various products which North American canneries extract from citrus fruit.

Juice Products.—The production of regular canned citrus juice, or partly concentrated and canned juice, or fully concentrated juice (concentrated *in vacuo* to about $\frac{1}{7}$ to $\frac{1}{8}$ of its original volume) has reached very large proportions in Florida, California, Texas, and Arizona. The original difficulties resulting from the changes which take place in the juice after removal from the fruit (through living organisms, enzymes, oxidation, and the presence of essential oil) have now been practically overcome, thanks to intensive research work on the part of biochemists, bacteriologists, and engineers. New methods of canning (flash pasteurization, etc.) and modern equipment have been introduced.

Concentrated orange juices and some concentrated lemon juices are both used quite extensively against scurvy in semimedicinal mixtures, designed to insure adequate dosages of the various vitamins in our daily diet. The concentrated juices serve not only to furnish vitamin C in ample quantities, but also to supply valuable mineral salts which insure proper alkalinization of the blood.

Canned Fruit Segments.—Details regarding the canning of grapefruit segments will be found in the section on "Oil of Grapefruit."

Essential Oils.—Essential oils extracted from citrus peel have attained great importance in the flavoring of all kinds of beverages, confectioneries, and baked goods. They are used also in perfumes, cosmetics, and for the scenting of soaps.

Citric Acid.—This, the first citrus by-product to be firmly established in California, has been produced there uninterruptedly since 1916. The basic process employed in its recovery is the classical Schiele method of precipitating citric acid as calcium citrate and decomposing the citrate with sulfuric acid. The principal basic material for the preparation of citric acid is lemon juice.

Pectins, Cattle Feed, and Molasses.—The residual pulp of citrus fruit, remaining after the extraction of juice, essential oil and citric acid, retains a good percentage of digestible nutrients. Hence, very large quantities of citrus pulp are used nowadays for the extraction of these nutrients. After removal of the essential oil, the waste peel is soaked in a hot solution of lime, and the pectins are gelatinized. The use of pectins in many kinds of food products, jellies, and in the cosmetic and pharmaceutical industries requires no further explanation. After isolation of the pectins, the pulp is submitted to high pressure between heavy cylinders to express the water. The peel is then comminuted, dehydrated, filled in sacks, and sold as cattle feed. The aqueous liquid, which contains a few per cent of sugar, is pumped into large evaporators and concentrated for molasses. During this process, that part of the essential oil which has remained in the peel after coldpressing is recovered by distillation in some canneries, but this oil has a very harsh off-odor and cannot be used for flavor work. However, it may serve for technical purposes, as a thinner in paints and lacquers, for example, replacing oil of turpentine. Large quantities of this type of distilled oil are produced, especially in Florida. The product, also referred to as "stripper oil," often consists of a mixture of distilled orange and grapefruit oils.

Description of American Citrus Juice and Oil Extraction Equipment.—The machines used today in North America (California, Florida, Texas, Arizona, etc.) for the recovery of citrus juice and essential oil are based upon the application of several principles. In most types the fruit is halved, the juice pressed out or reamed out, and the residual peel submitted to high pressure. In at least one type of machine the whole fruit passes over a grater surface where the oil glands are opened, and the freed oil is carried away in a spray of water. Other types of machines use other principles for juice and oil recovery, the most novel type being the F.M.C. Whole Fruit Extractor. All of these machines will now be described in more detail.

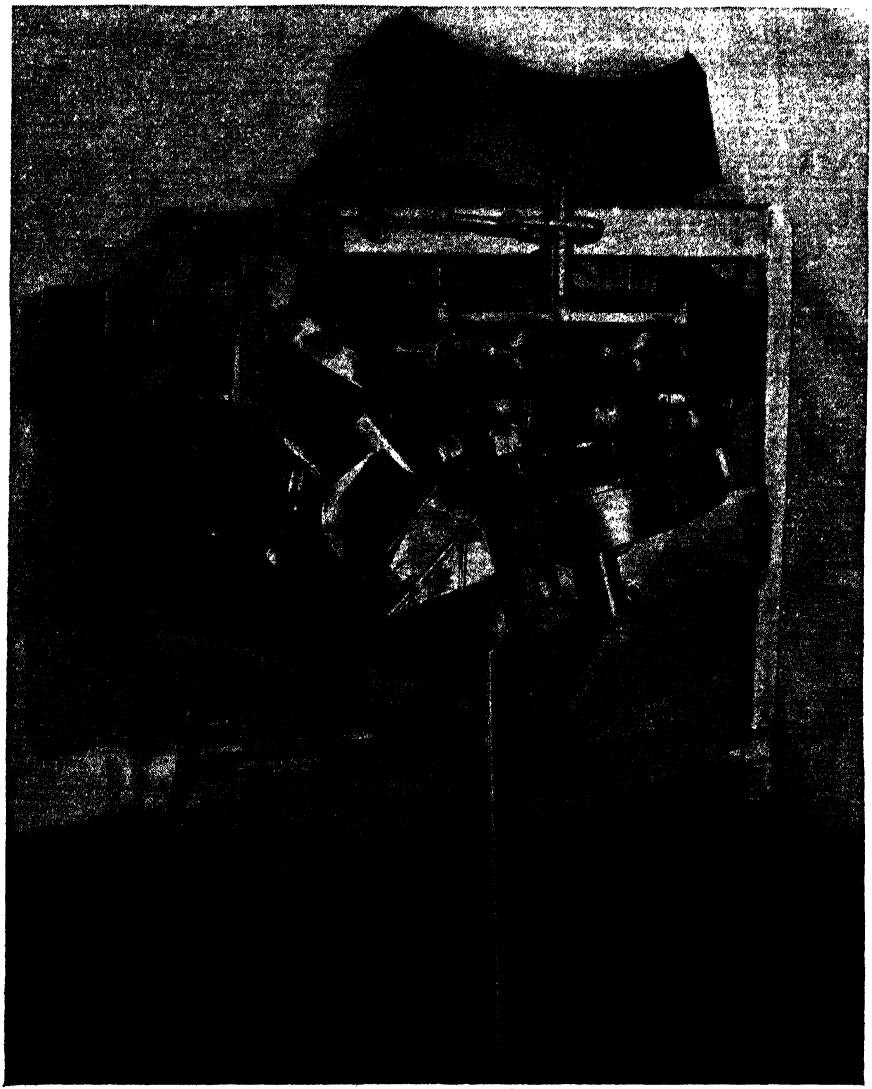
Concerning the yield of oil as obtained by coldpressing, it may be said that this depends on several factors—the variety, maturity, and condition of the fruit, for example, as well as the process of expressing the oil. One may employ several methods of treatment and obtain a yield of, say, ½ or 1 lb. of oil per ton of fruit; or, by varying the treatment, one may obtain a yield of 7 or 8 lb. of oil per ton. Treatment must be varied according to the condition and maturity of the fruit, and there exists no general formula which can be given with any degree of accuracy on this point. In the ordinary course of operation, one would obtain all the coldpressed oil possible from a given batch of fruit, and then distill the residual pulp to recover the remainder of the oil.

The Brown Automatic Citrus Fruit Juice Extractor.—The main objective in the designing of the Brown Automatic Citrus Fruit Juice Extractor [6] was to recover all the juice from oranges, lemons, and grapefruit, and to obtain a juice as free from oil as possible, all the oil to be retained in the peel. This juice extractor, constructed by the Brown Citrus Machinery Corporation, Whittier, California, employs rotating reamers or burrs which push into the halved fruit. The machines are constructed largely of stainless steel and bronze, with a high content (about 28 per cent) of nickel. A battery of Brown Automatic Citrus Fruit Juice Extractors consists of several units, the reamers of each unit being adjusted to the size of the halved fruit.

After being thoroughly cleansed by washing and rinsing, the fruit is conveyed on a belt to automatic sizers, which drop the smallest fruit into the hopper of the first juice extractor, fruit of next size into the second extractor, and so on, until all the fruit has been sized and fed into the proper juice extractor. In the hopper of each unit the fruit is taken up by cups mounted on an endless chain, each cup carrying one fruit. The cup chain carries the fruit through a stationary knife, halving the fruit and depositing each half, inverted, into a rubber cup on the right and left side of the machine. Each side of the machine has seven revolving burrs or reamers mounted on a revolving bowl. The unit carrying the rubber cups revolves with the cups directly above the burrs on the revolving bowl, but on a different plane, thus allowing the burrs to enter the cups on only a part of the revolution.

On entering the fruit to a certain depth, the reamers express the juice and some of the pulp, leaving all the oil in the peel and the juice free from oil. The reaming operation is adjustable to the extent that each side of the machine can be set by means of an adjusting screw, raising or lowering the

[6] The author is greatly obliged to Mrs. E. A. Silzle of the E. A. Silzle Corp., Anaheim, California, and to Mr. H. A. Zullig, Chief Chemist of Southern California Citrus Foods, Redlands, California, for information regarding this machine.



Courtesy of Brown Citrus Machinery Corporation, Whittier, California.

Brown automatic citrus fruit juice extractor.

rubbers on the burrs and allowing the burrs to drill to whatever depth the operator desires. The action of the revolving burr as it enters the fruit is very gentle, a special type of burr being used. The machine is closely synchronized.

Each unit will handle about 300 average sized oranges or lemons per minute, which means about 3¼ tons of oranges and 2¼ tons of lemons per hour, provided the machine runs at full capacity.

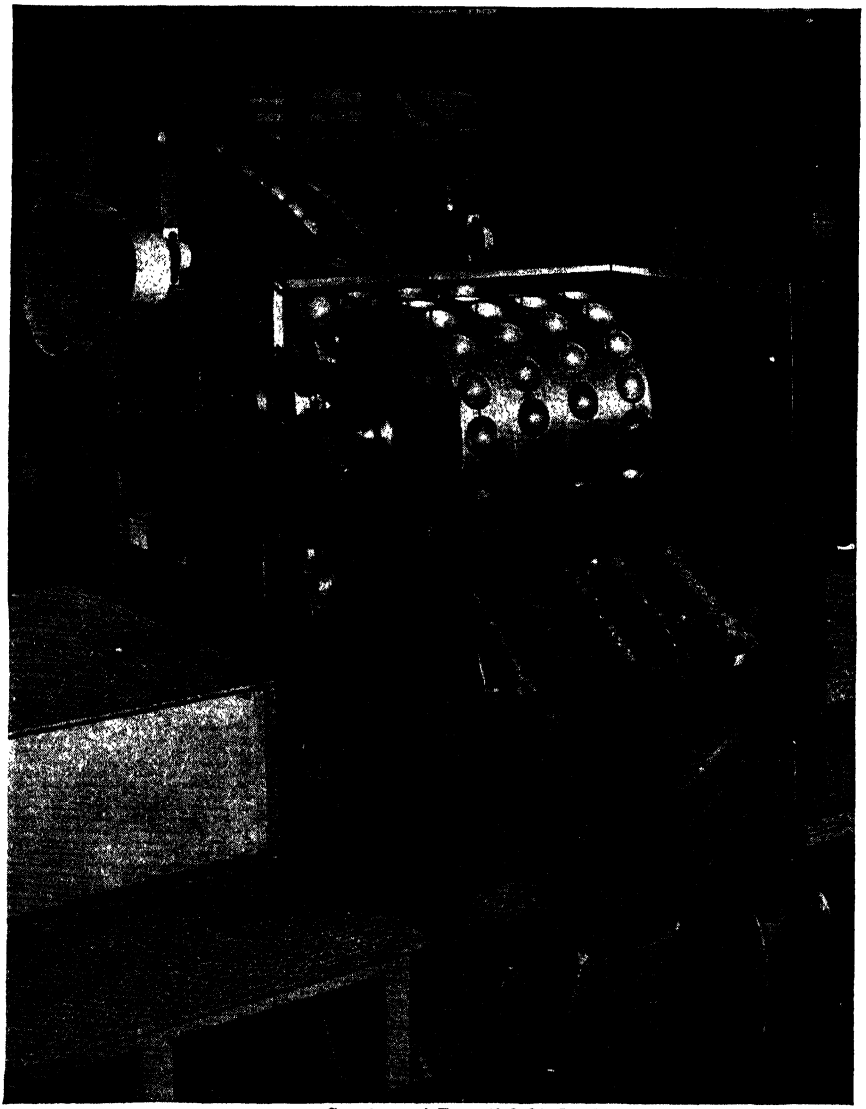
In order to remove seeds and excessive pulp, the juice is forced through a rotating finisher and then flows by gravity to stainless steel measuring tanks. From there the juice is directed either to the juice canning line or to the evaporators.

The peel, on the other hand, goes on a conveyer belt to the oil extraction room, where it is expressed in any type of citrus peel press (the tapered screw or Expeller type, for example).

The Brown Automatic Citrus Fruit Juice Extractor offers the advantage that it processes any type of fruit, including green and very ripe fruit. The juice contains relatively little essential oil, but nevertheless has to be de-oiled and de-aerated prior to canning. In 1947 there were about 50 of these machines in use.

The Rotary Juice Extractor.—The Rotary Juice Extractor [7] constructed by Juice Industries, Inc., Dunedin, Florida, is perhaps the most popular machine for the expression of juice from oranges, grapefruit, limes, etc. This machine consists of two horizontal, heavy, silicon-aluminum alloy cylinders making 10–18 rpm. The number of revolutions is governed by the amount of fruit to be processed. If there is an excess of one size of fruit, the press appropriate to that size must be speeded up to take care of it. Optimum juice recovery, however, takes place at the lower speeds. The lower cylinder is provided with protruding spherical knobs which, on rotation of the system, enter into a corresponding equal number of spherical cups or receptacles inserted in the upper cylinder. The fruit, after having been washed, is first automatically assorted according to size, and enters the Rotary Juice Extractor, where it is cut into halves by a sharp knife. The halves then pass between the two cylinders, held in the cups of the upper cylinder, while the protruding knobs of the other cylinder push into the halved fruit and remove the juice by pressing. It is a simple method of displacement, such as takes place when one pushes a fist into a glass filled with water. Since the smooth cup holding the halved fruit fully supports the thin membranes of the oil sacs in the flavedo during the expulsion of the juice, very little, if any, oil is projected into the juice.

[7] The author is greatly indebted to Mr. J. J. R. Bristow, Dunedin, Florida, for information regarding this machine.



Courtesy of Essential Oil Producers Inc., Dunedin, Florida.

Rotary juice extractor. This machine is used, particularly in Florida, for the expression of citrus fruit juices.

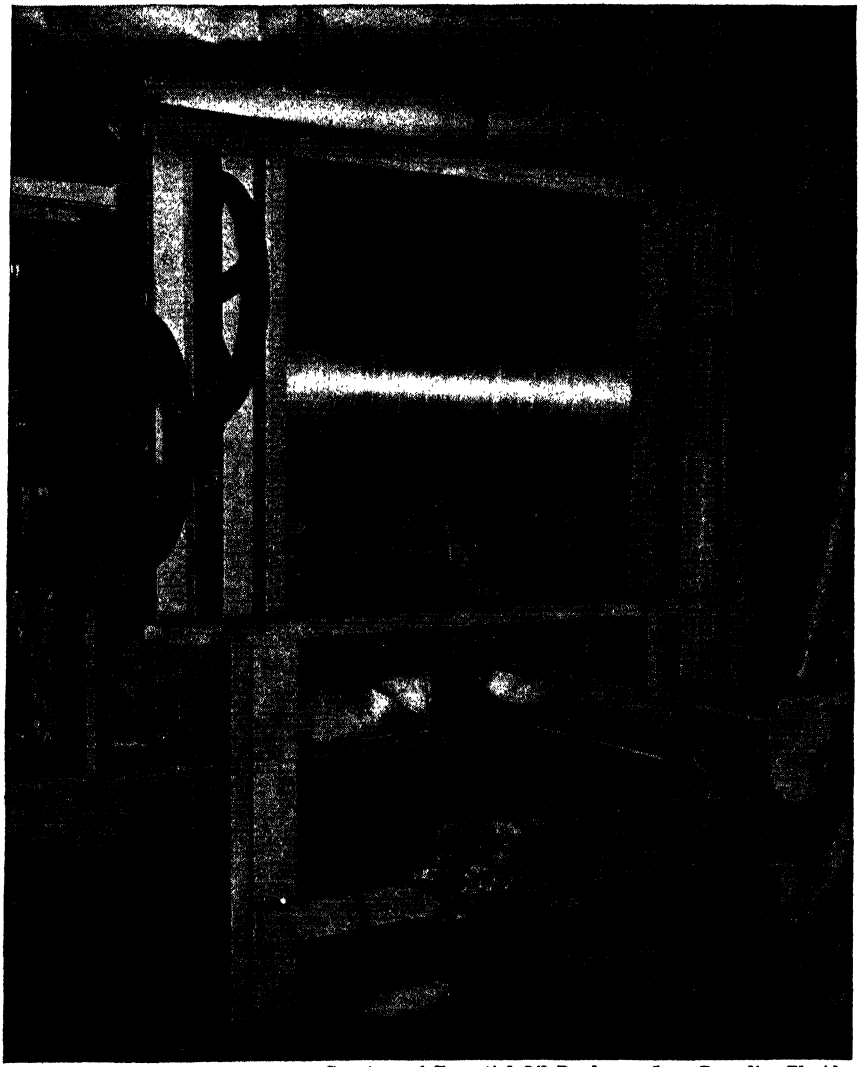
The machine is of very solid construction, simple to operate, and once adjusted requires very little servicing. Its capacity depends upon the size of the fruit. A battery of Rotary Juice Extractors consists of a number of individual machines, each adjusted to a certain size of fruit. The capacity of each unit, if kept full of fruit, is about 15 tons per hour, of oranges, grapefruit, or limes. Obviously, when operating at full speed, it will be almost impossible to keep any one machine operating at full capacity, because of the fact that the fruit runs in different sizes and the sizing has to be most carefully manipulated to prevent seepage of peel oil into the juice. If the fruit has been carefully sized, the juice will contain practically no essential oil and does not have to be de-oiled. A great many excess machines must thus be carried in the line so that the average fruit going through the total installation will yield the required amount of juice. The Rotary Juice Presses are constructed in eleven sizes, handling fruit from the smallest lime to the largest grapefruit. There will, of course, be more fruit receptacles on the presses handling the small sizes than on the ones handling large fruit. It is the larger number of receptacles on the cylinders that permits the machine to produce approximately the same amount of juice from small fruit as from large fruit.

Because of its many advantages, the Rotary Juice Extractor has become very popular, especially in Florida where in 1947 about 350 machines were in operation. Texas then had 30–40, and California 20–25 of these machines.

The Pipkin Peel Oil Press.[8]—This machine, constructed by Essential Oil Producers, Inc., Dunedin, Florida, is eminently suitable for expressing the essential oil from the residual, halved peel after removal of the juice (by the Rotary Juice Extractor, for example). As a matter of fact, the Pipkin Peel Oil Press attains its highest efficiency if operated in conjunction with the Rotary Juice Extractor.

Made of stainless steel, the Pipkin Peel Oil Press is a solid piece of machinery, ingeniously designed in its simplicity. It consists of two closely set, slowly rotating (5 rpm), very heavy, stainless steel cylinders provided with capillary grooves which run around the circumference of the cylinders and are sufficiently deep to receive the oil from the punctured cells and keep it out of contact with the crushed peel as the drums revolve. Under the high pressure (about 200 lb. per sq. in.) of the cylinders, which can be adjusted to the type of peel being processed, the oil glands of the flavedo are ruptured, the oil is ejected and runs off the cylinder through the capillary grooves, which prevent most of the oil from being re-absorbed by the sponge-like albedo of the crushed peel. No spray of water is required to

[8] *Ibid.*



Courtesy of Essential Oil Producers Inc., Dunedin, Florida.

Pipkin peel oil press. This machine is used, particularly in Florida, for the expression of citrus oils from the peel after the juice has been expressed from the halved fruit.

wash away the oil from the grooves, the aqueous cell liquid expressed from the peel and the very small quantities of juice adhering to the peel being sufficient to act as a carrier medium for the oil. This feature represents a great advantage over oil presses which require a spray of water (often in large quantities) to carry the oil away. As has been pointed out repeatedly, the oxygenated, and incidentally, the most important, flavoring constituents of the citrus oils are more water soluble than the (less important) terpenes and, therefore, will be lacking in the final essential oil if it has been in contact with too much water.

The emulsion of cell liquid and essential oil is then screened to remove solid particles, such as cell detritus, and finally separated in high-speed centrifuges.

The per hour capacity of the Pipkin Peel Oil Press is high. No assorting of the peel according to size being necessary, the machine can be kept operating at full capacity all the time. Each unit handles per hour the peel of about 7 tons of fruit.

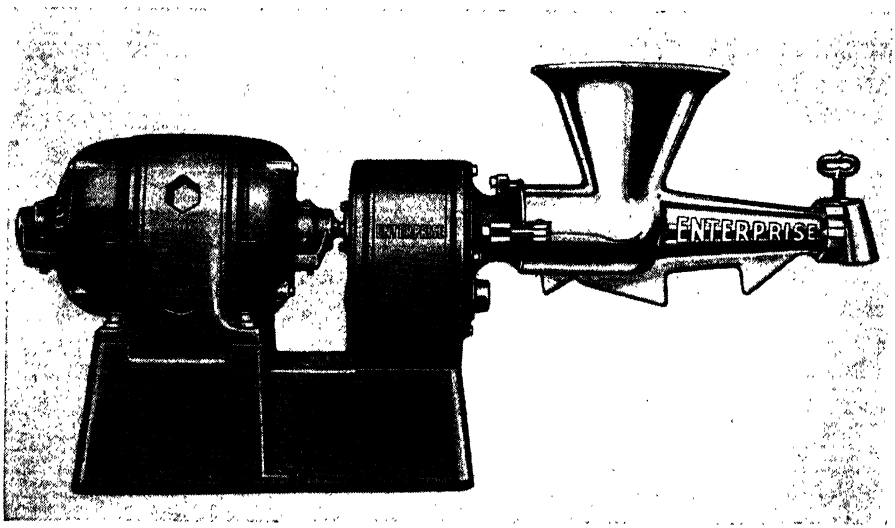
The yield of orange oil per ton of fruit obtained in Florida by the Pipkin Peel Oil Press varies from 3 to 4 lb., depending greatly, of course, upon the type of fruit processed, and upon the time of the season. Perhaps the yield would be higher (up to 6 lb.) with California oranges, which seem to contain more oil than Florida fruit.

In 1947 there were about 20 of these presses operating in Florida and none in California.

Like most machines used at present in Florida and California for the expression of citrus oils, the Pipkin Peel Oil Press has occasionally been criticized for giving a relatively low yield of oil, some of which seems to be absorbed and retained by the spongy albedo of the crushed peel, despite the action of the capillary grooves. Whatever may be the truth, it appears certain that in the case of grapefruit peel the Pipkin Peel Oil Press yields considerably more oil (up to 1.8 lb.) per ton of fruit than the tapered screw presses (1.2 lb.) because the oil glands of the grapefruit peel are buried much deeper in the peel than those of other citrus fruit, and the very thick layer of albedo in the grapefruit peel acts so much like a sponge that not even the strongest pressure can extract all the oil from the peel.

Oil Presses of the Tapered Screw (Expeller) Type.—This type of oil (and juice) press has in the past been quite popular, due to general adaptability and simplicity of construction, and is still being used widely in the United States, Mexico, and the West Indies. It represents the popular type of press adapted to the processing of all kinds of fruit, berries, etc., for the expression of the juices. By modifying the pressure, these machines can also be employed for the expression of essential oil from citrus peel only, after the juice has been removed from the fruit, by reaming, for example.

One unit consists simply of a horizontal tapered screw of the expeller type (with a progressively shallow depth of thread) fit snugly and turning within a tapered solid stainless steel, monel, or heavily tinned casing provided at the bottom with a strainer and slit through which the expressed fluid flows off, while the exhausted peel is expelled from a relatively small orifice at the end of the horizontally mounted casing. As the fruit or peel travels along its path between the tapered screw and cone-shaped casing, the pres-



Courtesy of the Enterprise Mfg. Co., Philadelphia, Pennsylvania.

Tapered screw press.

sure increases tremendously through the progressively diminishing area and attains its maximum just before the expeller nozzle. Several units can be attached to one shaft, the latter being driven by one powerful motor.

For example, the Enterprise Manufacturing Company of Pennsylvania, in Philadelphia, markets a motor-driven machine (model 958) and a pulley-driven one (model 58), which require a 2–3 h.p. motor and can process one box of oranges (90 lb.) in about 5 min. The size of these machines and the speed of their operation obviously determine their working capacity. Some of the tapered screw presses employed in Florida process about 3 tons of fruit peel per hour.

The P. & L. Welding Machine Works in Anaheim, California, have constructed a press consisting of two screw units, powered by one 10 h.p. motor. Each screw, 24 in. in length, is capable of handling 2 tons of fruit per hour, with an average recovery of about 60 per cent of the oil present in the peel.

The great advantage of these machines consists in the fact that they

process any type of fruit or peel, assorting according to size being unnecessary.

If whole citrus fruit is expressed in these tapered screw presses, the effluent will consist of an emulsion of juice, essential oil, and cell detritus. After removal of the solid particles by screening, the thin emulsion of juice and essential oil is centrifuged and separated into juice and oil. Such juice has to be de-oiled and de-aerated most thoroughly and carefully, as the large quantities of juice have a tendency to retain some of the oxygenated and more soluble constituents of the essential oil. On the other hand, oil obtained by this process will be deficient in the same constituents. For this reason the process of crushing and expressing whole fruit for juice and oil has lately been abandoned almost completely.

If only peel is processed in these tapered screw presses, after the juice has been expressed in other machines (by reaming in Brown Automatic Citrus Fruit Juice Extractors, for example), the quality of the oil and its yield will be substantially improved. However, the actual yield (3–4 lb. of oil per ton of oranges in Florida) will remain below the theoretical level, because the processing of the peel in the tapered screw presses brings about a mechanical disintegration, a breaking up and milling of the flavedo (containing the oil glands) with the very spongy albedo of the peel, which absorbs the oil after it has been expelled from the oil glands. For this reason the mass in the screw presses must be washed by a continuous spray of water to carry away the oil as rapidly as possible. Large quantities of carrier water may thus have to be used, in which event a good deal of the oil, and especially its oxygenated constituents, will be lost in the wash water. Water and oil, after removal of pulp and cell detritus by screening in a finisher, are finally separated by high-speed centrifuging, the first centrifuge (sludger) operating at 6,000 to 8,000 rpm and yielding an emulsion with a 70 per cent oil content. The second or "clarifying" centrifuge (polisher) operates at a bolt speed of 16,000 to 18,000 rpm. Approximately 0.1 per cent of oil remaining in the discharge water from the centrifuge can be recovered by distillation.

The problem resulting from absorption of the expressed essential oil by the sponge-like albedo is especially annoying in the case of grapefruit, which possesses a very thick albedo. Tapered screw presses are, therefore, not very well suited for the processing of grapefruit peel, although they give quite satisfactory results with thin-skinned limes and even tangerines.

The Oil Recovery Process of the Mission Dry Corporation.[9]—A machine employing the principle of the screw press, but in an improved form, operates as follows:

[9] The author is greatly indebted to Miss S. Blangsted, Chief Chemist, and to Mr. G. Bowen, Process Engineer, of that company for information regarding this process.

The juice has first to be expressed from the fruit, for which purpose any of the established processes may serve—extraction by reaming, for example. The residual halved peel passes through an "eliminator" tank, essentially a water-filled trough in which heavy contaminating objects separate from the peel before they can damage subsequent equipment; from this tank the cleaned peel goes to the oil presses, which were designed by the Mission Dry Corporation, Los Angeles, California, for the recovery of the essential oil from citrus peel. These oil presses are mounted vertically, with the motor drive and peel entry at the top. A pulsating pressure, provided by a varied pitch screw, forces a thin layer of peel between the central perforated hollow cone-shaped core of the machine and the outer wall, which consists of screened windows. The outer and inner surfaces of the machine are continuously washed with sprays of water, which float away the expressed oil. By pressing only a thin layer of peel, the absorption of oil by the spongy peel albedo can be held to a minimum. Breaker strips maintain the pressure and a continuous flow through the machine from top to bottom. The pressed peel is extruded through adjustable gates into a screw-type conveyer. The effluent, containing considerable solid material, then passes through a standard "pulper" and thence to continuous Sharples nozzle-jector separators, where the oil is removed as a heavy emulsion. This emulsion finally has to be broken down and clarified by Sharples Super-Centrifuges.

It is most important during operation to keep the oil machines full of peel, to adjust the water sprays for maximum oil recovery, and to adjust the peel extrusion gates for maximum pressing without damage to the screens in the outer wall of the machines. These screens are cleaned periodically to prevent clogging and are shielded by removable formed plates. Flow rates are so adjusted as to maintain continuous operation of the separators.

The working capacity of the oil press is 5 tons of peel per hour.

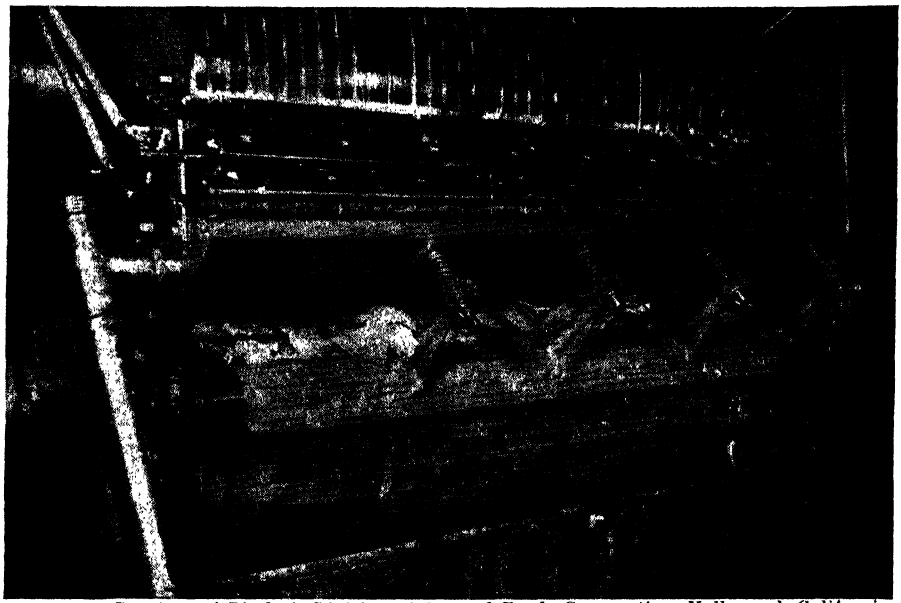
The percentage of oil removed by expression may be estimated as about 85 per cent for lemons, 50 per cent for Valencia oranges, and only 25 per cent for Navel oranges.

The average over-all yields of oil per ton of California whole fruit have been:

Lemons: 6 lb. of oil
Valencia oranges: 4–5 lb. of oil
Navel oranges: 1.0–1.5 lb. of oil

Interesting to note is the relatively low yield of oil from Navel oranges, due probably to the thicker peel of this type of orange.

The Citro-Mat Juice Extractor.—Another machine serving for the expression of citrus juices and for the extraction of the oils from the peel is the Citro-Mat Juice Extractor, patented and constructed exclusively by the Bireley's Division of General Foods Corporation, Hollywood, California.[10] The main feature of this all stainless steel machine consists in the close shaving of the flavedo (which contains the oil glands) from the albedo



Courtesy of Bireley's Division of General Foods Corporation, Hollywood, California.

Citro-Mat.

and the rest of the peel, after the juice has been removed from the halved fruit by expression. The Citro-Mat operates as follows:

The washed and cleaned fruit travels into the first part of the machine, which automatically halves it and expresses the juice by increasing the pressure upon the halved fruit. This is readily achieved by decreasing the distance between a strong grid and one of the large drums. To state it more clearly, the whole fruit is not simply crushed between two large rollers (as might appear from some pictures), but the juice is actually expressed from the halved fruit. After the juice has been removed, the peel of the halved fruit is held firmly in its path out of the machine by a grooved roller on one side and a smooth guide on the other side. During this operation, the peel is completely flattened out, and at the moment of flattening ex-

[10] The author is greatly indebted to Mr. W. Paul Arndt, Plant Manager of that firm, for information regarding this machine.

tremely sharp knives slice the outer portion (flavedo) of the peel from the underlying albedo. The knives accomplishing this feature are adjustable, so that the flavedo, which alone bears the oil glands, may be shaved away from the albedo just beneath the oil cells. Since the knives may be adjusted to cut to any desired degree of thickness, the operator can control, to a certain degree, the amount of albedo that will accompany the flavedo in this process. This bears a direct relation to the degree of emulsion trouble encountered later, if the shavings are too thick.

The removed flavedo is then chopped into small pieces approximately $\frac{3}{16}$ in. in diameter; simultaneously this minced mass is added to a rather large volume of water (the flavedo from 15 tons of fruit to 1,000 gal. of water), the water to act as the oil carrying medium. The mixture of triturated flavedo and water then passes through a counter-current extraction washing reel, which in turn removes the solids from the water. At this point additional fresh water (approximately 100 gal. more) is added, to effect almost complete washing of the chopped flavedo. The water and oil phase which flows from the screen of the counter-current backwashing reel then passes through a Sharples nozzle-jector which, in turn, produces a rather thick emulsion. The ring dam, as well as the nozzle phase of the centrifuge, are discharged to the sewer.

The emulsion from the nozzle-jector is mixed with additional water, occasionally at elevated temperatures, and run through a standard Sharples Super-Centrifuge to produce the final clear oil.

The Citro-Mat is an efficient machine of high capacity, employed mainly in California for the treatment of orange and lemon, and in Texas for grapefruit. It processes per hour 5 to 10 tons of oranges, 8 to 18 tons of grapefruit, or 3 to 6 tons of lemons. The wide ranges are due to the large difference in the fruit from various parts of the country and to the difference in varieties. For example, the large grapefruit of the Rio Grande Valley runs considerably faster than the much smaller grapefruit of California. Hard lemons, particularly those "out-of-round" are very difficult to process in the Citro-Mat, and therefore run much slower than well-matured, fairly rounded lemons. The same, obviously, applies to oranges.

The yields of oil per ton of fruit vary considerably also. Oranges yield 3 to 6 lb. of oil, grapefruit 1 to 2 lb., and lemons 2 to 5 lb. of oil per ton of fruit. These fluctuations in yield are caused by the actual variations in the fruit, as well as by the physical condition of the peel at the time the fruit is processed. For example, early northern (California) Valencia oranges usually yield 6 lb. of oil per ton of fruit, whereas late Navels yield at the most 2.5 lb. of oil.

The Citro-Mat has been criticized as using a relatively large volume of water to act as carrying medium. The constructors of the Citro-Mat are

well aware of the fact that the water has a tendency to extract from the oil certain of its constituents. In producing lemon oil they, therefore, recommend recirculating the water to a certain extent, but this is not advisable in the case of orange oil. Experience has shown that the water cannot be used over again because the solids discharged from the centrifuge will accumulate and, when this build-up reaches a certain amount, the yield of oil will fall to nothing.

The juice obtained in the Citro-Mat has to be de-oiled.

The Fraser-Brace Extractor.[11]—This machine has been developed primarily for the purpose of removing, by abrasion, the entire oil-bearing flavedo from the whole fruit, so that the juice expressed from the treated fruit contains practically no essential oil and does not require "de-oiling" by flash distillation. The grating effect is so thorough that the fruit leaving the machine looks almost as white as a tennis ball, but with a slightly yellowish tint.

The Fraser-Brace Extractor consists, in principle, of a corridor (tunnel) formed by four horizontal abrasive, carborundum-covered rolls revolving at high speed, and a baffle plate from which a fine spray of water plays upon the fruit as it passes through the extractor and is rapidly turned over and over on the abrasive rolls. The latter grind the entire flavedo off the fruit, and the spray water carries away the emulsion, consisting of cell detritus, solid particles, waxes, and essential oil. The emulsion is pumped to a screen, which removes the coarse particles, and then flows into a settling tank, where it is allowed to settle from 3 to 12 hr. The oil and suspended solids which have floated to the top are then passed through a centrifuge to separate the oil. The machine is completely enclosed and very little loss of oil occurs.

The Fraser-Brace Extractor offers one great advantage (aside from the fact that the juice of the treated fruit is free of oil): it recovers much more essential oil than any other machine or apparatus used for the extraction of citrus oils. In fact, it recovers almost all the oil present in the peel. During the 1947–1948 season, Kesterson and McDuff [12] observed an average yield of 9.7 lb. of orange oil per ton of *peel,* which was about twice the yield obtained in screw presses.

On the other hand, the quality of the oil suffers somewhat from the high yield. Oils recovered by the Fraser-Brace Extractor exhibit a dark red color, a high evaporation residue, a high specific gravity, refractive index, and ester content, caused by the high content of waxes. The optical rota-

[11] The author is greatly indebted to Mr. F. A. Barris, Fraser-Brace Engineering Co., Inc., Tampa, Florida, for information regarding this machine.

[12] "Florida Citrus Oils," *Univ. Florida, Agr. Expt. Sta., Gainesville, Fla., Tech. Bull.* No. 452 (1948).

tion is low. Because of the very large amount of spray and carrying water required to remove the emulsion of oil and cell detritus (100 gal. of water per gallon of oil) from the fruit, the oil is low in aldehydes. Moreover, settling of the oil and cell detritus emulsion for a period ranging from 3 to 12 hr. results in fundamental changes in the composition of the oil, due to enzymatic action, etc. (cf. the section on "Deterioration of Citrus Oils during Expression").

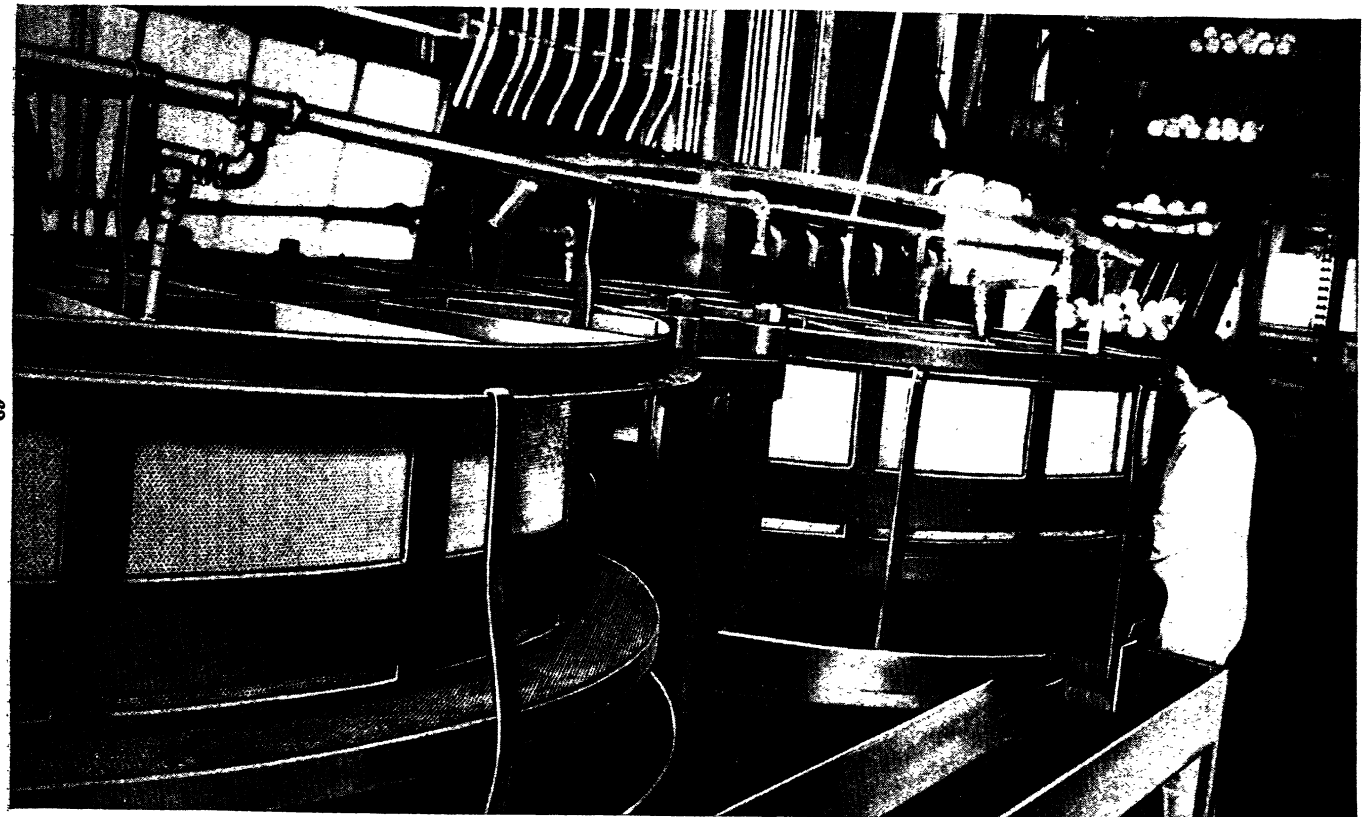
In all fairness, it must be said, however, that at the time of this writing (end of 1948), the Fraser-Brace Extractor has scarcely emerged from the experimental stage, and substantial improvements can be expected in the future. In fact, a large concern in Los Angeles manufacturing soft drinks recently installed several Fraser-Brace Extractors on a trial basis, and obtained very satisfactory results. The yield of oil has been exceptionally high. By reducing the spray and carrier water to a minimum the aldehyde content of the oil could be substantially increased. By keeping the oil in cold storage (−10° F.) for six months, and by centrifuging it several times during this period the wax content of the oil could be lowered materially.

The Citrus Oil Extractor of the Hyland-Stanford Corporation.[13]—In the Citrus Oil Extractor used by the Hyland-Stanford Corporation, Los Angeles, California, the whole fruit passes over a grated surface, which method punctures the oil glands and liberates the oil, which is then carried away in a spray of water and finally recovered by centrifuging. In principle this oil extractor resembles the Sicilian Avena machine, although its construction features depart radically from the Italian prototype.

The Citrus Oil Extractor used by the Hyland-Stanford Corporation consists of a continuous spiral, about 1 ft. high, with the inner surface partially punched through so as to form a grating surface, 60 ft. long (120 ft. for the two tables). This grater is suspended over two tables, 6 ft. 4 in. in diameter, and covered with the same grating surface as the spiral. The two tables revolve at a speed of from 60 to 200 rpm (the average is 100 to 120), whereas the grating spiral remains stationary. The whole equipment is constructed of stainless steel. Fruit feeds into the center of the left-hand spiral and, after having been grated, emerges from the center of the second spiral. A continuous spray of water, placed just above the spirals and playing upon the fruit while it is being grated, prevents the oil from being dissipated into the air, so that it will be carried to the overflow and storage tanks for centrifuging, after the effluent has been screened. It takes about 1 hr. before the mixture of oil and spray water reaches the centrifuge.

Depending upon the speed of the revolving tables, the capacity of this Citrus Oil Extractor ranges from 5 to 15 tons of whole fruit (oranges) per

[13] The author is greatly indebted to Mr. F. G. Stanford, President of the Hyland-Stanford Corporation, for information regarding this machine.



Courtesy of the Hyland-Stanford Corp., Los Angeles, California.

Citrus oil extractor.

hour. At a working capacity of 10 tons per hour, a ton of fruit passes through the extractor in 6 min. Processing oranges that weigh ¼ lb. each, the working capacity would be 80,000 oranges per hour, 1,333 per minute, or about 22 per second.

When a high production of juice was the primary object, the extractor was operated at a speed of 15 tons of fruit per hour, but this resulted in a considerably lower yield of oil than was obtained when the machine processed only 10 tons per hour. The yield of oil would probably increase further, if only 5 tons of fruit were processed per hour.

The extractor does not work so well with lemons because of their shape.

In general, the yield of oil depends upon several factors:

The type of orange, seasonal variations, etc. It is much higher early in the season than later in the season. The sharpness of the grating surface, too, plays an important part in the yield of oil. As this surface dulls, the yield is cut. Sufficient water in the form of a spray must be applied—if insufficient, some of the oil will be dissipated into the air. At present the Hyland-Stanford Corporation obtains on the average only 2 lb. of oil of orange per ton of whole fruit throughout the season. There is, however, every reason to believe that the yield can be materially increased by certain modifications which are being studied and experimented with.

After the grated fruit emerges from the oil extractor it is conveyed to the juice extractor, which is simply a press consisting of an upper and lower revolving disc through which the grated oranges pass continuously. The quality of the juice is controlled by regulating the pressure exerted by the press, as too much pressure affects the quality adversely.

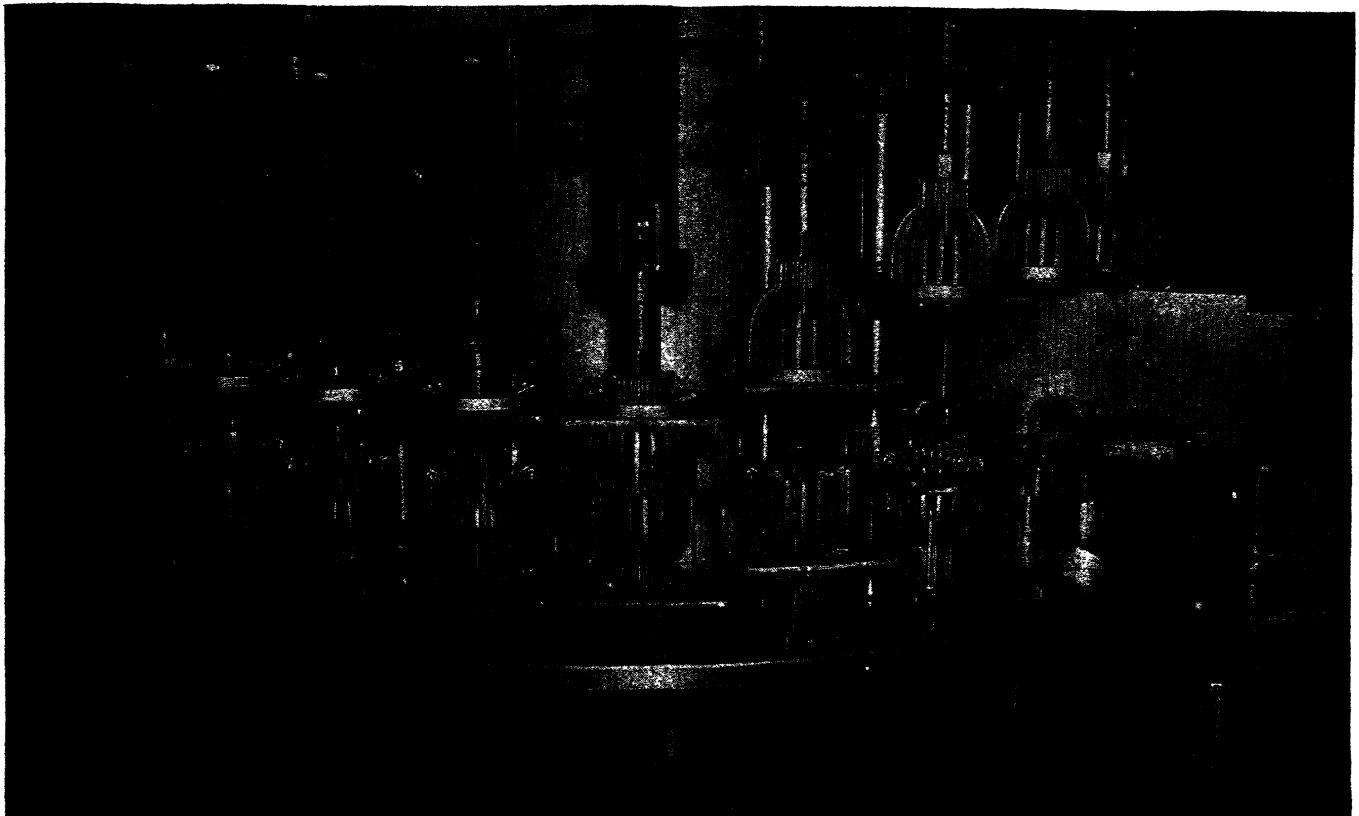
The juice does not have to be de-oiled because the Hyland-Stanford Corporation uses all the juice for the making of juice concentrates. For this purpose, the juice is flashed into vacuum pans and any oil present in the juice will be removed in the course of concentration.

The Citrus Oil Extractor of the Hyland-Stanford Corporation has the advantage of requiring no size grading of the fruit, as it handles all sizes simultaneously.

The F.M.C. Whole Fruit Extractor.—In 1947, an entirely new machine, differing in principle from any preceding type, was introduced by Food Machinery Corporation, San Jose, California.[14] The so-called F.M.C. Whole Fruit Extractor not only extracts juice, but simultaneously expresses oil emulsions from the peel, without the oil and juice coming in contact with one another.

The fruit, after being washed and assorted by size, is introduced into the bottom half of a divided sphere so designed that, when the upper and lower

[14] The author is greatly indebted to Mr. Paul C. Wilbur, Vice President and Director of Research of that firm, for information regarding this machine.



Courtesy of Food Machinery Corp., San Jose, California.

F.M.C. whole fruit extractor. This machine expresses citrus juices and the peel oil in one operation without contact of juice and oil.

halves meet, they form interlocking fingers, exerting almost perfectly distributed pressure. The support of the lower cup consists of a hollow shaft, with a cutter at the top. As the upper cup descends on the orange and applies pressure to it, the hollow shaft cuts a circular opening into the bottom of the orange, with the result that the juice flows out through the tube. With increasing pressure, the oil glands on the outside of the peel are ruptured, the ejected oil emulsion flowing off between the fingers of the cups and being collected in an outer trough. The juice flows into an inner trough. The dividing wall is sufficiently high to prevent any intermingling of these two products. Upon completion of extraction, the cup halves are drawn apart and the exhausted highly compressed fruit is ejected by flat plates, projections of which pass through the fingers of the fruit cups.

All the cups of one extractor are mounted circularly around a central shaft, and rotate at 20 rpm within a stainless steel enclosure which prevents spillage.

The F.M.C. Whole Fruit Extractor operates at 480 cups per minute. The actual output of the machine is determined by the efficiency of feeding and by the size of the oranges fed into the extractor. These two factors are probably responsible for the variations in capacity that have been reported. In actual experience, a machine equipped with 3-in. cups has shown a temporary capacity as high as 6 tons of oranges per hour. This may sound unusual, because for fruit approaching 3 in. in size, the normal feeding efficiency should be about 4.5 tons per hour. Of course, if small oranges are fed into the extractor, and if the efficiency of feeding drops off, the tonnage feed will be reduced. At present, the Whole Fruit Extractor is supplied with two cup sizes for oranges—viz., 3 in. and 4¼ in. in diameter. A grapefruit machine with 6 in. cups has also been designed.

The efficiency of extraction of the fruit will remain quite high, even though the orange is considerably smaller than the cup. Obviously, any oranges that are too large will be crushed; it is important, therefore, to assort the fruit into grades equal to or smaller than the cup size.

Because the oil is obtained by direct expulsion from the oil glands in the surface of the fruit, without the necessity of grinding the peel, there will be less chance of detritus and undesirable extractives from the other parts of the orange being removed with the oil and being incorporated into it. As an example: the wax content of orange oil extracted by this machine appears to be substantially lower than the wax content of oils removed by the conventional processes. Recovery of the oil from the emulsion is quite easy and economical, since only a centrifugal operation is required—all grinding and pressing being eliminated.

The main advantage of the F.M.C. Whole Fruit Extractor lies in the fact that during expression of the fruit there is absolutely no contact be-

tween juice and essential oil. The juice, therefore, does not need to be de-oiled. The yield of juice seems to be about 10 per cent higher than that obtained in the other juice presses, which may be due to the prevention of spillage in the Whole Fruit Extractor. The average yield of essential oil, also, appears to exceed that obtained in other types of oil presses, due, among other factors, to the clean oil separation by the centrifugal force exerted through the rotation of the whole machine. In general, the yield of oil per ton of oranges is extremely variable, depending upon the variety and condition of the fruit and upon the season. In commercial operation the following average yields of oil, per ton of whole fruit, have been observed:

	Pounds
California and Florida Valencia Oranges	4.5–5.5
Florida Oranges, Early and Midseason Varieties	5
Florida Grapefruit	1.25

Lately the F.M.C. Whole Fruit Extractor has also been adapted to lemon and lime, but yields of oil are not yet available at this writing.

The essential oils recovered by this machine are of excellent quality; their color is light, their content of waxes and other nonvolatile residue is low. Owing to the clean and direct separation of the oil from the peel (no contact of juice and oil, and no need of spraying water as carrier medium of the oil, except a little in the case of grapefruit), the essential oils are relatively rich in oxygenated constituents, particularly aldehydes, and lend themselves well to the preparation of concentrated and terpeneless oils.

On the other hand, it has been said that the Whole Fruit Extractor is a costly and very delicate machine, which requires constant attention by expert mechanics and is likely to give mechanical trouble, due to the many moving parts. This may have been true of the first models, but, with experience, "bugs" have been eliminated, and further improvements will undoubtedly be made. It has been stated that the Whole Fruit Extractor, in its original form, could not process very thin-skinned or overripe and puffy fruit, as the juice is likely to break through such peel; however, further improvements in the machine will probably overcome this difficulty too. As a matter of fact, the machine at present is being redesigned and a simplified model perhaps may be expected in the future.

Distilled North American Citrus Oils

As has been repeatedly pointed out, progressive citrus juice canneries in the United States endeavor to utilize their fruit for the recovery of *all*

possible by-products, which policy must be carried through to make the entire operation economically successful, especially in view of the heavy competition existing in the citrus canning industry.

As a result of the various processes to which the juice and the waste peel are subjected, a modern cannery of orange, lemon, grapefruit—and lately also of tangerine—obtains increasingly large quantities of distilled oil, of quite widely variant quality, and derived from the following operations:

1. Modern flash pasteurization and de-oiling of the juice (which still contains minute quantities of essential oil) yield a good quality of distilled oil, especially so if the de-oiling is carried out *in vacuo*. Since the quantities of pasteurized juice are enormous and increasing, substantial quantities of this type of distilled oil will be available.
2. Concentration of the juice yields distilled oils of good quality.
3. The peel, after expression of the oil by the usual methods, still contains substantial quantities of oil retained by the soft spongy albedo. It can be recovered by steam distillation of the waste peel (after expression). This oil is of mediocre quality, typical of distilled citrus oils.
4. After recovery of the oil by cold expression, the waste peel (the same as is used in process 3) is soaked in a hot solution of lime, whereby the pectins are gelatinized. The mass is then submitted to high pressure between heavy rolls, by which means the water is readily expressed. The peel is dehydrated, comminuted and filled into sacks to be marketed as cattle feed. The watery liquid, on the other hand, goes into large stills to be concentrated for the production of molasses, the peel containing about 6 per cent of sugar. During the process of concentration, substantial quantities of distilled oil can be recovered. This oil, also called "stripper oil," however, has a very harsh odor and cannot be used for flavor purposes. It may serve in technical products, in insect sprays, as a thinner of paints and lacquers, etc. Large quantities of this type of oil are available.

Because of the different methods by which these distilled oils are obtained, and because they are frequently offered as mixtures (even as mixtures of orange oil, grapefruit oil, and tangerine oil), it is difficult, in fact useless, to establish standards. Besides, physicochemical properties in this case have little meaning as to quality, and the final use of a distilled oil depends entirely upon its odor and flavor. If the distillation of the oil is carried out *in vacuo* (as by some canneries in the case of 1), and if proper precautions are taken, the odor of a distilled oil may be very good, indeed. Thus the author had occasion to examine distilled (with steam and *in vacuo* at 60° C.) tangerine oils which possessed a surprisingly good tangerine odor.

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CALIFORNIA CITRUS OILS

GENERAL ASPECT

Historical Development.—The exact date at which oranges were first introduced to California is not known, but doubtless some trees were grown by the early Franciscan missionaries during the latter part of the eighteenth century. In fact, the whole California fruit-growing industry traces its origin back to mission orchards and vineyards, where the Mission olive, the Mission fig, the Mission grape, and the Mission orange originated, and whence trees, vines, and seedlings were taken to be grown, on an ever-increasing scale, in private gardens and agricultural enterprises.

California's citrus industry actually began in 1804 or 1805, when about four hundred seedling trees were planted in an orchard of six acres at the San Gabriel Mission near Los Angeles for the personal use of the Mission's members. William Wolfskill is said to have started the first commercial orange orchard at Los Angeles in 1841. As early as 1870 a number of small plantings could be found from San Diego, in the south, to Butte County, northeast of San Francisco; and it appeared that many valleys of that extensive region were well adapted for growing fine quality citrus fruit.

Completion of the great transcontinental railroad lines, and the subsequent opening of fruit markets outside of California's boundaries, further advanced this new industry. Another factor contributing to its rapid growth was the development and fruiting, in Riverside, of the Washington Navel orange, a variety far superior to any other then grown; this occurred about 1878. By 1887 citrus fruit shipments amounted to about 900,000 cases. Since then the development of this industry has been quite phenomenal.

Producing Regions.—In California today, citrus fruit is produced commercially over a wide territory, extending from San Diego County, in the south, to Glenn County, north of San Francisco. The area involved is about 550 miles long and from 3 to 75 miles wide.

The principal growing regions are:

1. *Southern California,* including the coastal district from San Diego, Orange, Riverside, San Bernardino, Los Angeles, and Ventura, to Santa Barbara, the Santa Ana and San Gabriel River valleys, and the plantings in the Coachella and Imperial valleys. The climate in the two last named valleys is marked by extreme summer heat and dryness, the annual rainfall amounting to only about 2 in. The Santa Ana and San Gabriel valleys have a rather dry summer and bright days, like the northern and central sections of California, but with much cooler nights. The climate of the coastal region from San Diego to Santa Barbara is more temperate, due to the proximity of the sea, with cooler summers, milder winters, and frequent dews and fogs.

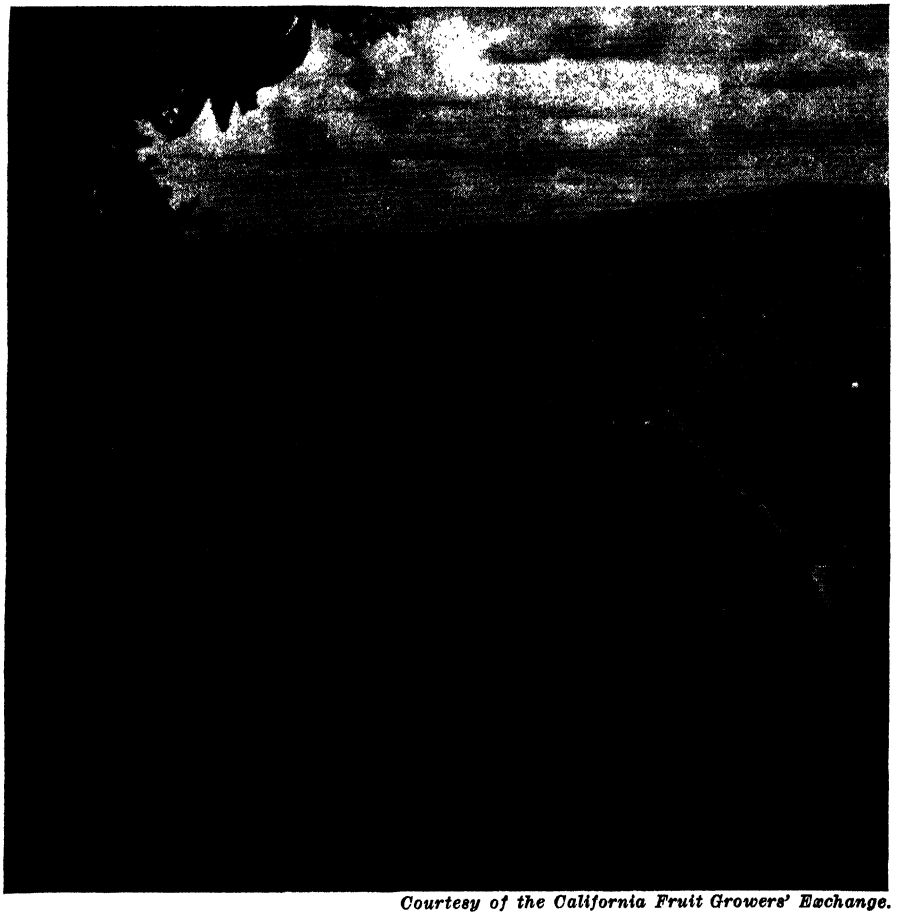
2. *Central California.* The next section is in the San Joaquin valley, principally in Tulare County. It ranges from Ducor up to Exeter and covers the territory eastward into the foothills from the Southern Pacific Railroad, which runs between the points mentioned.

3. *Northern California.* Less extensive plantations lie in parts of Butte and Sacramento counties, principally in the neighborhood of Hamilton City, Oroville, Maxwell, and their general vicinity. The climatic conditions in central and northern California are more continental, i.e., more extreme. The air is hot and dry in summer, the days clear and sunny without fog or dew. In winter, rain falls abundantly.

California's most important citrus fruit is the regular round, sweet orange, which comprises four-fifths of the commercial citrus acreage.

Planting and Cultivating.—The growing of reliable citrus trees has become a highly specialized industry, to which much work has been devoted. It would lead beyond the scope of this survey to attempt a comprehensive discussion of the agricultural methods employed today; they have been

thoroughly described in several standard works and in numerous bulletins of the California and U. S. Department of Agriculture, among them that of Shamel and Caryl.[1]



Courtesy of the California Fruit Growers' Exchange.

Citrus groves in California.

Climatic Conditions, Irrigation, Fertilization, and General Outlook.—In general, the climate of California is well suited to the successful cultivation of citrus trees. Located on a comparatively narrow strip of land between the Pacific coastline and the mountain range of the Sierras, the orchards are

[1] "Citrus Fruit Growing in the Southwest," *U. S. Dept. Agr., Farmers' Bull.* No. 1447, Revised, November (1930).

The most complete and recent work is that of H. J. Webber and L. D. Batchelor, "The Citrus Industry," 2 vols., Univ. of California Press, 1943–48.

fully exposed to California's warm sunshine, yet protected from cold winds by the high Sierras and many smaller hills. Against cold spells, which occasionally do hit California, the groves are now amply protected by artificial means, each orchard being equipped with sufficient ovens or "smudge pots" (one pot for every two trees) to weather frosts above 12° F. Such a low temperature, however, has never been observed in California, the lowest being 18° F. In addition, the meteorological service of California is most efficient, warning the growers by radio in ample time of any impending frost and advising them to light their "smudge pots."

Compared with the orange, the lemon tree requires a drier climate, as it is readily attacked by all kinds of rots and fungus diseases, which are so prevalent in a hot and humid climate. The orange tree grows best in a warmer, more humid climate; it requires ample rainfall or artificial irrigation. Because of climatic conditions, lemon cultivation in Florida has been a failure, whereas it is most successful in California. On the contrary, natural growing conditions for the orange are better in semitropical Florida, where artificial irrigation is greatly facilitated by the abundance of lakes and by the ease with which artesian wells can be dug. California has to conduct its irrigation water partly from the high Sierras, partly from the Colorado River; and in many parts of California new land which can be irrigated, and on which new orange groves could be started, is becoming increasingly scarce.

In certain years recently, the orange crop of California has been abnormally small, the Valencias being of subnormal size. Several explanations have been offered, but none is fully satisfactory. For instance, it has been claimed that for many years the California growers have used artificial and highly purified fertilizers lacking in certain minerals, trace elements, and other vital substances contained in natural fertilizers (compost or stable manure, for example). As a result of this practice, the soil of some of California's citrus groves has perhaps become slightly exhausted.

To conclude our general discussion of the California citrus industry, it should be mentioned also that since the outbreak of World War II its position has become somewhat more difficult. California is gradually being industrialized; during World War II many new industries (steel, aeroplane, and shipbuilding, etc.) moved into California and attracted hundreds of thousands of migratory workers, who, lured by California's natural beauty and agreeable climate, have settled permanently in the "Golden State." Real estate has been booming, new settlements are springing up everywhere, agricultural acreages have been converted into industrial sites, and prices of land have risen sharply. This development, obviously, cannot be without influence upon the position of California's citrus (and especially orange)

industry, in its competition with Florida, where enormous tracts of most fertile and readily irrigated virgin land still await cultivation.

Total Fruit Production.—Statistics on citrus fruit production in California and the other citrus growing states of the Union will be found in the monographs on the respective essential oils, viz., "California Orange Oil," "California Lemon Oil," "Grapefruit Oil," "Mandarin and Tangerine Oil," etc.

Regarding the quantities of fruit which have been shipped as edible fruit, and the quantities which have been used for the production of canned or concentrated juice, essential oil, citric acid, and all other by-products, it can be said that in 1942–1943, for example, about 80 per cent of California's orange crop was shipped as fresh fruit, and about 20 per cent processed for by-products. For lemons, in that particular year, the figures were 75 per cent and 25 per cent; for grapefruit, 50 per cent and 50 per cent. Even today these percentages are nearly correct for California, but not for Florida, because in Florida the production of canned orange and grapefruit juice has increased tremendously during and since World War II.

California Fruit Growers Exchange.—The spectacular growth of California's citrus industry, fostered by the research and experimental work of the United States Department of Agriculture, was due especially to the excellent producing and marketing organization of the California Fruit Growers Exchange, which may serve as an outstanding example to any agricultural enterprise in the world. The California Fruit Growers Exchange is a strictly cooperative, nonprofit, noncapital stock organization, formed under the laws of the State of California. The bulk of California's oranges, lemons, and grapefruit are today produced and handled by growers organized in the Exchange. The function of the organization is to advise on marketing, to lower the cost of selling, to collect accounts and damage claims, to improve production and packing, to increase the consumption of citrus fruit, to develop new markets, and, finally, to supply the public with good fruit at reasonable prices. The California Fruit Growers Exchange comprises many departments—orange sales, lemon sales, legal, traffic, field, accounting and advertising; and many subdivisions—claims, routing, research, education, inspection, growers' service, dealers' service, and by-products. The California Fruit Growers Exchange owns no fruit but is a marketing organization acting on behalf of its constituents by collecting information and distributing it daily to its affiliated associations. These, in turn, decide where and when their fruit shall be sold, and the price at which it will be sold.

The problem of most interest in this survey concerns the utilization of surplus fruit which cannot find a market or cannot be sold on account of slight damage (frost, culls). It has been estimated that from 5 to 10 per cent

of the citrus crop fails to reach market standards. This cull fruit is still valuable for the manufacture of essential oils and other by-products.

As Wilson [2] pointed out: "The need for the development of the citrus products industry in California is found in the economic fact that 100 per cent of the citrus crop cannot be packed and shipped to market over a period of years and sold for enough to cover the cost of production. This problem of handling surplus agricultural crops in a way that will not interfere with the orderly marketing of the main crop at a price that more than covers production cost was heavily stressed by the President of the American Institute of Cooperation at Berkeley in July, 1928. It was to take care of such surplus crops that Exchange Lemon Products Company was organized in February, 1915, the Research Laboratory of the Exchange in April, 1920, and The Exchange Orange Products Company in October, 1920."

It has been pioneer work from the start, because available literature on the manufacturing of citrus oils referred only to the rather antiquated methods used in the Sicilian citrus industry. The primitive handpressing methods, and even the small types of machines employed in Sicily and Calabria in hundreds of homes and small factories, would never do in California, where labor and living standards are high, and where enormous quantities of fruit are to be worked up each day in a few centrally located, large, and highly efficient factories. The young California citrus by-products industry has succeeded in developing not only its own modern machines for extracting the oils, but also certain by-products (concentrated juices, cattle feed, and especially pectins) which had previously been known little, if at all, in Italy. The task consisted in the development of new products and processes for better utilization of surplus fruit, in the supervision and control of the manufacturing processes, and in the development of new outlets.

The Exchange Orange Products Company of California Fruit Growers Exchange serves all Exchange orange shippers. Operating on a strictly nonprofit basis with such fruit as the Exchange shippers desire to send to it, its task is to work that fruit, which represents a very high percentage of California's total orange production, into staple products, and return to the shippers of the fruit whatever money remains, after the cost of production, shipment, and sale are deducted from the total sales value. The company makes no profit, never pays any dividends or interest on stock. The plant is located in Ontario, California.

Exchange Lemon Products Company, too, is a nonprofit cooperative group organized under California state laws in 1915 at Corona, California, where its plant is located. Its function is to salvage value from the surplus lemons

[2] "Relation of Chemistry to the Citrus Products Industry," *Ind. Eng. Chem., Ind. Ed.*, **20** (1928), 1302.

of its owners, the lemon-shipping associations of California Fruit Growers Exchange. These associations produce a very high percentage of all the lemons grown in California and send their surplus to Exchange Lemon Products Company, as they desire.

All products made by both of the above-mentioned companies are sold by Products Department of the California Fruit Growers Exchange, which department was organized for that special purpose.

The important products prepared from lemons are, of course, citric acid, lemon oil, pectin, canned or concentrated lemon juice, and lemon peel derivatives. Similarly, the products made from oranges are orange oil, pectin, canned or concentrated orange juice used both in the beverage field and in medicines, and orange peel derivatives (cattle feed and molasses). These various products move to every corner of the globe. The Products Department of California Fruit Growers Exchange operates its own sales offices in London, New York, and Chicago. About forty chemists, bacteriologists, engineers, and expert mechanics are continuously employed in the Corona and Ontario plants in connection with production and research work.

At first the quantity of fruit available for conversion varied enormously, but as production and sale of citrus by-products has become more firmly established, the amount of fruit for production has also become more regular, insuring a continuous supply of the products themselves. Many thousand tons of lemons and oranges per year are now available for processing in the Ontario and Corona plants.

Total Production of Oil.—As to the total production of citrus oils in California, it must be kept in mind that the oil is produced only from surplus fruit, the quantity of which varies tremendously.

The average sales figures of the California Fruit Growers Exchange have shown a tremendous increase in recent years. Particularly striking are the decided rise in the sales of lemon oil, and the smaller, but very important rise in orange oil. Without competition from the French Guinea, the Brazilian, and especially the Florida orange oils, the sales of California orange oil would probably have increased in a ratio similar to California lemon oil, the Sicilian orange and lemon oil having lost their former monopolistic position in the years prior to World War II. Of the total output of California's citrus oils, the California Fruit Growers Exchange produces by far the greater part.

Generally speaking, the amount of fruit available for the production of oil and other citrus by-products varies more or less directly with the total amount of fruit supplied. However, in years of a normal crop, like 1943, demands of the government for fruit and other products have been such that production of oil has been decreased despite the harvest of considerable fruit. Yet, even taking that into consideration, California's production has been

entirely ample to supply the need for lemon oil, but not for orange oil. Because of the remarkable development of citrus oil production in California and, more recently in Florida, the United States has become entirely independent of any imported lemon oil or orange oil; indeed, both of these products are now on an export basis.

Summary

When California coldpressed lemon and orange oils were introduced on the American market years ago, they were examined carefully and with some curiosity by consumers, because they differed in flavor character, and also in physical properties, from the imported oils, principally the hand "sponged" Italian, to which the users had been accustomed up to that time.

Orange Oil.—It soon became apparent, however, that California coldpressed orange oil, although different, was superior in flavor to the imported oils, having a more complete orange flavor, suggestive of both juice and peel, as contrasted with the strong peel-like note which characterized the other oils. There were some difficulties encountered because of its rather high content of solids, but these were gradually overcome as processes of extraction improved.

As the fine fruity flavor of this oil became more appreciated, it gradually supplanted the Italian oil in all its various applications, including the manufacture of soft drink extracts, the flavoring of confectioneries, baked goods, pharmaceuticals and, in fact, every type of product wherein imported orange oils had previously been employed. California orange oil has finally won such preference that now many manufacturers willingly pay a premium for it when scarcity advances its cost beyond that of the imported products.

Lemon Oil.—When California coldpressed lemon oil first appeared on the market, it also was treated with the distrust of unfamiliarity. It had a high solid content and, in addition, contained on an average only about 2½ per cent or more of citral, as distinguished from the imported oil, which has a minimum of 4 per cent. This naturally resulted in a somewhat different flavor character and, at the same time, placed the oil beyond the limits specified by the then current revision of the U. S. Pharmacopoeia. Likewise, the official definition of lemon oil, as promulgated by the U. S. Department of Agriculture, was found to be limited in its application to Italian oils.

Gradually, however, this different type of flavor came to be recognized as a better flavor and more suggestive of the domestic fruit, which has always been the most highly esteemed. It was observed that unidentified flavoring substances, which the Californian oil contains, more than compensated for the citral deficiency, and it was not long before the manufacturers perfected

a method of clarification by reducing the solid content so greatly as to render the oil even more soluble than the Italian oil.

Official agencies move very slowly, but eventually the merits of this oil forced recognition by the Department of Agriculture, whose standards for lemon oil were changed to include it. This was followed by a revision of the Pharmacopoeial specifications to the same end, so that the California coldpressed lemon oil is approved officially in every respect. Like the orange oil, California coldpressed lemon oil finds its way into every type of product requiring lemon flavor. It has replaced the Italian oil in all applications of the latter, and in recent years has come close to dominating the domestic market.

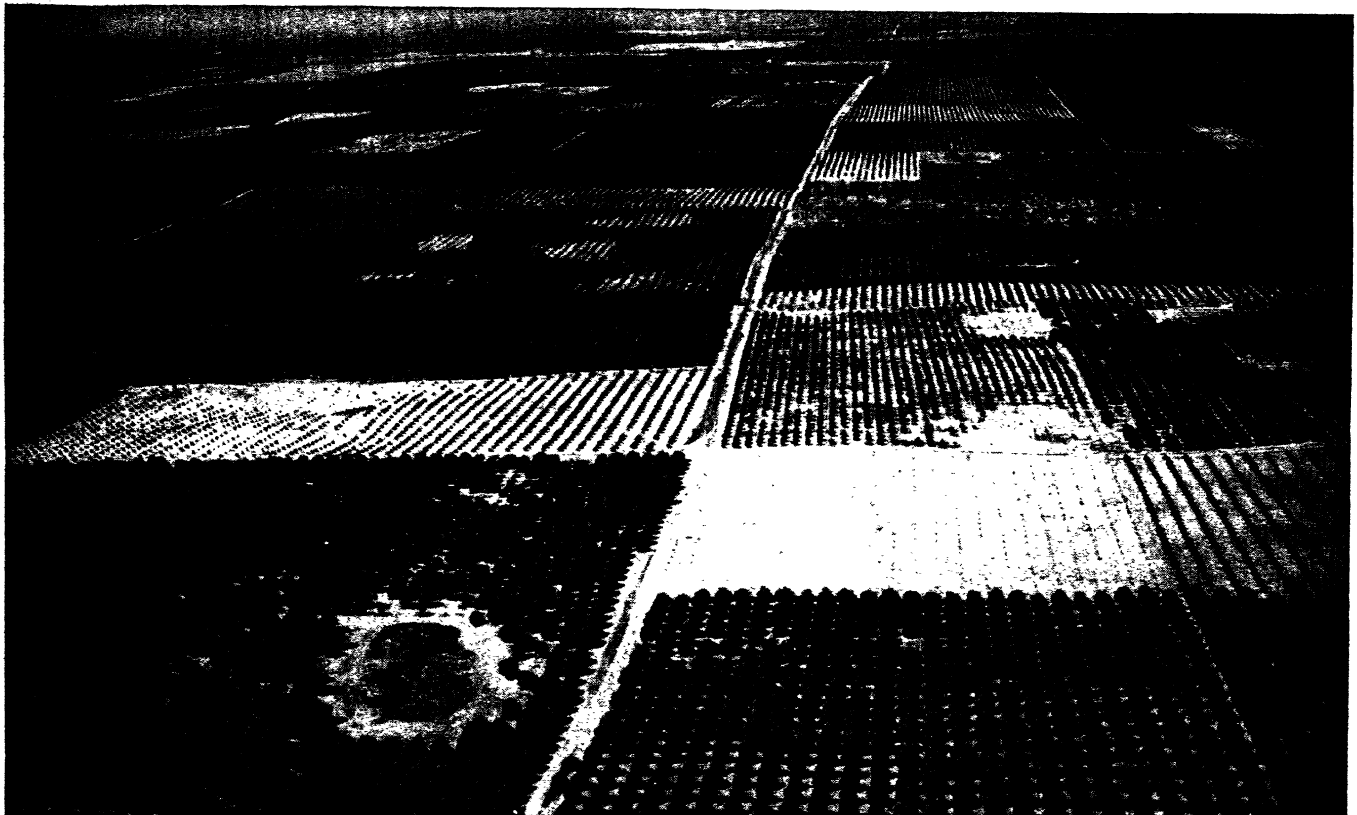
In those applications where whole orange or lemon oils have not proved suitable, the California coldpressed oils have provided splendid bases for the separation of concentrates suited for use in gelatin dessert powders, soft drink powders, cornstarch pudding powders, and other powdered food products.

To sum up briefly, the lemon oil consumption for all of the United States and Canada, and a great part of the orange oil consumption, are covered today by California production. Including the more recent production of Florida, the North American continent has become entirely independent of foreign imports of these oils; in fact is quite able to export considerable quantities to Canada, England, and to many other countries.

FLORIDA CITRUS OILS

General Aspect

Historical Development.—The early history of Florida's citrus industry is rather obscure; but from all evidence it appears that the first citrus trees were brought to Florida by Spanish missionaries and settlers more than 300 years ago. Prior to 1870, there existed only a few small groves in the northern part of the state, largely along the banks of the St. Johns River, the sole means of transport then being river boats. Most of these plantings consisted of orange trees; the grapefruit remained neglected until it began to grow popular in the late eighties. Today the grapefruit closely rivals the orange, so far as commercial importance is concerned. Next in production ranks the tangerine, a type of soft-skinned orange of good dessert quality.



Courtesy of the Florida Cypress Garden Association, Winter Haven, Florida.

Young and old citrus groves in Florida.

Limes, too, are being grown in the southern part of Florida; and since the fruit has found ready acceptance on the market, the acreage devoted to lime is being expanded.

Lemons cannot be grown in Florida because the humid, almost tropical, climate there makes it practically impossible to control lemon scab. This fungous disease causes a swelling of the skin of the fruit, and a change in the color of the peel, so that it comes to resemble a potato peel. Since lemons are most susceptible to this disease, lemon cultivation is generally carried on in areas that are not very humid while the fruit is young and growing. Also, certain bark diseases are quite prevalent in Florida; consequently lemon growing has been unremunerative in that state. As an added disadvantage it should be mentioned that under Florida's very humid and vigorous growing conditions lemons tend to be large and most difficult to cure. To summarize, in a country as hot and humid as Florida, lemons are subject to certain rots which do not exist in a dry climate like California's.

So far as oranges and grapefruit are concerned, the general conditions prevailing in Florida are most favorable for their successful cultivation. There is still plenty of virgin land available for further extension of citrus culture, soil which has never been broken; it is still covered with jungle growth, and, therefore, low-priced. The important problem of irrigation can be solved without too much difficulty by simply pumping water from the innumerable lakes, large and small, with which Florida abounds; or the water can be drawn from artesian wells. Rains are frequent and ample during certain periods of the year. The climate is warm, humid, and semitropical in the south—a factor most conducive to the growth of citrus.

The only drawback to the cultivation of citrus in Florida lies in the fact that Florida is occasionally visited by cold waves which, striking from the north and northwest, unchecked by any mountain barrier, may penetrate deep into flat Florida and do a great deal of damage to the crops. In past years Florida's citrus industry has repeatedly suffered disaster from severe frosts which, on several occasions, killed most of the trees and almost ruined the groves. The most damaging frosts occurred in 1835, 1886, 1894–1895, 1899, and 1917. Although Florida's citrus industry was thus seriously affected, it nevertheless learned many a valuable lesson and has now fully recovered from the setback. Research by the workers of the State [1] and United States Departments of Agriculture on the influence of "trace elements" upon citrus trees and their capability of resisting frosts proved of great benefit to the growers. Considerable improvements have thus been made in cultural methods, in the control of diseases and insects, and in regard to harvesting, handling, and shipping of fruit, with the result that

[1] The author is deeply indebted to Dr. A. F. Camp of the Citrus Experiment Station in Lake Alfred, Florida, for suggestions regarding the text of this chapter.

today Florida's citrus industry is on a more stable basis than ever. Like many agricultural industries, it is still confronted with the problem of disposing of surplus fruit and cull materials; indeed the profit on a whole crop may depend on the satisfactory handling of this part. The canning of orange juice, grapefruit juice, and grapefruit segments has helped considerably in solving the problem of overproduction.

There is hardly a citrus packing center in Florida which does not possess its own cannery utilizing surplus, dropped, scarred, over-sized, and other off-grade fruit that would otherwise go to waste or compete on the market with the better grades of edible fruit. Technically, Florida's citrus industry has reached a high degree of perfection in regard to canning of juices (straight canned juices, frozen canned juice concentrates, juice concentrates) and fruit segments (grapefruit "hearts," fruit salads, etc.) which, to operate on a profitable basis, involves the manufacture of all possible by-products, viz., essential oils (coldpressed and distilled), pectins, citric acid, cattle feed, molasses, alcohol, etc. The reader interested in details regarding the processing of these by-products, and in the canning of juice in general, is referred to the brochure by Chace, von Loesecke and Heid,[2] and to the publication of the Florida Department of Agriculture.[3]

During World War II there arose a tremendous demand for canned and concentrated juices on the part of the armed forces and lend-lease, and large sums of money were spent on research. Thanks to the improved methods of canning citrus juices (flash pasteurization, etc.), and the modern type of equipment used, the quality of canned juices is now far superior to the old-fashioned products and approaches that of fresh juice. These juices have an ever greater appeal among the consuming public, and the consumption is increasing rapidly. The Florida citrus canning industry is, therefore, in a position to extract large quantities of citrus oils as by-products of canning operations and at least to double its present output should the demand ever warrant it.

Producing Regions.—The citrus producing regions of Florida are divided into several sections, each section producing a slightly different type of fruit.

1. The first district is the Indian River section, which produces, perhaps, the best fruit in the entire state—a very thin-skinned orange rich in juice. The Indian River section extends from Daytona Beach in a very narrow strip along the east coast southward to Palm Beach.

2. The most important producing section is in Polk County. It includes the so-called Ridge, which runs from Haines City to Lake Placid, and the

[2] "Citrus Fruit Products," *U. S. Dept. Agr., Circular* No. 577, November (1940).
[3] "Citrus Industry of Florida," *Florida State Dept. Agr., Tallahassee, Florida* (1946).

high land around Winter Haven and Lakeland, as well as the lower, heavier soils from Bartow to Arcadia.

3. The third section runs from Ocala to Orlando, and includes Lake County and Orange County. Numerous orange groves there are located on hilly and sandy land, similar to that in the Ridge section; but much of it is heavier and of the so-called high hammock type.

4. The fourth section extends along the west coast in a narrow strip roughly from New Port Richey to Ft. Myers. The oranges there are all of about the same quality as the Ridge oranges, but the grapefruit of this section is more nearly akin to the Indian River grapefruit.

Total Fruit Production.—Statistics on citrus fruit production in Florida and the other citrus growing states of the Union will be found in the monographs on individual essential oils, viz., "California Orange Oil," "Grapefruit Oil," "Mandarin and Tangerine Oil," etc.

Economic Setup.—Various efforts made in Florida to organize its citrus industry on a cooperative basis, such as is exemplified in the California Citrus Growers Exchange, have been only partly successful. At present approximately 20 per cent of the entire crop is controlled by the Florida Citrus Exchange, a cooperative organization. The remaining 80 per cent of the crop is in the hands of individuals, growing perhaps 40 per cent of the crop, and of individual buyers purchasing the other 40 per cent for marketing on a speculative basis.

CITRUS PRODUCTION IN TEXAS AND OTHER SOUTHERN STATES

Outside of Florida and California, thousands of acres of citrus trees are planted in the lower Rio Grande Valley, irrigation water being drawn from the Rio Grande. This section, about 25 miles wide, extends from Brownsville north and along that river for 75 miles, Weslaco being the center. Ninety per cent of the acreage there is devoted to grapefruit, about 10 per cent to oranges, and approximately 1 per cent to lemons. The Texsun Citrus Exchange in Weslaco controls 20 per cent of the world's grapefruit production. Forty per cent of the grapefruit grown in that section is processed for canned juice, fruit segments, and cattle feed. Texas has not yet produced any oil of grapefruit commercially but could easily produce substan-

tial quantities every year. Plenty of fruit is available, and it will only be necessary to install the extracting equipment.

Small citrus plantings exist also in the Laredo-Winter Garden district, equally under irrigation, and in the northern Gulf Coast section of Texas, particularly in the vicinity of Houston and Beaumont.

In Alabama, some citrus groves are located in Mobile and Baldwin counties. In Mississippi, a few commercial plantings extend along the Gulf Coast.

Evidently these states, too, are potential producers of citrus oils.

OIL OF LEMON

Essence de Citron *Aceite Esencial de Limon* *Citronenöl*
Oleum Limonis

History.—The origin of the lemon, *Citrus limon* (Linn.) Burm. f., has been a mystery, although there exists some indication that it is a native of southeastern China, where it was known and cultivated before the Sung dynasty. Geographical distribution, as well as the names applied to the fruit, point toward the Eastern Himalayas as the home of the lemon. Webber [1] favors south China and upper Burma; but Swingle [2] claims that the true lemon is of recent introduction and still very rare in southern China. It may ultimately, however, prove to be a hybrid, or sport, of the so-called lemon of India. According to Swingle,[3] the lemon might also have the citron (*Citrus medica* Linnaeus) and the lime (*Citrus aurantifolia* Swingle) for parent species, being a hybrid of these two; or it might be considered as a satellite species of the citron.

Whatever its origin, it appears quite certain that the lemon, like the sour orange, was unknown to the Romans, despite the vast extent of their empire and its wide flung commercial relations with Asia Minor, Persia, and even India. Apparently the lemon was introduced to Persia and Palestine at the beginning of the twelfth century A.D., as it was then commonly grown in those countries and is described in many Arabian works of that period. In the following decades the lemon was brought to northern Africa, Spain, and

[1] H. J. Webber and L. D. Batchelor, "The Citrus Industry," Vol. I, 8, Univ. Calif. Press (1943).
[2] *Ibid.*, 400. [3] *Ibid.*, 399.

Sicily, probably by the Crusaders, who followed the activities of the Arabs in spreading citrus culture. References to the fruit begin to appear in Italian literature of this period.

As a result of this development, Sicily and Calabria, in southern Italy, became the leading lemon producing regions of the world, although the refinement of the industry has taken place chiefly in California.

As Webber [4] narrates in his fascinating chapter, "History and Development of the Industry," Columbus introduced citrus fruits, among them the lemon, into America in 1493, on the occasion of his second voyage to the New World. Sailing with seventeen vessels and two thousand men, he was prepared to establish settlements, bringing with him various seeds, plants, and domestic animals. Citrus seeds were planted on the island of Hispaniola (now Haiti and Dominican Republic), whence the citrus trees soon spread to other islands of the West Indies and to the mainland. Citrus fruits were first introduced into Florida sometime between 1513, when Ponce de Leon landed there, and 1565, when St. Augustine was established. Commercial lemon production in the United States was thus begun first in Florida, where it developed slowly. A disastrous freeze in 1894–1895 almost destroyed the industry. The humid climate of Florida has discouraged the growth of lemons there, and the successful extension of this industry, since the "great freeze," has been chiefly in semiarid countries, such as California, where the rainfall is light and the humidity low during hot spells of the curing season. The development of the lemon industry in California has thus been comparatively recent, although lemons have been grown there since the introduction by the padres toward the end of the eighteenth century. After Sicily and Calabria, in southern Italy, California is today the world's greatest producer of lemons and of the essential oil expressed from the rind. Spain, Brazil, and Argentina produce lemon oil in small quantities only.

California Lemon Oil

Introduction.—California is the only state in the Union in which lemons are grown successfully and on a large scale. Climatic and soil conditions in California are much more suitable to lemon cultivation than they are, for example, in Florida, the lemon preferring a somewhat drier climate and being easily attacked by all kinds of fungus diseases and rots, so prevalent in a hot and humid climate. (Cf. section on "Florida Citrus Oils, General Aspect.")

[4] *Ibid.*, 19.

Producing Regions.—California's lemon producing regions correspond quite closely to the orange areas and have been described in the section on "California Citrus Oils, General Aspect."

Varieties of California Lemons.—Two varieties of lemon are cultivated in California. The more extensively grown *Eureka* was originated in 1877 by T. A. Garey, as a selection from several trees grown from seeds of Sicilian lemons. The *Lisbon* lemon was introduced into California in 1874 or 1875, as a budded tree from Australia. The Eureka is a late spring and summer variety, while the Lisbon bears fruit in winter and earlier spring. The Lisbon tree seems to be more vigorous and hardy, as its denser foliage enables it to resist light frost, wind, and sunburn to a greater degree. The fruit of the Eureka and Lisbon differ somewhat in shape, but in both varieties there is such latitude in this respect that even an expert cannot always distinguish the two.

Total Fruit Production.—The reader interested in the latest and more detailed figures on fruit production in the United States is referred to the regularly published Crop Reports of the U. S. Department of Agriculture, Bureau of Agricultural Economics, Crop Reporting Board, Washington, D. C. The following data have been reported for the last few years:

California Lemons in Thousand Boxes

Average 1935–1944	*1944*	*1945*	*1946*	*1947*
11,520	12,550	14,500	14,700	12,200

The net content of one box of lemons in California is 79 lb.

Methods of Expressing the Oil.—California lemon oil is today expressed by the same processes and in the same type of machines as those used in the extraction of orange oil. They have been discussed at length in the section on "Modern, Large-Scale Citrus Juice and Oil-Pressing Equipment."

Yield of Oil.—On complete exhaustion by steam distillation, the peel from 1 ton of lemon fruit will yield about 14 lb. of distilled oil. Coldpressing yields much less oil, the average being only 6–7 lb. of oil per ton of fruit. As in the case of orange or grapefruit oil, a good deal of the oil will be retained by the sponge-like albedo of the peel. In general, however, lemon peel yields its oil somewhat more readily than orange peel, because the latter is softer, more spongy, and puffy. Obviously, the yield of lemon oil depends upon a good many factors, such as condition and maturity of the fruit, the method of expression, the type of oil press used, etc.

Total Oil Production.—California's total yearly production of coldpressed lemon oil averages about 600,000 lb. over a 10-year period. According to estimates by the U. S. Department of Agriculture, Production and Marketing

Administration, Fruit and Vegetable Branch, Washington, D. C.,[5] production was 800,000 lb. in 1943, 400,000 lb. in 1944, and 650,000 lb. in 1945. The bulk of this quantity is produced by Exchange Lemon Products Company, California Fruit Growers Exchange, in Corona, California. A description of this well-known cooperative organization will be found in a preceding section, viz., "California Citrus Oils, General Aspect."

Differences in the Quality of California Lemon Oil According to Region.—The quality of California lemon oil depends upon the region in which the fruit is grown, lemons from the foothills yielding oils of an odor and flavor somewhat different from those grown in coastal plains. To assure the supply of a uniform oil, therefore, Exchange Lemon Products Company, California Fruit Growers Exchange, in Corona, California, blend the two types of oil before marketing the well-known Exchange brand of lemon oil.

Physicochemical Properties of California Lemon Oil.—A thorough study on the physicochemical properties and composition of expressed California lemon oil was made by Poore,[6] who examined seventy-three samples of oil from lemons grown in seven counties of California. Poore determined the ester content as linalyl acetate according to the Seeker-Kirby[7] method, whereby the aldehydes are first eliminated with hydroxylamine hydrochloride so that alkali is consumed only for the saponification of esters, and not for the decomposition of aldehydes in addition. For the determination of citral, Poore employed the phenylhydrazine method of Kleber, which is discarded today in favor of the more accurate hydroxylamine method, because Kleber's method gives too high values. (Cf. Vol. I of this work, p. 285.)

Poore found that his samples of expressed California lemon oil possessed the properties shown in Table 1.2.

TABLE 1.2

	Specific Gravity 25°/25°	Total Solids	Refractive Index $n_D^{20°}$		Optical Rotation $\alpha_D^{20°}$		Citral Content Kleber Method	Ester Content
			Original	10% Distillate	Original	10% Distillate		
Minimum	0.8475	2.01%	1.4738	1.4726	+52° 43′	+46° 28′	2.0%	1.76%
Maximum	0.8525	4.52%	1.4749	1.4737	+70° 11′	+65° 44′	3.7%	3.12%
Average Properties	0.8497	2.96%	1.4743	1.4730	+62° 29′	+57° 54′	2.8%	2.38%

[5] Private communication.
[6] *U. S. Dept. Agr., Tech. Bull.* No. 241, March (1932).
[7] Unpublished. For details see the above cited paper of Poore.

Poore also studied the properties of California lemon oils produced in the various districts. He came to the conclusion that the averages of results by counties show a noticeable variance only in the lower optical rotation and higher percentage of citral from Ventura and Santa Barbara counties, which join one another. The highest average optical rotation was found in Riverside County and the next highest, in Los Angeles County. Otherwise the averages were fairly uniform. In optical rotation and citral content the difference between the maximum and minimum of all samples was large, the difference in optical rotation being 17° 28′ and the difference in percentage of citral (Kleber method) being 1.7.

The average is quite uniform, also, if commercial shipments of California Fruit Growers Exchange lemon oil are compared. This company has made it its policy to supply as uniform qualities as possible. Much emphasis is placed upon uniformity of flavor; but the properties, too, remain quite uniform throughout the years. This is possible only because enormous quantities of fruit originating from many counties and districts are worked up in one central factory, and large quantities of oils are bulked before shipping. Conditions in Italy are different not only because there is a marked difference in the oils produced in various sections of Sicily (in fact, by their characteristic properties Sicilian oils can often be recognized as originating from certain localities), but also because Sicilian oils are produced by numerous small operators and are often exported in small, nonbulked lots.

The large quantities of coldpressed California lemon oils, amounting to many hundred thousand pounds, analyzed by Fritzsche Brothers, Inc., New York, had physicochemical properties which varied within the following limits:

Specific Gravity at 25°/25°	0.849 to 0.855
Optical Rotation at 25°	+57° 0′ to +65° 36′, occasionally below +57°
Refractive Index at 20°	1.4742 to 1.4755
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	2.3 to 3.5%, usually around 3%, seldom as low as 2.3%
Evaporation Residue	1.5 to 1.8%
Solubility	Soluble in 3 vol. of 95% alcohol and more
Color	Lemon-yellow

Poore [8] also compared California lemon oils with imported Italian lemon oils and found that the California oils contained on an average about 0.5 per cent more solids, about 1.7 per cent less citral (Kleber method), and

[8] *U. S. Dept. Agr., Tech. Bull.* No. 241, March (1932).

about 0.6 per cent less esters (Seeker and Kirby method) than the Italian oils. In regard to optical rotation, the California oils were about 2° 24′ higher. However, these comparisons were based upon Italian oils imported quite some years ago, when they were made almost exclusively by handpressing. Since then, conditions in Sicily have changed, the bulk of Sicilian oils now being manufactured in small machines, which yield a little less citral and a somewhat higher evaporation residue than the old-fashioned method of handpressing.

Poore furthermore compared California lemon oils prepared experimentally by handpressing with the corresponding laboratory machine-made oils, and found that the latter contained from 0.3 to 0.5 per cent less citral. (In this connection see also "Physicochemical Properties of Italian Lemon Oils.")

It seems worth while to bring to the reader's attention a point in connection with the analysis of all citrus oils produced by the California Fruit Growers Exchange. Most government and commercial analysts, examining citrus oils to detect adulteration, approach the matter almost exclusively from that point of view. On the other hand, the chemists employed in the Corona and Ontario plants examine the oils for the purpose of determining their characteristics. These oils are known to be absolutely pure, there is no question of adulteration; nothing has been added to these oils, yet their analytical properties are determined. The two points of view—one aimed at finding out what is wrong with the oil and the other at trying to determine facts relative to pure oils—not infrequently lead to different conclusions.

Additional factors affecting the quality of California lemon oil are discussed in the section "California Citrus Oils, General Aspect—Summary."

Chemical Composition of California Lemon Oil.—The chemistry of California expressed lemon oil was investigated by Poore [9] who identified the following compounds:

α-Pinene. The first fraction (5%) consisted largely of α-pinene. Identified by its nitrosochloride m. 98°–99°, nitrolbenzylamine m. 121°–122°, and nitrolpiperidine m. 119°–120°.

β-Pinene. In the same fraction; characterized by oxidation to nopinic acid m. 125°–126°, according to Wallach's [10] method.

d-Limonene. The main constituent, b_{10} 57°–58°, n_D^{20} 1.4734; identified as tetrabromide m. 103°–104°.

γ-Terpinene. Small quantities only. Identified in the fraction b. 175°–185° or b_{10} 56°–66°. Oxidation with potassium permanganate, according to Wallach,[11] gave the erythritol $C_{10}H_{16}(OH)_4$, m. 238°–239° (corr.).

[9] *U. S. Dept. Agr., Tech. Bull.* No. 241, March (1932).
[10] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 354.
[11] *Ibid.*, 333.

Citral. Isolated as bisulfite compound from the oil obtained by steam distillation of the fractionation residue. When decomposed, an optically inactive oil of citral-like odor was obtained: b_{10} 105°–106°, n_D^{20} 1.4878.

Identified as α-citryl-β-naphthocinchoninic acid m. 199°–200° (corr.), α- and β-citral semicarbazones m. 134°–135°, and α-citral semicarbazone m. 163°–164°.

Octyl Aldehyde and Nonyl Aldehyde. Prolonged treatment of the limonene fraction with a 40 per cent bisulfite solution, and decomposition of the compound gave an oil resembling in odor octyl- and nonyl-aldehyde. Positive test with fuchsin aldehyde reagent.

d_{25}^{25} 0.8333, α_D^{20} +1° 23′, n_D^{20} 1.4252.

Semicarbazone m. 91°, naphthocinchoninic acid compound m. 238°–239°.

Poore could not find any methyl heptenone in California lemon oil, although this compound had been reported earlier by Schimmel & Co.[12] in Italian lemon oil (see Chemical Composition of Italian Lemon Oil).

Geraniol. Isolated as primary alcohol by the phthalic anhydride method; b_{10} 109°–110°, d_{25}^{25} 0.8801, n_D^{20} 1.4746, optically inactive.

Oxidation with chromic acid gave a strong citral note. Diphenylurethane m. 81°–82°. "A diphenylurethane prepared from geraniol obtained from Fritzsche Brothers, Inc., melted at 81°–82° and a mixture of the two melted at the same temperature."

Linaloöl. Traces were indicated in the corresponding fractions obtained after the primary alcohols had been eliminated by the phthalic anhydride method. Oxidation with chromic acid mixture gave a few drops of an oil with a characteristic citral odor.

A Tertiary Alcohol(?) $C_{10}H_{18}O$. Found in the same fraction after it had been freed from geraniol. This alcohol yielded to none of the tests for linaloöl and terpineol.

An Aldehyde(?). Obtained as a white crystalline precipitate in the fourth of the main fractions, b_3 45°, α_D^{20} +11° 47′, n_D^{20} 1.4647.

The crystalline precipitate melted at 58°–59°, after desiccation over sulfuric acid at 64°–65°. Positive test with fuchsin aldehyde reagent; reduction of ammoniacal silver nitrate solution. It is perhaps the same compound, the anhydrous form of which was found by Romeo[13] to possess the empirical formula $C_{10}H_{18}O_2$.

Acetic Acid, Caprylic Acid, and Capric Acid. The ester fractions obtained by steam distillation of the fractionation residue were freed from citral and saponified. The liberated acids were identified as acetic acid by preparation of the *p*-nitrobenzyl ester m. 77°–78°; no depression when mixed with synthetic *p*-nitrobenzyl acetate (see Reid[14]).

Caprylic acid and capric acid, the latter predominating, were determined as silver salts. No formic acid was found.

Bisabolene. Identified in the high boiling sesquiterpene fractions, as trihydrochloride m. 79°–80°.

[12] *Ber. Schimmel & Co.*, October (1902), 35.
[13] *Ann. chim. applicata* **15** (1925), 305.
[14] *J. Am. Chem. Soc.* **39** (1917), 124.

Cadinene. Present very likely in traces. The corresponding fractions gave a positive color test, according to the method of Wallach.[15] The nitrosate test was not successful.

Evidently the higher boiling portions of California lemon oil consist largely of bisabolene, with probably a trace of cadinene.

An Amorphous Compound(?). Found in the paste-like substance remaining after steam distillation of the fractionation residue. The white powder m. 71°–72° obtained by purification with various solvents failed to crystallize; it is not identical with citroptene (limettin) which melts at 146°.

Italian Lemon Oil

Introduction.—In Sicily and Calabria lemon cultivation and lemon oil production are still practiced as a primitive, scattered, village and family industry. Innumerable orchards, many of them showing age and neglect, are owned by countless small growers, who either sell their crops to small packing houses and oil producers in neighboring villages, or press the oil themselves, using the old-fashioned sponge process or small, locally constructed machines. Despite efforts of the Italian government to improve it and despite some real progress, the whole industry has remained somewhat primitive, conforming with the general pattern of low living standards prevalent in Sicily. Many orchards have suffered from attacks of *mal secco*. This disease, for which no remedy has yet been found, causes the leaves and twigs to dry up and the tree finally to die.

Producing Regions.—Almost 90 per cent of Italy's lemon fruit is grown in Sicily; the remainder is cultivated in neighboring Calabria, and in Campania, Apulia, Liguria, and Sardinia. In Sicily, the lemon producing regions form an almost continuous belt, lying between the sea and the coastal mountains, and stretching from the southeastern point of the island to the northeastern tip near Messina, and along the northern coast to Palermo. These regions can be classified in order of importance:

1. District of Mount Etna, most important center for the production of oil. (Catania and surrounding territory, Acireale, Giarre, Carruba, Fiumefreddo, Giardini.)
2. District of Messina. (S. Teresa di Riva, Nizza di Sizilia, the territory surrounding and to the west of Messina.)
3. District of Palermo. (Termini Imerese, Bagheria, Palermo, and surrounding territory, Monreale, Carini, Cinisi, Portinico.)
4. District of Siracusa. (Pachino, Rosolini, Noto, Avola, Siracusa and surrounding territory, Floridia, Priolo, Melilli, Augusta, Lentini.)

[15] *Liebigs Ann.* **238** (1887), 87.

5. District of Barcellona. (Barcellona, Patti, S. Agata di Miletello, S. Stefano.)

6. District of Vittoria. (Biscari, Vittoria, Comiso, Chiaramonte, Gulfi.)

Climate, Soil and Altitude.—The lemon tree requires a warm, sunny climate, a fertile, well-drained soil, and protection from storms or cold winters. It thrives especially well in the valleys and terraced slopes of the coastal mountains, but not above 2,500 ft., since above that altitude the winters are too cold, and irrigation during the long hot summers is too difficult.

Planting, Cultivating, and Irrigating.—Until about the middle of the last century, the lemon, like other citrus species, was propagated from seed. In 1862 root rot and gum disease destroyed practically all citrus orchards except those of the bitter orange tree. After that, lemons were grafted on the more resistant stock of the sour, or bitter, orange (*Citrus aurantium* Linn., subsp. *amara* Linn.). In cultivation the trees are planted in spaces of 15 ft. by 15 ft. The ground must be thoroughly hoed every year, or at least every other year, the Sicilian farmers still employing the primitive, almost timeless *zappa* for this purpose. For fertilization, stable manure, and chemicals such as ammonium sulfate and potassium sulfate, are freely applied. The most important factor, however, is proper irrigation, which demands considerable skill and experience, if root disease is to be avoided. Irrigation begins in June and continues at regular, sometimes weekly, intervals until the autumn rains set in. The water is conducted from higher reservoirs, through a system of ditches, to the trees on the terraces, after the soil around the trees has been loosened by hoeing. Proper irrigation, in combination with manuring and fertilizing, are the chief factors in maintaining vigorous life in the trees. Regular pruning eliminates dead wood, over-abundant branch growth, and allows for sunlight.

Five years after grafting, the tree bears about 200 lemons; and at the age of 15 or 20 years, about 1,000 lemons. A full grown healthy tree bears several thousand fruit yearly.

Harvesting.—The lemon harvest continues almost uninterruptedly throughout the year, but its importance varies with the seasons. The ripening of the fruit depends upon the period of blooming, for which reason there exist two types of fruit—winter lemons and summer lemons.

Winter Lemons.—The first bloom begins about the end of April and reaches its climax by the middle of May. Fruits of this bloom are harvested from the latter part of September to the end of October and represent 10 to 20 per cent of the entire crop. The second bloom extends from the end of May to the middle or latter part of June. Fruits from these blossoms are harvested from mid-November throughout December and represent about 40 per cent of the total harvest. This fruit, *frutta di durata,* is very hardy,

keeps well for months, and is, therefore, best adapted for export. The third bloom lasts from late June to early July and produces fruits which ripen during January and February of the following year. It amounts to about 30 per cent of the total production. This crop is not suitable to export, but serves for the production of oil and citric acid. There is a last and smaller bloom during July, the light colored fruits of which mature during March and April of the following year. These lemons, *bianchetti,* are used for export, chiefly, because the oil obtained from them is low in citral content, and has an optical rotation below the Pharmacopoeial limit.

Summer Lemons.—By a special method of cultivation, it is possible to grow a summer crop of lemons. The trees are kept dry without irrigation until the end of July, at which time irrigation is resumed. The trees bloom abundantly in August and September, and the fruit, called *verdelli* because of its green-yellow color, is harvested the following summer. This method of cultivation imposes considerable strain on the trees, and reduces their normal longevity of eighty years to fifty, or even forty years; however, the greater profits derived from the export of *verdelli* fruit offset this disadvantage.

Only the damaged or second grade of *verdelli* fruit is used for oil extraction, first, because the export of edible summer fruit brings very good returns, and second, because the properties of oil of *verdelli* lemons usually exceed the limits of normal lemon oil. Oil recovered from summer lemons for various reasons—such as damage to the fruit, high oil prices, low stocks of oil, heavy demand for oil, low prices for export fruit—is usually mixed with stocks remaining from the previous winter, to impart a certain freshness to old oil made from winter lemons.

The last fruits of the *verdelli* harvest are called *bastardoni.* Their oil, like that of the *verdelli,* has a low optical rotation; it is not exported as such, but usually bulked with the stock of normal oil.

Export of Edible Fruit and Expression of Surplus or Inferior Fruit.—Sicilian growers prefer to export their crop as edible fruit, this being quite remunerative; but only sound, well-shaped fruit, *frutta di durata,* can be used for this purpose. Light yellow, oval shaped, thin-skinned lemons containing few seeds are considered best. Windfalls, damaged fruit, second quality, *scarto,* and surplus fruit are processed for oil. Obviously, the age and condition of the orchards, as well as the climatic conditions to which the districts are exposed, play a deciding role in the production of first and second quality fruit.

As has been said, many of the Sicilian lemon groves are old and neglected, very little replanting having been done in past years to recover the monopoly on fruit export which Sicily once held. Hence, Sicily produces relatively much more second-grade fruit, fit only for oil pressing, than do California

and Spain. On the average, the northern coast of Sicily between Messina and Palermo produces 75 per cent of edible, and 25 per cent of second-grade, fruit. Conditions on the east coast vary; in the province of Siracusa about 25 per cent of the total lemon production in normal years is second grade, which proportion increases up to 75 and 80 per cent in the region around Mount Etna and north toward Messina. Calabria, too, produces some lemons which, however, are processed mostly in Calabrese machines (see also "Oil of Bergamot").

Total Production.—In the years prior to World War II, Italy produced from 600,000 to 800,000 kg. of lemon oil per year. The total yearly production fluctuates considerably and depends primarily upon climatic conditions and the demand for export fruit. In the years 1940 to 1947, the average annual production of Italian lemon oil was 350,000 kg.

Methods of Expression.—Years ago Sicily's lemon oil was produced exclusively by handpressing ("sponge method"), as described in a previous section. This simple method was in accordance with the primitiveness of the whole industry, scattered over wide areas where lack of roads prevented transport of fruit to centrally located factories. The industry, composed of isolated family units, permitted every member of the family to participate in the work; it provided employment for a great number of people; and last, but not least, it resulted in an excellent oil, better than that extracted in most machines.

In those days (not so long ago), a visitor to the coastal towns in Sicily was again and again confronted with this scene: citrus groves; picturesque villages—in which nothing had changed since time immemorial; and dim cellars where women and children cut the fruit in half, tearing out the pulp, while men, sitting for endless hours on low stools amidst heaps of citrus peels, pressed the oil from the peels into sponges held above earthen pots. However, the technical progress of our age penetrated slowly even to the remote villages of Sicily, bringing about a gradual transformation, a mechanization of the old "sponge process." Primitive, rather clumsy machines were introduced, most of them the products of local mechanics. Today the bulk of Sicily's lemon oil is extracted in the so-called *sfumatrici* and *pellatrici*, detailed descriptions of which have been given previously. It will be remembered that the *sfumatrici* treat only the peel from which the pulp has been removed, while the *pellatrici* (rotary rasping machines) treat the whole fruit. Some of these machines, especially the *sfumatrici*, produce oil almost as good as "sponge" oil, but the latter is still considered superior in appearance, flavor, preservative qualities, and citral content. Toward the end of 1939, Dr. F. La Face, the well-known authority on Italian citrus oils, told the author in Messina that only about 20 per cent of Italian lemon oil was then made by hand ("sponge pressing"), the balance being produced by ma-

chines. The war and resulting labor shortage accelerated the trend toward mechanization. Obviously, the change from "sponge pressing" to machines has not been without influence upon the quality of Italian lemon oil, especially since some of the older models still employed yield oils of inferior quality.

Variations in Quality.—The quality of Italian lemon oil depends upon several factors—the locality of production, annual variations in weather conditions, season of growth, conditions of the orchards and fruit, methods of extraction, etc. It is difficult, if not impossible, to obtain exact data on these variations, because of the scattered nature of the whole industry, the quality of oil from a certain village always being affected by more than one factor. The fruit processed in a village usually originates from several orchards, some of the trees being old or slightly diseased, whereas others are vigorous and healthy. Several types of machines may be employed in one village; but even with the same type of machine, the oils may vary according to the care and skill of the operator. Small lots may even consist of the produce of more than one grower.

The innumerable data published on the variations in quality of Italian lemon oil should be regarded with some measure of doubt. At best they give an approximate idea of conditions influencing the variations.

1. Yearly Variations.—The physicochemical properties of Sicilian lemon oils, and especially their optical rotation and citral content, vary slightly from year to year, depending upon climatic and weather conditions.

2. Seasonal Variations.—Oils made at the beginning of the main harvest period (extending from the end of November through December) are the finest in quality; they show the highest citral content and rotation, the

TABLE 1.3

Period	Condition of Fruits	Specific Gravity at 15°	Optical Rotation at 20°	Citral Content (Kleber's Method) (%)	Evaporation Residue (%)	Yield of Oil per 100 kg. of Fruit (g.)
End of October, 1925...	Green	0.8589	+61° 41′	4.65	3.97	413.6
March, 1926.....	Yellow (best quality)	0.8577	+61° 24′	4.35	4.54	263.2
End of June, 1926.....	Yellow (very ripe)	0.8586	+54° 38′	4.14	5.89	158.2

lowest evaporation residue. As the season progresses and the fruit ripens, the citral content and rotation decrease, whereas the evaporation residue increases.

Ajon [16] made the observations shown in Table 1.3.

From various sources in Messina, the author gathered the following information about the seasonal increase and decrease in the citral content of handpressed Messina lemon oil:

	Citral Content (%)
December to beginning of January	Up to 6.0
January to February	5.0 to 5.5
March	5.0 to 4.5
April	4.0 to 3.8

The properties of summer oils (*bianchetti, verdelli,* and *bastardoni*) differ from those of winter oils. The summer oils usually show a lower citral content, a lower specific gravity, and lower optical rotation. On the other hand, the odor and flavor of *verdelli* oils are excellent, sometimes even superior to the winter oils. For this reason *verdelli* oils are frequently used in Sicily for bulking with winter oils from the previous season.

Table 1.4 gives the properties of *verdelli* lemon oils that have been reported.

TABLE 1.4

Author	Specific Gravity at 15°	Optical Rotation	Citral Content (%)
Romeo (1924) [a]	0.8596	α_D^{20} +50° 47′	4.29
Berté (1926) [b]	0.8580 to 0.8600	α_D^{15} +50° 0′ to +55° 0′	3.0 to 4.0
Guenther (1929) [c]	0.8597	α_D^{20} +54° 50′	3.5

[a] *Prof. Ital.* **3** (1925), 304.
[b] *Camera di Commercio e Industria, Messina* (1927). *Ber. Schimmel & Co.* (1928), 38.
[c] *Am. Perfumer* **24** (1930), 729.

3. Geographical Variations.—The properties of Italian lemon oil vary considerably according to the different regions of production, especially in regard to optical rotation, which is characteristic for each region. Table 1.5 [17] gives a fair indication.

[16] *Annali della R. stazione sperimentale di agrumicoltura e frutticoltura, Acireale,* **8** (1926), 106.
[17] *U. S. Dept. Commerce, Special Circ.* No. 41, Washington, D. C., through *Ber. Schimmel & Co.* (1925), 34.

TABLE 1.5

District	Specific Gravity ($d_{15.5°}$)		Optical Rotation ($\alpha_D^{15.5°}$)		Evaporation Residue (%)		Citral Content (%)	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Siracusa	0.8593	0.8558	+67° 45′	+59° 27′	2.90	1.90	5.65	3.45
Acireale to Giardini	0.8588	0.8562	+64° 51′	+58° 51′	2.94	1.80	5.10	3.60
Santa Teresa	0.8602	0.8570	+63° 36′	+54° 33′	3.10	1.84	5.80	3.85
Messina	0.8602	0.8570	+63° 57′	+55° 33′	3.08	1.76	6.00	4.00
North Coast Barcelona to Orlando	0.8598	0.8562	+64° 54′	+57° 48′	2.82	1.78	5.00	3.40
Palermo	0.8593	0.8568	+64° 12′	+55° 6′	2.92	1.80	4.85	3.50

4. Various Extraction Methods.—The most important cause for variation in the quality and properties of Italian lemon oil lies in the method of expression.

Some years ago, La Face [18] published figures given in Table 1.6 showing the variations in the properties of handpressed and machine-pressed oils.

Since then, some of the machines have been improved considerably, but a number of the old models are still in use. La Face's table shows that in all machine made oils the citral content is lower, and the nonvolatile residue higher, than in the corresponding "sponge" oils, and that, although the specific gravity is increased, the optical rotation is decreased. The ester content is not affected much. These differences are more pronounced in the oils from rotary rasping machines (*pellatrici*) than in those from *sfumatrici;* in other words, the slower operating *sfumatrici* yield oils more closely resembling hand sponged oils than those made in *pellatrici.* Variations in the quality of machine oils are considerable, but published tables do not cover the common extent of variation, the range being too wide for a definition of limits. In fact, most of the data are rather misleading because:

1. There is a marked natural variation in the oil from one district to another.

[18] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **5** (1930), 182; quoted by Donovan, "Extraction of Citrus Oils," *Perfumery Essential Oil Record,* Special Issue (1937), 25.

TABLE 1.6

Method of Extraction	Specific Gravity at 15.5°	Optical Rotation at 15.5°	Citral Content (%)	Ester Content (%)	Non-volatile Residue (%)
1. Sponge	0.8578	+60° 36′	4.51	3.09	2.40
Vinci Machine	0.8590	+59° 37′	4.07	2.76	3.05
2. Sponge	0.8580	+58° 52′	5.78	3.31	3.15
Avena Machine	0.8590	+57° 48′	4.33	3.27	4.46
3. Sponge	0.8589	+59° 40′	5.26	3.49	2.70
Speciale Machine	0.8600	+57° 53′	4.51	3.38	4.93
4. Sponge	0.8580	+60° 35′	4.65	3.21	2.23
Cannavò Machine	0.8593	+59° 23′	3.75	3.10	4.96

2. One type of machine may be used in widely distant places, or it may be restricted to certain individual districts.

3. The results obtained with the same type of machine, using similar fruit from the same district, have varied enormously from one producer to another, according to his degree of care and skill. There is even variation in the same factory from one operator to another working with the same machines.

Donovan,[19] who studied the problem thoroughly, gave the properties shown in Table 1.7 for commercial Italian lemon oils produced in 1931.

The same author then wrote that, in general, the rotary rasping machines, which at that time were growing in popularity because of their ease and economy of operation and high yield, gave oils with a very high nonvolatile residue (usually over 5 per cent and quite often reaching 6 per cent, sometimes even 7 per cent and more). The citral content seldom exceeded 4 per cent, and often fell to 2.5 per cent and less against roughly 4 to 5.5 per cent in "sponge" oils. Such oils were useless for direct sale and were seldom, if ever, seen abroad. Their presence was easily detected in admixture; and, for the most part, they were concentrated in the usual way, the resulting terpenes and concentrates being marketed as such, or more commonly reconstituted or admixed with other oils. Oils of better quality were occasionally to be found, where greater care in processing had been used.

[19] *Perfumery Essential Oil Record,* Special Issue (1937), 26.

TABLE 1.7. EXAMPLES OF COMMERCIAL LEMON OILS, 1931

Process	Specific Gravity 15.5°	Optical Rotation 15.5°	Citral Content (%)	Non-volatile Residue (%)
Sponge	0.8580	+61° 33′	4.80	2.36
	0.8576	+59° 36′	4.60	2.16
	0.8574	+62° 9′	4.45	2.34
	0.8589	+58° 12′	4.35	2.60
	0.8562	+63° 24′	4.10	2.00
	0.8575	+62° 21′	3.90	2.46
Cianciolo	0.8570	+61° 42′	3.80	2.60
	0.8573	+59° 51′	3.55	2.72
	0.8584	+60° 12′	3.35	2.68
Morasca	0.8559	+63° 39′	4.20	1.94
	0.8566	+60° 27′	4.00	2.24
	0.8574	+59° 48′	3.90	2.30
	0.8577	+58° 30′	3.55	2.08
Andronaco	0.8567	+60° 12′	3.90	1.74
Vinci	0.8577	+59° 30′	4.70	2.90
	0.8574	+61° 48′	4.55	3.44
Rotary Rasping Machines (various types)	0.8573	+60° 33′	3.35	4.34
	0.8579	+61° 33′	3.10	4.68
	0.8582	+61° 15′	2.65	5.34
Do. Bennett Method	0.8587	+59° 12′	4.80	3.36

As would be expected from the low citral content of these oils, there was a marked weakening of the typical lemon fragrance. Moreover, the rotary machine oils were lacking in freshness and were characterized by the presence of a flat, sweetish, foreign note, sometimes described as "grassy." This grassy note varied in strength, so that 5 per cent of machine-made oil in admixture with "sponge" oil could be detected at once by the nose. In a few oils this off-note was almost imperceptible. Vinci oils were generally superior in odor, the best having the typical, fresh lemon note more or less weakened.

In color, again, there were great variations—from a brownish or greenish yellow tint to a heavy muddy brown or dark green, sometimes with a persistent turbidity.

From the above it will be gathered that the quality of the earlier machine-pressed lemon oils never, or only rarely, approached that of hand-sponged oils. When discussing these machines in a previous section, we noted that a number of factors contributed to the general lowering of quality in machine-pressed oils—catalytic action of the metal surfaces upon color and several

constituents, oxidation of alcohols and aldehydes by contact with air and certain enzymes, and hydrolysis of esters by contact with acid water. The prolonged action of pectinous and mucilaginous substances also has some influence upon the oil phase, with the result that machine-made oils contain an elevated percentage of resins and compounds of objectionable odor.

A detailed description of the various machines, their construction and principles of operation, and their merits, will be found in the above-mentioned paper of Donovan and, in more general terms, in a previous section of this work. Improvements have constantly been effected by progressive machine constructors in Sicily, through the extensive research in the Experimental Station in Reggio Calabria and through the work of Bennett.

The smaller, scattered, often backward, producing units have been slower to abandon older machines and methods, and during the past years oils of all types have continued to be produced. There has been a steady general improvement, however, and in this respect several government regulations have had a good effect. A few examples in Table 1.8 given by Donovan indicate the data for various lemon oils in 1935 and 1936; under Avena machines control analyses of the bulk production from a large factory using the Bennett-Cusmano process are listed.

In a comparatively recent paper, Bennett,[20] a leading authority on Italian citrus oils, reported that the grating machines which came into use about twenty years ago, and by 1930 were responsible for a considerable part of the production, certainly caused much deterioration in the quality of the oil. Instead of the normal amount of nonvolatile residue, the machine-made oils contained 4 to 5 per cent and upward and, instead of 4 to 5 per cent of citral, 3.0 to 3.5 per cent, and even less. These oils were not commercially acceptable and the machines are no longer used in the original way. A suitable modification of the method of working (Bennett-Cusmano process), however, enabled them to produce oils approaching the characters of sponged oil and with this change they have given quite satisfactory results.

The later machines, *sfumatrici*, by which the greater part of the Sicilian lemon oil is now produced, do not cause so much alteration. There is some loss of citral and the specific gravity and nonvolatile residue are also somewhat lower. Much of the oil produced in this way was of the range: citral 3.6 to 4.0 per cent, specific gravity 0.856 to 0.8575, residue 2.0 to 2.3 per cent.

It is probable, however, that but for the war the working of these machines also would have been improved and the results brought nearer to those of sponged oil. The existence of a standard such as that of the Pharmacopoeia was a strong inducement to seek improvement in methods of working.

[20] *Ibid.* **35** (1944), 308.

TABLE 1.8. LEMON OILS OF 1935 AND 1936

Type	Specific Gravity 15.5°	Optical Rotation 15.5°	Citral Content (%)	Non-volatile Residue (%)
Sfumatrici	0.8567	+62° 48′	4.80	2.00
Unspecified	0.8568	+62° 33′	4.65	2.22
	0.8587	+59° 12′	4.55	2.60
	0.8581	+61° 39′	4.45	2.48
	0.8571	+62° 21′	4.25	1.98
	0.8560	+68° 15′	3.85	2.12
	0.8551	+66° 48′	3.30	1.80
Sfumatrici	0.8570	+61° 45′	5.15	1.96
Morasca	0.8562	+63° 12′	4.90	1.68
	0.8561	+62° 57′	4.70	1.68
	0.8564	+62° 51′	4.30	2.36
	0.8569	+60° 57′	3.60	2.74
Sfumatrici	0.8564	+63° 9′	4.70	1.86
Andronaco	0.8563	+62° 9′	4.55	2.02
	0.8571	+62° 36′	4.45	2.04
	0.8561	+63° 42′	4.10	1.82
	0.8556	+63° 45′	3.95	2.18
Sfumatrici Cannavò	0.8562	+64° 42′	4.35	2.20
Peratoner	0.8532	+65° 54′	3.60	...
Process	0.8530	+63° 54′	3.35	...
(Distilled)	0.8544	+63° 48′	2.00	...
Rotary Rasping	0.8578	+61° 24′	4.45	4.00
Unspecified	0.8559	+67° 36′	4.15	2.68
	0.8584	+63° 30′	4.10	4.38
	0.8582	+59° 27′	3.85	3.72
	0.8578	+63° 12′	3.70	4.24
	0.8591	+60° 30′	3.55	4.54
	0.8589	+59° 21′	3.20	5.00
	0.8589	+60° 48′	2.40	5.76
Do. Centrifuged (but Not Bennett-Cusmano Method)	0.8580	+63° 0′	3.90	4.64

TABLE 1.8. LEMON OILS OF 1935 AND 1936 (*Continued*)

Type	Specific Gravity 15.5°	Optical Rotation 15.5°	Citral Content (%)	Non-volatile Residue (%)
Cannavò	0.8575	+62° 48′	4.40	4.06
(Whole Fruit)	0.8586	+62° 12′	4.00	4.94
	0.8572	+67° 42′ [a]	3.65	4.68
	0.8586	+61° 18′	3.30	5.02
Speciale (Whole Fruit)	0.8581	+61° 9′	4.05	4.86
Do. Bennett-Cusmano Process	0.8571	+63° 54′	4.65	2.80
Avena	0.8591	+59° 6′	4.35	4.00
(Whole Fruit)	0.8578	+60° 57′	4.35	3.64
	0.8573	+61° 15′	4.20	3.54
	0.8599	+58° 18′	4.10	4.74
	0.8579	+61° 21′	3.70	4.22
	0.8577	+59° 27′	3.10	5.54
Do. Bennett-Cusmano Process				
Dec.-Jan. Production, 1936 [b]	0.8568	+62° 51′	5.05	3.50
Jan.-Feb. Production, 1936	0.8567	+62° 24′	4.92	3.52
Feb.-Mar. Production, 1936	0.8570	+62° 48′	4.50	3.32
Sponge	0.8575	+62° 39′	4.80	2.50
	0.8563	+64° 36′	4.80	2.34
	0.8578	+61° 18′	4.45	2.54
	0.8561	+64° 0′	4.35	2.00
	0.8569	+63° 54′	4.05	2.34

[a] Siracusa oils.

[b] Control analyses of plant: bulks of around 4,000 lb.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[21] the properties of Italian lemon oil produced in the years up to 1930 varied within the following limits:

Specific Gravity at 15°/15° ..... 0.856 to 0.861; in some cases as low as 0.854
Optical Rotation at 20° ..... +57° 0′ to +61° 0′; in some regions of Sicily as low as +56° 0′ and as high as +67° 0′
Refractive Index at 20° ..... 1.474 to 1.478

[21] "Die Ätherischen Öle," 3d Ed., Vol. III, 34.

Citral Content (Improved Hydroxylamine Hydrochloride Method)	3.5 to 5.0%
Evaporation Residue	2.1 to 4.0% in handpressed oils; 5.0 to 6.6% in machine-pressed oil
Acid Number of the Evaporation Residue	19 to 39
Ester Number of the Evaporation Residue	100 to 214. When small quantities of oil (5 to 10 g.) are evaporated the ester number of the evaporation residue is not below 150; if larger quantities are evaporated the ester number has been observed as low as 100, probably because a part of the oil is resinified during the longer period of evaporation
Solubility	Usually not completely soluble in 6 to 8 vol. of 90% alcohol, because of the presence of mucilaginous and wax-like constituents. Clearly soluble in 0.5 to 1 vol. of 95% alcohol. Soluble in any proportion in absolute alcohol, sulfuric ether, chloroform, benzene and amyl alcohol. The solutions in carbon disulfide and benzene are usually slightly turbid because of the presence of water in the oil

Shipments of genuine Italian lemon oils, analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within the following limits:

Specific Gravity at 25°/25°	0.849 to 0.855
Optical Rotation at 25°	+57° 0′ to +65° 36′
Refractive Index at 20°	1.4742 to 1.4755
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	3.7 to 5.0%, in exceptional cases even higher. On the average it is 4.0%
Evaporation Residue	1.5 to 2.2%, usually 1.6%
Solubility	Soluble in 3 vol. of 95% alcohol and more

(Note that, in commercial usage, the terms "citral" and "aldehyde" content are often used interchangeably, even though they are not synonymous. The aldehydes contained in lemon oil consist chiefly of citral. By the hydroxylamine hydrochloride method, the *total* aldehyde content is determined; but the value is calculated as citral. Hence the commercial term "citral content.")

Bennett [22] suggests these limits for genuine Italian lemon oil produced up to 1944:

Sponge-Pressed Oils

Specific Gravity at 15.5°/15.5°	0.856 to 0.8595, usually 0.857 to 0.859
Aldehyde Content, Calculated as Citral	Usually 4 to 5%, occasionally less than 4%
Nonvolatile Residue	Usually between 2.2% and 2.8%, very rarely below 2%

[22] *Perfumery Essential Oil Record* **35** (1944), 308.

Italian Lemon Oil
(in general)

Specific Gravity at 15.5°/15.5°	0.8560 to 0.8595
Citral Content	Minimum 3.6%
Nonvolatile Residue	2 to 3%

Analysis.—Analysis of lemon oil should comprise determination of the specific gravity, optical rotation, refractive index, citral content, evaporation residue, and solubility; detailed procedures for these determinations may be found in Vol. I of this work.

When determining the optical rotation it is important to consider the temperature, as the angle of rotation changes with temperature, being reduced with increasing temperature. In order to obtain data for purposes of comparison of various oils, it is necessary to record the exact temperature at which an observation is made, and to recompute the angle of rotation for 25° (see Vol. I of this work, p. 242).

Examination of the evaporation residue may lead to interesting conclusions in cases where doubt exists as to the purity of the oil. It may be advisable to determine, also, the acid number and ester number of the evaporation residue.

The distillation test of the USP XIII (wherein the optical rotation of the first 10 per cent fraction is compared with the optical rotation of the original oil) serves no useful purpose today, as lemon oil is no longer adulterated with turpentine oil, other terpenes being much more suited for this purpose. For the same reason the test for pinene, suggested by Chace,[23] has lost much of its practical value.

The content of citral has remained an important criterion, especially for lemon oils imported directly from Italy. Many methods have been suggested and adopted in the course of years, each method giving somewhat different results. In fact, in recording the citral content of an oil, a notation of the method used in its determination should be included. The most exact procedure generally employed today is a titrimetric method using an alcoholic solution of hydroxylamine hydrochloride. In most of the commercial laboratories of Sicily and Calabria, this is the method now employed. Detailed instructions for this procedure may be found in Vol. I of this work, p. 285.

It is a well-known fact that lemon and orange peel oils easily spoil if improperly stored, especially when exposed to light and air. According to Naves,[24] this spoilage is caused by the formation, through autocatalytic

[23] *J. Am. Chem. Soc.* **30** (1908), 1475. *Ber. Schimmel & Co.*, October (1908), 53. "The Occurrence of Pinene in Lemon Oil," *U. S. Dept. Agr., Bur. Chemistry, Circ.* No. 46, October 30 (1909). Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 65.

[24] *Parfums France* **12** (1934), 314.

action, of peroxides, the percentage of which should not exceed 0.32 in good oils. The rate of oxidation of orange or lemon oil appears to be dependent upon the initial peroxide content. Naves [25] suggested a method of determining the content of peroxides by means of titanium III salts. Strausz [26] ventured the opinion that the spoilage of poorly stored lemon oil is caused by autoxidation (in the presence of air and moisture) of *d*-limonene to carvone and carveol,[27] but that the odor of these two compounds in the autoxidized oil is masked by the presence of *p*-cymene which, in turn, originates from the oxidation of isocitral. (For details, see the monograph on "Citral," Vol. II of this work, p. 326.)

Adulteration.—The examination of lemon oil for purity is one of the most difficult tasks confronting the essential oil chemist because of the ease with which this oil can be adulterated to meet all routine tests. Former crude forms of adulteration with turpentine oil are no longer encountered, much more efficient and equally low-priced adulterants now being available for this purpose. The terpenes and sesquiterpenes obtained as by-products of the preparation of terpeneless and sesquiterpeneless, or concentrated, lemon oils offer an ideal means of sophistication. Deficiencies in the evaporation residue, a result of the addition of terpenes and sesquiterpenes, can be remedied by the addition of the natural waxes which are also obtained in the making of concentrates. A lowered citral content is easily made up by the addition of synthetic citral. Lemon oil has, therefore, remained an article of strict confidence, to be purchased only from reliable sources. In many cases careful organoleptic tests and comparison with standard samples of unquestioned purity will furnish the expert a better indication of quality than a routine analysis.

The reputation of Italian lemon oil, in the years following World War I, fell to such a low that the Italian government was obliged to take energetic measures. In order to safeguard Sicily's citrus oil industry a number of laws were promulgated, establishing strict control of all outgoing shipments, and aiming at suppression of adulteration by unscrupulous producers and exporters. The importation of synthetics or natural isolates which might be used for sophistication—citral, linaloöl, linalyl acetate, and similar constituents of citrus oils, was prohibited; makers of terpeneless and sesquiterpeneless citrus oils must keep strict account of their manufacturing activities; and all terpenes, sesquiterpenes, and residual waxes must be

[25] *Ibid.*

[26] *Perfumery Essential Oil Record* **38** (1947), 260.

[27] In the author's opinion, the oxidation of *d*-limonene to carvone and carveol, although theoretically possible, has not been actually proved to occur during the spoilage of lemon oils.

delivered to the Italian government. These measures exert a wholesome influence upon the quality of Italian citrus oils, and it is to be hoped that they will not be relaxed.

Chemical Composition.—Investigations of the chemistry of lemon peel oil began as far back as 1820, but the results were confusing because the oils examined had occasionally been adulterated with turpentine oil, a common practice for many years. More reliable results were obtained toward the end of the last century by several workers, especially by the chemists of Schimmel & Co. whose findings are reported in the *Berichte* of that firm. Since then our knowledge regarding the composition of this oil remained almost stationary until Bohnsack [28] in 1944 carried out a new investigation of the chemistry of Messina lemon oil and identified some constituents hitherto not observed.

Octylene(?). Examining the lowest boiling compounds of lemon oil, Burgess and Page [29] isolated a hydrocarbon possessing these properties:

b_{768}	123°–124°
d	0.7275
α_D	±0°
n_D^{15}	1.4066
Mol. Refr.	38.54

Combustion analysis and determination of the molecular weight indicated the empirical molecular formula C_8H_{18} or C_8H_{16}. Oxidation with potassium permanganate gave butyric acid, which led Burgess and Page to assume that the hydrocarbon in question is octylene, and that octylene is a normal constituent of lemon oil.

α-Pinene. Investigations by Schimmel & Co.,[30] and by Burgess and Child,[31] led to the conclusion that traces, or very small quantities, of α-pinene occasionally occur in some normal lemon oils; in some oils it is absent. No explanation has, as yet, been found for the curious fact that the lemon tree produces α-pinene.

For the determination of traces of α-pinene in lemon oil, see Vol. I of this work, p. 337.

Camphene. Burgess and Child [32] reported the presence of camphene in lemon oil by preparing isoborneol from the corresponding fraction.

β-Pinene. Gildemeister and Müller [33] established the occurrence of β-pinene in lemon oil by oxidizing the fraction b. 165°–168° to nopinic acid m. 126°, and to nopinone. The latter yielded a semicarbazone m. 188°.

[28] *Ber.* **77B** (1944), 428.
[29] *J. Chem. Soc.* **85** (1904), 1328.
[30] *Ber. Schimmel & Co.*, April (1897), 19; October (1897), 22; April (1902), 24; October (1902), 33.
[31] *J. Soc. Chem. Ind.* **20** (1901), 1176.
[32] *Chemist Druggist* **62** (1903), 476.
[33] *Festschrift Otto Wallach*, Göttingen (1909), 441. *Ber. Schimmel & Co.* Oct. (1909), 49.

β-Phellandrene. Identified first by Schimmel & Co.[34] as nitrite m. 102°, and later confirmed by Gildemeister and Müller.[35] Oxidation with a dilute potassium permanganate solution gave a liquid glycol; boiling of this glycol with dilute acid yielded a hydrogenated cuminaldehyde, semicarbazone m. 203°–204°.

Methyl Heptenone. Isolating the aldehydes and ketones from lemon oil with bisulfite solution, and fractionating the regenerated aldehydes and ketones, Schimmel & Co.[36] found methyl heptenone in the foreruns b. 174°–179°; semicarbazone m. 136°–137°.

γ-Terpinene. This terpene was identified in an essential oil, for the first time, when Gildemeister and Müller oxidized the hydrocarbons of lemon oil boiling above 173°. The product of oxidation proved to be the erythritol of γ-terpinene, m. 237°.

d-Limonene. The main constituent of lemon oil; identified as tetrabromide m. 104°–105° by Wallach.[37]

Tilden's [38] claim that limonene occurs in lemon oil in a less pure form than in sweet orange oil and that the limonene fraction (Tilden's so-called "citrene") also contains cymene, $C_{10}H_{14}$, was disproved by Schimmel & Co.,[39] and by Gildemeister and Müller.[40] These workers contended that Tilden, in the course of his investigation, had used concentrated sulfuric acid, which undoubtedly reacted upon some of the constituents of lemon oil—e.g., upon phellandrene or γ-terpinene—thereby creating cymene. Gildemeister and Müller finally showed that cymene is not present in a lemon oil which has not been treated with sulfuric acid.

Octyl Aldehyde, Nonyl Aldehyde, Decyl Aldehyde, and Lauric Aldehyde. According to Burgess,[41] lemon oil contains an aldehyde; b_{15} 80°–85°. Von Soden and Rojahn [42] prepared the semicarbazone and came to the conclusion that this aldehyde consists in reality of two aldehydes—these being nonyl aldehyde and octyl aldehyde, the former predominating.

Elze [43] found that lemon oil contains also small quantities of *n*-decyl aldehyde (thiosemicarbazone m. 99.5°; oxidation of the aldehyde to decylic acid) and of lauric aldehyde (oxidation to lauric acid m. 44°), as well as traces of other aldehydes and ketones which could not be identified. Bohnsack arrived at similar conclusions in his investigation cited above.

Citronellal. The presence of citronellal in lemon oil was established by Doebner;[44] identified as citronellal-β-naphthocinchoninic acid m. 225°. Doebner's findings were later confirmed by von Soden and Rojahn. The aldehyde fraction of the oil (b. around 200°) gave a semicarbazone m. 83°–84°.

[34] *Ber. Schimmel & Co.*, October (1897), 22.
[35] *Festschrift Otto Wallach*, Göttingen (1909), 441.
[36] *Ber. Schimmel & Co.*, October (1902), 35.
[37] *Liebigs Ann.* **227** (1885), 290.
[38] *Pharm. J.* [3], **8** (1877), 190; **9** (1879), 654.
[39] *Ber. Schimmel & Co.*, October (1897), 23.
[40] *Festschrift Otto Wallach*, Göttingen (1909), 451.
[41] *Proc. Chem. Soc.* 17 (1901), 171.
[42] *Ber.* **34** (1901), 2809.
[43] *Riechstoff Ind.* (1926), 181. *Ber. Schimmel & Co.* (1927), 43.
[44] *Arch. Pharm.* **232** (1894), 688. *Ber.* **27** (1894), 352.

Barbier and Bouvault,[45] as well as Burgess and Child,[46] disputed the claim that citronellal occurs in lemon oil.

α-Terpineol. Schimmel & Co.[47] identified α-terpineol, phenylurethane m. 110°, among the higher boiling constituents of lemon oil, after having freed it from aldehydes with bisulfite. According to Paolini,[48] the α-terpineol is laevorotatory, $[\alpha]_D$ −2° 55′.

Citral. This aldehyde, discovered by Bertram,[49] is the most important and characteristic constituent of lemon oil, so far as odor and flavor are concerned. Italian lemon oils contain from 3.5 to 5.5 per cent citral, whereas California oils contain somewhat less.

Some authors have ventured the opinion that the citral occurring in lemon oil is not citral *a* and *b*, but some other isomer like γ-citral or isocitral which is supposed to possess a milder and finer odor. (For details, see the monograph on "Citral," Vol. II of this work, p. 326.)

The presence of citral in Italian lemon oil has been confirmed by Bohnsack.[50]

Linalyl Acetate and Geranyl Acetate. According to Umney and Swinton,[51] lemon oils from Messina and Palermo contain geranyl acetate. Removing the aldehydes from the terpeneless and sesquiterpeneless oils with hot bisulfite solution, saponifying the nonaldehydic constituents, and separating acetic acid from the saponification lye, these authors obtained a fraction which, upon oxidation, gave citral and a solid compound with calcium chloride. The substance in question is geraniol, which was originally present in the oil as acetate. Treating lemon oil from Palermo in the same fashion, Umney and Swinton isolated *l*-linaloöl aside from geraniol. They came to the conclusion that the variance in odor between the Palermo and Messina oils is caused by the different ratio between citronellal and citral, and by the presence of linalyl acetate in oils originating from the Palermo region.

After careful fractionation of Messina lemon oil, Bohnsack [52] arrived at the conclusion that this lemon oil contains no linaloöl, nor linalyl acetate.

Geraniol (Probably as Acetate). The same author isolated geraniol b_{15} 115°–116° as calcium chloride compound and characterized this alcohol by the preparation of the diphenylurethane m. 81°–82°, and by oxidation to citral *a* b_{20} 118°–120°, the latter identified as semicarbazone m. 162°–164°.

Nerol (Probably as Acetate). Bohnsack identified this alcohol b_{14} 114°–116° by the preparation of its tetrabromide m. 120°–121° and also characterized it by oxidation, with chromic oxide, to citral *b*, b_{20} 117°–119°. The latter could be identified as semicarbazone m. 166°–168°.

Citronellol (Probably as Acetate). Characterized by the same author through oxidation with chromic oxide to citronellal, the latter identified as semicarbazone m. 82°–84°.

A Compound, $C_{10}H_{18}O_2 + 3H_2O$. Romeo [53] observed that a terpeneless lemon oil suddenly separated crystals m. 58°, $[\alpha]_D$ +39° 26′ (after recrystallization in

[45] *Compt. rend.* **122** (1896), 85.
[46] *Chemist Druggist* **60** (1902), 812.
[47] *Ber. Schimmel & Co.*, Oct. (1902), 34.
[48] *Gazz. chim. ital.* **55** (1925), 804.
[49] *Ber. Schimmel & Co.*, Oct. (1888), 17.
[50] *Ber.* **77B** (1944), 428.
[51] *Pharm. J.* **61** (1898), 196, 370.
[52] *Ber.* **77B** (1944), 428.
[53] *Ann. chim. applicata* **15** (1925), 305.

water). The compound was odorless but had a slightly bitter taste. Combustion analysis pointed toward the molecular formula $C_{10}H_{18}O_2 + 3H_2O$. Keeping the substance above concentrated sulfuric acid gave the anhydrous compound $C_{10}H_{18}O_2$, m. 69°–71°. Treatment of a hot, aqueous, saturated solution with sulfuric or hydrochloric acid yielded a light yellow oil which possessed an odor resembling oils of thyme and peppermint. Combustion analysis of this oil pointed toward an isomeric compound $C_{10}H_{18}O_2$.

Bisabolene. Oliveri [54] first reported the presence of this sesquiterpene in lemon oil. Schimmel & Co.[55] determined the constants of this hydrocarbon and called attention to its surprisingly low specific gravity. Burgess and Page [56] prepared a hydrochloride m. 79°–80°. Gildemeister and Müller [57] showed that the sesquiterpene is identical with bisabolene, identified previously in bisabol-myrrh oil. The presence of bisabolene in the fraction b_{15} 130°–138° of Messina lemon oil has been confirmed more recently by Bohnsack.[58]

Cadinene. Bisabolene is accompanied by a higher boiling sesquiterpene, which also gave a hydrochloride. Gildemeister and Müller [59] did not have sufficient material available to raise the melting point above 110°–113° by repeated recrystallization. The behavior of this compound, however, was similar to that of cadinene.

More recently Bohnsack [60] confirmed the occurrence of cadinene in the fraction b_{15} 130°–138° of Messina lemon oil.

A Primary(?) Sesquiterpene Alcohol. The same author observed the presence of a probably primary sesquiterpene alcohol in the fraction b_{15} 165°–168° of Messina lemon oil. This alcohol had an odor resembling that of cedarwood oil.

Acids. Shaking lemon oil with a sodium bicarbonate solution, acidifying the solution with dilute sulfuric acid, and extracting with ether, von Soden and Rojahn [61] isolated small quantities of acids, partly volatile with steam, partly nonvolatile. The latter showed a faintly blue fluorescence and were soluble in alkali carbonates with a light blue color. In a more recent investigation of Messina lemon oil, Bohnsack [62] established the presence of the following acids:

Acetic Acid. Identified as anilide m. 113°–114°.

Capric Acid. In the fraction b_{16} 155°–160°; identified as amide m. 98°.

Lauric Acid. In the fraction b_{16} 172°–176°; identified as amide m. 97°–98°.

Methyl Anthranilate(?). Parry [63] expressed the belief that traces of this ester are present in lemon oil.

Limettin (Citroptene). Upon prolonged standing, coldpressed lemon oil separates a soft, mucilaginous, waxy mass, which also remains in the evaporation residue if

[54] *Gazz. chim. ital.* **21**, I (1891), 318.
[55] *Ber. Schimmel & Co.*, October (1903), 26.
[56] *J. Chem. Soc.* **85** (1904), 416.
[57] *Festschrift Otto Wallach*, Göttingen (1909), 448. *Ber. Schimmel & Co.*, October (1909), 50.
[58] *Ber.* **77B** (1944), 428.
[59] *Festschrift Otto Wallach*, Göttingen (1909), 449.
[60] *Ber.* **77B** (1944), 428.
[61] *Ber.* **34** (1901), 2809.
[62] *Ber.* **77B** (1944), 428.
[63] *Chemist Druggist* **56** (1900), 993.

the oil is rectified or concentrated. Early investigations offered no clue as to the nature of this compound, but later limettin was identified as 5,7-dimethoxycoumarin. For details the reader is referred to the monograph on "Limettin" in Vol. II of this work, p. 669. The presence of limettin m. 147°–148° in the non-volatile residue of Messina lemon oil has been confirmed more recently by Bohnsack.[64]

A Phenol(?). Aside from citroptene, the lemon oil residues, according to Schmidt,[65] also contain a phenol m. 89°, which is soluble in sulfuric acid, with deep red color. It does not react with ferric chloride.

Terpeneless and Sesquiterpeneless Italian Lemon Oil

Leone [66] studied the best conditions under which the oxygenated compounds of essential oils could be separated from the terpenes. Thus Leone treated 5 kg. of natural Italian lemon oil containing 5.35 per cent of citral by repeated fractional distillation at 25 mm. pr. and obtained 4.440 kg. of terpenes and 0.401 kg. of oil free of terpenes, but not of sesquiterpenes. This oil had a citral content of 40.5 to 43.2 per cent.

The sesquiterpenes were eliminated by a second fractional distillation at 20 mm. pressure, and by collecting only the fraction having a specific rotation of 0° to −4°. The oil thus obtained had a citral content of 60.5 per cent and was soluble in 1 to 1.5 vol. of 70 per cent alcohol. The yield was 5.36 per cent, calculated upon the original complete oil.

According to Bennett,[67] Italian lemon oil has a much greater range of natural variations than orange oil. When prepared by the sponge process or by those mechanical processes which do not cause any alteration in its composition, the content of citral in a freshly made oil may vary in the same season from 3.8 to 5.5 per cent according to the district in which the fruit was grown. It is natural, therefore, to find considerable differences in the yield of terpeneless oil and some difference in its composition. For example, see Table 1.9.

Nos. 1 and 2 were sponge-made oils, Nos. 3 and 4 machine-made oils of good quality with the natural properties unaltered.

The optical rotation of such terpeneless oils is usually in the neighborhood of −7°.

When the oils have been expressed by a mechanical process which causes change in their composition, quite different results are obtained. Such oils often contain only from 2 to 3 per cent of citral; but this loss of citral is accompanied by a large increase in the percentage of free alcohol, and the

[64] *Ber.* **77B** (1944), 428.
[65] *Apoth. Ztg.* **16** (1901), 619. *Arch. Pharm.* **242** (1904), 288.
[66] *Rivista ital. essenze profumi* **28** (1946), 5. *Perfumery Essential Oil Record* **38** (1947), 78.
[67] *Perfumery Essential Oil Record* **25** (1934), 111.

TABLE 1.9

No.	Citral in the Original Oil (%)	Yield of Terpeneless Oil (%)	Composition of the Terpeneless Oil		
			Citral (%)	Ester (%)	Free Alcohol (%)
1	5.05	6.70	53.90	13.70	14.15
2	4.15	5.80	44.85	. .	16.60
3	4.45	6.15	52.05	16.90	13.00
4	5.00	7.10	51.70	. . .	9.80

yield of concentrate is not greatly reduced but its composition (and flavor) is changed (Table 1.10).

TABLE 1.10

Citral in the Original Oil (%)	Yield of Concentrate (%)	Composition of Concentrate		
		Citral (%)	Ester (%)	Free Alcohol (%)
2.95	5.25	29.65	21.95	31.40
2.20	5.10	24.70	21.10	27.80
2.40	6.40	23.35	21.50	28.00
2.60	5.65	30.80	19.55	21.20

In good oils the relation, free alcohol/citral, is about 0.3; in deteriorated oils it varies from 0.7 to 1.2. This change, which is naturally accompanied by a change in flavor, makes it possible to detect the presence of this type of oil.

The optical rotation of terpeneless oils of this kind is generally $-3°$ to $-4°$.

Terpeneless lemon oils contain from 10 to 20 per cent of sesquiterpenes. When these are removed as far as possible the resultant oil may contain from 58 to 66 per cent of citral if made from unaltered oils rich in aldehyde, whereas, from the deteriorated oils mentioned above, the concentrate may have little more than 30 per cent of citral with an equal or greater amount of free alcohol.

Bennett also described a third kind of concentrate (occasionally encountered in commerce) prepared from the oil of green summer lemons (*verdelli*). Such concentrates are rich in esters and in sesquiterpenes. For example, a *verdelli* oil on distillation yielded 5.8 per cent of concentrate with these properties:

Optical Rotation	−10° 21′
Ester Content	25.90%
Free Alcohol Content	11.30%
Citral Content	31.15%

The supply of these *verdelli* concentrates fluctuates. They are often mixed with lots of lemon concentrates made from regular lemon oil (winter oil).

To conclude, it can be said that, in general, it is very difficult to establish precise or even satisfactorily close limits for concentrated, terpeneless, and sesquiterpeneless citrus oils. This applies particularly to lemon and bergamot oils which, due to provenience and method of expression of the natural oil, may be of variable chemical composition. As La Face [68] recently stated, a natural lemon oil containing, for example, 3 per cent aldehydes, may yield a terpeneless oil with 30 per cent aldehydes and 30 per cent free alcohols; whereas another lot of natural lemon oil, containing 5 per cent aldehydes, may give a terpeneless oil with 51 per cent aldehydes and 10 per cent free alcohols.

Regarding the methods of preparing concentrated, terpeneless and sesquiterpeneless citrus oils, the reader is referred to Vol. I of this work, pp. 218 ff.

We should not close this discussion without citing also the physicochemical properties of terpeneless and sesquiterpeneless Italian lemon oils given years ago by Romeo,[69] although these limits today no longer can be adhered to in a strict sense. They apply to sponge pressed oils which at the time of Romeo's writing formed the bulk of the Italian production.

Terpeneless Italian Lemon Oil

Specific Gravity at 15°	0.8935 to 0.900
Optical Rotation at 20°	−5° 0′ to −8° 30′
Refractive Index	About 1.481
Citral Content (Romeo Method)	40 to 52%
Ester Content, Calculated as Linalyl Acetate	16 to 25%
Sesquiterpene Content	20 to 24%
Solubility	Soluble in 1 vol. of 80% alcohol; soluble in 3 to 8 vol. of 75% alcohol

[68] Private communication of Dr. F. La Face, Reggio Calabria.

[69] *Atti congresso naz. chim. pura applicata* **2** (1928), 870. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 38.

Some oils are dextrorotatory because the terpenes have not been removed completely in order to preserve the natural bouquet of the original, complete oil.

Sesquiterpeneless Italian Lemon Oil

Specific Gravity at 15°	0.898 to 0.902
Optical Rotation at 20°	−3° 27′ to +1° 0′
Citral Content (Romeo Method)	60 to 65%
Ester Content, Calculated as Linalyl Acetate	15 to 25%
Sesquiterpene Content	Traces
Solubility	Soluble in 6 to 15 vol. of 60% alcohol; soluble in 1 to 3 vol. of 70% alcohol

Spanish Lemon Oil

The production of oil of lemon in Spain was started in 1937.

The main producing regions are located in the provinces of Murcia and Malaga, centers of production being Murcia, Alquérias, Alcantarilla, and Molina in the province of Murcia, and Alora and Pizarra in the province of Malaga.

The oil is produced by two methods, viz., sponge pressing, and puncturing of the oil glands in the flavedo with a mechanically driven needle.

The process of sponge pressing is carried out by girls, as the employment of men for this purpose would make the oil too expensive. Depending upon her skill, one girl can produce daily from ½ to 1½ liters of oil. One metric ton of common lemons "limón cumún" (which are processed from November to February) yields from 3 to 4 kg. of sponge-pressed oil; whereas "verna" lemons (which are processed from April to September) yield only 2.5 kg. of oil.

The average citral content of oil recovered from common lemons by sponge pressing varies from 4 to 4.5 per cent; the oil from "verna" lemons obtained by the same process averages only 3 per cent of citral.

The production of sponge-pressed lemon oil in Spain was 2 metric tons in 1945–1946, and 9 tons in 1946–1947.

The other means employed in Spain for the recovery of lemon oil involves the scraping or puncturing of the oil glands in the skin with a mechanically driven needle while the fruit rotates and is being held between two rapidly turning spindles. A more detailed description of this process will be found in the monograph on "Spanish Sweet Orange Oil."

By this method one girl can process about 2,000 lemons a day, obtaining approximately 750 g. of oil; a metric ton of fruit thus yields 3.26 kg. or about 7 lb. of lemon oil. The oil is collected in a receiver beneath the

fruit and separates usually in three layers. The top layer consists of clear light colored oil, the intermediate layer of a turbid liquid which must be filtered, and the lower layer of an emulsion containing much cell detritus, cell liquid, and essential oil, which has to be separated by pressing (or is sometimes distilled).

The quality of this type of oil cannot be considered to be as fine as that obtained by hand sponging, yet is fairly good at the beginning of the season (November–December) when the citral content amounts to 4.5 to 5 per cent. During the latter part of the season (January–March), however, the citral content falls to about 2 per cent.

In the year 1944–1945, Spain produced 45 tons of machine scraped lemon oil. In the year 1945–1946, 8 tons were produced, and in 1946–1947, 7 tons. From these figures it may be seen that Spain can be self-sustaining as far as oil of lemon is concerned. As a matter of fact, in years of reduced fresh fruit export the Spanish lemon oil could even compete with Italian lemon oil. The main difficulty in the production of regular quantities of Spanish lemon oil lies with the high prices of the fruit in periods when the export as fresh fruit is possible.

Physicochemical Properties.—Three samples of Spanish lemon oils examined in the laboratories of Fritzsche Brothers, Inc., New York, had the properties given in Table 1.11.

TABLE 1.11

	Sponge-Pressed Oil	Oil Obtained by Needle Scraping	
		Upper Layer	Intermediate Layer
Specific Gravity at 25°/25°	0.851	0.851	0.852
Optical Rotation at 25°	+62° 42′	+57° 23′	+59° 32′
Refractive Index at 20°	1.4748	1.4743	1.4745
Evaporation Residue	Insufficient sample	3.7%	4.1%
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	4.5%	3.4%	3.4%

Due to its usually high price, little, if any, Spanish lemon oil has been exported to the United States. The oil is used mainly on the local market for the flavoring of all kinds of food products, beverages, etc.

Brazilian Lemon Oil

The development of lemon oil production in Brazil has paralleled that of orange oil.

Fruit Varieties.—The fruit most suitable for the expression of oil is closely related to the Californian Villa Franca and Eureka, the latter a type of Sicilian fruit. Another variety grown in Brazil is the so-called Gallego (a sort of lime) which, however, yields practically no oil and is produced for local consumption as fresh fruit.

Producing Regions.—In the favorable and frost-free climate of Brazil, the lemon tree grows readily and produces abundant fruit, particularly in fertile soils. If it is possible to control the verrucosis, which appears in so many lemon groves, a large harvest of excellent export fruit can be expected. The lemon tree grows at medium altitudes but not in the tropical lowlands on the seacoast, nor at altitudes above 1,000 m. Near the city of São Paulo, and in the interior of the state of São Paulo, where altitudes average 400 to 600 m. and a favorable semitropical climate prevails, the tree flourishes beautifully.

The first lemon plantations were laid out near the city of São Paulo, but they were small, seldom comprising more than 500 trees, and the fruit was consumed locally. Later much larger groves were started in the departments of Limeira and Pitangueiras, the main producing regions of the orange also. Here the farming population is experienced in the growing and cultivating of citrus fruit. In some of the industrially organized orchards of Limeira and Pitangueiras, the number of lemon trees reaches about 500,000, most of the fruit being of excellent export quality.

Development.—The first attempts to press lemon oil from surplus fruit date back to 1936–1938, when a few plantings were started for that special purpose. With the outbreak of World War II, Brazil's young and rapidly growing soft drink, bakery, confectionery, and flavor industry in general found itself cut off from the supply of lemon oil and citric acid, which previously had been imported mainly from Sicily. Considerable effort was made, therefore, to produce these vital flavoring ingredients in Brazil and to process the fruit itself which, because of a shortage of shipping space, could no longer be exported.

Method of Production and Yield of Oil.—Today Brazilian lemon oil is expressed in the type of machine described in the section "Brazilian Orange Oil." Three hundred and sixty kilograms of lemons (whole fruit) yield on the average 1 kg. of oil, the yield depending upon and varying with weather conditions, advancing season, and ripeness of the fruit.

Physicochemical Properties.—A sample of genuine Brazilian lemon oil examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°/25°	0.851
Refractive Index at 20°	1.4746
Optical Rotation at 25°	+63° 5′
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	2.0%
Evaporation Residue	3.8%

By comparison with Italian or California lemon oil, this Brazilian oil exhibited a low citral content and a high evaporation residue, which indicates that the emulsion of essential oil, spray water, cell liquid, and cell detritus was probably separated not by centrifuging, but in settling tanks.

Total Production.—In 1944 Brazil produced almost 25,000 kg. of lemon oil, in 1945 about 14,500 kg. and in 1947 about 6,000 kg. By complete utilization of the presently existing lemon plantations in the state of São Paulo, 30 to 40 metric tons of lemon oil could be produced annually and without much difficulty. Additional lemon plantings have been started lately, but the future development of Brazil's lemon oil industry will depend upon several factors—competition of the California and Italian oils, consumption of fresh fruit on the home market, and export of fresh fruit from Brazil. Relatively little of the Brazilian lemon oil has been exported thus far, except to Argentina, chiefly because of the inflated price of the Brazilian oil, but also because the domestic flavor industry has been absorbing a large part of the oil. In 1946, 3,010 kg. of lemon oil were exported from the port of Santos.

Palestine Lemon Oil

For the past few years Palestine has been producing substantial quantities of lemon oil which were exported mainly to the United Kingdom (16 tons in 1941–1942).

The bulk of the oil was formerly expressed by the *écuelle* method, but now several types of machines, chiefly of Italian construction, are being employed. The crude oils are clarified by settling or, preferably, by centrifuging and filtering.

Efforts are being made to organize the lemon industry of Palestine in such a way as to convert the fruit into all its by-products, viz., citric acid, pectins, concentrated juice, and essential oil.

According to Davidsohn,[70] the physicochemical properties of Palestine lemon oil fall within those specified by the British Pharmacopoeia.

An examination of six Palestine lemon oils by Islip and Major [71] showed that they met the requirements of the British Pharmacopoeia in all respects except the following. The optical rotation was higher in every case than that allowed. The amount of citral in all six lemon oils fell into line with the requirements of the Pharmacopoeia, but in each case the figure was below the minimum of the ranges for Sicilian lemon oil quoted by Gildemeister and Hoffmann, and by Parry. The optical rotation of the Palestine oils was generally higher than that of Sicilian oils. The odor and flavor of Palestine oils were different from those of Sicilian oils.

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[70] *Soap, Perfumery & Cosmetics* **17** (1944), 337.
[71] *Bull. Imp. Inst.* **44** (1946), 5.

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Use of Lemon Oil

Oil of lemon is one of the most important flavoring oils, used widely in all kinds of beverages, soft drinks, soft drink powders and tablets, and in baked goods, such as cakes, pastries, pie fillings, confectionery, soft and hard center candies, gelatin desserts, ice creams, etc.

The oil is also employed in perfumes, toilet waters, eaux de Cologne, and in cosmetics to which it imparts a refreshing top note.

Handpressed Italian lemon oil is the type best suited for the making of terpeneless oil.

OIL OF PETITGRAIN LEMON

(Lemon Leaf Oil)

Essence de Petitgrain Citron *Aceite Esencial Petitgrain Limon*
Petitgrain Citronenöl

The leaves, petioles, and twiglets trimmed from the lemon tree, *Citrus limon* (Linn.) Burm. f., are occasionally subjected to steam distillation (cf. section on "Oil of Petitgrain Bigarade") by which means the so-called Oil of Petitgrain Lemon is obtained. Very small quantities are produced in Sicily, but production could be increased should the demand warrant it.

The yield of oil diminishes as the season advances, according to La

Face,[1] who reported a yield of 0.205 per cent in March and 0.181 per cent in April, the two months during which the lemon trees are trimmed in Sicily.

The oil has a petitgrain-like odor with a lemon "by-note" which is due to the presence of citral.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[2] the properties of the oil vary within the following limits:

Specific Gravity at 15°	0.867 to 0.894
Optical Rotation	+14° 0′ to +35° 0′
Saponification Number	14 to 46
Aldehyde Content	13.0 to 30.0%
Solubility	Occasionally soluble in 1 vol. of 80% alcohol; sometimes up to 19 vol. are required

Glichitch and Naves[3] suggested these properties:

Specific Gravity at 15°	0.865 to 0.888
Optical Rotation	+18° 16′ to +30° 52′
Refractive Index at 20°	1.4719 to 1.4751
Acid Number	Up to 1.5
Ester Number	30.52
Citral Content (Bisulfite Method)	9.0 to 18.0%
Solubility	Soluble in 4 to 6 vol. of 85% alcohol with slight turbidity; soluble in 0.5 vol. of 90% alcohol, without turbidity upon addition of alcohol

Trabaud[4] reported the following properties for four oils of lemon leaf distilled on the plantations of Nadel and La Sala near Labé, in the highlands of French Guinea (West Africa):

	I	*II*	*III*	*IV*
Specific Gravity at 15°	0.8663	0.8730	0.8690	0.8700
Optical Rotation	+52° 18′	+46° 52′	+31° 28′	+48° 20′
Acid Number	2.7	3.1	1.8	0.5
Ester Number	19.14	19.9	14.9	20.5
Ester Content	6.69%	6.93%	5.2%	7.1%
Aldehyde Content (by Oximation), Calculated as Citral	25.15%	27.83%	28.04%	29.1%
Solubility in 85% Alcohol	15 and over	6, slightly cloudy	6, cloudy	5.5, slightly cloudy
Solubility in 90% Alcohol	0.6 and over	0.5 and over	0.5 and over	0.6 and over

[1] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* (1942), No. 4–6, 7.
[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 75.
[3] *Parfums France* **7** (1929), 60.
[4] *Perfumery Essential Oil Record,* **27** (1936), 356.

According to Trabaud, the French Guinea petitgrain lemon oils are similar to the Italian, except that the rotation is generally higher in the former. The citral content is also higher in the Guinea oils; this seems to be one of their characteristics, as Trabaud never observed a Guinea oil with less than 25 per cent of citral, whereas the upper citral limit in Italian oils is lower. In exceptional cases, Guinea oils have been observed with as high as 51 per cent of citral, but these limits cannot be considered as normal. According to Trabaud, oil of petitgrain lemon is subject to various changes, due, probably, to the period of distillation. This is rather important, especially in Guinea, where the raw material can be collected almost all the year around.

Chemical Composition.—The chemistry of petitgrain lemon oil was first investigated by Schimmel & Co.,[5] who found that this oil contains citral. Later Litterer [6] and, still more recently, Glichitch and Naves,[7] established the presence of the following constituents:

Identified as:

d-α-Pinene. Pinonic acid semicarbazone m. 202° (corr.).

Camphene. Isoborneol m. 210°.

d-Limonene. Tetrabromide m. 104°; α-nitrosochloride m. 103°.

Dipentene. Tetrabromide m. 124°.

Citral. α-Citryl-β-naphthocinchoninic acid m. 199° (corr.).

Cineole. Iodole compound m. 112°–114°.

l-Linaloöl. α-Naphthylurethane m. 52°.

Geraniol. Diphenylurethane m. 80°–81°; tetrabromide m. 72°–73°; oxidation to citral.

Nerol. Tetrabromide m. 118°–118.5°; allophanate m. 101°.

α-Terpineol. Phenylurethane m. 111°–112°.

A Sesquiterpene Alcohol(?)

A Phenol(?). It possesses a guaiacol-like odor; phenylurethane m. 133°–134°; benzoyl compound m. 107°–108°.

A Sesquiterpene(?).

Pyrrole.

Furfural.

Geranic Acid. Isomerization to isogeranic acid m. 103°.

[5] *Ber. Schimmel & Co.*, October (1896), 59; April (1902), 81.
[6] *Bull. soc. chim.* [3], **33** (1905), 1081.
[7] *Parfums France* **7** (1929), 60.

Acetic Acid. Analysis of the silver salt.

A Nitrogenous Base(?). Traces only

According to Glichitch and Naves,[8] the composition of the oil is as follows:

	Per Cent
Terpenes	55
Free *l*-Linaloöl	4
Free Geraniol and Nerol, in Equal Parts	3
Linaloöl and α-Terpineol, as Acetates	2
Geraniol and Nerol as Geranates and Acetates	10
Citral	15
Sesquiterpene Compounds	2
Acids in Ester Form (Acetic and Geranic)	3

These authors arrived at the conclusion that the aromatic qualities of lemon petitgrain oil must be attributed mainly to the relatively high proportion of free and esterified nerol which it contains. It is a well-known fact that nerol possesses, to a much higher degree than geraniol, the property of communicating to the compounds in which it occurs, a peculiar pungency and tenacity. Oil of lemon petitgrain contains altogether certainly 7–8 per cent of nerol (the analytical estimate being necessarily slightly deficient), that is to say, more than any other known natural oil except that of neroli and of helichrysum.

Use.—Oil of petitgrain lemon is used in some Eaux de Cologne, perfumes and soaps to impart a strong and refreshing lemon note.

OIL OF SWEET ORANGE

Essence d'Orange Portugal *Aceite Esencial Naranja Dulce*
Süsses Orangenschalenöl (Portugalöl) *Oleum Aurantii Dulcis*

Introduction—History.—The sweet orange, *Citrus sinensis* (Linn.) Osbeck, is probably a native of southeastern Asia, more specifically of northeastern India and Pakistan or, perhaps more likely, of southern China and Indo-China. It has been cultivated so widely and for such a long time that the sweet orange is no longer known in a truly wild condition. However, most of the varieties now grown commercially originated in those

[8] *Ibid.*

countries into which this orange was introduced. Strangely enough, the sweet orange reached the Mediterranean basin at a much later date than the bitter (sour) orange or the lemon. Indeed, there exists no reference to the sweet orange preceding the thirteenth century. The path by which this delicious fruit, the most important of all citrus, first reached Europe is difficult to trace. Swingle,[1] the eminent citrologist, believes it highly probable that the superior varieties of the sweet orange, such as we now cultivate, were first brought from southern China by the Portuguese, about 1520, shortly after they occupied Macao, near Hong Kong, where very choice varieties of sweet oranges are grown. Similarly, Killermann[2] expressed the opinion that the sweet orange was introduced into southern Europe by the Portuguese navigators returning from India by the newly discovered route around the Cape of Good Hope. Apparently, the general application of the vernacular name Portugal orange to the sweet orange resulted from a belief that the first sweet orange tree in Europe was planted at Lisbon in the garden of the Count St. Laurent. Webber[3] concludes that the sweet orange in its introduction came by nearly the same route as the citron, the sour orange, and the lemon, but at a much later date, and through different agencies, reaching Europe sometime in the early part of the fifteenth century, probably over the Genoese trading route. Whatever the truth, there is abundant evidence to show that the sweet orange had become well established and had assumed commercial importance in southern Europe by the beginning of the sixteenth century. It does not seem to have been cultivated there until toward the middle of the fifteenth century.

The sweet orange, along with the lemon, was introduced to the New World on the occasion of Columbus' second voyage. Both spread to the West Indian Islands and to Florida, now one of the world's most important producers. The date of the introduction of the sweet orange to California, another great orange producer, may properly be considered as 1769, when the first mission was established in San Diego. Portuguese settlers brought the sweet orange to Brazil, and Spanish missionaries transported it to Paraguay where the tree was planted extensively and escaped cultivation, growing therefore semiwild over many sections of South America. Sweet oranges are today cultivated in all sections of the world where climatic conditions are favorable and are grown on a much larger acreage

[1] H. J. Webber and L. D. Batchelor, "The Citrus Industry," Vol. I, Univ. Calif. Press (1943), 411.

[2] *Naturw. Wochenschr.* **31** (1916), 201–208. H. J. Webber and L. D. Batchelor, "The Citrus Industry," Univ. Calif. Press, Vol. I (1943), 977.

[3] "The Citrus Industry," Vol. I, Univ. Calif. Press (1943), 12.

than any other citrus species. In importance of production, the principal orange growing countries shortly before the outbreak of World War II may be listed as follows: United States, Spain, Brazil, China, Japan, Italy, Palestine, North and South Africa, Egypt, Paraguay, and the West Indies.

In French Guinea (West Africa), wild and semiwild orange trees grow over wide areas, but none of the fruit is exported due to lack of roads in the interior; hence no figures as to quantities of fruit available have ever been assembled. Since about 1930 the fruit harvested by the natives in French Guinea has been processed for essential oil.

As far as the essential oil from the peel of the sweet orange is concerned, the producing countries may be listed approximately as follows:

United States (California and Florida)
French Guinea (Fouta Djallon)
Brazil (São Paulo and Rio de Janeiro)
Italy (Sicily and Calabria)
West Indies (Puerto Rico, Jamaica, etc.)
Spain (Southeastern Coast)
Palestine
Japan

Suggested Additional Literature

Y. R. Naves, "Analysis of Oil of Lemon and of Oil of Sweet Orange. Observations on the Determination of Aldehydes," *Parfums France* **10** (1932), 198.

"Analysis of Oil of Lemon and of Oil of Sweet Orange. Mechanism and Evaluation of Their Deterioration or Alteration," *Parfums France* **10** (1932), 225.

"Analysis of Oil of Lemon and of Oil of Sweet Orange. Measuring the Deterioration of the Oils by Oxidation," *Parfums France* **12** (1934), 314.

A. R. Feliu, "Composition and Physiochemical Analysis of Essential Oil of Sweet Orange," *Ion* **3** (1943), 111.

A. Laurence Curl, "Comparison of Several Types of Apparatus Devised for the Determination of Volatile Oil in Citrus Juices," *J. Assocn. Official Agr. Chem.* **30**. No. 3 (1947), 567.

J. Deshusses, "Estimation of Essential Oils in Lemon and Orange Peels as well as Dried, Grated Lemon Peel," *Mitt. Lebensm. Hyg.* **36** (1945), 316.

B. E. Proctor and E. M. Kenyon, "Objective Evaluation of Odor Deterioration in Orange Oil," Paper presented at the Ninth Annual Meeting of the Institute of Food Technologists, San Francisco, July 13, 1949.

California Sweet Orange Oil

Producing Regions.—California's orange producing regions have been described in the section "California Citrus Oils, General Aspect."

Varieties of California Oranges.—California produces principally two types of oranges, viz., the Washington Navel and the Valencia.

The *Washington Navel* was introduced into the United States in 1870 through the U. S. Department of Agriculture. It probably originated about 1820 at Bahia, Brazil, as a bud mutation from the Portuguese variety *Laranja selecta*. The Washington Navel has a smooth textured rind, is seedless, of attractive appearance, and of very good color and flavor. An excellent table fruit, it does not lend itself too well to the canning of juice, as such juice has a tendency to turn bitter on standing. As table fruit, however, the Washington Navel has attained great popularity and has always managed to command a premium price, which is a very important factor in the economy of the California orange industry. The Washington Navel ripens in California from late November to May.

The *Valencia* orange was introduced into California in part directly and in part via Florida, about 1876, by an Englishman, Thomas Rivers, of London. It contains very few seeds (up to 6), and is adapted particularly to the canning of juice, the juice of the Valencia being of superb quality. Originally the Valencia orange was adopted as a complementary variety for summer and fall requirements. Even when mature, the fruit remains on the tree for a prolonged period and has thus encouraged large-scale cultivation.

As has been pointed out, the quality of the juice from the Valencia orange differs considerably from that of the Washington Navel. So far as the odor and the physicochemical properties of the essential oil are concerned, the difference is only slight, as we shall see in the section "Physicochemical Properties of California Orange Oil."

With these two main orange varieties, California can supply the fresh fruit market all year round. This has been a most important factor in the rapid and enormous growth of the California citrus industry.

There exist in California also a few minor varieties of orange, such as the Ruby Blood, Malta Blood, Mediterranean Sweet, St. Michael, etc., but they have been extremely variable and difficult to market in uniform grades. In addition, they are small and seedy, and the red flesh does not seem to appeal to the American public, although the flavor of the St. Michael, for example, is very fine indeed. Furthermore, the tender rind of this variety is subject to much damage in handling and shipping.

Total Fruit Production.—The reader interested in the latest and more detailed figures on fruit production in the United States is referred to the regularly published Crop Reports of the U. S. Department of Agriculture, Bureau of Agricultural Economics, Crop Reporting Board, Washington, D. C. The following data have been reported for the last few years:

Oranges in Thousand Boxes

	Average 1935–1944	*1944*	*1945*	*1946*	*1947*
California	45,410	60,500	44,180	53,700	47,100
Florida	29,640	42,800	49,800	54,500	56,000
Texas	2,540	4,400	4,800	5,300	5,800
Arizona	600	1,150	1,210	1,270	760
Louisiana	280	360	330	390	300
Total	78,470	109,210	100,320	115,160	109,960

The orange crops of all states, with the exception of Florida, include also small quantities of tangerines.

The net content of boxes varies in the different producing regions. In California and Arizona, one box contains 77 lb. of oranges, in Florida and the other states, 90 lb.

Methods of Expressing the Oil.—Some years ago the principal method of expressing the essential oil from oranges and lemons used in California consisted in crushing the whole fruit between heavy stainless steel cylinders and in separating the essential oil from the juice by centrifuging. This method now is rarely employed and only on occasion, because it gives a somewhat inferior yield and quality of oil. In general, California's canneries and essential oil producers now use much more advanced processes and machinery, a detailed discussion of which will be found in the section on "Modern, Large-Scale Citrus Juice and Oil Pressing Equipment."

Yield of Expressed Oil.—When completely exhausted by steam distillation, the minced peels from 1 ton of California oranges yield from 11 to 15 lb. of oil. In the case of coldpressing, however, the yield of oil will always be lower, as a part of the oil remains in the peel. The yield of oil depends upon several factors, such as maturity, and condition of the fruit, the method of expression, the type of machines used, etc. Thus, the yield of oil per ton of fruit may vary from ½ to 8 lb. The treatment of the fruit must be modified according to its condition, and no general formula can be given. It may be stated that with modern coldpressing equipment, the yield of oil from one ton of normally sound fruit averages 4 to 5 lb. Compared with Florida oranges, California fruit seems to contain slightly more oil.

It is claimed that after a severe frost the fruit, on coldpressing, yields up to 50 per cent more oil than undamaged fruit would yield. Whether this is due to rupture of the cell walls by the frost, or to the fact that during a cold spell the fruit develops more oil, as protection against frost damage, has not yet been explained.

Bartholomew and Sinclair [4] have found that the yield of volatile oil per unit area from Valencia orange peel shows very little change from the time the fruit is half grown until it is mature, but the yield per fruit increases in proportion to the increase in surface area of the peel. After maturity the oil content of the peel appears to be governed more by climate and physiological conditions than by any change in the surface area of the fruit. Thus, the oil content of Valencia and Navel peel is highest in the inland fruits, and progressively lower in those grown nearer the coast. Large fruits yield more oil than small fruits when expressed as yield per surface area, but the reverse is true when the yield is expressed on a tonnage basis. The oil in the peel of Valencias increases progressively from the stem end to the stylar end of the fruit. In general, similar conditions hold true for Navels but not to such a marked extent.

Total Oil Production.—The total yearly production of California cold-pressed orange oil in normal years ranges from 350,000 to 400,000 lb., a very high percentage of which is produced by The Exchange Orange Products Company, California Fruit Growers Exchange, in Ontario, California. A description of this well-known cooperative organization will be found in a preceding section, viz., "California Citrus Oils, General Aspect."

With planned improvement, California's yearly production of coldpressed orange oil may easily reach 500,000 lb.

Physicochemical Properties of California Sweet Orange Oil.—Poore [5] made comparative studies on oils produced in different counties from Washington Navel and Valencia oranges and established the average for the period 1923 to 1926 as shown in Table 1.12.

Poore concludes that the averages, by counties, of the Valencia oils are uniform, except that the refractive index is higher and the citral content lower in the oils from San Bernardino than in those from the other two counties. His tabulation by seasons shows even more uniformity than by counties. The averages, by counties, of the Washington Navel orange oils are exceptionally uniform, so that no striking differences are noted. Comparison of averages of the Valencia and Washington Navel oils shows that the content of aldehydes in the Valencia oil is 0.6 per cent higher than that in the Washington Navel oil by the Kleber method, and the content of esters is about 0.5 per cent lower. The physical properties, however, are fairly uniform.

Comparing California sweet orange oils with imported Italian oils, Poore found for the latter a lower refractive index, lower content of esters and

[4] *Calif. Citrograph* **31** (1946), 293.

[5] "Analysis and Composition of California Lemon and Orange Oils," *U. S. Dept. Agr., Tech. Bull.* No. 241, March (1932).

TABLE 1.12. COMPARATIVE STUDIES ON OILS

All Counties	Specific Gravity 25°/25°	Total Solids (%)	Refractive Index at 20°		Optical Rotation at 20°		Aldehyde Content Calculated as Citral (Kleber Method) (%)	Ester Content (%)
			Original	10% Distillate	Original	10% Distillate		
CALIFORNIA VALENCIA ORANGE OILS								
Minimum [a]	0.8413	1.93	1.4728	1.4718	+95° 43′	+97° 56′	0.8	0.44
Maximum [a]	0.8482	6.26	1.4746	1.4727	+99° 35′	+100° 26′	2.2	1.76
Average Properties [a]	0.8440	3.61	1.4735	1.4723	+97° 47′	+99° 13′	1.4	0.83
CALIFORNIA WASHINGTON NAVEL ORANGE OILS								
Minimum [b]	0.8419	1.49	1.4731	1.4721	+94° 11′	+97° 31′	0.6	0.49
Maximum [b]	0.8503	8.17	1.4748	1.4727	+99° 19′	+99° 35′	1.0	2.58
Average Properties [b]	0.8455	4.53	1.4738	1.4724	+96° 56′	+98° 43′	0.8	1.38

[a] Sixty-three samples.
[b] Thirty-one samples.

residual solids, but a higher content of aldehydes (calculated as citral). As in the case of Italian lemon oils, the properties described by Poore for Italian sweet orange oils apply to oils made exclusively by the handpressing method.

The figures given in the following table are based upon analyses, carried out in the laboratories of Fritzsche Brothers, Inc., New York, of many hundred thousand pounds of coldpressed California oils.

Specific Gravity at 25°/25°	0.842 to 0.846; usually 0.844 to 0.845
Optical Rotation at 25°	+94° 0′ to +98° 15′; usually +95° 10′ to +97° 0′
Refractive Index at 20°	1.4723 to 1.4742; usually 1.4737 to 1.4741
Evaporation Residue	3.5 to 5.5%; occasionally as high as 7%
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	Average 1%
Solubility	Incompletely soluble in 95% alcohol, up to 10 vol.
Color	Orange to reddish-orange

Obviously, the evaporation residue of the oil depends upon the type of presses used for the extraction of the oil and upon the length of time the oil is permitted to stay in the cold room for precipitation of the waxes.

The California Fruit Growers Exchange keeps the properties and especially the flavor of sweet orange oils as uniform as possible by bulking large quantities; but, naturally, some allowance must be made for slight variations of properties caused by seasonal and climatic conditions. To keep up this uniform standard, these orange oils reach the market in bulked form as "Coldpressed California Orange Oils."

Chemical Composition of California Sweet Orange Oil.—The chemistry of coldpressed California orange oil was investigated by Poore [6] who found that the oils from Valencia and from Washington Navel oranges are similarly composed. Poore identified the following constituents:

d-Limonene. This is the main constituent, the oil containing about 90% of limonene, b. 175°–176°, α_D^{20} + 100° 58′, n_D^{20} 1.4728; identified by tetrabromide m. 103°–104°.

Decyl Aldehyde. Isolated as bisulfite compound from the oil obtained by steam distillation of the first fractionation residue; b_{756} 205°–207° (corr.).

The aldehyde contained in the Valencia oil: d_{25}^{25} 0.8256, n_D^{20} 1.4283, optically inactive; identified as naphthocinchoninic acid compound m. 238°-239° (corr.), and as semicarbazone m. 101°-102°.

The aldehyde contained in the Washington Navel oil: d_{25}^{25} 0.8352, n_D^{20} 1.4296, optically inactive; naphthocinchoninic acid compound m. 242°-243° (corr.).

Elementary analysis confirmed that the aldehyde is decyl aldehyde. According to Poore, it is the only aldehyde present in California sweet orange oil.

Nelson and Mottern [7] identified citral in the oil of Florida Valencia oranges by using the sodium sulfite method of Tiemann [8] because, with sodium bisulfite, citral may go into solution as stable dihydrodisulfonic acid compound from which it cannot be regenerated. This is probably the reason why Poore was unable to identify citral in California sweet orange oil.

Citral. Guenther and Grimm [9] showed that California sweet orange oil, as expressed from Valencia and from Washington Navel oranges, contains α- and β-citral (citral *a* and *b*). Employing the neutral sulfite method, Guenther and Grimm first separated decyl aldehyde from the terpeneless oil. The remaining aldehydes proved to be a mixture of α- and β-citral. Identified as α-citryl-β-naphthocinchoninic acid m. 199°. From the mixture of α- and β-semicarbazones, these authors isolated the α-compound, the crystals of which melted at 163°. The presence of β-citral was indicated by the formation of a semicarbazone compound of the citral mixture, m. 130°–131°.

Octyl Alcohol. Poore isolated small quantities of octyl alcohol, by the phthalic anhydride method, from the oil remaining after saponification of the aldehyde-free fractions; oxidation with chromic acid mixture gave caprylic acid. Confirmed by analysis of the silver salt.

An Olefinic Alcohol, $C_{10}H_{18}O$. Closely related to linaloöl, this alcohol was isolated from the oil remaining after removal of the primary alcohols with phthalic an-

[6] *U. S. Dept. Agr., Tech. Bull.* No. 241, March (1932).
[7] *J. Am. Chem. Soc.* **56** (1934), 1238.
[8] *Ber.* **31** (1898), 3318.
[9] *J. Am. Chem. Soc.* **60** (1938), 933.

hydride. The fraction b_{10} 84°–88° was especially examined for linaloöl and terpineol, but all attempts to prepare the phenylurethane, nitrosochloride, and terpin hydrate gave negative results. After the fraction had remained for four months in a sealed tube in the icebox, a phenylurethane m. 60°–61° was obtained.

Linaloöl. Oxidizing a small portion of the same fraction and isolating the aldehydes with sodium bisulfite, Poore obtained a drop of oil with the odor of citral. This indicates that only very little linaloöl is present in California sweet orange oil.

It seems worth while that these alcohol fractions be studied once more. Naves,[10] investigating the oil pressed from French Guinea oranges, found the corresponding fraction (freed from aldehydes and primary alcohols) to consist of *d*-linaloöl b_{10} 80°–82°, d_4^{17} 0.8684, α_D +17° 15′, n_D^{17} 1.46225; phenylurethane m. 66°. Linaloöl is accompanied in Guinea orange oil by a little *d*-α-terpineol b_{10} 98°–101°, n_D^{20} 1.4831; phenylurethane m. 111°–112°.

Formic Acid. Reduction of mercuric chloride to mercurous chloride; formation of a precipitate and mirror when warmed with mercurous nitrate.

Acetic Acid. Preparation of *p*-nitrobenzyl acetate m. 77°–78°, according to the method of Reid.

Caprylic Acid and Capric Acid. Like acetic acid, these acids were found after the fractionation residue had been steam distilled, and after the resulting oil had been freed from aldehydes with sodium bisulfite and saponified. Analysis of the silver salts indicated capric and some caprylic acid.

A White Amorphous Compound. According to Poore, it was present in the distillation residue but did not yield to crystallization, m. 62°–63°. (Cf. "Auraptene" in Vol. II of this work, p. 672.)

Because of the methods used in the United States for the expression of the oil from the fruit which involves considerable pressure, it appears quite possible that the California as well as the Florida orange oil contains also minute quantities of some pulp constituents which are absent in the hand-pressed Italian or African (French Guinea) oils. Investigating the pulp and locular tissue of the sweet orange for their fatty constituents, Matlack[11] identified oleic, linoleic, linolenic, palmitic, and stearic acids. The presence of an acid with a chain of 26 carbon atoms, and probably mixed with another acid containing 24 carbon atoms, was indicated. This would constitute what has frequently been reported as "cerotic acid." Glycerol, a phytosterol (sitosterol), a phytosterolin and a hydrocarbon, which seemed to be only slightly impure pentacosane, were isolated. The amount of glycerol found appeared to be too small to combine with all the acids present, whereas the amount of phytosterol was relatively large. This suggests that the fatty acids may be present partly in combination with the sterols. The composition of the pulp fat is quite similar to that of the peel (cf. Italian Orange Oil) with the exception that ceryl alcohol was

[10] *Parfums France* **10** (1932), 175.
[11] *J. Organic Chem.* **5** (1940), 504.

found in the peel but not in the pulp, and pentacosane in the pulp but not in the peel. That the oil occurring in the peels of oranges, lemons, and grapefruit contains minute quantities of acetaldehyde was proved by Biale and Weiss.[12] These workers suggested that most of the aldehyde is produced in the rind during the process of respiration and is not formed by the breakdown of substances during the course of the distillation. This contention can be substantiated by the presence of aldehyde in air passed through frozen ground peel or over whole fruit.

Evidently acetaldehyde cannot be present in the commercial citrus oils as this highly water-soluble aldehyde is extracted from the oil by the aqueous cell liquid, or by the juice or spray water during the process of pressing the peel according to the different methods.

It seems quite probable that the California sweet orange oil contains still other components which were not observed in the above-cited investigations but which have been more recently identified in French Guinea, Brazilian, and Italian sweet orange oils. The reader is, therefore, advised to consult also the monographs on these last-named types of oil.

Steam-Distilled California Orange Oils.—In the general discussion of the processes used for the recovery of citrus oils, we have seen that the peel does not yield all of its essential oil upon pressing. The press residue is therefore steam distilled, and large quantities of oil are obtained. In the case of oranges, the proportion of oils distilled by this process is even higher; the opposite is true in the case of lemons, however.

Steam-distilled orange oils have thus become of considerable importance. They are lower priced than the coldpressed oils and therefore find application where the higher price of the pressed oils may be an obstacle. Steam-distilled orange oils are used not only in flavor work, but also for perfuming—of soap, for example—where they serve as a low-priced yet excellent substitute for the pressed oils. Very large quantities of these oils are used yearly by the soap and cosmetic industries.

Examining a great many lots of steam-distilled California orange oils during the past few years, Fritzsche Brothers, Inc., found that their properties varied within these limits:

Specific Gravity at 25°.....	0.840 to 0.842
Optical Rotation at 25°.....	+97° 28′ to +99° 10′
Refractive Index at 20°.....	1.4714 to 1.4734; usually 1.4725 to 1.4730
Evaporation Residue.....	0.2 to 1.4%
Solubility.....	Incompletely soluble in 95% alcohol up to 10 vol.

[12] *J. Am. Chem. Soc.* **61** (1939), 635.

Florida Sweet Orange Oil

Producing Regions.—Florida's orange producing regions have been described in the section "Florida Citrus Oils, General Aspect."

Varieties of Florida Oranges.—According to Vosbury and Robinson,[13] the early citrus groves in Florida, Louisiana, and other Gulf states consisted almost entirely of seedling trees. Some of the old seedling groves remain and contribute heavily to the total fruit production, but they are disappearing, seedlings no longer being planted in Florida, except in a few localities where they are considered hardier than budded plants.

Largely as a result of the numerous varieties grown, Florida's orange output has been much less uniform in appearance and quality than that of California, where only two varieties, the Washington Navel and the Valencia, are extensively grown. Every district in Florida possesses its own variety of fruit, considered best adapted to the locality. The Parson Brown orange, for example, matures earlier and colors up more fully in the Hammock sections of north central Florida than in localities farther south. The Valencia variety, on the other hand, is less desirable for northern Florida, because it ripens late and the groves may be injured by frost. In general, however, there has been a marked tendency in the last thirty years to standardize, exploiting fewer varieties and limiting plantings to a few types only (the older varieties now being shipped together with the new ones). The reader interested in details regarding Florida's orange types will find ample information in the booklet "Citrus Industry of Florida."[14]

According to Camp,[15] the varieties of Florida orange fall into three general classes, viz., early varieties, which will pass the maturity test, required by law, during late October and November; midseason varieties, which are shipped from December to February; and late varieties, ready for packing at the beginning of March and shipped up to early summer. In the following brief description, we shall deal only with the principle varieties; at the same time it should be kept in mind that in Florida the essential oil is usually extracted only from those orange varieties which serve for the canning of juice, the oil in general being a by-product of canning operation.

(a) *Early Varieties.*—The *Parson Brown,* one of the older varieties, of relatively large size, contains 10 to 19 seeds, has a fairly coarse-textured flesh, and yields a deep yellow juice. The color of the peel tends to remain a dark green until late in the fall; but the green tint readily changes to yellow in the coloring room on treatment with ethylene gas. The tree, a

[13] "Culture of Citrus Fruits in the Gulf States," *U. S. Dept. Agr., Farmers' Bull.* No. 1343, September (1929).
[14] *Florida State Dept. Agr., Tallahassee, Florida* (1946).
[15] *Ibid.,* 30.

very vigorous, upright grower, is quite resistant to cold weather. The production of fruit has remained heavy, as among old plantings the Parson Brown still constitutes the most important orange. It is shipped from October to November but, under modern cultural practices, may carry well into December and January.

The *Hamlin,* one of the newer early varieties, is a rather small, slightly oval fruit, with a very smooth-textured peel, containing very few (1 to 5), or no, seeds. Rather insipid, and very sweet, the juice is not too well adapted for canning and storing over long periods. When grown under most favorable conditions, the fruit has proved to be of good dessert quality. A vigorous and heavy grower, the tree is more susceptible to cold spells than the Parson Brown. Many new plantations of the Hamlin have been started in recent years—more, in fact, than of any other early variety. If produced on rough lemon or on sour orange stock, the fruit may be held on the tree through January.

The *Washington Navel,* in California a standard, seedy variety of great importance and of superb quality as edible fruit, has never been satisfactory in Florida, where it dries up and loses its juice, especially under favorable vegetative conditions during a wet season. Experiments to develop a good strain of Washington Navel are being conducted in Florida. The present fruit is of medium to large size and ripens early. Under most favorable growing conditions, the fruit has proved to be of excellent quality, salable on the fancy fruit market but not practical for juice canning.

(b) *Midseason Varieties.*—The *Pineapple,* the leading and most widely grown midseason variety, derives its name from the rich and distinct pineapple flavor which fully ripened fruit often possesses. It is probably the best flavored of all Florida orange varieties. Usually round or slightly oblate, with a thin, deep red peel, the Pineapple contains 13 to 20 seeds, which constitutes something of a disadvantage. The trees produce heavily.

The *Homosassa,* a large orange-yellow fruit, round or slightly oblate, with a fairly coarse peel and flesh, contains 20 to 24 seeds. The flavor of pulp and juice is excellent. Because of its seediness, the Homosassa has not been planted recently on a large scale, but the old acreage remains considerable.

The *Jaffa,* a rather large orange-red fruit, round to slightly oblong, contains 6 to 9 seeds and abundant deep orange colored juice of excellent flavor. The tree, a vigorous grower, is very resistant to cold weather. The acreage has been increased in recent years.

Seedlings. As has been mentioned above, the early citrus groves of Florida consisted mostly of seedling trees, comprising innumerable varieties. Although no new plantings of seedling oranges have been started lately, the fruit from old seedling groves still constitutes a very large pro-

portion of midseason shipments. In general, the fruit is large, the rind smooth, the acid and sugar content high, and the juice of excellent quality. The number of seeds in the fruit varies, amounting usually to 20 or more. Groves planted with seedling trees produce heavily and consistently until neglected.

The *Temple,* another midseason variety, should be mentioned as the finest Florida orange for eating purposes. Being probably a natural hybrid between a sweet orange and some kind of mandarin (loose-skinned orange), the Temple contains a pulp and a juice markedly different from those of any regular sweet orange. The deep red, smooth or pebbly and thin peel can be detached from the fruit quite easily. Of medium size, oblate, usually slightly tapering toward the stem end, the fruit has a deep orange colored flesh and contains about 20 seeds. The slightly dwarfish tree, bearing a very round top, is quite susceptible to cold and requires a warm climate. The plantings have been increased considerably in recent years.

(c) *Late Varieties.*—The *Valencia* is now Florida's principal late variety, grown on a large scale, with production increasing. Of medium to large size, slightly oval, possessing a smooth, hard peel of deep orange color when mature, the Valencia contains an orange colored flesh and few (0 to 6) seeds. The highly colored juice is of most excellent quality. The peel seems to contain more essential oil than the peel of other orange varieties. The fruit is now shipped from March to June, even July, and with modern cultivation methods may be held on the trees until later. Vigorous and quite resistant to cold spells, the tree grows well on most soils and stocks.

Total Fruit Production.—Statistics on fruit production in Florida and other states of the Union will be found in the monograph on "California Sweet Orange Oil."

Florida Sweet Orange Oil, a By-Product in the Canning of Orange Juice.—As has already been explained, Florida produces enormous quantities of canned orange juice, the waste peel remaining after the expression of the juice being utilized for the extraction of its essential oil. The best equipped canneries possess their own oil processing installations; others sell their waste peel to independent operators who specialize in the expression of oil from peel which they purchase from canneries in the vicinity. Often such peel must be trucked over considerable distances and, under the influence of Florida's warm weather, may start to undergo slight fermentation while on the heavily loaded trucks. Obviously the quality of the oil depends greatly upon the condition of the peel and will be best if the oil is expressed from the peel immediately after the juice has been removed. In this respect, then, the independent operators who purchase their peel from canneries will be at a slight disadvantage. Such peel material also occasionally contains over-ripe or rotten fruit, which has been condemned by the Gov-

ernment inspectors, who strictly supervise and control the quality of all fruit to be processed for juice in the canneries. Some canneries neither process, nor sell, their waste peel but simply throw it away without paying any attention to the oil. Such practice, however, cannot contribute to the economic operation of a cannery. Besides, the disposal of the waste peel has become an increasingly serious problem in Florida. It cannot simply be thrown into the rivers, as it poisons the fish. The material must be buried in the ground, and that involves labor. Most of the modern canneries, therefore, now process their waste peel for the isolation of all by-products, viz., essential oils, pectins, cattle feed, and molasses.

Methods of Oil Recovery.—The methods employed today in Florida for the recovery of orange oil from the fruit were described in the section "Modern, Large-Scale Citrus Juice and Oil Pressing Equipment." For additional information the reader is referred to the work of Kesterson and McDuff [16] which gives valuable information on commercial production methods and properties of Florida citrus oils.

After expression from the peel, the oil is separated centrifugally from the aqueous phase, by passing the emulsion through a sludger (8,000 to 10,000 rpm) and then through a polisher (16,000 to 18,000 rpm). Following separation, the oil is placed in cold storage tanks and kept at 32° to 40° F. for a period varying from 1 to 12 weeks, during which time undesirable waxy materials separate as sediments of gummy consistency. The clear oil is decanted into stainless steel storage tanks or tin-lined containers, which are then maintained at a storage temperature of about 40° F. To prevent deterioration, air must be excluded from the containers by filling them full of oil or by displacing the air with carbon dioxide. Prior to shipping, another treatment of the oil in a centrifugal polisher may be necessary.

Yield of Expressed Oil.—As has already been pointed out on several occasions, the yield of oil depends upon several factors—primarily the season, the type and condition of the fruit, and the type of equipment used for the expression of the oil from the peel. As a rule, the peel of Florida oranges appears to contain less oil than the peel of California grown fruit.

Data gathered by the author while surveying Florida citrus oil production on several occasions, particularly in 1947 and 1948, indicate that the yield of oil varies considerably with the season, due probably to differences in the varieties of fruit processed in the course of the season. It has never been possible to determine the exact commercial yield of oil for each variety for the simple reason that the varieties overlap as they mature and several varieties usually arrive in the cannery at the same time. The only place

[16] "Florida Citrus Oils," *Univ. Florida, Agr. Expt. Sta., Gainesville, Fla., Tech. Bull.* No. 452 (1948).

to determine the commercial yield of oil is in a large juice cannery, but while in heavy production a cannery could never manage to separate definite varieties of fruit, which arrives from the groves in very large quantities. As a matter of fact, some varieties resemble one another so closely that even the expert would be unable to distinguish them.

The yield of oil described below was observed in one of the largest canneries of Florida. All the oil, at that time, was expressed from the peel in the same type of press (a kind of tapering screw press) after the juice had been removed in Rotary Juice Extractors.

1. Parson Browns, Hamlins and other early varieties:
   12 to 14 boxes [17] yielded 1 lb. of oil, which means 1.75 to 2.0 lb. of oil per ton of fruit.
2. Pineapples, Seedlings and other midseason varieties:
   12 boxes yielded 1 lb. of oil, which means 2.0 lb. of oil per ton of fruit.
3. Valencias and other late varieties:
   8–9 boxes yielded 1 lb. of oil, which means 2.7 to 3.0 lb. of oil per ton of fruit.

This yield obviously does not represent the total amount of oil contained in the peel (12–15 lb. of oil per ton of fruit), most of which is retained by the spongy albedo and can be completely isolated only by steam distillation of the minced peel.

As has been said, the yields mentioned above were obtained in one, rather obsolete, type of oil press; they are therefore only relative and refer to the different orange varieties as they mature during the season. Much better yields (4 to 5 and even 6 lb. of oil per ton of fruit) have been obtained in more modern oil presses—in the Pipkin Peel Oil Press, for example, or in the FMC Whole Fruit Extractor. A more detailed description of these novel oil presses will be found in the section, "Modern, Large-Scale Citrus Juice and Oil-Pressing Equipment."

For the three months, March, April, and May, 1948, during which period only Valencia oranges were processed, Kesterson and McDuff [18] observed average yields ranging from 1.85 to 9.70 lb. of oil per ton of *peel* (the peel, pulp, rag, and seeds amount to about one-half the total weight of the fruit). The yield of oil varied greatly with the type of press used for oil recovery and had a considerable influence upon the physicochemical properties of the oil (see below).

[17] One box of oranges in Florida contains 90 lb. of fruit.

[18] "Florida Citrus Oils," *Univ. Florida, Agr. Expt. Sta., Gainesville, Fla., Tech. Bull.* No. 452 (1948).

Hood [19] found a wide variation in the oil yield of Florida oranges, reporting values of 0.11 to 0.58 per cent of oil calculated on the weight of the whole fruit. Hood stated that the oil content does not reach its maximum until the oranges are fully matured, but occurs in commercial quantities before the fruit is ready for harvest. The same author also noted that a decrease in oil content immediately follows a period of rainfall.

Total Oil Production.—According to statistics supplied by the Florida Citrus Commission, State of Florida, Lakeland, the following quantities of coldpressed orange oil have been produced in Florida during the past few years:

	Pounds
1942–1943	170,150
1943–1944	198,509
1944–1945	244,553
1945–1946	281,991
1946–1947	335,726

As far as distilled orange oil is concerned, the following quantities were produced in Florida during the same years:

	Pounds
1943–1944	18,977
1944–1945	13,249
1945–1946	5,831
1946–1947	Not available

Florida's output of orange oil, expressed and distilled, could be increased very largely if the demand should ever warrant it.

In general, it is difficult to obtain reliable statistics on citrus oil production. The above given figures are undoubtedly correct for expressed orange oil, but the figures for distilled oil appear low, and probably do not include the large quantities of distilled oil (of inferior quality) which are recovered in the making of cattle feed and molasses from the waste peel.

Physicochemical Properties of Florida Orange Oil.—In a study of the "Physical Characteristics of Florida Orange Oil Produced During 1937–38 Season," von Loesecke and Pulley [20] came to the conclusion that there exists no variation in the physical characteristics of the oils prepared commercially from different varieties of Florida fruit. Neither is there any correlation between time of commercial production and physical properties of the oil. Oils produced from fruit grown in five different counties

[19] *Ind. Eng. Chem.* **8** (1916), 709.

[20] *Food Research Division Publication* No. 414, *U. S. Dept. Agr., U. S. Citrus Products Station,* Winter Haven, Florida.

showed no variation in physical characteristics, with the possible exception that oil from fruit grown in Hardee County may have a higher total solid content.

However, the method of expression has a marked effect upon the physical properties of the oil. The properties of orange oil obtained by different methods of extraction (Valencia variety only) during 1937–1938 are shown in Table 1.13.

TABLE 1.13

Method	No. of Samples Analyzed	Specific Gravity 25°/25°	Refractive Index at 20°	Total Solids (%)	Optical Rotation at 25°	10% Distillate	
						Optical Rotation at 25°	Refractive Index at 20°
Pipkin Machine	10	0.8435	1.4726	3.99	+96° 23′	+97° 32′	1.4720
Screw Press	10	0.8434	1.4723	3.76	+97° 12′	+97° 43′	1.4722
Rasping	6	0.8471	1.4742	10.27	+93° 37′	+98° 19′	1.4725

According to the same authorities, there has been difficulty in some instances in disposing of the Florida orange oil because certain batches did not meet the U. S. Pharmacopoeia standards and because there appeared to be a lack of uniformity among different lots. This may be due in part to the fact that in Florida production of oil has not always been under laboratory control, and an attempt is not always made to examine each batch with the thought of subsequent blending to obtain a product of uniform quality.

Samples and shipments of Florida coldpressed orange oil analyzed in the New York laboratories of Fritzsche Brothers, Inc., during the past years had properties which varied between the following limits:

Specific Gravity at 25°/25°	0.842 to 0.846
Optical Rotation at 25°	+96° 0′ to +99° 0′
Refractive Index at 20°	1.4723 to 1.4742
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	0.8 to 2.1%
Evaporation Residue	1.6 to 4.5%
Solubility	Incompletely soluble in 95% alcohol, up to 10 vol.
Color	Orange to reddish orange

The wax content of the Florida orange oils is in general lower than that of the California oils, probably because California has a dryer climate.

The above cited remarks of von Loesecke and Pulley regarding the quality of Florida orange oil no longer hold true. During the last few years the leading canneries in Florida have installed very modern equipment for the recovery of citrus oils and have given much attention to the production of high quality oils with the result that many lots of Florida orange oil now reaching the market are of very good odor and flavor and possess normal physicochemical properties.

In their recent and detailed study of the commercial production methods and properties of Florida citrus oils, Kesterson and McDuff [21] arrived at very interesting conclusions, not all of which, however, can be accepted as final because the work of these authors covers only one producing season (1947–1948) and will be continued for another year or two. For details the reader should consult the original paper of Kesterson and McDuff; suffice it here to summarize the tentative conclusions drawn by these investigators:

(*a*) *Relation of Yield of Oil to Properties and U.S.P. Specifications.*— The factor which was found to influence the physical and chemical properties of coldpressed oil of orange to the greatest extent was the yield of oil secured from the peel. As the yield increased, the values for the specific gravity, evaporation residue, and refractive index also increased, but the values for the optical rotation decreased. Thus the percentage of the total amount of oil that is actually extracted from the peel determines the characteristics of the oil and, therefore, its final quality. As the yield of oil is increased, more high boiling, high molecular weight constituents are evidently extracted, and the presence of a greater percentage of these compounds in the oil causes a reduction in the percentage of *d*-limonene, resulting in lower optical rotation values, since *d*-limonene is the most optically active component in the oil. A high yield results particularly in a high evaporation residue of the oil.

The yield of oil obtained by the various methods of processing varied from 1.85 lb. per ton of peel to 9.70 lb. per ton of peel. Commercial plants often have more peel than it is possible for them to process and still obtain the maximum amount of oil recoverable from the peel. This being the case, the plants are operated in such a manner as to produce the maximum amount of oil on an hourly basis. To do this they partially extract the oil from a large quantity of peel, rather than secure the maximum recovery of oil from a smaller quantity of peel. By operating in this manner they may secure very low yields of oil despite the fact that they are capable of

[21] "Florida Citrus Oils," *Univ. Florida, Agr. Expt. Sta., Gainesville, Fla., Tech. Bull.* No. 452 (1948).

obtaining much higher yields with the use of the same equipment. For example, the yields of oil secured when using the Pipkin Peel Oil Press and the Screw Press methods of extraction appear to be low when compared with the yields obtained by the other methods of extraction, but this is caused by the operation of the equipment from an efficiency standpoint on an hourly rather than a yield basis. Quality of the oil depends upon its properties, which are influenced by the yield obtained; the latter in turn is determined by operational procedure of the equipment used and other processing techniques.

Analyses of expressed oils of orange procured during the 1947–1948 season indicated that the oil produced by some of the oil recovery processes at certain times during the season did not meet the U.S.P. specifications, because some of the processes resulted in yields which were either too low or too high. However, it is apparent that if oil is extracted in such a manner that the yield falls within a certain range, then the oil will meet the U.S.P. specifications. If the yield falls below the minimum of this range, then the values for specific gravity, refractive index, and evaporation residue will be below the U.S.P. requirements. If the yield is above the maximum of this range, then the differences between the optical rotation and refractive index values of the original oil and the 10 per cent distillate will not meet the U.S.P. standards. Utilization of data obtained by Kesterson and McDuff will make it possible for any processor to produce an oil which will meet the U.S.P. specifications, provided that he is willing to change his oil recovery procedures. He may still use available equipment in such a manner that he will secure a yield of oil having these properties which are indicative of good quality. Excessively high or low yields should be decreased or increased by the mode of operation of the extraction equipment. Based upon the data accumulated by Kesterson and McDuff in 1947–1948, it may be estimated that a yield of 6.5 to 8.5 lb. of oil per ton of peel from midseason oranges or the extraction of 45 to 60 per cent of the total amount of oil present in the peel of any variety of fruit of good maturity will result in a coldpressed oil of orange that will meet the specifications of the United States Pharmacopoeia. It might also be added that oil extracted about the middle of May from Valencia oranges which had considerably passed peak maturity did not meet the U.S.P. standards. The reason that this late season oil was of lower quality was that low yields of oil were obtained with this type of fruit, because the peel had become soft and pliable, making the extraction of the oil more difficult.

(*b*) *Effect of Aqueous Phase on Aldehyde Content of the Oil.*—The flavor quality of oil of orange depends upon the numerous constituents of which it is composed. The aldehyde content of the oil, although not included in the U.S.P. specifications, is indicative of the *flavoring* qualities of the oil,

and although other constituents are also very important from a flavor standpoint, aldehydes are a predominant factor in orange and other citrus oils. The data obtained by Kesterson and McDuff show that the aldehyde content decreases as the amount of aqueous phase, which comes in contact with the oil during processing, is increased. The average aldehyde content of the expressed oils of orange, which were secured during March, April, and May from the four plants at which material balance studies were made, varied from 1.47 to 1.93 per cent. In one plant, where, at the suggestion of Kesterson and McDuff, the water used in the process was reduced from extremely large quantities to an amount sufficient to give 100 gal. of aqueous phase per gallon of oil produced, while other variable factors were kept constant, the aldehyde content increased from 1.08 to 1.64 per cent (an increase of 52 per cent). Thus, it appears that in order to produce an orange oil of high aldehyde content, the amount of aqueous phase that is allowed to come in contact with the oil during processing should be reduced to as small a quantity as is practically possible under operating conditions.

Aqueous Phase in Gal. per Gal. of Oil	*Aldehyde Content Calculated as Decyl Aldehyde* (%)	*Method of Extraction*
12.5	1.93	F.M.C. Whole Fruit Extractor
21.5	1.91	Pipkin Peel Oil Press (Roll)
100.0	1.58	Fraser-Brace Extractor
190.0	1.47	Screw Press

(*c*) *Relation of Fruit Variety to Properties.*—Consideration of the data obtained by Kesterson and McDuff shows that the oils recovered by any one process fell within a particular category of their own and remained there throughout the season. The differences in the physical properties of expressed orange oils that were obtained from different varieties of fruit by any particular process were not significant.

The aldehyde content of coldpressed oils of orange was highest when derived from Valencia oranges, particularly in March and April, but decreasing toward the end of the producing season. Mixtures of Pineapple and Seedling oranges gave an oil with a lower aldehyde content, and mixtures of Hamlin and Parson Brown varieties yielded oil of lowest aldehyde content. (The Parson Brown, Hamlin, Pineapple and Seedling varieties are early oranges, being processed from the end of October to the end of March; from then on to the end of June the fruit consists exclusively of Valencias.)

The variety of the fruit apparently had very little effect on the ester content of the orange oils. Oil of orange produced by the Fraser-Brace

Extractor from midseason varieties that were partially green in color was considerably higher in ester content than that recovered by the same process later in the season from the same varieties that were completely orange in color; the oil was also higher in esters than oils produced by the other methods. High evaporation residue values were found for the oils produced by the Fraser-Brace Extractor.

(*d*) *Storage of Fruit Prior to Oil Extraction.*—Results obtained by Kesterson and McDuff indicate that the length of time fruit was stored, prior to the extraction of the oil, was another factor which influenced the characteristics and quality of the oil. There were no significant differences in the physical properties of coldpressed oils of orange extracted from fruit on the same day it was harvested, and those extracted from fruit having been stored in fruit bins for three to five days before the oils were extracted. However, significant differences were found in the chemical properties. The ester content of the oil secured from stored fruit was 31.3 per cent higher than that extracted from fruit which had not been stored. The evaporation residue of the oil from stored fruit was 9.6 per cent greater, and the aldehyde content was 4.6 per cent smaller than that of the oil from fruit which had not been stored.

(*e*) *Effect of Maturity on Properties.*—In the studies of the effect of fruit storage on oil quality, all samples of orange oil were extracted by the same process and secured from the same variety of fruit. Therefore, over a period of four months information was obtained in reference to the effect of maturity on the properties of the oil. Here, again, differences were noted in the chemical characteristics rather than in the physical properties. The aldehyde content of Valencia orange oils increased as the maturity increased, reached a maximum when extracted during the early part of the Valencia season from fruit that just passed the maturity standards, and then decreased after peak maturity had been reached. The ester content of these oils was lowest when extracted during the early part of the Valencia season and gradually increased as the fruit became more mature. Valencia oranges that had passed peak maturity produced an oil with the highest ester content of any oils secured during the year.

In Table 1.14 Kesterson and McDuff give the maximum and minimum values which they found for the physicochemical properties of coldpressed orange oil produced in Florida by various methods of oil recovery, in the 1947–1948 season.

Before closing the discussion of the physicochemical properties of Florida orange oil, it might be of interest to mention briefly the influence which cold storage of the fruit, prior to the extraction of the oil, exerts upon the characteristics of the oil.

TABLE 1.14

Type of Oil	Coldpressed									
Method of Extraction	All Methods		Pipkin Peel Oil Press		Screw Press		Fraser-Brace Extractor		F.M.C. Whole Fruit Extractor	
Number of Samples Analyzed	35		4		8		6		17	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Specific Gravity at 25°/25°	0.8458	0.8416	0.8425	0.8420	0.8426	0.8416	0.8458	0.8441	0.8433	0.8420
Refractive Index at 20°	1.4734	1.4718	1.4722	1.4718	1.4724	1.4719	1.4734	1.4730	1.4729	1.4722
Refractive Index of 10% Distillate	1.4715	1.4703	1.4711	1.4708	1.4712	1.4707	1.4713	1.4703	1.4715	1.4707
Difference	0.0031	0.0008	0.0013	0.0009	0.0015	0.0008	0.0031	0.0017	0.0015	0.0010
Optical Rotation at 25°	+97.76°	+95.16°	+97.76°	+97.16°	+97.59°	+96.69°	+96.30°	+95.16°	+97.57°	+96.19°
Optical Rotation of 10% Distillate	+98.70°	+96.81°	+98.19°	+97.52°	+98.32°	+97.24°	+98.70°	+96.96°	+97.89°	+96.81°
Difference	2.44	0.00	0.85	0.01	0.73	0.03	2.44	1.51	1.30	0.00
Aldehyde Content (Calculated as Decyl Aldehyde) (%)	2.04	0.92	2.02	1.70	1.55	0.92	1.65	1.08	2.04	1.17
Ester Content [a] (%)	1.63	0.04	1.01	0.15	0.95	0.04	1.63	0.35	1.09	0.08
Evaporation Residue (%)	4.93	1.07	1.57	1.07	2.20	1.38	4.93	3.12	2.59	1.85

[a] Determined by the Seeker and Kirby Method as reported by Poore, *U. S. Dept. Agr., Tech. Bull.* No. 241 (1932), 1–30.

Investigating orange oil derived from South African fruit, which had been kept in cold storage for periods longer than six weeks, de Villiers [22] observed an increase in the specific gravity, optical rotation, iodine number, and saponification number, and a decrease in the aldehyde content of the oil.

So far as the distilled oils are concerned, Kesterson and McDuff [23] examined nine vacuum steam distilled Florida orange oils, obtained in the de-oiling of the juice, during the 1947–1948 season, and reported these values:

Specific Gravity at 25°/25°	0.8400 to 0.8464
Optical Rotation at 25°	+95.92° to +98.56°
Refractive Index at 20°	1.4715 to 1.4732
Aldehyde Content (Calculated as Decyl Aldehyde)	1.72% to 2.48%
Ester Content (Seeker and Kirby Method) [24]	0.22% to 1.38%
Evaporation Residue	0.08% to 1.24%

Chemical Composition of Florida Orange Oil.—The aldehydes occurring in Florida orange oil were first identified as *n*-decyl aldehyde and citral by Nelson and Mottern.[25] According to these authors, the early investigations of Italian sweet orange oil failed to prove the presence of citral because citral, upon treatment of the oil with sodium bisulfite solution, goes into solution as stable dihydrodisulfonic compound. A more thorough examination of the Florida oil was undertaken by Foote and Gelpi [26] who established the presence of the following constituents:

d-Limonene. Identified as α-nitrosochloride m. 102°–103°, as β-nitrosochloride m. 100°–101°, and as tetrabromide m. 103°.

The physical properties of the limonene fraction b. 175°–177° closely agreed with those recorded for *d*-limonene. The Florida oil investigated by Foote and Gelpi contained 90.4 per cent of limonene.

n-Decyl Aldehyde. Identified in the fraction b. 206° as semicarbazone m. 101°, and as 2,4-dinitrophenylhydrazone m. 104°.

Citral. Identified in the fraction b_{20} 110° as semicarbazone m. 161°, as naphthocinchoninic acid derivative m. 195°, and as 2,4-dinitrophenylhydrazone m. 107°.

Nonyl Alcohol (Probably). 3,5-Dinitrobenzoate m. 50° (instead of 52°).

[22] *Farming in South Africa* **4** (1930), 515, 529.
[23] "Florida Citrus Oils," *Univ. Florida, Agr. Expt. Sta., Gainesville, Fla., Tech. Bull.* No. 452 (1948).
[24] Reported by Poore, *U. S. Dept. Agr., Tech. Bull.* No. 241 (1932), 1–30.
[25] *J. Am. Chem. Soc.* **56** (1934), 1238.
[26] *J. Am. Pharm. Assocn.* **32** (1943), 145.

Linaloöl. Presence indicated by the similarity of the physical properties of this alcohol to those recorded for linaloöl.

b_{765} 180°, d_{25}^{25} 0.8654, $[\alpha]_D^{25}$ −12° 48′, n_D^{20} 1.4683. The fraction had a slight rose-like odor.

Most probably, the sweet orange oil produced in Florida contains still other compounds which were not discovered in the above cited work of Foote and Gelpi but which have been observed in other types of sweet orange oil, for example in the oils from French Guinea, Brazil, Italy, and California. The reader, therefore, should consult also the monographs on these last-named types of sweet orange oil.

French Guinea Sweet Orange Oil

Development.—One of the most startling developments in the essential oil industry is that of sweet orange oil in French Guinea, West Africa, the production of which rose from the modest beginning of a few kilograms in 1928 to about 275,000 kg. in 1939. Within a period of only ten years the Guinea oil assumed such importance that it outranked the Sicilian oil which previously had held the world's monopoly, and at times even challenged the position of the California oil. The latter has been able to withstand the competition of the Guinea oil because it is produced by very modern technical processes, and by one of the finest agricultural cooperatives in the world. The Guinea oil, on the other hand, is the product of an utterly primitive village industry in the remote highland region of French Guinea. Indeed, the methods employed in the production of California and of French Guinea orange oils afford an interesting study in contrast, unparalleled in the industry.

Botany.—According to a study by the French botanist, A. Chevalier,[27] the principal varieties of orange found in Guinea are *Citrus sinensis* Osbeck, var. *limo-viridis* Chev. and *Citrus sinensis* Osb., var. *djalonis* Chev. There also exist countless intermediary types, all resulting from the degeneration of *Citrus sinensis* Osb. The sweet Valencia orange is said to represent a type of the latter. It was originally introduced to Guinea several hundred years ago by early Portuguese navigators and explorers. Although the orange tree degenerated north and south of Guinea, it grows abundantly (partly cultivated, partly wild) in the highlands of the Fouta Djallon, where climate and soil conditions are ideal for its development. The orange tree of the Fouta Djallon is a large tree, 20 to 30 ft. high. In size and shape it resembles the apple tree of northern France. The smooth, ash-

[27] *Rev. botan. appl. agr. trop.* **15** (1935), 658.

colored trunk, 6 to 10 ft. high, is often bi- or trifurcated at the base. The crown consists of a large head with dark green foliage and abundant fruit on branches exposed to the light; the inner branches do not bear. If pruned, the tree would undoubtedly be more productive. The trees usually grow around villages and belong to the native community, but many are scattered over the interior of the country in small groups marking the former locations of abandoned Peul villages.

So far only fruit from trees around the villages has been exploited, and the many trees scattered over the interior are not touched. It is estimated [28] that there are more than 1,500,000 orange trees in the Fouta Djallon. They grow from seeds thrown away when the fruit is eaten, or from fallen fruit. The seedlings developing next to the mother tree are simply transplanted a little farther away and surrounded with thorny bushes to protect them from the teeth of grazing goats and cattle. The orange tree grows rather rapidly; at the age of five it measures 2.5 to 3.0 m. and begins to flower. When eight to ten years old it bears a substantial fruit crop, but full productivity is reached only in the twelfth to fifteenth years.

The trees are planted mainly for their fruit, which is very popular. A native consumes up to thirty and more oranges daily, especially during the months of November to March, when food is scarce. The juice, which they simply suck from the fruit, serves as a refreshing beverage. In this connection, it is interesting to note that compared with other native tribes many of the Peuls have very bad front teeth, partly destroyed, and it is said that this is due to excessive consumption of the acid juice.

Most of the orange trees in the Fouta Djallon are thirty to ninety years old, but there are also younger ones which have been planted recently, in line with the government's policy of encouraging the growing of citrus fruit and the production of oil. A full-bearing, healthy, twenty-year-old tree produces 1,000 to 1,500 and even 2,000 oranges per year.

The existence in French Guinea of so many local orange varieties is due to the fact that the natives are not familiar with the art of selection and grafting, and simply plant at random, exclusively from seed. Chevalier [29] said: "The Fouta Djallon district could provide us with oranges, lemons, mandarins and grapefruit, but practically nothing has yet been done to establish our colonial citrus cultivation."

In West Africa there are only old, indigenous types of citrus plants which can be used for grafting. To remedy this situation, the French colonial government maintains nurseries and tree schools, selects the best strains,

[28] Communication du Gouvernement Général de l'Afrique Occidentale Française, Agence Economique, No. 2768D, Paris, June 19, 1937.

[29] *Rev. botan. appl. agr. trop.* **15** (1935), 658.

and offers the young plants to the natives, teaching them also how to grow and cultivate properly. Of course, the indolence of the natives makes this educational campaign long and difficult.

Main Producing Regions.—The orange tree flourishes in all kinds of soil, especially on poor laterite gravel. It prefers altitudes above 800 m., but grows from 500 to 1,200 m. In the Mamou district of the Fouta Djallon, 80,000 orange trees were in full production in 1937, and in the Labé district 106,000 orange trees. During 1936, 20,000 new trees were planted in the region of Mamou and 52,000 in the region of Labé. These figures were given to the author by Mr. Jean Guilloteau of the École Pratique d'Agriculture du Fouta Djallon and are based upon counts by the natives; the figures suggested in former years by Chevalier were based only upon estimates, which date back as far as 1907. Even the data given by Guilloteau are inexact, however, because the natives, for fear of being taxed, are inclined to conceal the actual number of their trees.

Many orange trees grow outside of the Fouta Djallon—in the Kankan region of Upper Guinea and in the Kindia region of Lower Guinea, for example—but the fruit of these trees serves mainly as food for the natives, and not for the recovery of oil. Even in the Fouta Djallon only a part of the estimated 1,500,000 orange trees is actually exploited. Production of oil could be greatly increased, probably to a total of 800 tons in the interior. But there labor is scarce, and oil production would encounter many difficulties.

Producing Seasons.—There are two main harvesting periods—the winter and the summer. The winter harvest lasts from October–November to March–April and produces about 50 per cent of the total crop; whereas the summer harvest lasts from June–July to August–September and yields about 25 per cent of the crop. Weather conditions greatly affect flower development and, consequently, ripening of the fruit. A prolonged dry season before the winter harvest, for instance, may delay fruit development, with the result that fruit of that harvest matures only in June–July—or, in other words, at the beginning of the following summer season. There is thus really a year-round harvest, the production between the main seasons amounting to about 25 per cent of the total harvest.

The spherical fruit has a diameter of 5 to 7 cm. The skin is smooth, fairly thick, and adherent, and stays green for a long time; upon ripening it turns deep orange-yellow. The flesh is firm, yellowish, and very juicy. There exist varieties with either a very acid, fairly acid, or sweet juice, some of which equal the best edible oranges. Fruit of very good qualities could be raised by proper plant selection and grafting.

The natives prefer to extract orange oil only when there is no more

urgent work—such as harvesting cereal crops, or guarding the fields against grasshoppers, which attack in clouds and frequently devour entire crops in November. The extraction of the oil is, therefore, sometimes delayed until quite late in the season with a consequent poor yield. On the other hand, when in need of cash, the natives frequently work up fruit prematurely. Thus, the oil lots which accumulate in the trading centers are not uniform.

Expression of Orange Oil.—Since there exist only few good roads in Guinea, it is impossible to transport the fruit from the widely scattered groups of trees to producing centers. This, in turn, prevents the use of machines, because mechanical extraction would require transport of the fruit to centrally located plants.

The Guinea orange oil is obtained in a very simple way by scraping the orange with a tablespoon. The native holds the fruit between two fingers of the left hand, his thumb usually on the navel, and, while slowly turning the orange with the left hand, he scrapes the surface of the peel with a spoon held very short in the right hand. The spoons are sometimes sharpened on the edges or slightly dented so as to rupture the cells of the peel more quickly. The oil accumulating in the hollow of the spoon is dropped into a small enamel beaker which the native, squatting on the ground, holds between his legs. This work goes on for hours, usually in the shade of a tree to prevent exposure of the oil to the sun. Sometimes the workers use a banana leaf as funnel above the beaker so that no oil is spilled from the spoon. A skillful worker can extract the oil from one orange in 15 to 20 sec., which is quite remarkable. The oil slowly accumulates in the cup and is then carefully decanted from the aqueous cell content which, together with the oil, has been scraped from the peel cells. Instead of decanting, the natives sometimes pour the mixture of oil and cell liquid into a bottle which stands in front of them, partly imbedded in the ground to keep it upright and prevent exposure of the oil to light. Oil and water separate in two layers and, by turning the bottle and holding the thumb over the opening, the native can let the aqueous liquid drip out until only oil remains in the bottle. Some workers use a kind of primitive separating funnel made from the conical end of a dried gourd (calabash).

After repeated decanting from separated water and impurities, the clear oil is finally stored in bottles. The natives, never in a hurry, take plenty of time for this slow decanting; and their primitive method is, therefore, almost as efficient as filtration. If corks are not available, they twist a fresh orange peel around the mouth of the bottle and let it dry until it closes like a cellophane cap. Thus filled, the bottles are stored and sometimes even buried in the ground for protection from light and heat.

From the foregoing description, it is evident that the conditions under which the oil is extracted are unsatisfactory and not very sanitary because of too much contact of the oil with the fingers of the workers. The influence of light and air upon the oil slowly accumulating in the beakers easily brings about oxidation; and the bottles in which the oil is kept have sometimes served previously for kerosene, palm oil, or fat without being thoroughly washed. The government of the colony, aware of these conditions,



Courtesy of Fritzsche Brothers, Inc., New York.

Scraping of oranges in French Guinea.

has been trying to regulate the scraping of fruit and the storing of oil according to certain standards—for instance, prescribing the use of enameled or, preferably, aluminum funnels and the washing of the bottles with hot water and ashes prior to filling them with oil. It has also been suggested that the oil be transported in carboys of 10 to 15 liters at the most, which must always be well filled and properly corked. Decanting into a carboy of 10 liters, for instance, should be permitted only if the natives have actually produced 10 bottles of 1 liter each. This is about all that can be demanded of the natives; from this point on, the oil enters into circulation, passing through many hands, the fewer, of course, the better.

In the interior of French Guinea, all dealings in orange oil are made in liters and not by weight which is too complicated for the natives to understand.

According to Drouet [30] a highly skilled worker can extract 1.3 liters of oil in 7 hr., an average worker 0.6 to 0.7 liters. One thousand oranges yield from 1.0 to 1.2 liters of oil.

In the opinion of Guilloteau,[31] a healthy twenty-year-old tree produces yearly from 1,500 to 2,000 oranges which, in turn, give 1.0 to 3.0 liters, on the average 1.5 to 2.0 liters of oil.

According to de Tourris,[32] an orange tree bears from 1,250 to 1,500 oranges which yield 1 kg. of oil.

Trabaud [33] stated that 1,200 oranges yield about 1 liter of oil,[34] whereas in Sicily 2,000 fruit are required to produce the same amount of oil.

The fruit must be picked when well developed and, if possible, when it begins to mature and to turn from green to golden yellow. At that period the fruit seems to yield the maximum of oil which is, incidentally, of best quality. The natives are well aware of this fact and try to arrange the harvest accordingly unless, as mentioned before, they are occupied with other more important tasks. Early November fruit seems to give the highest yield and best quality of oil.

Transport of the Oil.—When the natives have a number of bottles ready, they pack them into baskets and, carrying the load on their heads, walk to the nearest trading center to sell the oil. Sometimes the trip takes days, but this is considered no hardship; on the contrary, it seems to appeal to their nomadic habits. The bottles of oil may represent the total output of an entire village and, therefore, the messenger is often accompanied by a representative of the chief who supervises the selling and guarantees the safe return of the money. The bottles may also be held in the village until a Syrian dealer with his merchandise truck arrives in the vicinity and buys the oil in exchange for goods which the natives need. Sometimes small lots of oil remain in the hands of natives for many weeks; traders and speculators, too, may hold the oil until market prices are sufficiently attractive.

Buying the Oil.—The large European trading companies of West Africa operate chain stores all over the country. These bazaars, located in the more important settlements, resemble in a way the general stores of the old American West or the present trading posts in northern outposts of Canada. The white manager of the store buys the oil from the natives with cash at the prevailing market value. Prices fluctuate from day to

[30] Conversation with Mr. Hubert Drouet in Mamou, French Guinea.

[31] Conversation with Mr. Jean Guilloteau at the Government Experiment Station near Mamou, French Guinea.

[32] Conversation with Mr. G. de Tourris, Ingénieur Agricole of the Chamber of Commerce in Conakry.

[33] *Riechstoff Ind.* **13** (1938), 119.

[34] The same yield is indicated in a report of the French Colonial Government, June 19, 1937.

day according to demand and supply, and news of such changes seems to travel quickly throughout the region. With the cash received the natives, in turn, buy merchandise in the store. During the height of the harvest hundreds of natives arrive daily with oil, and, if one day their number diminishes, the store manager knows that some competitor offers higher prices or that a Syrian barterer has arrived in the vicinity paying above the current market price. A messenger sent to investigate usually confirms this assumption.

Aside from these European owned and managed trading stores, one finds in the interior of Guinea a much lower type of store, usually run by Syrians, which prior to World War II used to sell low-priced Japanese merchandise.

A third group of buyers are the Syrian merchants who travel by truck from village to village and deal with the natives. The trucks are loaded with all kinds of finished goods for the natives and represent a lower type of the house-to-house canvassing system operating in the American Middle and Far West. These traders are usually financed with funds advanced in the form of merchandise by their Syrian or Greek mother houses in France. Starting out from Conakry, they drive all over the country bartering with the natives and finally return to Conakry, their trucks filled with native products. Unfortunately, not all of these barterers from Asia Minor enjoy a good reputation. They are said to be partly responsible for the unhealthy speculation from which the Guinea orange oil market has suffered so much.

One must see the sordid condition of some of the Syrian bazaars in Mamou or Labé to realize that European import and export houses cannot compete with them. Therefore, the Syrians are frequently in a position to offer the oil at slightly lower prices, although this advantage is usually counteracted by a poor quality oil, contaminated with kerosene, or adulterated with old, resinified lots. Many of these Syrian trading shops are located on the outskirts of a village, and the natives prefer to sell the oil there, for fear of being taxed if the officials in town should see them entering the village with a few bottles of oil. The government of the colony, aware of the damage inflicted upon its economy by overshrewd trading practices of some of the Syrian merchants, is ready to meet them, if necessary, with strict measures.

A fourth group of buyers consists of one or two organizations which simply buy the oil from the natives with cash without selling them anything. These houses are reliable because they specialize in buying and exporting orange oil and are expert at evaluating quality.

Storing and Filtering of Orange Oil.—In the ordinary trading shops the oil is treated like any other native product, without the special care which a delicate article, such as orange oil, requires. The managers of these stores



Courtesy of Fritzsche Brothers, Inc., New York.

Native shops and trading centers in villages of French Guinea's highlands (West Africa).

are young European employees, usually French, who have to serve a few years in the colonies before the mother house in France advances them to higher positions at home. Having no special experience with essential oils, they cannot be expected to evaluate orange oil properly. A simple odor and solubility test and sometimes a determination of the specific gravity by the hydrometer method is all they can do to determine whether the various bottles of oil are acceptable. Daily, hundreds of bottles are brought to the store during the producing season, and the busy manager cannot give the contents of each bottle a close examination. Thus, the small oil lots slowly accumulate in the trading stores and are bulked in drums.

The proper storing of orange oil under the primitive conditions and in the hot climate of French Guinea presents a rather difficult problem. Heat and the action of metal have a deteriorating effect upon orange oil and, unfortunately, the drums used by the dealers in the Fouta Djallon, especially by the Syrian merchants, are frequently of very poor quality, some of them having served previously for kerosene, lubricating or palm oil.

Filtration, too, should be done with great care because contact with air causes oxidation and resinification of the oil. The government of the colony, guided by the Chamber of Commerce in Conakry, has been making real efforts to improve the quality of Guinea orange oil by strict regulations in regard to proper storage and filtration.

According to de Tourris,[35] the practice of filtering the oil in broad daylight is wrong, particularly if repeated several times. Filtration should be carried out in enclosed vessels to avoid, as much as possible, exposure of the oil to air and light. The best method would be to let the oil settle for a number of days in filled drums and then to filter it very slowly. Filtration, however, should be carried out as soon as possible after extraction because the mucilaginous material, always present in orange oil, tends to give the oil a poor odor. The sediment in the bottoms of the drums, consisting of mucilage and wax, should be treated separately and should be very thoroughly filtered. It should not be left too long in the drums after the supernatant, clear oil has been drawn off, because contact with air causes it to oxidize and to turn rancid. Many lots of oil are damaged by the addition of these residues which are frequently left in the containers. The empty containers should be washed with lye solutions and thoroughly rinsed with fresh, hot water immediately after the oil has been removed from them. The bottoms where the residue is likely to adhere should be specially cleaned with fine cloth attached to a stick. The empty containers should be dried completely before being used again.

[35] "Étude sur L'Essence d'Oranges Guinée," Conakry, August 20, 1937. Private communication.

According to de Tourris,[36] galvanized iron drums are not practical because they have an unfavorable effect upon the keeping qualities of the oil. He suggested metal drums, plated inside with pure tin. Furthermore, he advised removing the small layer of air above the oil in the filled drum by blowing an inert gas, such as carbon dioxide, through the oil before closing the drum. The most important point is to fill the containers as completely as possible, leaving a space of about 1 in. to allow for expansion of the oil during transport.

Export of the Oil.—The oil drums accumulating in the trading centers of Mamou and Labé are finally transported to the port of Conakry and stored in warehouses of the large import and export companies, the main offices of which are located in England and France, especially in Marseilles and Bordeaux. Their Conakry branches fill shipping orders only upon instructions from the home offices in Europe. The same procedure holds true for the buying of oil through their smaller branches in the interior of French Guinea. Most oil is shipped from Conakry to France and transshipped to other parts of Europe or to America, but the mother houses in Europe frequently instruct their branches in Conakry to ship the oil direct to America. It is in the interest of the American buyer to receive shipments direct from Conakry or under international transit whereby the oil does not leave the customs warehouses in the French ports, if transshipment via France is unavoidable. Unscrupulous shippers in France might adulterate the oil before it leaves the country; the seal of the Chamber of Commerce in Conakry offers much greater assurance of purity.

Production Figures.—Production of French Guinea orange oil has developed from the experimental beginning of only a few kilograms in 1928 to about 260,000 kg. in 1939, quite a unique and spectacular record.

In general, production in the district of Mamou is larger than that in the district of Labé, but exact statistics are impossible because of the oil trading between the two regions. The region of Teliméné (Kindia) produces very little oil. There are still many unexploited regions farther inland, but the scarcity of labor in these sections would necessitate organizing large crews of skilled workers to process the fruit there. Thus, the present method of extracting the oil with spoons would probably make production in the interior too expensive. The problem, therefore, seems to suggest the introduction of simple, small, and portable machines. It is possible that some of the latest Sicilian machines, especially the *sfumatrici,* would suit the purpose.

The entire French Guinea orange oil production is influenced by the fact that the natives are rather indolent and work just enough to keep alive,

[36] *Ibid.*

purchase the necessities of life—such as dry goods, simple utensils, and wives—and pay their taxes. They are not interested in additional work, even if tempted by higher wages and a higher standard of living. During World War II, when French Guinea was isolated from the rest of the world and could no longer import or export, production of orange oil fell to almost nil, because the natives lost interest, being no longer able to purchase or barter any goods against their oil. In 1946, however, production increased again, reaching about 150,000 kg. For 1947 the figure was 170,000 kg. Most of this went to Europe, because for the United States the prices quoted were too high, prior to the devaluation of the French franc.

In 1948–49, the total fell to 60,000 kg. Production of orange oil in French Guinea is subject to extreme variations, depending chiefly upon the price of the oil on the world market, and upon demand.

A total yearly production of 300,000 kg. of oil is possible in French Guinea, provided demand and prices on the world market warrant it.

Quality Control by the Government.—The development of the orange oil industry in Guinea progressed quite satisfactorily for a number of years. Then suddenly grave complaints were registered by the users abroad because many lots were found to be adulterated with kerosene. This nuisance became so widespread that the reputation of the Guinea oil suffered a most serious setback. Lots containing 10 per cent of kerosene and more were not unusual; and, of course, such lots were absolutely worthless for use in flavors. If pure, the Guinea orange oil is a good product which compares favorably with the Sicilian sweet orange oil, but the widespread adulteration with kerosene seriously threatened its position. The primitive conditions existing in the remote regions where the oil is produced and the natives' lack of knowledge in handling essential oils facilitate adulteration, together with the fact that the oil passes through so many unreliable hands before it is shipped abroad. The natives found it easy to add kerosene to the oil and make a few pennies of added profit, but the most disturbing factor seemed to be the Syrian intermediaries, some of them unscrupulous and not too eager to follow ethical business principles. As a matter of fact, these Syrian barterers were blamed most for the widespread adulteration practiced at one time.

The situation became so serious that the French government had to take rigorous steps in order to suppress adulteration. These measures were of great benefit to the entire Guinea orange oil industry and the qualities reaching the consumers abroad became much better than those of years ago.

General Properties of Guinea Orange Oil.—Oil extracted from green fruit has an olive-green color; oil from the ripe fruit displays a yellow color; whereas oil oxidized and colored through contact with metal and rust shows

reddish to brownish tints. The oil from ripe fruit is "sweeter," and that from green fruit has a decidedly fresher note. Like all citrus oils, Guinea orange oil is extremely sensitive to the influence of air and light which affect its quality by oxidizing the terpenes and, its most important constituents, the aldehydes. Such oxidized lots lose considerably in value.

Physicochemical Properties.—According to Naves,[37] the properties of Guinea orange oil vary within the following limits:

	Extreme Limits	*Narrower Limits*[38] *Applying to About 90% of the Oils*
Specific Gravity at 15°	0.8480 to 0.8520	0.8485 to 0.8510
Optical Rotation at 20°	+95° 30′ to +98° 40′	+96° 0′ to +98° 0′
Refractive Index at 20°	1.4720 to 1.4740	1.4724 to 1.4735
Evaporation Residue	1.17 to 3.10%	1.52 to 2.6%
Acid Number of Residue	21.0 to 38.0	27.4 to 35.5
Ester Number of Residue	92.0 to 160.0	130.5 to 152.8
Saponification Number of Residue	122 to 190	150 to 185
Aldehydes as $C_{10}H_{20}O$ (Hydroxylamine Method)	1.1 to 2.9%	1.2 to 2.2%
Solubility in 90% alcohol	Soluble in 4 to 20 vol., sometimes less	Soluble in 4 to 16 vol.
Solubility in 95% Alcohol	Soluble in 0.5 to 5 vol.	Soluble in 0.5 to 4.5 vol. and more

In 1935, the same author indicated that the upper limit of the optical rotation is +99° 16′, and that of the evaporation residue, 4 per cent.

Oils extracted from fully matured fruit exhibit a higher specific gravity, refractive index, aldehyde content, and evaporation residue, but a lower optical rotation than oils pressed from green fruit. Evidently, the altitude, also, influences the quality and properties of the oil; the odor of oils originating from Labé (average altitude 1,100 m.) differs from that of oils from the Mamou region (average altitude about 800 m.). Definite data on the properties of the two types of oil are not available, however, because the commercial lots usually consist of mixtures from the two regions where the oil changes hands frequently.

The numerous lots of Guinea orange oil analyzed in the New York laboratories of Fritzsche Brothers, Inc., during the past years had properties which varied within these limits:

Specific Gravity at 25°/25°	0.843 to 0.845
Optical Rotation at 25°	+93° 47′ to +97° 45′
Refractive Index at 20°	1.4721 to 1.4735
Evaporation Residue	1.2 to 2.7%

[37] *Parfums France* **10** (1932), 163.

[38] These limits applied also to Guinea orange oil of 1940 harvest, according to a private communication from Mr. de Tourris, Conakry.

The quality of the pure Guinea orange oil compares favorably with that of the Sicilian oil.

The Guinea oil lends itself very well to the preparation of terpeneless oils, provided it does not contain even the slightest trace of kerosene or mineral oil, which would show up as a most disagreeable by-odor in the concentrated terpeneless and sesquiterpeneless oil. Bennett [89] found 40 to 45 per cent of aldehydes in the terpeneless Guinea oil and only 29.5 to 36.6 per cent in the terpeneless Italian oils.

Adulteration.—There are three forms of adulteration of which the user of Guinea orange oil must be aware.

1. The usual addition of orange terpenes obtained as by-products in the preparation of terpeneless and sesquiterpeneless oils. Such adulteration is done outside of Guinea, chiefly in Europe, by dealers who are versed in the more advanced forms of sophistication. This "art" is not known in Guinea; besides, terpeneless oils not being produced there, no orange oil terpenes are available. Furthermore, the Custom House and the Chamber of Commerce in the relatively small port of Conakry would quickly notice any imports of orange terpenes and would act to prevent their use. It is advisable, therefore, that the foreign buyer receive shipments of Guinea orange oil directly from the colony, or at least as international transshipment under customs seal. The government's analytical control in Conakry prevents that type of adulteration.

2. Adulteration with petroleum, kerosene, or mineral oil. Thanks to the strict control exercised by the Conakry Chamber of Commerce, outright adulteration of Guinea orange oil with kerosene has become rare. Unfortunately, however, one still encounters small quantities of kerosene, due perhaps to the use of contaminated vessels for storing the oil.

3. As a third form of adulteration, we should mention the addition of old, oxidized, and resinified oils to good lots. It is said in the colony that the Syrian dealers, particularly the small barterers operating in the interior, sometimes buy inferior, resinified oils at substantially lower prices and add them to better lots. Here again the control of the Chamber of Commerce has been of great help and the quality of the oil has improved.

Analysis.—Addition of substantial quantities of terpenes to orange oil may be suspected if the oil possesses an unusually low specific gravity and low evaporation residue. Such deviations, however, can quite easily be compensated by other additions and, therefore, adulteration with *d*-limonene, if cleverly done, is most difficult to detect. Deviations in the

[89] *Ber. Schimmel & Co.* (1936), 68.

ratio of the various physicochemical properties permit serious doubt as to the authenticity of the oil under investigation.

According to Naves,[40] the addition of oxidized and resinified oils is revealed by the presence of peroxides. The content of oxidized compounds, calculated as $C_{10}H_{16}O_2$, should not be higher than 0.30 to 0.32 per cent.

The most important test for Guinea orange oil is that for detecting added kerosene or mineral oil. According to Trabaud,[41] an addition of 2 per cent of kerosene lowers the optical rotation by about 3°, making it abnormal. It also lowers the specific gravity by 0.0018. It has been the experience of Fritzsche Brothers, Inc., however, that the addition of 2 per cent of kerosene will lower the specific gravity by only 0.0007.

Igolen [42] suggested a test—based upon the solubility of the oil in 94.8 per cent alcohol at different temperatures—by which 0.5 per cent of petroleum can be detected by slight turbidity. Schimmel & Co.[43] recommended testing for the presence of petroleum by fractionating the oil in fractions of 10 per cent and determining the optical rotation of each fraction.

The presence of relatively large quantities of kerosene can be established easily, but the problem is to identify traces of kerosene which are so often present. So far the determination of such traces has required a thorough and lengthy examination of the oil. The control laboratories in Conakry can hardly submit every drum to a complicated procedure, and there has been great need for a simple and reliable method.

The New York laboratories of Fritzsche Brothers, Inc., employ a relatively simple method, which permits one chemist to examine as many as twenty-five samples daily. The following procedure is recommended:

Distill a 50 cc. sample of the oil in question at reduced pressure until 92 to 93 per cent of the oil has come over. If necessary, this distillation may be carried out at atmospheric pressure, but the sensitivity of the test suffers thereby. A flavor test in acidified syrup is then carried out on the residual 7 or 8 per cent of the oil. (See Vol. I of this work, p. 306.)

The analyst tasting the syrup with the added solution of orange oil should notice no musty kerosene character, but a clean, terpeneless orange oil note. An expert accustomed to this test will detect as little as 0.01 per cent of a kerosene fraction. For actually identifying kerosene in the suspected sample, a larger quantity should be examined further by distilling off 92 to 93 per cent from the orange oil, and testing the residual 7 or 8 per cent by means of the oleum test described in the chapter, "The Examina-

[40] *Parfums France* **12** (1934), 314.
[41] *Riechstoff Ind.* **13** (1938), 120.
[42] *Rev. Marques—Parfums France* **16** (1938), 87.
[43] *Ber. Schimmel & Co.* (1939), 73.

tion and Analysis of Essential Oils, Synthetics, and Isolates," Vol. I of this work, p. 332.

Any form of adulteration, and even the slightest contamination, may have grave repercussions upon the reputation of Guinea orange oil and cause much trouble for the users abroad. It was, therefore, important that the government of French Guinea suppress any fraudulent action which might depreciate this important source of revenue. Obviously, then, the problem for the government was to re-establish the standing of a product which had been seriously undermined a few years before. The decrees of January 17, 1935, and June 18, 1937, were designed for this purpose and stipulate in brief that the export of Guinea orange oil be permitted only under the following conditions:

The oil must be clear, of light or orange-yellow color; it must not contain any foreign matter in solution or suspension and must not be mixed with any liquid. The odor of the oil should be clean and resemble that of fresh orange juice without any rancid taste. The physicochemical properties must remain within the limits indicated by Naves [44] (see above). The containers should be very clean and not have served previously for products such as petroleum, mineral or fatty oils, acids, etc. Furthermore, they should be plated or enameled inside. Proper labels must permit quick identification of the drums. Every drum or container which is marked for export must be analyzed in the control laboratories of the Chamber of Commerce and remain untouched until a decision as to its quality has been reached. Any drum of oil which in appearance or odor does not conform to standard is rejected without even being analyzed. If a routine analysis shows that an oil is suspicious, a second sample is drawn and submitted to a more minute examination. For each lot a bulletin of the analysis is made out with additional details as to number of containers, quantity, brand, net weight, and analytical figures. This bulletin bears either of the following notices, "Natural Oil Recognized as Pure" or "Oil Recognized as Impure," followed by the account and other useful information. The customs officials authorize the shipping of a lot only after seeing this document and after having confirmed the validity of the seals and the stamp of the Chamber of Commerce. Additional regulations have been planned in regard to purchasing and transporting the oil, all with a view toward exporting a product which is as carefully made as the primitive conditions prevailing in French Guinea permit.

These government decrees actually resulted in an improvement in the quality of Guinea orange oil, as may be seen from the figures quoted by de

[44] *Parfums France* **10** (1932), 163.

Tourris [45] in a communication to the author: 1,431 drums of orange oil, each containing 200 liters, were analyzed during the 1939–1940 production. Of all the drums, 99.2 per cent showed an optical rotation of from +96° 0′ to +98° 0′ at 20°, and 98.1 per cent had a specific gravity of 0.8485 to 0.8510 at 15° which, according to Naves,[46] represent the narrower limits for Guinea orange oil. Less than 1 per cent of all the drums showed a specific gravity above 0.8520, the officially admitted upper limit; these oils were, therefore, denatured by the addition of color which made them unsalable.

Chemical Composition.—The chemical composition of Guinea orange oil does not differ much from that of the Sicilian oil. According to Naves,[47] the Guinea orange oil is composed of the following constituents:

95–96% Terpenes:

Myrcene.

d-Limonene.

Terpinolene(?).

A Terpene(?). Still unknown.

An Aliphatic Terpene. Possibly Ocimene(?). b_{10} 64°.

1.6% Aldehydes:

Octyl Aldehyde(?), Nonyl Aldehyde, Decyl Aldehyde, and Citral. Traces only.

0.6–0.8% Volatile Alcohols and Esters:

n-Nonyl Alcohol. Amounting to 20 per cent of the alcohols and esters.

n-Decyl Alcohol(?). Presence probable.

Nerol.

Geraniol(?). Perhaps present.

d-Linaloöl. Amounting to 50 per cent of the alcohols and esters.

d-α-Terpineol. Amounting to 15–20 per cent of the alcohols and esters.

Farnesol or Nerolidol. Traces only.

These alcohols are present partly in free form, partly as formates, acetates, caprylates and caproates.

Methyl Anthranilate(?). Presence possible.

Sesquiterpenes. The oil contains traces of sesquiterpenes as indicated by the formation of cadinene dihydrochloride.

Free Higher Fatty Acids. Present only in traces.

Phenols.

[45] Note sur la Campagne d'Essence d'Orange, 1939–1940, Chambre de Commerce, Conakry, Sept. 19, 1940.
[46] *Parfums France* **10** (1932), 163.
[47] *Ibid.*, 181.

0.8% Residue:

Caprylic, Palmitic, and Cerotic Acid. In ester form.

A Phytosterol.

Ceryl Alcohol.

Carotene.

A Xantophyllic Compound.

A Yellow Substance. M. 108°–110°.

In the course of a more recent investigation, the same author [48] found that the aldehydes present in Guinea sweet orange oil consist of

n-Dodecanal. Identified by means of its semicarbazone m. 105°–105.5°.

n-2-Decen-1-al. Semicarbazone m. 161.5°–162°.

n-2-Dodecen-1-al. Characterized by oxidation (with silver nitrate and sodium hydroxide) to 2-dodecenoic acid and by further oxidation (with potassium permanganate) to dihydroxylauric acid m. 123°–123.5°.

According to Naves,[49] these aldehydes cannot be isolated from orange oil by treatment with bisulfite solution. He concluded from his studies that the aldehyde fraction of sweet orange oil has the following composition:

	Per Cent
n-Octanal	31.0
n-Decanal	27.0
n-Dodecanal	6.0
n-2-Decen-1-al	4.0
n-2-Dodecen-1-al	3.0
Citral	7.5

These values are in varying degrees lower than the actual values, due principally to losses during distillation and to unequal yields in the regeneration from derivatives. *n*-2-Decen-1-al and *n*-2-dodecen-1-al have so far been encountered only in essential oil from certain *Umbelliferae* plants, such as coriander. It is quite remarkable that in oil of orange these aldehydes co-exist with *n*-octanal and *n*-decanal from which they can be formed by condensation with acetaldehyde.

As Naves points out, the absence in orange oil of traceable proportions of the corresponding unsaturated alcohols, free or esterified, is an interesting fact, biochemically.

[48] *Perfumery Essential Oil Record* **38** (1947), 237, 295. In a private communication, Dr. Y. R. Naves, Geneva, pointed out that the same aldehydes also occur in Brazilian sweet orange oil.

[49] *Ibid.*

Investigating the aldehyde fraction of Guinea sweet orange oil, Benezet and Igolen,[50] on their part, found that the aldehydes consist chiefly of *n-octyl aldehyde* (75 to 80 per cent), and some *nonyl aldehyde, decyl aldehyde,* and *citral.*

Export Figures.—According to de Tourris,[51] the production and export figures of Guinea orange oil during 1939 to 1940 read as follows:

	Kg.
Exports from January 1 to August 31, 1940.....	234,524
To deduct from the previous harvest.....	2,930
	231,594
Stocks in Conakry on September 15, 1940.....	18,832
Stocks in the interior.....	21,782
Evaluation of the harvest.....	272,208

The production for 1939–1940 was, therefore, about equal to the exports of the previous year which amounted to 275,437 kg.

Future Outlook.—At present it is difficult to predict the future of the entire Guinea citrus industry. If World War II had not intervened, some white planters would have continued to develop and expand the new orange and lemon orchards which they had started from selected and grafted varieties promising fruit of excellent quality. The wild-growing oranges from the Fouta Djallon are not sufficiently good for export as edible fruit, even if there were adequate transport facilities from the interior to the coast. France has always been an importer of oranges and lemons from Spain, Sicily, Brazil, and California, and her own colony, Guinea, seemed to offer a good source of supply. Thus far, certain sections of Guinea have specialized in the growing of bananas, a very speculative and perishable product; and citrus fruits seem to offer a desirable extra crop, especially because they are not easily attacked by locusts, that dreaded and deadly plague of West Africa.

Quite a number of new citrus orchards were started by progressive white planters prior to the outbreak of World War II, many of which did come into actual production. It is possible that the export of selected citrus fruit from Guinea to France and perhaps to other parts of Europe would have developed as spectacularly as the production and export of orange oil during the last ten years. However, the entire program has been jeopardized and paralyzed by the effects of the war which brought about unexpected conditions in French Guinea. For several years no consumer

[50] *Bull. soc. chim.* (1946), 359.

[51] Note sur la Campagne d'Essence d'Orange, 1939–1940, Chambre de Commerce, Conakry, September 19, 1940. Private communication.

goods were imported to French West Africa, with the result that the natives had absolutely nothing to buy and lost all incentive for earning money. They simply reverted to their own limited agricultural activities of raising the most essential foodstuffs for themselves and stopped producing orange oil. This picture, however, has changed again with the renewed, although limited, availability of consumers goods, and since 1947 substantial quantities of orange oil have been exported, chiefly to Europe. In addition, numerous orange groves, owned by white planters, have come into bearing and it may be expected that part of their crop, especially damaged or surplus fruit, will be converted into canned orange juice and essential oil, which will have to be expressed by mechanical means.

Suggested Additional Literature

A. Chiris, "Terpeneless and Sesquiterpeneless Oil of Orange from French Guinea," *Rev. marques parfums France* **17** (1939), 30. *Chem. Abstracts* **33** (1939), 4376.

Brazilian Sweet Orange Oil

Development.—Citrus fruits were introduced to Brazil in 1549, when Portuguese Jesuit missionaries arrived in Bahia and set about transforming the grounds around their settlements into beautiful orchards, including many orange and lemon trees. The production of Brazilian citrus fruit, especially oranges, thus goes back many years; it was only in the decade prior to the outbreak of World War II, however, that Brazil became one of the world's greatest growers and exporters of oranges. The adaptation of scientific grove methods, dating from that period, resulted in a steady improvement in the yield and quality of the fruit. The peak of the export trade, which went mainly to Europe, was reached in 1939, with about 5.5 million cases of oranges (a standard case weighing about 45 kg.). To this must be added millions of cases for local consumption, if some idea of the scale of production is to be gained. The outbreak of World War II and the ensuing shortage in shipping space practically stopped exports, except for small quantities to Argentina.

The home market alone could not consume the great surplus of fresh fruit, and the situation became almost catastrophic for the growers, who were forced to sell their fruit at any price. Many packing houses, and even very small suppliers, then decided to install oil pressing equipment to process a large quantity of the orange crop for oil, for which there seemed to be a good demand in South America and particularly in the United States, as the formerly important French Guinea orange oil was no longer available.

The idea of expressing oil from the peel of the Brazilian citrus fruits was actually nothing new, as some commercial attempts to this effect had been made in 1930. At that time, some producers, probably immigrants from Sicily, had tried to introduce the Sicilian sponge method which, however, proved too costly, and had to be replaced by mechanical means, described below. As a result of this mechanization in conjunction with the very low cost of the fruit, producers were able to recover their oil at favorable prices. At the same time, their output was quickly absorbed by exports, especially to the United States, and left good profits. Oil production in Brazil thus increased rapidly, but on a quite speculative basis, until it reached the surprisingly high quantity of 400 tons in 1942. This amount was so far in excess of potential consumption by North and South America that oil prices dropped to levels which were actually unprofitable to the oil producers, even though they could still obtain their fresh fruit from the growers almost for the asking. Completely discouraged, many packing houses, and most of the small suppliers, stored away their oil-making equipment and, because of a lack of export facilities, closed shop or limited their production to small quantities of oil. It took several years to dispose of the large surplus of oil made in 1942, which was gradually exported, in admixture with the limited quantities of oil produced annually after 1942. In these years, there were in Brazil altogether about 200 packing houses and small operators equipped for the expressing of oil, most of them (about 170) located in the state of São Paulo (around Limeira) and the remainder in the states of Rio de Janeiro and Rio Grande do Sul.

In the meantime, Brazil's orange fruit and oil industry gradually took an unfavorable turn, caused by several factors—primarily the end of World War II. During all those years, when the fresh fruit could no longer be disposed of profitably, the growers neglected their orchards, as they could no longer afford to spend money on fertilizers, sprays, and other necessities of cultivation. Insect pests and diseases invaded the once beautiful groves, many of which were ruined. In numerous cases oranges were replaced by other, more profitable, crops. As a result, fruit production diminished considerably. On the other hand, the war years brought about higher wages, an increase in the purchasing power of the masses in Brazil, and a general inflationary movement which was reflected in a much larger demand for fresh fruit on the local markets. The end of hostilities eased the shortage of shipping space, and Brazil could resume its exports of fresh fruit, shipping about 500,000 cases in 1946, and at very high prices. In 1947, the home market of fresh fruit continued to strengthen, and fruit production declined further, which factors did not encourage the production of oil. As a matter of fact, it appears that in future only large packers and exporters of fruit will be in a position to produce orange oil, as they will always have limited

quantities of rejects, unfit for consumption as edible fruit, which can be salvaged by conversion into by-products and particularly essential oils. In 1946 Brazilian orange oil production amounted to 100–120 tons; in 1947, to 60 tons only. In the meantime, a number of new orange groves have been started by progressive growers but, due to lack of nursery stock, labor, etc., these orchards will not come into production for several years.

In general, it should be pointed out, however, that in normal times Brazil's citrus industry is favored by many factors, such as excellent climate, absence of frost, rich soil, little need for irrigation, and relatively low-priced labor. On the other hand, from the beginning, the orange trees in Brazil's orchards have been planted too closely, and many diseases (mal di gomma, psorosis, leprosis, fruit scab, etc.) have done a great deal of damage.

Brazilian Orange Varieties.—The two orange varieties most extensively grown in Brazil are the Bahia or Baia, an early Washington Navel which makes up almost nine-tenths of the exports, and the late ripening Pera or Pera do Rio. The Pera, a small, nearly seedless, oval, and well-colored orange with a small greenish zone around the stem, resembles the Valencia. More recently a new navel orange, the so-called Bahianinha (little Bahia) has also been planted, especially around São Paulo. It has a smaller fruit, a smaller navel, and a thinner skin than the regular Bahia. Navarro de Andrade [52] considers it an ideal type for export.

Producing Regions and Climatic Conditions.—Citrus groves extend over a large part of Brazil's inhabited sections, especially along and not far inland from, the Atlantic coast. The principal growing areas are in the State of São Paulo and Rio de Janeiro, with smaller plantings in Rio Grande do Sul, Bahia, Espirito Santo, Pernambuco, and Minas Geraes. In the latter state, however, most fruit is consumed locally, as lack of roads prevents shipping of the fruit to the coast.

A. São Paulo.—The largest producing area is on the high rolling table lands (1,500 to 2,500 ft. altitude) of the State of São Paulo, about 100 miles inland from the coast, and 50 miles from the city of São Paulo, in the following departments:

1. Limeira—the principal center, 3 hr. by railroad from São Paulo
2. Campinas
3. Araras
4. Rio Claro
5. Sorocaba

The temperature in that subtropical climate almost never falls sufficiently low to damage the fruit. In the São Paulo section, about 80 per cent of the orange trees are of the Bahia variety, some 8 per cent of the Pera

[52] *Manual de Citricultura I*—Edicão da Chacaras e Quintaes, São Paulo (1933); through Webber and Batchelor, "The Citrus Industry," Univ. Calif. Press, Vol. I (1943), 984.

variety, the balance being largely Valencias. The Bahias ripen from April to June and are shipped to reach Europe after the peak of the Spanish orange season and just before the South African Navels arrive. The Peras of São Paulo are harvested from June to October. Regarding exports of fresh oranges, São Paulo is less important than Rio de Janeiro, the population of São Paulo consuming more fruit locally. As far as oil production is concerned, São Paulo far exceeds Rio de Janeiro, because the fruit grown in Rio de Janeiro (chiefly of the Pera variety) yields only half the quantity of oil, which thus becomes too costly, and cannot compete with the oil from São Paulo. About 70 per cent of Brazilian orange oil, therefore, is expressed from the Bahia or Washington Navel orange, and only 30 per cent from the Pera.

B. Rio de Janeiro.—In the state and federal district of Rio de Janeiro, the orange plantations are grouped quite closely, and located mainly in the tropical lowlands near the Bay of Rio de Janeiro, 20 to 50 miles from that great and beautiful city. Most of the fruit grown there is of the Pera variety (Pera do Rio) which, under normal conditions, is mainly exported as fresh fruit. The harvest takes place from August to December. Compared with São Paulo, Rio de Janeiro produces much less oil.

Methods of Oil Recovery.—As has been said, the first experiments of expressing orange oil in Brazil were made by using the Sicilian hand-sponge method which, however, had to be abandoned as too cumbersome and costly. Later several types of machines were imported from Messina—primarily the Avena, which gave good results and was, therefore, quickly imitated by local constructors. In the opinion of Brazilian producers, the firm Irmãos Ruegger in Araras, Est. de São Paulo, even succeeded in improving the Avena. Today, about 300 to 400 such models exist in Brazil. The larger producers, mainly fruit packing houses, are usually equipped with several machines, arranged in battery form.

Before being charged into the feeder, the fruit is soaked and washed, but not brushed, in water, which facilitates and accelerates oil extraction.

The extractor of the machine, constructed of iron, contains two horizontal rotating discs, one above the other, and 1.15 m. in diameter, which are covered with glass plates containing many protruding points. The inner walls, too, are lined with curved and pointed glass plates. Some operators employ pointed stainless steel plates, but the rasping action in this case is more violent, the somewhat higher yield of oil being offset by the formation of a heavier emulsion, and by an oil with a higher evaporation residue (higher content of waxy matter), and a darker color. About three-quarters of a case of oranges is charged through the feeder upon the two plates, which turn at a speed of 50 to 80 rpm. The speed of rotation and quantity of fruit charged must be controlled carefully, or the fruit might be

crushed or broken. The fruit tumbles and brushes against the pointed horizontal discs and vertical side walls, lacerating the oil sacs and liberating the oil. Depending upon the condition of the fruit, treatment of one charge lasts about 2 min., riper and softer oranges requiring less time than greener and harder ones. The speed of rotation can be adjusted through the pulleys of the motor (3 h.p.) or through the axle wheel. While the fruit turns and tumbles in the extractor, a continuous spray of water, injected above the discs, carries the emulsion of liberated oil, aqueous cell liquid, and cell detritus into a system of strainers. This consists of several metal screens of progressively finer mesh. The emulsion is thus freed from the coarser particles of solids. The remaining liquid emulsion must then be broken up into oil and water, a very important procedure, as we shall see below. The carrier (spray) water is used over and over again for about 10 hr. and then is replaced by fresh water. It is returned to the spray nozzle above the rotating discs by a pump of 15 to 20 liters capacity per minute.

The working capacity of one machine varies from 300 to 400 cases of fruit in 10 hr. of operation.

Separation of the Effluent.—The complete and rapid separation of the outflowing emulsion consisting of oil, aqueous cell liquid, carrier water, and fine cell detritus (mainly colloidal and waxy matter) presents considerable difficulties and is one of the principal factors affecting the quality of the final oil. The less time the oil stays in contact with water, the better will be its quality. Two methods are generally applied, viz., separation by decanting in large settling tanks and centrifuging.

A. Separation by Decanting.—After being strained, the effluent is pumped into a series of large wooden tanks where the fine emulsion is permitted to settle until it separates, which often requires several days. During this period, forces of oxidation, fermentation, hydrolysis, and polymerization, activated by enzymes, are at play and, in the warm climate of Brazil, may cause serious degradation in the delicate constituents of the oil. Some of the oxygenated compounds, incidentally, are more soluble in water than the terpenes and may, therefore, be lost in the large quantities of carrier water, especially at the prevailing temperature. The mass finally separating above the water layer is by no means clear; often it represents a heavy emulsion of oil, colloidal matter, and some water, which can be broken by packing the mass into hydraulic presses and pressing it through heavy cloth lined with cotton or sponges. This method of separating the effluent, although on the whole not very satisfactory, has unfortunately been adopted by many operators, especially the smaller ones, who are limited in regard to cost of installation. The oils thus obtained usually have a dark color, a high evaporation residue (content of waxy matter), and frequently an "off" odor.

B. Separation by Centrifuging.—Progressive, well-equipped manufacturers separate the extractor effluent in high-speed centrifuges, in De Laval machines, for example.

After the bulk of solid particles has been removed by being run through a system of metal sieves, the liquid emulsion flows into a large supercentrifuge which separates it into water, waxy matter, and crude oil. The latter then runs directly into a smaller centrifuge, where it is clarified and freed from any suspended water (about 20 per cent). All separated water is pumped into a large tank, returned to the extractor, and injected again as carrier water (see above).

The different clarified oil lots should finally be bulked into uniform lots and stored airtight in well filled containers in cool, dark rooms.

Quality of Brazilian Orange Oil.—In the past the quality of Brazilian orange oil not infrequently caused disappointment on the part of buyers abroad. This was due primarily to lack of experience and to poor equipment employed by the numerous small operators who, after the outbreak of World War II, started to produce large quantities of oil to dispose of their surplus fruit. The causes for the poor quality of the large stocks of Brazilian orange oil accumulated during World War II may be summarized as follows:

I. In most cases the separation of the extractor effluent, consisting of essential oil, aqueous cell liquid, and colloidal matter was effected by decanting and standing for a prolonged time in large settling tanks, which procedure causes considerable degradation of the oil. As explained above, the most efficient method of breaking up this emulsion is by running the effluent directly into a system of high-speed centrifuges.

II. Frequently the accumulated stocks of oil were stored improperly, often in half-filled drums not hermetically sealed against access of air. Orange oil easily oxidizes under those conditions, especially in the warm climate of Brazil. It is not surprising that after a lapse of several years those old stocks became of quite inferior quality, no longer suited for flavor work.

III. Not all Brazilian operators possessed the facilities for bulking their oil into uniform large lots, with the result that the importer abroad received shipments in which each drum represented a different quality.

These shortcomings, however, have been remedied. As a matter of fact, some of the leading producers in Brazil have been able to ship qualities which, although not equal to the best grades of handpressed oils, nevertheless compare very well with machine-pressed oils from other countries. As Brazilian orange oil producers acquire more experience, eventually they

will be able to supply lots more superior in quality and uniformity than those which had been shipped during World War II.

Brazilian Orange Oil a "By-Product" of the Brazilian Citrus Industry.—As has been pointed out, the Brazilian orange packers, in the processing of their surplus fruit for oil, sought a means to alleviate the plight of the growers and exporters during World War II when they no longer could ship their crops of fresh fruit to Europe. However, to recover Brazilian orange oil on an economical basis, the fruit must be converted into all possible by-products (orange oil being only one of them). For this purpose, some of the leading Brazilian packing houses, especially around Limeira in the State of São Paulo, have acquired the most modern equipment, imported mainly from the United States and installed by American engineers. Aside from the standard equipment for packing fresh fruit, these houses possess machinery for producing concentrated juices, pectins, citric acid, and cattle feed from the exhausted peel. The sweetened juice may be fermented and the orange wine distilled into orange brandy, both products being quite popular in Brazil.

Yield of Oil.—According to information gathered by the author in Brazil, the yield of orange oil varies from 3 to 5 kg., the average being about 4 kg. per metric ton of fruit. At the beginning of the harvest, when the fruit is firm and green, the yield of oil amounts to about 0.5 per cent, but it may fall to as low as 0.25 per cent toward the end of the harvest when the fruit becomes mature and too soft for complete recovery of the oil.

Physicochemical Properties.—The physicochemical properties of Brazilian orange oil, like those of all orange oils, change in the course of the harvest. As the fruit matures, the evaporation residue increases while the optical rotation decreases. The Bolsa de Mercadorias de São Paulo, Laboratorio de Tecnologia [53] reports as follows:

Type Bahianinha Oranges—Decanted Oil

Date of Production	*Specific Gravity at 25°*	*Optical Rotation at 22°*	*Refractive Index at 20°*	*Evaporation Residue (%)*	*Color*
4/10/42	0.8445	+98° 6′	1.4735	2.20	Green-yellow
4/30/42	0.8437	+97° 29′	1.4732	2.33	Yellow-green
5/30/42	0.8437	+97° 27′	1.4730	2.75	Amber
6/30/42	0.8470	+96° 12′	1.4734	4.22	Amber
		Type Baia Oranges—Centrifuged Oil			
5/6/42	0.8425	+98° 27′	1.4725	1.44	Yellow-green
5/16/42	0.8429	+97° 33′	1.4725	1.48	Yellow
6/3/42	0.8433	+97° 15′	1.4725	1.77	Amber
6/12/42	0.8433	+96° 41′	1.4730	2.14	Amber

[53] *Oleo de Laranja*, São Paulo (1942), 30.

From these tables, it also appears that the evaporation residue is generally higher in the oils obtained by decanting the oil-water emulsion than in centrifuged oils.

During 1942, the Laboratorio da Secção de Fiscalização de Adubos e outros Produtos Agricolas, da Divisão de Fiscalização e Classificacão de Produtos Agricolas do D.P.V. da Secretaria de Agricultura [54] analyzed 238 samples of Brazilian orange oils made from Baia oranges and obtained the following results:

Specific Gravity at 25°	Minimum 0.8416
	Maximum 0.8470
	Average 0.8435
Optical Rotation at 25°	Minimum +93° 52′
	Maximum +97° 58′
	Average +96° 17′
Refractive Index at 20°	Minimum 1.4719
	Maximum 1.4738
	Average 1.4729
Evaporation Residue	Minimum 1.00%
	Maximum 6.41%
	Average 2.90%

Genuine Brazilian orange oils examined by Fritzsche Brothers, Inc., New York, had properties which varied within these limits:

Specific Gravity at 25°/25°	0.842 to 0.848
Optical Rotation at 25°	+94° 30′ to +97° 52′
Refractive Index at 20°	1.4723 to 1.4747
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	0.5 to 2.2%
Evaporation Residue	2.0 to 4.8%

The color of Brazilian orange oil is usually deep orange, but may vary from green to light yellow.

According to Maffei,[55] samples of genuine Brazilian orange oil showing normal organoleptic properties often fail to meet tests prescribed in the United States Pharmacopoeia. These abnormalities are in part traceable to differences in maturity of the fruit: oil from partly ripened oranges shows smaller nonvolatile residues than oil from over-ripe fruit. The effects of differences in maturity may be masked by long exposure of the fruit to light in regions of intense insolation. Storage tests showed that the oil, when protected from light, may be kept up to three years with little change.

[54] *Ibid.*, 32.

[55] *Anais assoc. quím. Brasil* **5** (1946), 61. Through *Chem. Abstracts* **41** (1947), 5262.

Normal oils left for three months in the laboratory exposed to light, and in some cases to air, underwent the following changes:

Specific Gravity at 25°	From 0.845 to 0.874
Optical Rotation at 20°	From +98° 36′ to +86° 0′
Refractive Index at 20°	From 1.4740 to 1.4780
Distillation Residue	From 4 to 12.5%

An oil exposed (*A*) in a closed glass flask to ultraviolet light from a Hanau lamp with a focus of 30 cm., and (*B*) in an open crystallizer, for different lengths of time showed these changes:

A

	Original	*40 Hr.*	*48 Hr.*
d_{25}	0.841	0.843	0.852
α_{20}	+97° 24′	+96° 30′	+92° 12′
n_D^{20}	1.4729	1.4734	1.4751
Residue	1.6%	2.27%	6.5%

B

	Original	*40 Hr.*	*48 Hr.*
d_{25}	0.842	0.845	0.850
α_{20}	+96° 48′	+95° 54′	+93° 30′
n_D^{20}	1.4727	1.4739	1.4745
Residue	1.7%	2.4%	4.8%

As the percentage of nonvolatile residue increases, the refractive index also increases. The addition of cottonseed oil raises the specific gravity and markedly decreases the refractive index; a high nonvolatile residue is thus not necessarily an indication of fraud.

Other circumstances that produce characteristics beyond the pharmacopoeial limits are genetic (the variety "Bahia" is prone to show refractive indexes above the limits), or they may be caused by a difference in the methods of extraction: oils obtained by centrifuging rasped orange peel in aqueous suspension have lower refractive indexes than oils produced by pressing.

Maffei criticizes the specifications of the United States Pharmacopoeia: while a lower limit (1.7%) is fixed for nonvolatile residue no upper limit is imposed directly, but indirectly the maximum is fixed at 4 per cent by reason of other specifications. This excludes many oils of undoubted genuineness. The purposes of inspection would be well served by determinations of only the refractive index and the optical rotation on the original oil, dispensing with the official method of comparing the indexes of the original oil with the indexes of the first 10 per cent fraction.

In connection with the conclusions reached by Maffei, the author would like to comment that, in respect to odor and flavor, Brazilian orange oils

possessing a high evaporation residue and a low optical rotation are generally not so fine as freshly prepared oils having normal properties.

Simmons [56] has reported that in shipments of Brazilian orange oil the aldehyde content (calculated as decyl aldehyde) at one time attained well over 1 per cent (up to 1.7 per cent); more recent imports have contained only 0.5 to 0.8 per cent aldehyde, results as low as 0.37 per cent having been observed. With earlier samples the nonvolatile residue ranged from 2 to 3 per cent, but it has now gone up considerably, as much as 4.5 to 5.0 per cent being encountered. Simmons [57] also described some recent samples with most abnormal properties (optical rotations below +90°, and nonvolatile residues above 7 per cent). These samples had a particularly poor odor.

Such abnormalities may be explained as due to improper methods of extraction and storage, with ensuing spoilage—all of which have been described above.

Chemical Composition.—To the author's knowledge, no detailed study on the chemical composition of the Brazilian type of sweet orange oil has been published. However, it may be assumed that the chemistry of this oil is closely allied to that of sweet orange oils from Italy, French Guinea, California, and Florida (see the monographs on these oils).

Suggested Additional Literature

Evaldo de Oliveira, "Study of *Citrus Aurantium, Linnaea* subsp. *sinensis*, Gallesio, and Its Essential Oil," *Rev. quím. farm. Rio de Janeiro* **12,** No. 5, 9–40, No. 6, 17–49 (1947). *Chem. Abstracts* **41** (1947), 7057.

Italian Sweet Orange Oil

Until about twenty-five years ago, Sicily and adjacent regions on the tip of the Italian mainland (Calabria) held almost a monopoly on the production of sweet orange oil. Since then the United States (California and Florida), French Guinea, and Brazil have entered the field as competitors, with the result that the Italian production, in comparison, has become almost negligible. Still, the Italian oil, which is recovered mostly by hand-pressing, has remained in demand because of its high quality. For the preparation of terpeneless and sesquiterpeneless oils, the Italian oil is equaled only by the Guinea oil and by some American oils expressed by very modern processes.

[56] *Perfumery Essential Oil Record* **38** (1947), 265.
[57] *Ibid.*

Producing Regions.—Production of fruit in various regions of Italy is distributed approximately as follows:

	Per Cent
Sicily	57.0
Calabria	20.0
Campagna	16.0
Apulia	3.0
Liguria	0.7
Other regions	3.3

Most of the crop is exported as edible fruit to Central Europe and England, whereas second-grade and surplus fruit is processed for essential oil and other by-products.

The best fresh fruit is grown probably in the province of Catania, on the island of Sicily (around the villages of Paternò, Biancavilla, Adernò, and Bronte), and also in Calabria, on the Italian mainland (around the villages of Gallico and Rosarno). So far as the production of oil is concerned, the villages of Radicena, Varapodio, Oppido, and Cittanova, located in the higher altitudes of the province of Reggio in Calabria, and the village of Barcellona on the northern coast of Sicily, supply the finest quality. These centers produce almost 80 per cent of the total output of Italian sweet orange oil. A third center is located around the villages of Francofonte, Scordia, and Palagonia.

Harvesting.—Orange trees are able to withstand a somewhat more severe climate than lemon trees. They bloom only once a year, in May. The harvest of fruit which is to be processed for oil begins early in October and lasts until the end of December, whereas the harvest of edible or export fruit begins in December and lasts until April, sometimes even up to the middle of May. The Italian producers, in general, differentiate between first-class fruit, suitable for export, and a second, somewhat lower quality for the pressing of oil. These two qualities may originate from different geographical regions or from different groves which, according to their age and condition, yield a higher or lower grade of fruit.

A young, vigorous, and well-kept orange grove usually produces good healthy fruit, which can stand packing into cases for export to Central Europe or England. Obviously the profits on edible fruit are higher than those on second-grade fruit from an old or neglected orchard, which can at best be used for the extraction of oil. Frosts and storms may considerably increase the quantity of second-grade fruit for pressing of oil, bad weather doing more damage to old and neglected orange groves than to vigorous

ones. The percentage of windfalls in a well-cultivated orchard will always be much lower than in an old one.

There exist no strict rules in regard to the two qualities of fruit and, under certain circumstances, part of the second quality may be used for home consumption as edible fruit and even for export whenever there exists a heavy demand. On the other hand, healthy, first-class fruit is also used for pressing of oil whenever there is a strong demand for oil and whenever high oil prices permit pressing of first-class fruit. The entire matter is closely related to the question of price calculation in the extraction of the oil.

Expression of Oil.—The bulk of Italian orange oil is still produced by handpressing (sponge method), but certain types of *sfumatrici* have been found to give good results with oranges.

Yield of Oil.—A skilled laborer can press in the course of an 8-hr. working day about 5 Sicilian lb.,[58] or 3½ American lb. of oil. One thousand oranges weigh 110 to 120 kg. (about 242 to 264 American lb.) and yield from 1½ to 2 Sicilian lb. (about 1 lb. ¾ oz. to 1 lb. 6½ oz. American). This corresponds to an approximate average yield of about 0.4 to 0.5 per cent, varying with the season and the condition of the fruit. The producers in Sicily claim that the green-yellow oranges of the early harvest give a considerably higher yield of oil than the mature yellow-reddish fruit.

Orange Juice—A By-Product.—The utilization of the orange juice in Sicily and Calabria has by no means reached the degree of importance that it has, for example, in California and Florida, where the oil is more or less a by-product in the extraction of the juice. In Sicily, the fruit pulp, which has been removed before pressing of the peel, is subjected to pressure in rather primitive spindle or hydraulic presses. The juice is then protected from fermentation by the addition of a small percentage of formic acid or other preservative and exported to Central Europe.

Total Production of Italian Sweet Orange Oil.—While the total yearly production of Italian sweet orange oil in former years (e.g., in 1928–1929) varied from 200,000 to 300,000 American lb., it amounted to only about 36,000 lb. in 1935–1936, 43,000 lb. in 1936–1937, and 53,000 lb. in 1937–1938. In the years 1940 to 1946 the average annual production of Italian sweet orange oil was 25,000 kg. (about 55,000 lb.).

Physicochemical Properties of Italian Sweet Orange Oil.—According to Gildemeister and Hoffmann,[59] the properties of the Italian oils vary within the following limits:

[58] A Sicilian pound contains 317.621 g., whereas the American pound contains 453.590 g. This makes the Sicilian pound about 12 oz., as compared to 16 oz. American.

[59] "Die Ätherischen Öle," 3d Ed., Vol. III, 78.

Specific Gravity at 15°	0.848 to 0.853
Optical Rotation at 20°	+95° 30′ to +99° 0′
Optical Rotation of the First (10%) Fraction	Not, or only very little, lower than the optical rotation of the original oil
Refractive Index at 20°	1.473 to 1.475
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	1.0 to 2.7%
Solubility	Soluble in about 1.5 vol. of 95% alcohol. Usually not clearly soluble in 90% alcohol (7–8 vol.)
Boiling Range	The oil starts to boil at 175°; nine-tenths distill over, up to 180°
Evaporation Residue	1.5 to 4.2%
Acid Number of Evaporation Residue	11 to 28
Ester Number of Evaporation Residue	118 to 157

When determining the optical rotation of lemon or orange oil, it is important to consider the temperature. According to Gildemeister and Hoffmann,[60] the angle of rotation of these oils changes with the temperature, being reduced with increasing temperature. To obtain comparable data, it is, therefore, necessary to record the exact temperature at which the observation was made and to recompute the angle of rotation for a standard temperature. For details see the chapter on "The Examination and Analysis of Essential Oils, Synthetics, and Isolates," Vol. I of this work, p. 242.

Genuine oils imported from Sicily and Calabria and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied between the following limits:

Specific Gravity at 25°/25°	0.843 to 0.846
Optical Rotation at 25°	+95° 50′ to +97° 8′
Refractive Index at 20°	1.4728 to 1.4739
Evaporation Residue	1.6 to 3.3%
Solubility	Incompletely soluble in 95% alcohol, up to 10 vol.

According to Bennett,[61] the composition of sweet orange oil is more nearly constant than that of any other citrus oil. The figures published over a period of many years have shown that practically the whole of the Sicilian production falls within these limits:

Specific Gravity at 15.5°	0.848 to 0.850
Optical Rotation at 15.5°	+98° 0′ to +99° 30′
Nonvolatile Residue	1.5 to 2.0%

[60] *Ibid.*

[61] *Perfumery Essential Oil Record* **25** (1934), 111.

In the opinion of Bennett, the quite erroneous figures given in some Pharmacopoeias seem to be due to a confusion between sweet and bitter orange oils, the latter being quite different in flavor and composition.

During prolonged storage a certain amount of oxidation and resinification takes place, but if the conditions of storage are satisfactory the above cited figures for specific gravity and residue will only be slightly exceeded (Bennett).

Adulteration.—At one time, Italian orange oils frequently were adulterated with turpentine oil; routine analytical control immediately detects such crude falsification by a pronounced lowering of the optical rotation. Consequently such adulteration seldom is encountered today.

A much more dangerous and subtle form of adulteration is the addition of natural terpenes from orange oil; such terpenes are obtained in large quantities as a by-product from the preparation of terpeneless oils and concentrates. Small additions are difficult, if not impossible, to prove. Large additions cause changes in the physicochemical properties of the oil, e.g., a lowering of the evaporation residue. Furthermore, the odor and flavor become weak, the aldehyde note less pronounced, and the oil fails to have the strength and body of a normal unadulterated oil.

Chemical Composition of Italian Sweet Orange Oil.—Wallach [62] showed that sweet orange oil consists mainly of *d*-limonene, whereas Stephan [63] investigated the oxygenated compounds which amount in the oil to only a few per cent.

Italian sweet orange peel oil is composed of the following constituents:

d-Limonene. According to Wallach;[64] identified as dihydrochloride m. 49°–50°; tetrabromide m. 104°–105°.

The oil, according to the same author, contains at least 90% of *d*-limonene.

Reducing *d*-limonene, $[\alpha]_D^{14}$ +116° 6′, with hydrogen and nickel catalyst, and oxidizing the nonreducible portion with ozone, Escourrou [65] obtained products of decomposition (formic acid and acetone), the determination of which led Escourrou to the conclusion that crude limonene, as obtained by vacuum distillation from sweet orange oil, consists approximately of 80% pure limonene.

Terpinolene(?). 12% of terpinolene and

α-Terpinene(?). 8% of *α*-terpinene, probably.

n-Decyl Aldehyde. Treating a terpeneless oil with bisulfite solution, Stephan [66] isolated an oil b_{12} 93°–94°; naphthocinchoninic acid derivative m. 237°. This oil upon oxidation gave *n*-capric acid.

[62] *Liebigs Ann.* **227** (1885), 289.
[63] *J. prakt. Chem.* [2] **62** (1900), 523.
[64] *Liebigs Ann.* **227** (1885), 289.
[65] *Parfums France* **3** (1925), 94. *Chimie & industrie* **14** (1925), 519.
[66] *J. prakt. Chem.* [2], **62** (1900), 525.

Citral(?). According to Stephan, Italian sweet orange oil does not contain any aldehydes other than *n*-decyl aldehyde. Semmler [67] had claimed the presence of citral in Italian orange oil, but very likely his oil was adulterated with lemon oil. Nelson and Mottern [68] definitely established the presence of citral in Florida sweet orange oil, the chemical composition of which is undoubtedly quite similar to that of the Italian oil. Nelson and Mottern contended that in previous investigations of sweet orange oil no citral had been found because shaking of the oil with sodium bisulfite solution results in a stable dihydrodisulfonic acid compound which remains in solution. Guenther and Grimm [69] proved the presence of α- and β-citral (citral *a* and *b*) in California sweet orange oil. Naves [70] reported about the presence of citral in Guinea sweet orange oil.

d-Linaloöl. Identified first by Parry; [71] b. 199°–200°; oxidation to citral.
d-Linaloöl was later identified also by Stephan.[72] Oxidation to citral; conversion with formic acid to *l*-terpineol m. 35°–36°.

n-Nonyl Alcohol. According to Stephan; oxidation yielded nonyl aldehyde and nonylic acid m. 15°.

d-Terpineol. The same author also proved the presence of *d*-terpineol m. 38°–40°; identified as nitrolpiperidine m. 154°–155°, and as phenylurethane m. 111°–112°.

n-Caprylic Acid. Stephan showed that these alcohols are present in the oil partly in free form, partly esterified with *n*-caprylic acid; m. +15°· b_{762} 236°–237°; analysis of the silver salt.

Methyl Anthranilate. Parry [73] explained the fluorescence of the terpeneless sweet orange oils by the presence of methyl anthranilate. The Schimmel laboratories [74] confirmed Parry's contention.

Auraptene. This coumarin derivative $C_{15}H_{16}O_4$, m. 91°, was identified in sweet and bitter orange oil by Böhme and Pietsch.[75] (Cf. Vol. II of this work, p. 672.)

Otherwise, comparatively little is known about the nonvolatile residue of Italian sweet orange oil, which is only slightly soluble in alcohol. When boiled with alcohol to remove foreign substances, the compound, according to Stephan, had a melting point of 67°–68°, and a saponification number of 65. After saponification, a saturated solid acid m. 77°–78° could be extracted from the saponification lye; the barium salt of this acid, when analyzed, pointed toward cerotic acid $C_{26}H_{52}O_2$. Extraction of the saponification lye with ether yielded a neutral compound, m. 138°, which is possibly a sapogenin. Elementary analysis of this compound suggested $C_{28}H_{48}O_2$; when dissolved in chloroform it gave the cholesterin reaction of Liebermann.[76] An explanation for the decomposition of such complex

[67] *Ber.* **24** (1891), 202.
[68] *J. Am. Chem. Soc.* **56** (1934), 1238.
[69] *Ibid.* **60** (1938), 933.
[70] *Parfums France* **10** (1932), 160.
[71] *Chemist Druggist* **56** (1900), 462, 722.
[72] *J. prakt. Chem.* [2], **62** (1900), 530.
[73] *Chemist Druggist* **56** (1900), 462, 722.
[74] *Ber. Schimmel & Co.*, April (1900), 18.
[75] *Arch. Pharm.* **276** (1938), 482.
[76] *Ber.* **18** (1885), 1804.

molecules was suggested by Dodge.[77] (See also Chemical Composition of "West Indian Sweet Orange Oil.")

Aside from an alkali soluble pigment, according to Zechmeister and Tuzson,[78] orange and mandarin peels contain also an ether soluble carotinoid which can be split into a hydrocarbon and an ester, the latter predominating. Alkaline hydrolysis of the ester gives a crystalline xanthophyll variety, which turns blue with moderately diluted acids. It is probably a viola-xanthin.

Present-day knowledge of the chemistry of Italian orange oil is undoubtedly incomplete, no new investigations having been undertaken since the above cited earlier works of Wallach and of Stephan. Quite probably the chemical composition of Italian sweet orange peel oil is closely related to, if not identical with, that of oils from other countries—e.g., French Guinea, California, Florida, Brazil, and the West Indies. The latest discoveries as to the composition of these oils probably apply also to the Italian oil. (See the respective sections.)

Spoilage of Sweet Orange Oil.—According to Strausz [79] the spoilage of poorly stored orange oil is caused by autoxidation (in the presence of air and moisture) of *d*-limonene to carvone and carveol which impart to the spoiled oil a slight "by-note" of caraway.

West Indian Sweet Orange Oil

The sweet orange tree, *Citrus sinensis* (*Linn.*) *Osbeck*, was introduced to the West Indies by Spanish explorers and settlers, probably at a very early date. Today the tree is widely distributed, growing wild, semiwild, and cultivated on most of the islands, particularly in Jamaica, Puerto Rico, and Haiti.

The oil is recovered by various methods, on Jamaica and other islands chiefly by the *"écuelle"* method. On Puerto Rico, a native of Palermo, Sicily, taught his workers the Sicilian "sponge" method and has succeeded in producing a very good quality of oil. Compared with the production of French Guinea, California, Florida, Brazil, and Sicily, the output of sweet orange oil in the West Indies has remained small. The oil, however, is usually of good quality, well suited for the making of concentrates, terpeneless, and sesquiterpeneless oils. West Indian sweet orange oil has been regularly imported to the United States for quite a number of years.

Genuine West Indian sweet orange oils imported and analyzed by

[77] *Am. Perfumer* **38**, December (1938), 34.
[78] *Naturwiss.* **19** (1931), 307. *Chem. Zentr.* I (1931), 3477.
[79] *Perfumery Essential Oil Record* **38** (1947), 260.

Fritzsche Brothers, Inc., New York, had properties which varied within the following limits:

	Puerto Rico Oils	*Oils from Other West Indian Islands*
Specific Gravity at 25°/25°	0.843 to 0.844	0.842 to 0.847
Optical Rotation at 25°	+96° 21′ to +98° 18′	+94° 37′ to +98° 52′
Refractive Index at 20°	1.4723 to 1.4733	1.4720 to 1.4740
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)		1.5 to 2.2%
Evaporation Residue	1.6 to 2.1%	1.0 to 3.9%
Solubility	Incompletely soluble in 95% alcohol up to 10 vol.	

Chemical Composition.—Dodge [80] isolated from West Indian orange oil a compound which crystallized from petroleum ether in snow-white crystals m. 88°, α_D −38° 0′; Dodge named it *meranzin*. The compound occurs also in West Indian and African bitter orange peel oil and is identical with auraptene.

Undoubtedly, the chemical composition of the West Indian type of sweet orange oil is closely akin to that of oils from Italy, French Guinea, Brazil, California, and Florida, and most probably contains also the compounds discovered in those oils (see the respective monographs).

Use.—The West Indian sweet orange oil has always been esteemed for its good quality. As said, it lends itself particularly well to the making of concentrated, terpeneless, and sesquiterpeneless oils.

Spanish Sweet Orange Oil

Spain is one of the world's greatest shippers of fresh oranges, exporting large amounts of excellent edible fruit (chiefly to Central Europe and England). The citrus belt in Spain extends in a long narrow strip from Castellón, on the Mediterranean Coast, south to Malaga. This belt can be divided into two main regions—"La Ribera," in the province of Valencia, stretching south of Valencia toward Puebla Larga and La Encina, with its center around Carcagente, and the other, "La Plana," in the province of Castellón, stretching north of Valencia toward Castellón, with its center around Burriana and Villarreal.

The Spanish citrus groves are generally well cultivated, healthy and prosperous; in this respect they differ considerably from the Sicilian and Calabrian orange groves, many of which have an appearance of old age and neglect. The Spanish citrus orchards resemble our California groves; in fact, even the countryside between the Mediterranean and the mountains

[80] *Am. Perfumer* **37**, No. 12 (1938), 34.

further inland recalls Southern California. The orange groves of Spain are generally in such good condition that they produce excellent fruit, which can be exported at a profit greater than that to be gained by processing the fruit for essential oil.

For the extraction of oil of orange, three qualities of fruit are recognized in Spain. The best oil is obtained from the "Naranja Blanca" or "Comun," a second quality from the "Sanguina," and a third from the "Verna," which is not so well suited for the expression of oil. Since most of the fruit is exported, only damaged fruit is processed for oil. The term "damaged" includes windfalls, fruit attacked by insects (*piojos rojos*), and fruit that has suffered from cold weather. Frost does the worst damage, sometimes affecting the peel to such an extent that it becomes soft and causes trouble in the recovery of oil.

The price of damaged fruit depends upon its condition and the general demand for fresh fruit; in case of heavy export demand, slightly damaged fruit is sometimes sold as edible on the local markets. On the other hand, it frequently happens that practically no damaged fruit is available at all; the oil producers then have to use sound fruit which obviously limits the output of oil because of too high a price.

Methods Used in Spain for the Recovery of Citrus Oils.—Wages paid to male labor in Spain are substantially higher than the wages prevailing in Sicily; therefore, any handpressing (sponge process) of citrus fruit in Spain would have to be done by female labor. As a matter of fact, since 1945 small quantities of orange and lemon oil have been produced in Spain by women employed in small and medium sized processing plants. The bulk of the oil, however, has always been produced in labor saving machines of local construction. The prosperous citrus growing regions of Spain possess a network of fairly good roads, on which the fruit can be trucked or carted to conveniently located processing plants.

Until about 1945 practically all Spanish orange oil was produced by a process based essentially upon the removal, by rasping, of the flavedo from the peel of the whole fruit and upon the expression of the removed flavedo with the help of hydraulic presses. This process gave the Spanish orange oil its particular character (high wax content, reddish color, long lasting odor, etc.) which distinguished it from all other types of orange oil. We shall refer to this method of oil recovery as the "old" process. It is still employed in Spain, but on a rapidly diminishing scale, giving way to the "new" process, which consists of puncturing the oil glands with a mechanically moved needle while the fruit rotates rapidly on a horizontal spindle. The new process yields an oil of entirely different character, approaching hand-sponged oils.

Before describing the new process, we shall discuss the old method and the oil obtained by its use.

On a small encased apparatus, one or two girls hold two or four oranges with both hands through a round opening against a horizontally mounted rapidly rotating (400 rpm) grated disc, which scrapes the flavedo off the fruit in a few seconds' time. The peel gratings, which contain the oil glands, drop to the bottom of the apparatus, where they are collected. One girl can "peel" daily 30 to 40 arrobas of oranges (345 to 460 kg. or about 760 to 1,000 American lb.). The soft orange peel gratings then are packed into heavy hair bags and pressed in a hydraulic press. This is done 24 hr. after grating to bring about a softening of the cell walls. The pressure, about 50 kg. per sq. cm. at the beginning of the operation, is gradually increased up to 100 and 150 kg. The oil and the aqueous phase are thereby expressed from the oil glands, which had previously been broken up by the process of grating.

The dark emulsion of essential oil and aqueous cell liquid filtering through the cloth packing is collected. After a few hours' standing, oil and water separate, and the oil is filtered and stored in the dark. After a period of at least fourteen days, the oil begins to develop its characteristic, delicate flavor.

The press cake remaining in the hydraulic press is submitted to steam distillation, which yields a second-grade (distilled) oil of orange. In the days when the recovery of oil was carried out chiefly by farmers and small producers, this distilled oil was usually added to the expressed oil, and the mixture sold on the market as "coldpressed oil." However, since the development of larger and more modern enterprises, controlled by progressive exporters, the pure expressed oil of orange is offered and marketed separately from the distilled oil.

Yield of Oil.—By this process, 22 to 25 arrobas of oranges (about 558 to 634 American lb.) on the average give 800 g. (1 lb. 12 oz.) of expressed oil, and 200 g. (7 oz.) of distilled oil. This represents a yield of 0.277 to 0.318 per cent expressed oil, and 0.318 to 0.344 per cent expressed *and* steam distilled oil (combined).

The yield of oil obtained in Spain by the above described process appears rather small when compared with that obtained in Sicily and Calabria by handpressing. It would seem that the high pressure of 100 to 150 kg. applied in the old Spanish process should recover more oil than the gentle process of sponge pressing used in Sicily. It is possible that the Spanish oranges contain less oil than those of Southern Italy; or the reason for the comparatively small yield obtained in Spain by the old process may lie in the fact that, in the course of grating, not only the flavedo containing the

oil glands, but also a part of the sponge-like white albedo, is removed from the fruit, and this albedo absorbs and retains a great deal of oil, while the gratings are submitted to hydraulic pressure. Furthermore, the Spanish producers use a great percentage of fully ripe yellow fruit, whereas the Italians prefer early green-yellow fruit because the latter yields more oil. Sponge pressing of Spanish oranges (by hand), before they have reached full maturity, has at times yielded 700 g. of oil per 200 kg. of oranges. This represents an oil yield of 0.35 per cent, calculated upon the whole fruit.

The Spanish oil recovered by this process possesses a full, rich, and soft flavor, which is very lasting because of the high percentage of waxy constituents acting as natural fixatives. The Spanish product gives excellent results in confectionery (soft center candies) and especially in hard candies.

The old type Spanish oil, however, is not suited for use in alcoholic or non-alcoholic beverages, due to its poor solubility. Neither can the old type Spanish oil be employed for preparing concentrated, terpeneless, and sesquiterpeneless oils, the waxes causing much trouble by formation of emulsions.

Physicochemical Properties of Spanish Sweet Orange Oil.—The method of extracting orange oil in Spain from ripe fruit under hydraulic pressure

TABLE 1.15

Specific Gravity at 25°/25°	Optical Rotation at 25°	Solubility at 25°	Evaporation Residue (%)
		EXPRESSED OILS	
0.8575	Too dark	Cloudy in 10 vol. alcohol. Sediment of oil and wax	14.0
0.853	+87° 26′	Not clearly soluble in 95% alcohol up to 10 vol.	12.1
0.8506	+90° 14′	Opalescent in 10 vol. alcohol. No oil separation	9.8
0.850	+90° 40′	Ditto	9.3
0.850	+90° 54′	Ditto	9.2
0.8494	+91° 34′	Ditto	8.5
0.8487	+91° 38′	Soluble in 6 vol. alcohol. Wax separation	7.9
0.8483	+92° 0′	Ditto	7.4
0.8482	+92° 34′	Soluble in 5 vol. alcohol. Wax separation	6.2
0.8458	+94° 39′	Soluble in 4 vol. alcohol. Wax separation	4.95
		DISTILLED OIL	
0.8427	+98° 36′	Soluble in 1 vol. and more of alcohol. Very slightly opalescent	0.44

up to 150 kg. per sq. cm. explains the marked characteristics of the old type Spanish oils, viz., their deep yellow-red color, their high content of waxy substances (evaporation residue up to 12 and 14 per cent), their high specific gravity, and their somewhat low optical rotation.

Samples of Spanish sweet orange oils prepared under the author's own supervision during a stay in the Spanish producing regions in 1929 showed the properties given in Table 1.15.

A high evaporation residue corresponds to a high specific gravity, low optical rotation and poor solubility, and vice versa. Oils originating from the region of "La Ribera" seem to possess a lower evaporation residue and a lower specific gravity than oils produced in the region of "La Plana."

Shipments of genuine Spanish sweet orange peel oils, expressed by the above-described method and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

Valencia Oils

Specific Gravity at 25°/25°	0.847 to 0.852
Optical Rotation at 25°	+90° 0′ to +93° 27′
Refractive Index at 20°	1.4750 to 1.4760
Evaporation Residue	6.6 to 9.6%

Two lots of Spanish sweet orange peel oils, expressed in the province of Murcia, had these properties:

	I	*II*
Specific Gravity at 25°/25°	0.856	0.857
Optical Rotation at 25°	+85° 40′	+51° 40′
Refractive Index at 20°	1.4772	1.4755
Evaporation Residue	16.3%	31.4%

The abnormally low optical rotation of these oils, especially of Number II, is caused by their very high wax content (evaporation residue).

According to Luna Arenes,[81] the Spanish oil, when compared with the Italian product, contains less aldehydes, a higher saponification number, a "softer" aroma, a deeper red color and a larger evaporation residue. Luna Arenes ascribes these differences to the more advanced stage of ripeness of the Spanish oranges when harvested.

A distilled Spanish sweet orange peel oil analyzed as follows:

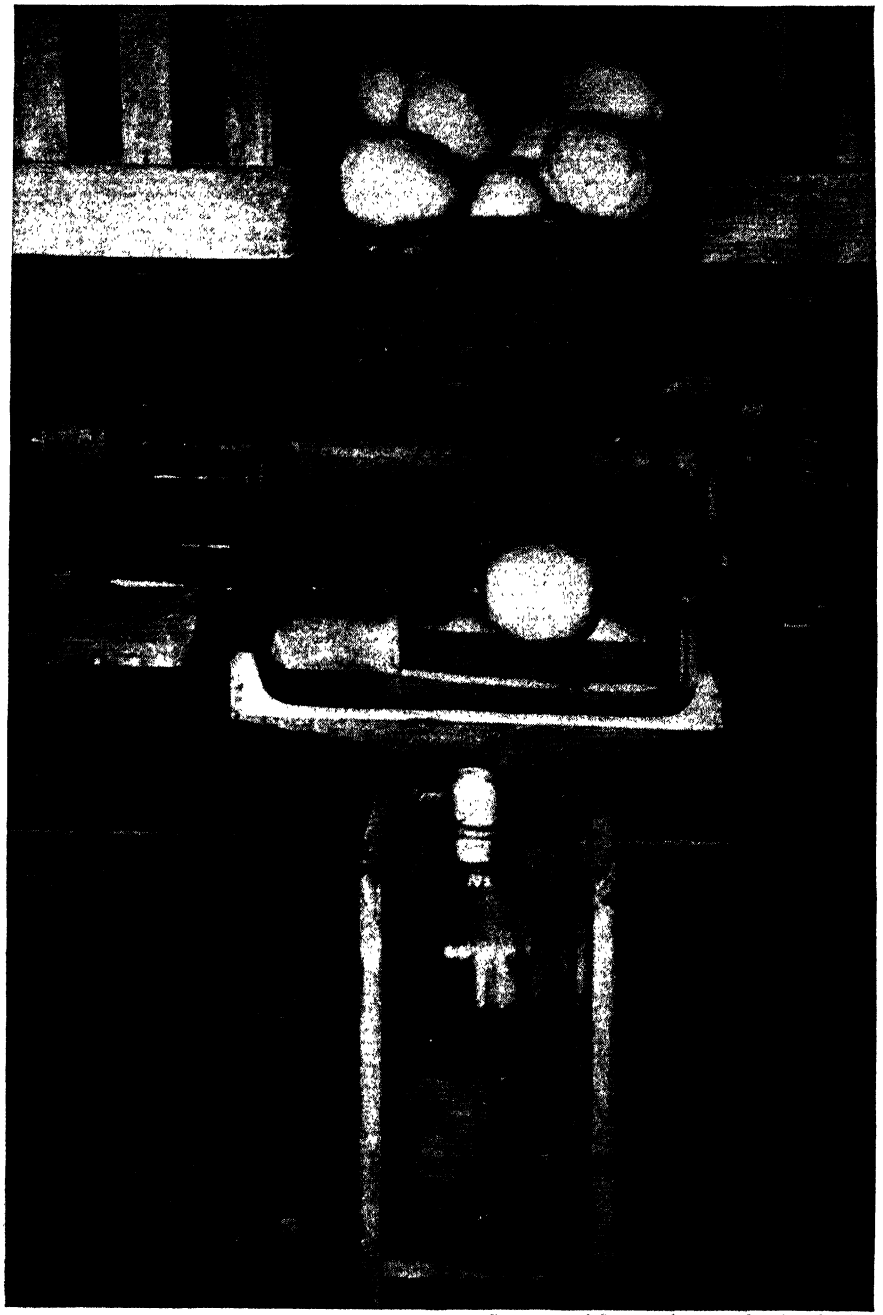
Specific Gravity at 25°/25°	0.841
Optical Rotation at 25°	+97° 33′
Refractive Index at 20°	1.4723
Evaporation Residue	0.4%
Solubility	Incompletely soluble in 95% alcohol, up to 10 vol.

[81] *Afinidad* **17** (1940), 29. *Chem. Abstracts* **35** (1941), 4158.

New Method of Oil Recovery.—As has been pointed out, a new method of recovering the oil from the whole fruit was introduced in Spain in 1945 and is rapidly replacing the old process described above. The machines employed for this purpose are of local construction and have never been used outside of Spain. They process oranges as well as lemons. The machine consists essentially of a central, motor-driven, horizontal shaft which drives five small divisions on each side of the shaft. Each division is attended by a girl. The fruit first passes into a box on top of the whole machine, and from there drops by gravity through a hopper into the girl's right hand. Quickly she places the fruit between two rapidly rotating (600 rpm) spindles which hold and rotate the fruit while a needle attached to a lever is moved horizontally across the surface of the peel, left and right, with sufficient force to scratch the whole peel and to puncture the oil glands. The rotating spindles and the horizontally moving needle are so synchronized that one fruit is processed within a few (5–7) seconds. The oil glands are punctured only lightly and with only sufficient force to scratch the surface, without penetrating into the albedo. The oil freed from the glands drops into a funnel and receiver standing beneath the rotating fruit. The fruit from which the oil has been removed is detached from the spindles, thrown into a basket and used for expression of the juice. The essential oil and aqueous cell liquid separate in three layers, viz., a light colored top layer, consisting exclusively of oil; an intermediary layer which has to be filtered; and an emulsified lower layer containing some cell detritus, essential oil, and water, which has to be filtered under pressure, or is occasionally distilled. The oil obtained by this somewhat primitive scratching method is of excellent quality and of normal aldehyde and low wax content—very different from the oil recovered by the old process of grating. One girl can process per day about 2,000 fruit which, in the case of lemons, yield about 750 g. of oil, and, in the case of oranges, 850 to 950 g. of oil.

In general it can be said that this machine produces a much better quality of oil than the old process of grating. On the other hand, the quality is not quite equal to that of the hand-sponged oil, being somewhat lower in aldehyde content. It can easily be seen that, during the scratching of the peel, even though this lasts for only a few seconds, the liberated oil is exposed to the oxidizing influence of the air on a large surface. As a matter of fact, the girls operating these machines must protect their eyes and noses by tying handkerchiefs to their faces; otherwise the fine spray of oil inhaled for any length of time would be dangerous to their health.

During the producing season—November, 1946, to February, 1947—the yield of oil, as obtained by the above-described method of needle scraping, was 3.7 kg. per ton of whole fruit.



Courtesy of Ramon Bordas, Sevilla, Spain.

Needle machine for the extraction of orange and lemon oil.

A sample of sweet orange oil (upper layer) prepared by this method and analyzed by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 25°/25°	0.845
Optical Rotation at 25°	+96° 31′
Refractive Index at 20°	1.4732
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	1.0%
Evaporation Residue	4.0%

The Spanish orange oil produced by the new process, or by sponge pressing (see below) resembles the Italian product; being of excellent flavor and normal solubility, it can be used for many purposes.

Handpressed Spanish Sweet Orange Oil.—According to Bordas,[82] Spain has lately been producing sponge-pressed oil also, the total production of this type of oil amounting in 1946–1947 to about 2,000 kg., which was absorbed entirely by the domestic market. Provided the fruit is not too ripe, the yield of oil is good (about 350 g. from 100 kg. of fruit) and the same can be said of the quality, the oil assaying about 2.5 per cent of aldehydes. During the producing season—November, 1946, to February, 1947—the yield of oil by the sponge-pressing method as carried out in Spain was 3.3 kg. per ton of whole fruit.

For the purpose of sponge pressing, the fruit is first cut in halves in specially designed machines; girls then remove the pulp with a special kind of spoon (see in this connection the section on "Handpressing by the Sponge Process," described in the introductory chapter on "Italian Citrus Oils"), the peel is exposed to the air on trays for 24 hr., and finally sponge pressed by women. Depending upon her skill, one girl can produce daily from 500 to 800 g. of oil.

Adulteration.—Expressed Spanish sweet orange oil is occasionally adulterated with distilled orange oil. The presence of a moderate percentage of distilled oil in expressed oils cannot be easily proved, particularly in view of the fact that the properties of Spanish orange oils are subject to greater variations than the Sicilian, Guinea, California, or Florida oils and, therefore, allow some leeway for the adulterator. The properties of Spanish orange oils are not very well defined and depend a great deal upon the process of extraction; their evaluation, therefore, is never complete without thorough organoleptic tests.

Total Production.—The annual production of Spanish sweet orange oil varies greatly and depends, as was explained above, upon several factors, viz., the condition and price of the fruit, the export market, etc.

[82] Private communication by Mr. Ramon Bordas, Sevilla, Spain.

In 1945–1946 Spain produced 35 tons of orange oil expressed by the old grating process, 1.5 tons of oil recovered by the new process of puncturing the peel, and 200 kg. of handpressed oil. In 1946–1947 only 2 tons of "old process" oils were produced, 3 tons of "new process" oil, and 2 tons of handpressed oil.

Under normal circumstances, and provided the price of the fresh fruit is not too high, Spain could easily produce 40 tons of orange oil per year, and this according to the new process described above.

Chemical Composition of Spanish Sweet Orange Oil.—Not much has been published about the chemistry of Spanish sweet orange oil, and no thorough investigations have been undertaken, probably because it is generally assumed that its chemical composition closely resembles that of the Italian product.

Palestine Sweet Orange Oil

The climate of Palestine is eminently suited to the cultivation of citrus fruit; indeed, the growing of oranges has been one of Palestine's stable industries. During the years of World War II, the development of the citrus industry in Palestine was hampered by lack of fertilizers, insufficient irrigation, and high labor cost. Government, however, came to the assistance of growers, and postwar developments have raised the status of Palestine citrus juices and oils to a high level. Produced on a relatively small scale in the years prior to World War II, citrus oils are now exported from Palestine in substantial quantities. During the 1942–1943 season, for example, Palestine exported 53,000 lb. of sweet orange oil to the United Kingdom, Egypt, India, Australia, and Iraq.[83] Davidsohn [84] reported a production of 55 tons of orange oil for the year 1941–1942.

According to Nicholls,[85] the varieties of orange most suited to the climate and to the soil conditions of Palestine are the Valencia and Chenauti types of *Citrus aurantium var. sinensis* (sweet orange). The latter type is cultivated in no other country, and forms the early crop; the Valencia comprises the late crop. The trees are grown in groves and are planted and vigorously pruned to give maximum light and air for resistance to disease and parasites.

The yield of oranges from a full grown tree amounts to about 2,000. The thick skin popularly associated with the Jaffa orange is due to cultivation in new groves, but as the industry is more firmly established the peel becomes thinner.

[83] *Drug, Vitamin Allied Ind.* **31** (1945), 21.
[84] *Hadar* **17** (1944), 337.
[85] *Perfumery Essential Oil Record* **38** (1947), 240.

TABLE 1.16

Properties	Sample 1, Machine Pressed	Sample 2, Hand Pressed	Sample 3, Machine Pressed	Sample 4, Machine Pressed
Specific Gravity at 15.5°/15.5°	0.8500	0.8565	0.8524	0.8490
Optical Rotation at 20°	+97° 48′	+96° 48′	+96° 30′	+99° 0′
Refractive Index at 20°	1.4742	1.4750	1.4749	1.4746
Aldehyde Content, Calculated as Decyl Aldehyde	1.28%	0.94%	1.33%	1.15%
Nonvolatile Matter	3.16%	3.84%	5.43%	2.28%

The picking of the fruit begins early in November, when a high proportion of the oranges is sold for export. The fruit chosen for extraction of juice and essential oil is first washed by sprays of water on a conveyer belt, then gently spun against a set of revolving, minute, stainless steel spikes which puncture the oil cells. The oil finally runs through a sieve below the spikes straight to the centrifuge, which separates the oil from the attendant water. This process is based upon the principle of the old *écuelle* method, but has been fully mechanized, several types of machines (some of them of Italian design) being used. After the extraction of the oil, the fruit is halved and sent to the juice extraction plant. Efforts are being made in Palestine to organize the orange production in such a way as to utilize the fruit for all its by-products, viz., canned juice, concentrated juice, pectins, essential oil, and cattle feed. To maintain the flavor of the juice, only one-third of the oranges are treated for oil; the remaining two-thirds go straight to the juice extraction plant.

According to Braverman and Monselise,[86] the oil content of Shamouti (Chenauti) oranges during the 1939–1940 season ranged from 4.26 to 6.18 kg. per ton of whole fruit.

The properties of orange oil samples in the factory throughout that season varied within these limits:

Specific Gravity	0.8480 to 0.8498
Optical Rotation	+96° 0′ to +100° 0′
Refractive Index	1.4744 to 1.4760
Dry Residue	1.058 to 1.227%

Braverman [87] reported the following analysis of a Palestine sweet orange oil:

[86] *Hadar* **13** (1940), 225. *Chem. Abstracts* **35** (1941), 6392.
[87] *Hadar* **6** (1933), 62. *Chem. Abstracts* **28** (1934), 5926.

Specific Gravity at 15.5°	0.8488
Optical Rotation	+98° 51′
Refractive Index at 20°	1.4710
Aldehyde Content, Calculated as Decyl Aldehyde	1.4%
Evaporation Residue	2.76%

Islip and Major[88] investigated several samples of handpressed and machine-pressed orange oils and found the properties given in Table 1.16.

A sample of Palestine orange oil analyzed in 1948 by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 25°	0.845
Optical Rotation at 25°	+96° 26′
Refractive Index at 20°	1.4730
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	1.6%
Evaporation Residue	3.9%
Color	Orange

According to Nicholls,[89] Palestine orange oil has a dark brown color and possesses the following characteristics:

Specific Gravity at 15.5°/15.5°	0.850 to 0.852
Optical Rotation	+97° 0′ to +99° 0′
Refractive Index at 20°	1.473 to 1.4745
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	1.5 to 1.9%
Residue at 100°	3.2 to 3.8%

The oil contains about 90 per cent of *d*-limonene, traces of *d*- and *l*-terpineol, linaloöl, nonyl alcohol, and caprylic esters. Methyl anthranilate could not be detected, although it has been reported in Spanish and West Indian orange oils.

In the opinion of Nicholls,[90] the Palestine orange oil possesses a flavor similar to that of the Rhodesian product, but the former is more delicate, its aroma fresher. Since the oxygen-containing components of an orange oil are generally recognized to be the determining factors for flavor, Nicholls suggested a method of obtaining comparative results. This method is based upon a comparative quantitative estimation of the steam volatile oxygenated compounds soluble in diacetin, in which terpenes are only slightly soluble. Advantage is taken of the nonvolatility of diacetin.

[88] *Bull. Imp. Inst.* **45** (1947), 15.
[89] *Perfumery Essential Oil Record* **38** (1947), 240.
[90] *Ibid.*

Fifty milliliters of the oil under test are shaken with 50 ml. diacetin in a separating funnel and allowed to stand for 4 hr., to give complete separation of the two phases. The lower layer, which consists of a solution of the oxygenated compounds in diacetin, is run off into a 1 liter distillation flask with a side arm. The extraction is repeated with a further 50 ml. diacetin, and, after standing, the second diacetin extraction is added to the first. Five hundred milliliters of water are added together with a few pieces of pumice to insure even boiling, and the oxygenated bodies determined in Short's apparatus for the determination of essential oils in plants.

The volatile oxygenated compounds are collected in the graduated receiver, and the distillation continued until the volume of oil remains constant. Since the diacetin is not volatile it remains in the distillation flask.

The volume of oil in the receiver is then read off. The following results were obtained:

	Per Cent
Palestine Orange Oil (20 Samples Examined)	4.9–5.4
Sicilian Oil (3 Samples Examined)	5.1–5.3
Rhodesian Oil (8 Samples Examined)	4.7–5.5
West Indian Oil (4 Samples Examined)	3.9–4.5
Brazilian Oil (6 Samples Examined)	3.8–4.3
Spanish Oil (2 Samples Examined)	4.1 and 4.2

Results obtained from this method indicate whether an oil is suitable for the preparation of concentrated oil.

Suggested Additional Literature

A. Laurence Curl, "Comparison of Several Types of Apparatus Devised for the Determination of Volatile Oil in Citrus Juices," *J. Assocn. Official Agr. Chem.* **30**, No. 3 (1947), 567.

J. B. S. Braverman, "Citrus Products," New York, Interscience Publishers, 1949.

Jacob Feigenbaum, "Les Essences de Citrus en Palestine," *Ind. Parf.* **4**, No. 2 (1949), 37.

Japanese Sweet Orange Oil [91]

Introduction.—For many years Japan used to fill her requirements of orange oil by imports from Italy; but, with the outbreak of World War II, she had to become self-supporting and developed her own orange oil industry. In the years 1940 to 1945, from 35 to 50 metric tons of orange oil were produced per year; but in the first season after the end of hostilities—oil pressing begins in December and ends in April of the following year—production of oil fell to nothing. It rose to 1 ton of oil in 1947 and to 3–5

[91] Often referred to in literature as Japanese grapefruit oil.

tons in 1948. A further increase may be expected as economic conditions in Japan improve. There are two reasons for the severe drop in the production of orange oil in Japan at the end of the war: lack of fertilizers, and demand for oranges as food, which eliminated any use of the fruit for technical purposes.

Japan's principal orange producing regions are located in the South, viz., on Kyushu, Shikoku, and the southern parts of Honshu.

In Japan there exist two types of oranges, i.e., (I) *Citrus aurantium* L., subsp. *natsudaidai* Hayata, and (II) *Citrus unshiu* Marcovitch. The former is used for the production of expressed orange oil, the latter for the production of distilled orange oil. Both types of oranges are harvested from December to April.

I. Expressed Orange Oil

Citrus aurantium L., subsp. *natsudaidai* Hayata (locally called "Natsumikan" or "Natsu-daidai"—*natsu* meaning summer, and *mikan* meaning orange) has a thick skin and somewhat resembles our grapefruit. In fact, chemical literature often refers to the oil derived from this fruit as grapefruit oil. An average sized fruit weighs 370 g., a large one up to 550 g.

The total annual production of this orange in normal years has averaged 75,000 metric tons, the planted area being about 3,000 hectares. Eighty to ninety per cent of the harvested fruit is sold as edible fruit, and the balance (10 to 20 per cent) is processed for the expression of essential oil and the recovery of citric acid. Centers of this industry are Wakayama and Yamaguchi. In 1944 and 1945, 37.5 tons and 52.5 tons of expressed orange oil were recovered from 9,375 tons and 13,120 tons of fruit, respectively.[92]

For the recovery of the oil from the peel, the fruit is first cut into four parts and the pulp is removed, all this work being done by hand. One skilled woman can treat five oranges per minute. Then the peel is steeped in warm water for several minutes and crushed between heavy cylinders rotating at 20 to 30 rpm. The effluent, an emulsion of essential oil and aqueous cell liquid, flows into a settling tank where the oil and water separate. To eliminate solid particles, cell detritus, etc., the oil phase is squeezed through canvas bags. Finally, the oil is decolorized by means of active carbon [93] and filtered.

The average yield of oil from the whole fruit is 0.4 per cent.

[92] Private information, courtesy Dr. Teikichi Hiraizumi, Tokyo.

[93] A dangerous procedure, as active carbon affects some of the oil constituents and influences the quality of the oil (the Author).

Physicochemical Properties.—Komatsu et al.[94] reported these properties for an oil expressed from the peel of *Citrus aurantium* L., subsp. *natsudaidai* Hayata.

Specific Gravity at 25°/4°	0.8486
Optical Rotation	+87° 45′
Refractive Index at 25°	1.4748
Acid Number	1.9
Ester Number	17.2
Ester Number after Acetylation	20.8
Methoxyl Number	2.2
Evaporation Residue	3.0%

Chemical Composition.—Komatsu and Tanaka[95] also investigated the chemical composition of the oil expressed from *Citrus aurantium* L., subsp. *natsudaidai* Hayata and found that it consists of—

d-Limonene		94.6%
Linaloöl, Terpineol	49.8	0.8%
Nonyl Alcohol	4.3	
n-Decyl Aldehyde	29.5	
Auraptene	17.0	

From the nonvolatile portions (0.01 per cent) of the oil these workers isolated *umbelliferone, methylumbelliferone,* and *auraptene*[96] $C_{16}H_{20}O_3$, m. 68° (umbelliferone-4-heptyl ether).

Auraptene is as characteristic of oil of *Citrus aurantium* L., subsp. *natsudaidai* Hayata as citraptene is of lemon oil, and bergaptene of bergamot oil.

II. Distilled Orange Oil

Citrus unshiu Marcovitch is well known in North America as a Satsuma orange, a type of loose-skinned orange. In Japan it is called "Mikan" or "Unshiu-mikan." There has been considerable confusion regarding the classification and nomenclature of this orange. For a time it was considered a variety of *Citrus nobilis;* later it was recognized to be an independent horticultural species and named, by Marcovitch, *Citrus unshiu* Marc.

The fruit is smaller than *C. aurantium* L., subsp. *natsudaidai* Hayata, and averages 100 g. in weight. *C. unshiu* in Japan is a most popular winter fruit for eating and for canning purposes. In the canning operation, the peel of the Unshiu-mikan is dried for 2 to 3 days and then steam distilled, 2,200 to 3,000 metric tons of dried peel yielding 7 to 9 metric tons of

[94] *J. Chem. Soc. Japan* **51** (1930), 478. *Chem. Abstracts* **26** (1932), 717.
[95] *Ibid.*
[96] Not to be confused with "auraptene" occurring in bitter orange peel oil. (Cf. the monograph on "Auraptene" in Vol. II of this work, p. 672.)

distilled oil, which used to be the annual production prior to World War II. The yield of oil, calculated upon the dried peel, therefore, amounts to 0.3 per cent, on the average. To this production of 7 to 9 tons of orange oil distilled from *C. unshiu* must be added a few tons of oil distilled from the residual peel (after pressing) of *C. aurantium* L., subsp. *natsudaidai* Hayata, so that the total production of distilled orange oil in Japan in normal times amounts to 10 to 15 tons annually. The so-called "Mikan" oil or "Tohi" oil is low priced, and in respect to odor and flavor quite inferior to the oil expressed from the peel of *C. aurantium* L., subsp. *natsudaidai* Hayata. The center of distillation is in Shizuoka.

East Indian Sweet Orange Oil

Nigam and Dutt [97] reported on the properties of distilled and coldpressed Indian orange oil.

According to these authors, the orange tree grows to a height of 20–30 ft. and yields on the average 500–600 fruit. There are two orange crops. The first flowers in October and matures before the following September. This is the smaller, or so-called "puncha," crop. The second crop flowers in April or May, matures from November to March, and is the large, so-called "nancha," crop.

On steam distillation, the raw peels of the puncha oranges yield about 1 per cent of oil, which is of low quality; and the peels of the nancha oranges yield 2–3 per cent of oil of superior quality. The oil is obtained by grinding the fresh peel in a mincer, and by steam distilling the whole mass.

In coldpressed oil the above-named authors established the presence of caprylic esters of linaloöl and of nonyl alcohol and found them to be largely responsible for the characteristic odor of orange.

On ripening of the fruit, the limonene contained in the peel oil was observed to be converted to open chain compounds, a natural breaking down of ring structures which could not be performed in the laboratory.

Nigam and Dutt [98] established the following properties for an oil expressed from the ripe peel:

Specific Gravity at 18°	0.8553
Optical Rotation [99] at 23° (in Chloroform)	+114° 18′
Refractive Index at 18°	1.4730
Acid Number	2.42
Saponification Number	11.9
Saponification Number after Acetylation	28.65

[97] *Indian Soap J.* **11** (1946), 245. *Perfumery Essential Oil Record* **38** (1947), 65.
[98] *Ibid.*
[99] This undoubtedly means Specific Optical Rotation (the Author).

Nothing has been published, to the author's knowledge, about the export of this oil which is probably used locally in soft drinks, for the flavoring of confectionery, etc.

Comparison of Various Types of Sweet Orange Oil

It is at present very difficult, if not impossible, to establish definite standards, based upon physicochemical properties, of the numerous types of sweet orange oil, according to geographical origin, for the simple reason that these properties depend upon several factors, viz., the variety of fruit, climatic and soil conditions, seasonal variation, and, most of all, the process of extraction.

Thus, French Guinea orange oils contain only a small percentage of waxes, because they are made by scraping the outside of the peel with a spoon so that no pressure is applied. The same was true of the old-fashioned Italian orange oils, which were obtained by sponge pressing. The wax content is substantially higher in the Brazilian and those Italian orange oils which are extracted by rasping the whole fruit in machines (the Avena *pellatrice,* for example). The wax content of the present California and Florida orange oils depends a great deal upon the type of machine and the working method used. The latest juice and oil presses, such as the Whole Fruit Juice Extractor constructed by Food Machinery Corporation, San Jose, California, have reached a high degree of perfection and yield oils with a lower wax content than that of oils made in other oil presses. Conditions will undoubtedly change again as still more novel types of juice and oil presses appear on the market. The wax content of an oil depends also upon the extent to which the oil has been de-waxed by storage at very low temperature, by filtering, or centrifuging ("polishing," etc.).

Obviously, the percentage of wax contained in an orange oil will influence the other physicochemical properties of the oil—its specific gravity and the refractive index, for example. It should be noted in this connection that the refractive index of coldpressed orange oil increases slightly as the oil ages.

Concentrated, Terpeneless, and Sesquiterpeneless Sweet Orange Oil (Preparation of Sesquiterpeneless Sweet Orange Oil)

To obtain sesquiterpeneless orange oil Nicholls [100] suggests preparing first a ten times concentrated oil by vacuum distillation and transferring this concentrated oil to a gas-heated still fitted with an efficient fractiona-

[100] *Perfumery Essential Oil Record* **38** (1947), 241.

tion column, and with joints well sealed, to obtain the highest possible vacuum. If the pressure in the still exceeds 1 mm., the resulting oil is likely to be "burned" and of inferior quality. The contents of the still are then slowly distilled, collecting about twenty equal fractions, using some modification of the Perkin triangle to maintain the vacuum in the still while the receiver is being changed. The various fractions are numbered and tested for solubility in 80 per cent alcohol. Those fractions, which show a solubility at 20° of one part of oil in 9 volumes of alcohol, are bulked together and form the sesquiterpeneless oil.

The yield in the case of Palestine oil is usually 2.5 per cent, West Indian oil yields 2 per cent, and Rhodesian orange oil yields 2.5 per cent, the percentage being calculated on the original oil used. The preparation of this sesquiterpeneless oil is in accordance with the tendency in recent years to utilize better and finer raw materials in the manufacture of flavoring extracts. Its use in the preparation of fruit squashes prevents the formation of the objectionable "ring" found on the necks of bottles containing inferior products and gives the squash a fresher and purer flavor. Laboratory control is necessary at all stages to insure uniformity of quality in the final product, and the task should be tackled with understanding of the variability within limits of the oil from natural sources.

According to Bennett,[101] sweet orange oil consists largely of terpenes (more than 90 per cent) and about 2 per cent of resinous and coloring matter. The mixture of oxygenated bodies which constitute terpeneless orange oil can be obtained by careful distillation (*in vacuo*) with a yield varying from 1.2 per cent to 1.5 per cent. The orange oils from Africa and Palestine which have entered the (British) market in recent years have been found to differ little from the Sicilian type.

Bennett [102] reports the following limits, established for a number of terpeneless orange oils:

Specific Gravity at 15.5°	0.8926 to 0.9094
Optical Rotation at 15.5°	+27° 0′ to +33° 0′
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	29.50 to 36.65%
Free Alcohol Content	37.0 to 44.9%
Ester Content	8.0 to 12.0 %

The free alcohols are chiefly *d*-linaloöl and *d-terpineol.*

Bennett [103] also examined terpeneless orange oils from French Guinea, Palestine, and South Africa and found them all to be characterized by a

[101] *Ibid.* **25** (1934), 111.
[102] *Ibid.*
[103] *Ibid.*

high proportion (40 to 45 per cent) of aldehydes and a notably lower proportion (20 to 30 per cent) of free alcohols in the concentrates. This naturally gave them a flavor somewhat different from that of the Sicilian oils.

Bennett also pointed out in the same paper that by distillation or by extraction with dilute alcohol, etc., it is possible to obtain various fractions of terpeneless orange oil of a composition different from that given above as representing the total recoverable flavoring matter. Samples particularly soluble in dilute alcohol are sometimes offered commercially as "sesquiterpeneless orange oil," but it has not been ascertained that orange oil contains any recognizable quantity of sesquiterpenes. There is thus no analogy with lemon oil in which sesquiterpenes are present to the amount of about 1 per cent and can be separated from the concentrate without loss of any fraction of the flavoring matter. (In this connection the reader is also referred to Vol. I of this work, pp. 218 ff.)

Years ago Bertè [104] recorded these properties for terpeneless sweet orange oils prepared in Italy:

Specific Gravity at 15°	0.8831 to 0.9000
Optical Rotation at 15°	+31° 0′ to +42° 20′
Aldehyde Content, Calculated as Citral	25.34 to 43.35%
Ester Content, Calculated as Linalyl Acetate	14.80%
Solubility	Soluble in 75% and in 80% alcohol

Shortly afterward Romeo [105] suggested these figures for concentrated sweet orange oils (Italian):

Specific Gravity at 15°	0.886 to 0.900
Optical Rotation at 15°	+20° 0′ to +35° 0′
Aldehyde Content, Calculated as Citral (Sulfite Method of Romeo)	30 to 40%
Solubility	Soluble in 2 to 4 vol. of 70 to 75%, or in 80% alcohol

These limits, however, are now somewhat obsolete because at the time of Bertè's and Romeo's writing all the Italian sweet orange oil was recovered by hand (sponge) pressing, whereas today a part of the production originates from the use of *sfumatrici* which yield a slightly different type of oil.

Use of Sweet Orange Oil

Orange oil is an important ingredient for flavoring all kinds of food products, confectionery, alcoholic and nonalcoholic beverages. It is also

[104] *Rivista ital. essenze profumi* **4** (1922), 112. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 82.

[105] *Atti congresso naz. chim. pura applicata* **1** (1923), 326.

employed in pharmaceutical and oral preparations in order to cover objectionable odors, and in perfumes, lotions, eaux de Cologne, creams, soaps, powders, lipsticks, and many other toilet preparations.

OIL OF PETITGRAIN SWEET ORANGE

(Sweet Orange Leaf Oil)

Essence de Petitgrain Portugal *Aceite Esencial Petitgrain Naranja Dulce*
Petitgrain Portugalöl

The leaves, petioles, and twiglets trimmed from the sweet orange tree, *Citrus sinensis* (Linn.) Osbeck, are occasionally steam distilled, like those of the bitter (sour) orange tree (see "Oil of Petitgrain Bigarade" and "Oil of Petitgrain Paraguay"). The oil, also called Portugal petitgrain oil, is little used, only very small quantities being produced occasionally in Algeria and before World War II on the plantations of Nadel and La Sala, near Labé, French Guinea (West Africa).

Three samples analyzed by Trabaud [1] had these properties:

	I	*II*	*III*
Specific Gravity at 15°	0.855	0.8554	0.8515
Optical Rotation	+37° 30′	+39° 24′	+44° 58′
Refractive Index at 20°	1.4725	...	...
Acid Number	0.4	1.3	0.9
Ester Number	13.0	9.33	8.4
Ester Content	4.5%	3.26%	2.93%
Aldehyde Content (by Oximation), Calculated as Citral	0.75%	...	...
Solubility in 90% Alcohol (in Vol.)	2.3 and over	3 and over	1 and over
Solubility in 85% Alcohol (in Vol.)	7 with light cloud	15 with light cloud	4 with light cloud

Glichitch and Naves [2] examined an oil of petitgrain Portugal distilled in Algeria from the shoots of sweet orange trees which were obtained at the Spring pruning. This oil had the following properties:

Specific Gravity at 15°	0.8585
Refractive Index at 20°	1.4726
Optical Rotation at 26.5°	+40° 55′

[1] *Perfumery Essential Oil Record* **27** (1936), 356.
[2] *Parfums France* **7** (1929), 223.

Acid Number	0.98
Ester Content, Calculated as Linalyl Acetate	2.33%
Aldehyde Content (Hydroxylamine Hydrochloride Method)	10.6%
Free Alcohol Content (by Cold Formylation of the Oil Deprived of Aldehydes)	29.2% (of the whole oil)
Primary Alcohol Content (Phthalization at 80°)	3.1%
Solubility	Soluble in 8 vol. and more of 85% alcohol, and in 1 vol. and more of 90% alcohol

Chemical Composition.—Examining the above-mentioned oil of petitgrain Portugal distilled in Algeria, Glichitch and Naves[3] found that the oil is composed qualitatively as follows:

Pinene	Traces
Limonene, Dipentene, Aliphatic Hydrocarbons	53%
d-Linaloöl, Free	22%
α-Terpineol, Free	4%
Geraniol and Nerol, Free	4%
Linalyl Acetate, Terpinyl Acetate, Geranyl Acetate, Neryl Acetate	2.3%
Citral *a* and *b*, with Small Quantities of Other Aldehydes or Ketones	10.6%
Sesquiterpenes (Bisabolene?)	2%
Sesquiterpene Alcohols (Farnesol)	0.5%
Free Phenols, Furfural, Methyl Anthranilate, Methyl Anthranilic Acid Methyl Ester, Unsaponifiable Basic Compounds (Pyrrole, etc.)	Traces
Geranic and Palmitic Acid, Free and Combined	Traces
Acetic Acid and Soluble Higher Acids, Combined	...

Petitgrain oil from sweet orange trees thus differs in composition from the petitgrain oils of the bitter orange and of the bergamot tree, the latter oils being rich in esters and free alcohols. According to Glichitch and Naves, the petitgrain oil from the sweet orange tree resembles the lemon petitgrain

[3] *Ibid.*

oil, at least qualitatively. Differences to be specially noted are that the petitgrain oil from the sweet orange tree is slightly poorer in aldehydes, it contains much less esters, and the total geraniol-nerol content is distinctly inferior to that observed in the lemon petitgrain oil. It may be noted also that the oil of petitgrain from the sweet orange tree contains dextrorotatory linaloöl, like the oil from the flowers of the sweet orange tree; whereas in all the other citrus oils the laevorotatory linaloöl predominates.

SUGGESTED ADDITIONAL LITERATURE

G. A. Fester, "Some South American Volatile Essential Oils," *Rev. facultad quim. ind. agr.* (*Univ. nacl. litoral, Sante Fé, Argentina*) **7** (1938), 118. *Chem. Abstracts* **33** (1939), 7958.

Otto Richard Gottlieb, "Étude des Produits Odorants des Feuilles de l'Oranger Doux." *Ind. parfum.* **4** (1949), 9.

SWEET ORANGE BLOSSOM OIL

(Oil of Neroli Portugal)

Essence de Neroli Portugal *Aceite Esencial Neroli Naranja Dulce*
Neroli Portugalöl

Unlike the blossoms of the bitter (sour) orange tree, those of the sweet orange tree, *Citrus sinensis* (Linn.) Osbeck, are usually left on the trees to develop into fruit, which is either exported as edible fruit or processed for juice and oil (oil of sweet orange peel). For this reason, the blossoms of the sweet orange tree are very seldom employed for distillation purposes. Sweet orange flower oil, known also as oil of neroli Portugal, is, therefore, not a regular article of commerce, the localities around Valencia and Murcia in Spain being perhaps the only regions where small quantities (about 80 kg. yearly) of the oil have been regularly produced. The collecting of the flower material is done in a rather careless and crude way, as only the flowers which dropped naturally are picked up from the ground. The blossoms are not hand-picked from the trees, nor are the trees shaken or the branches beaten with sticks to cause some of the flowers to drop to the ground.

The distillation of the flowers is carried out similarly to the distillation

of bitter (sour) orange blossoms. Seven hundred kilograms yield about 1 kg. of oil which, as to be expected, is of rather poor quality.

Two authentic samples collected by the author in Andalusia during 1930–1931 had the following properties:

	I	*II*
Specific Gravity at 15°/15°	0.853	0.855
Optical Rotation	+44° 0′	+48° 20′
Ester Content, Calculated as Linalyl Acetate	4.2%	2.9%
Solubility	Soluble in 0.5 vol. of 90% alcohol; turbid with more	Soluble in 4 vol. of 90% alcohol; turbid with more

Two oils distilled from the blossoms of the sweet orange tree in Sevilla and analyzed by Fritzsche Brothers, Inc., New York, had these properties:

	I	*II*
Specific Gravity at 25°/25°	0.849	0.853
Optical Rotation	+44° 0′	+46° 56′
Ester Content, Calculated as Linalyl Acetate	2.9%	4.2%
Solubility	Soluble in 4 vol. of 95% alcohol	

Sweet orange flower oil possesses a lower specific gravity, a lower ester content, and a considerably higher optical rotation than bitter (sour) orange flower oil (neroli bigarade).

In Sicily and Spain, neroli Portugal oil is occasionally used as an adulterant for the higher priced neroli bigarade oil; but any such adulteration considerably affects the physicochemical properties of the oil, as was shown above. The same alteration is exhibited if sweet orange blossoms are added to those of the bitter (sour) orange tree, and the mixture distilled, as is sometimes done in Sicily, Calabria, Andalusia, and Haiti (West Indies).

Chemical Composition.—The chemistry of sweet orange flower oil has not been investigated very thoroughly, probably because the oil is commercially much less important than bitter (sour) orange flower oil (oil of neroli bigarade). Theulier[1] established the presence of the following compounds:

d-Camphene. Characterized by conversion into isoborneol m. 212°.

d-Limonene. Identified as tetrabromide m. 105°.

d-Linaloöl. Oxidation of the corresponding fraction to citral; α-citryl-β-naphthocinchoninic acid m. 198.5°.

Theulier did not investigate the fractions boiling above linaloöl.

[1] *Bull. soc. chim.* [3] **27** (1902), 278.

d-Linalyl Acetate(?). That the oil contains esters, probably linalyl acetate, is evident from the ester value.

Methyl Anthranilate. According to Schimmel & Co.[2] a Spanish sweet orange flower oil contained about 0.3 per cent of this ester. Benzoyl compound m. 100°–102°· picric acid compound m. 105°–106°.

BITTER ORANGE OIL

Essence d'Orange Bigarade *Aceite Esencial Naranja Amarga*
Bitteres Orangenschalenöl *Oleum Aurantii Amari*

Botany, History and Description.—Details about the botany of the true bitter (sour), Seville, or bigarade orange tree, *Citrus aurantium* Linnaeus, subsp. *amara* Linn., its origin, and its introduction to the Old and New World may be found in the chapters on Neroli Bigarade Oil (bitter orange flower oil) and Petitgrain Bigarade Oil (bitter orange leaf oil).

The peels of the true bitter (sour) orange fruit are widely employed in the manufacture of marmalades, so popular among the English-speaking peoples. Like the peel of the sweet orange, *Citrus sinensis* (Linn.) Osbeck, the bitter orange contains an essential oil of a somewhat bitter flavor, and slightly mandarin-like odor, which may be expressed by various methods.

The production of bitter orange oil has remained very small, compared with that of the sweet orange oil. The oil is produced today in several parts of the world—principally in Sicily, Spain (Andalusia), and in some of the West Indies (Puerto Rico, Jamaica, and Haiti).

In Italy the oil is expressed chiefly by the old "sponge" method; in Spain by various processes (see "Spanish Sweet Orange Oil"); and in the West Indies (Jamaica) by the *écuelle* method. In Puerto Rico, a native of Palermo introduced the Italian "sponge" process, teaching it to his native workers and producing limited quantities of a very good oil.

Samarskii [1] reported that the U.S.S.R. also is producing bitter orange oil, which does not differ from that of the Italian product in its physicochemical properties. The yield of the Russian bitter orange oil exceeds that of the Italian, according to Samarskii.

In Sicily numerous plantations of the bitter (sour) orange tree are lo-

[2] *Ber. Schimmel & Co.*, October (1903), 81.
[1] *Sovet. Subtropiki* (1938), No. 12, 53. *Khim. Referat. Zhur.* (1939), No. 6, 117. *Chem. Abstracts* **34** (1940), 3879.

cated in the provinces of Messina (Barcellona and Patti), Palermo (Bagheria and Corleone) and Siracusa (Siracusa and Avola). Often the trees are planted in rows (espaliers) on the dividing line of individual properties. In Calabria scattered plantings are to be found in the province of Reggio Calabria, especially in the bergamot belt. Following an old custom, the bitter orange trees are cultivated there in rows around the bergamot groves to protect the latter from cold winds. The bitter orange and the bergamot tree flower simultaneously, and it is commonly believed that the presence of the bitter orange tree benefits the bergamot tree by pollinating the blossoms of the latter by a genetic affinity. Individual plantations of bitter orange exist also in the plain of Rosarno and near Cittanova, Taurianova, and Polistena; these have recently been reduced, however, the producers preferring to grow the sweet orange.

In Sicily and Calabria the fruit of the bitter orange tree is harvested in January and February and sometimes in March. The oil is recovered from the peel by handpressing (sponge method) but it may also be extracted with a Ramino machine. If the latter method is used, however, the exhausted peel cannot be exported in brined form, which actually is the most important and remunerative feature of the Italian bitter (sour) orange industry. One thousand bitter oranges (one quintal [2]) yield on the average only 150 g. of oil. If the fruit were to be expressed while still unripe (green), the yield of oil would be 330 g., but the exhausted peel no longer could then be used for brining, and for export as brined peel. The residual fruit pulp is utilized for the extraction of citric acid. The annual production of bitter orange oil in Sicily and Calabria varies considerably. The average is 8,000–10,000 kg. for Sicily and 1,000–1,500 kg. for Calabria.

Physicochemical Properties.—The physicochemical properties of bitter (sour) orange oil differ from those of sweet orange oil principally in regard to the optical rotation, which is lower in the former than in the latter.

Gildemeister and Hoffmann [3] report the following limits:

Specific Gravity at 15°/15°	0.852 to 0.857, usually from 0.854 to 0.856
Optical Rotation at 20°	+88° 0′ to +96° 0′, usually between +89° 0′ and +94° 0′
Refractive Index at 20°	1.473 to 1.475
Aldehyde Content, Calculated as Decyl Aldehyde (Phenylhydrazine Method)	About 1%
Evaporation Residue	2.5 to 5.0%. Data regarding acid number and saponification number of the evaporation residue are incomplete; both probably resemble those of sweet orange oil
Solubility	Soluble in 7 to 8 vol. of 90% alcohol with turbidity

[2] One quintal = one hundred kilograms.

[3] "Die Ätherischen Öle," 3d Ed., Vol. III, 86.

Shipments of genuine bitter (sour) orange peel oils analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within these limits:

Specific Gravity at 25°/25°	0.845 to 0.851
Optical Rotation at 25°	+91° 0′ to +96° 21′
Refractive Index at 20°	1.4730 to 1.4760
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	Average 1%
Evaporation Residue	2.2 to 4.7%
Solubility	Soluble in 4 vol. and more of 95% alcohol

According to Igolen and Sontag [4] the oil expressed from the fruit of *Citrus bigaradia* Risso, grown in France, has the following properties:

Specific Gravity at 15°	0.857 to 0.860
Specific Rotation at 20°	+87° 13′ to +92° 24′
Refractive Index at 20°	1.4745 to 1.4770
Aldehyde Content	0.60 to 0.78%
Evaporation Residue	5.3 to 6.3%

Adulteration.—Adulteration of bitter orange oil, if practiced, is carried out usually with citrus terpenes resulting, as low-priced by-products, from the preparation of terpeneless oils.

Chemical Composition.—Except for the high boiling constituent which causes its bitter taste, the chemical composition of bitter orange oil resembles that of sweet orange oil. This being so, no detailed chemical investigation of the components present in bitter orange oil was undertaken for a long time. It was only in comparatively recent years that Böhme and Pietsch,[5] and Igolen and Sontag [6] studied the oil more thoroughly and identified its most important constituents.

Investigating an oil produced in the Golfe Juan-Vallauris section (Alpes Maritimes, Southern France) by treatment of the fruit in an Avena machine, Igolen and Sontag [7] established the presence of the following substances:

A Compound(?), $C_{25}H_{25}O_{10}$. Treatment of the oil with a 5% solution of sulfuric acid yielded a very small quantity of fine, white needles, m. 142°. The odorless substance, which had the empirical formula $C_{25}H_{25}O_{10}$, could not be identified.

d-Limonene. In the terpene fraction; identified by means of its tetrabromide m. 104°. Treatment of the limonene fraction with hydrogen chloride in ethereal solution at low temperature gave dipentene hydrochloride m. 50°–51°. The oil itself, however, did not contain any dipentene, nor any myrcene or ocimene.

[4] *Chimie & industrie* **45** (1941), 157.
[5] *Arch. Pharm.* **276** (1938), 482.
[6] *Chimie & industrie* **45** (1941), 157.
[7] *Ibid.*

A Sesquiterpene(?). The high boiling fractions of the oil contained a sesquiterpene d_{15} 0.921, α_D^{23} −37°, n_D^{20} 1.4980, which did not yield a hydrochloride.

Hesperitin(?). Treatment of 13.3 kg. of oil with a 3% solution of sodium carbonate yielded 13 g. of partly crystallized phenols and 8 g. of acids.

From the phenolic portions a yellow, crystalline substance m. 210° (decomposition), probably hesperitin, was isolated.

A Phenol(?), $C_{16}H_{16}O_4$. Another phenolic constituent, m. 62°–63°, had the molecular formula $C_{16}H_{16}O_4$, but could not be identified.

Formic Acid, Acetic Acid, Pelargonic Acid and Cinnamic Acid. Formic, acetic, pelargonic and cinnamic acids were characterized by preparation of their *p*-bromophenacyl esters, m. 135°, m. 85°, m. 61°–62°, and m. 146°–147°, respectively.

Nonyl Aldehyde, Decyl Aldehyde, and Dodecyl Aldehyde. The aldehydes were isolated from the terpenic fractions, as well as from the oxygenated constituents of the oil, by treatment of the fractions with a 2% bisulfite solution.

Nonyl, decyl, and dodecyl aldehydes were then identified by preparation of their semicarbazones, m. 100°, m. 101°–102°, and m. 104°–105°, respectively. Decyl aldehyde clearly predominated in the mixture of aldehydes; nonyl aldehyde was present in substantial quantities, dodecyl aldehyde in small amounts.

Linaloöl and *d*-α-Terpineol. These alcohols were identified by the preparation of the following derivatives:
linalyl phenylurethane m. 64°; *d*-α-terpinyl phenylurethane m. 111°–112°.

Linalyl Acetate, Neryl Acetate, Geranyl Acetate, Citronellyl Acetate and Decyl Pelargonate. The alcohol radical in these esters was identified through:

Linalyl Phenylurethane	m. 64°
Neryl Allophanate	m. 101°
Geranyl Allophanate	m. 111°
Citronellyl Allophanate	m. 105°
Decyl Naphthylurethane	m. 62°–63°

Decyl alcohol and pelargonic acid, which predominated in all ester fractions, were present probably in the form of decyl pelargonate. Geraniol, citronellol, and nerol occurred in the oil mostly as acetates; linaloöl free and as acetate; terpineol in free form.

Igolen and Sontag did not study the 6.3 per cent of nonvolatile residue obtained by steam distillation of the concentrated oil after the acids and phenols had been eliminated (see above) and after the terpenes and sesquiterpenes had been removed by vacuum distillation.

Igolen and Sontag arrived at the conclusion that oil of bitter orange has this composition:

Phenols	
0.09%	Hesperitin(?) A solid phenol m. 63° (not identified)

Free Acids 0.05%	Formic Acetic Pelargonic Cinnamic
Terpenes 92%	*d*-Limonene
Sesquiterpenes 0.03%	Not identified
Aldehydes 0.78%	Nonanal Decanal Dodecanal
Free Alcohols 0.37%	Linaloöl Terpineol
Esters 2.1% (Calculated as Linalyl Acetate)	Linalyl acetate (1% of the oil) Decyl pelargonate Neryl, geranyl, and citronellyl acetate

The substance causing the bitter taste of the oil is apparently contained in the evaporation residue.

When stored for a time, sweet and bitter orange peel oils deposit a brown, semicrystalline sediment. Boiling this deposit with petroleum benzene, Böhme and Pietsch [8] isolated a crystalline substance which they named "auraptene." It had the empirical molecular formula $C_{15}H_{16}O_4$. The same authors established the occurrence of auraptene in orange peel oils of various origin. When purified, auraptene consisted of colorless tuft-like crystals m. 91°, easily soluble in alcohol and other organic solvents, except petroleum ether and ligroin, $[\alpha]_D^{20}$ −33° 24′. Auraptene is a coumarin derivative (see Vol. II of this work, p. 672).

Terpeneless Italian Bitter Orange Oil.—Romeo [9] indicated the following physicochemical properties of concentrated Italian bitter orange oil:

Specific Gravity at 15°	0.9083 and 0.8921
Optical Rotation at 20°	+10° 5′ and +8° 10′
Aldehyde Content, Calculated as Citral (Romeo Method)	25.03% and 17.27%
Ester Content, Calculated as Linalyl Acetate	47.46%
Solubility	Soluble in 1.2 vol. of 75% alcohol, and in 1.5 vol. of 80% alcohol

[8] *Arch. Pharm.* **276** (1938), 482.

[9] *Atti congresso naz. chim. pura applicata* **2** (1926), 870. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 31.

These figures, however, can no longer be adhered to in a strict sense because at the time of Romeo's writing all Italian bitter orange oils were produced by sponge pressing while today some lots are expressed in *sfumatrici* (cf. section on "Italian Sweet Orange Oil").

According to Bennett,[10] the composition of natural bitter orange oil is not so uniform as that of the sweet oil. The percentage of aldehydes is much lower, that of the esters much higher. The optical rotation of bitter orange oil varies from +90° 0′ to +97° 0′, oils from the province of Syracuse showing the higher figures. The yield of terpeneless oil from bitter orange oil ranges from 1.6 to 2.5 per cent and thus is notably higher than that from the sweet oil.

Bennett [11] recorded these properties for typical cases of terpeneless bitter orange oils:

Specific Gravity at 15.5°	0.8951 to 0.9223
Optical Rotation at 15.5°	+7° 12′ to +20° 0′
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	17.95 to 24.15%
Free Alcohol Content	14.5 to 41.5%
Ester Content	30.85 to 42.15%

(See also the section on "Concentrated, Terpeneless, and Sesquiterpeneless *Sweet* Orange Oil.")

Use.—Bitter orange oil is a valuable adjunct in the flavoring of beverages (alcoholic and nonalcoholic), confectionery, and baked goods. It serves very well also in perfumes, toilet waters, and cosmetics to which it imparts interesting notes.

Suggested Additional Literature

L. Trabaud, "Aromatic Products from French Guinea," *Riechstoff Ind.* **13** (1938), 116.

[10] *Perfumery Essential Oil Record* **25** (1934), 111.
[11] *Ibid.*

OIL OF PETITGRAIN BIGARADE

(Bitter Orange Leaf Oil)

Essence de Petitgrain Bigarade *Aceite Esencial Petitgrain Bigarade*
Petitgrain Bigaradeöl

Botany, Producing Regions and Quality.—As was explained in the monograph on Oil of Neroli Bigarade, the blossoms of the true bitter (sour) orange tree, *Citrus aurantium* Linnaeus, subsp. *amara* L., on being distilled, yield neroli bigarade oil. If, on the other hand, the leaves and petioles of the same tree are distilled, oil of petitgrain bigarade is obtained. It should be emphasized, however, that only the oils produced at present in Southern France, Italy, Spain, and Africa fit the definition of true petitgrain bigarade oils, because in those regions the leaf material used for the distillation of this oil is derived primarily, if not exclusively, from the true bitter (sour) orange tree. In Haiti (West Indies), where considerable quantities of this oil are produced, the leaf material originates partly from the true bitter (sour) orange tree, and partly from the so-called bitter-sweet variety (see below). The Paraguayan oil, which constitutes the bulk of petitgrain oil production, cannot properly be called a bigarade oil because the leaf material distilled in that country originates mainly from the bitter-sweet variety (see "Oil of Petitgrain Paraguay"). This bitter-sweet or Paraguay variety, as Webber [1] calls it, developed as a hybrid between the true bitter (sour) orange and the true sweet orange, after they had escaped cultivation and started to grow semiwild and wild in the interior of South and Central American countries and in some parts of the West Indies.

This section will be devoted to a description of the true petitgrain bigarade oils, including the Haiti type.

The quality of a petitgrain bigarade oil depends upon several factors:

1. The leaf material to be distilled should originate exclusively from the true bitter (sour) orange tree. Charabot and Pillet [2] showed that such oils will have a relatively high laevorotation and that the presence of leaves from sweet orange trees will result in oils of lower laevorotation, or even of dextrorotation, if the leaves from the sweet orange tree predominate.

2. The leaf material should not contain any wooden branches, nor any small (unripe) fruit. The presence of any such fruit in the leaf material will also result in oils of lower laevorotation, or even of dextrorotation.

[1] "The Citrus Industry," Vol. I, 499, Univ. Calif. Press (1943).
[2] *Bull. soc. chim.* [3], **19** (1898), 853; **21** (1899), 74.

3. The leaf material should be distilled rapidly and with direct steam, generated in a separate steam boiler. It must not be immersed in boiling water, as this will cause hydrolysis of linalyl acetate, the most important constituent of petitgrain oil. If properly distilled, the oil will have a high ester content.

The quality of a petitgrain bigarade oil can thus be evaluated quite properly by its physicochemical properties. A low laevorotation, and particularly a dextrorotation, in a petitgrain oil proves that the original plant material contained either leaves from the sweet orange tree or small unripe fruit. This can occasionally be observed in Italian, Spanish, and North African oils. A low ester content, on the other hand, indicates that the oil has been distilled improperly.

French Petitgrain Bigarade Oil

Producing Regions.—As will be explained in our section on oil of neroli bigarade, the true bitter (sour) orange tree is cultivated principally in the small coastal section of Southern France, between the Alpes-Maritimes and the Mediterranean, with Cannes-Grasse as the western boundary, and Cagnes-Vence as the eastern.

Harvesting.—In Southern France and, in fact, in all producing sections of Southern Europe and North Africa, the bitter (sour) orange tree blooms in May and June, and the blossoms, on distillation, yield oil of neroli bigarade. From late June until early October, the trees are pruned, and the resulting leaf material is used for the distillation of oil of petitgrain bigarade.

Distillation.—In Southern France, the leaves are charged into stills of 1,500 to 2,000 liter capacity, and live steam is injected for about 2 to 2½ hr. The operation is carried out in such a way that 800 g. of distillation water are collected per kilogram of plant material charged. Five hundred kilograms of leaves yield about 1 kg. of petitgrain bigarade oil.

Quality.—In quality the French oil surpasses all other petitgrain oils, because the producers in Southern France employ for distillation only the leaves and petioles, eliminating any wooden branches or small fruit. Since neither the sweet nor the bitter-sweet orange tree is grown at all in Southern France, the plant material used there for the distillation of petitgrain bigarade oil cannot possibly contain any leaves other than those of the true bitter (sour) orange tree, a fact not always true in other producing regions.

Total Production.—Southern France produces annually about 800 kg. of petitgrain bigarade oil. Cost of production in Southern France is high and,

therefore, the French oil cannot readily compete with other types despite its very high quality.

Physicochemical Properties.—Genuine petitgrain bigarade oils distilled under the author's supervision in Southern France had properties varying within the following limits:

Specific Gravity at 15°/15°	0.891 to 0.896
Refractive Index at 20°	1.4574 to 1.4584
Optical Rotation	−4° 50′ to −5° 38′
Ester Content, Calculated as Linalyl Acetate	64.4 to 68.8%
Solubility in 70% Alcohol	Soluble in 3.5 to 4.5 vol. and more, sometimes with opalescence

In 1930, Chiris [3] indicated these properties for French petitgrain bigarade oils:

Specific Gravity at 15°	0.8844 to 0.8965 (one oil had 0.901)
Optical Rotation	+3° 7′ to −6° 15′
Refractive Index	1.459 to 1.4634
Acid Number	Up to 2.2
Ester Content	41.6 to 69.3%
Solubility	Soluble in 2.8 to 4.5 vol. of 70% alcohol, rarely with opalescence, but more often with precipitation of paraffins

A few years later, the same workers [4] reported that lately the properties of French petitgrain bigarade oils had undergone certain changes and cited the following four examples:

	I	*II*	*III*	*IV*
Specific Gravity at 15°	0.8948	0.8989	0.8960	0.897
Optical Rotation	−6° 38′	−5° 52′	−7° 24′	−6° 10′
Refractive Index at 20°	1.4570	1.4578	1.4574	1.4568
Acid Number	0.42	0.56	0.56	0.56
Ester Content (%)	67.18	69.58	70.1	70
Free Alcohol Content, after Formylation in the Cold (%)	18.8	16.23	15.48	16.1
Oxygenated Products (%)	85.98	85.81	85.58	86.1

These properties approach those noted by the author and described above.

Adulteration.—Because of its relatively high price, genuine French petitgrain bigarade oil is not infrequently adulterated with cheaper petitgrain oils (oil of petitgrain Paraguay, for example), or with linaloöl and linalyl

[3] *Parfums France* **8** (1930), 73.
[4] *Ibid.* **14** (1936), 49.

acetate. These admixtures lower the laevorotation of the original French oil; to raise it, laevorotatory oil of shiu (ho oil) is occasionally added. Such adulteration can scarcely be detected by routine analysis. Hence French petitgrain oils should always be submitted to a careful organoleptic examination and comparison made with standard samples of unquestioned purity.

Spanish Petitgrain Bigarade Oil

In Spain, oil of petitgrain bigarade is distilled mostly in Sevilla, the annual production of about 1,000 kg. being absorbed by the home market. Five hundred kilograms of leaf material yield, on the average, 1 kg. of oil.

Italian Petitgrain Bigarade Oil

The production of Italian petitgrain bigarade oil is, in normal years, limited and irregular—averaging between 200 and 250 kg. However, during the recent war, when former sources of supply (notably Paraguay) were shut off, distillation was substantially increased. Italian production areas lie in Sicily and Calabria; they have been described in the section on "Bitter Orange Oil" (Italian). The bulk of commercial Italian petitgrain bigarade oil is produced in the province of Reggio Calabria.

The plant material used for the distillation of the oil is obtained during the regular process of pruning the trees—which, in the case of the bitter (sour) orange tree, lasts from February to April.[5]

Distillation is carried out both in distilleries equipped with direct steam stills and in field distillation posts consisting of directly fired stills. The oil from the latter is of somewhat inferior quality.

The yield and quality of the oil depend upon several factors. According to La Face,[6] leaves from young trees yielded 0.290 per cent of oil; leaves from trees in full growth yielded only 0.205 per cent of oil. Freshly cut leaves on distillation gave a yield of 0.280 per cent of oil; whereas leaves of the same origin, but stored and withered for three days, gave 0.225 per cent of oil. In commercial production such storage (and consequent withering) is often necessary because of an accumulation of work. La Face obtained a lower yield of oil (0.260 per cent) from chopped leaves than from whole leaves (0.285 per cent); he believed this apparent abnormality to result from the fact that the chopped material piles up in the stills and obstructs the passage of steam—which means longer hours of distillation and hydrol-

[5] F. La Face, *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **20**, Nos. 4, 5, 6 April–June (1942).
[6] *Ibid.*

ysis of esters (linalyl acetate [7]). For the same reason the oil obtained from whole leaves contained 68.56 per cent of linalyl acetate, that from chopped leaves only 64.80 per cent of linalyl acetate.

The yields of oil during the harvesting period were: February, 0.193 per cent; March, 0.182 per cent; and April, 0.244 per cent. The highest yield of oil was thus obtained toward the end of the season. Minimum and maximum yields in the various months were:

February		*March*		*April*	
Minimum	*Maximum*	*Minimum*	*Maximum*	*Minimum*	*Maximum*
0.180%	0.196%	0.161%	0.227%	0.180%	0.294%

The yield of oil also depends upon the method of distillation (water distillation, water *and* steam distillation, and direct steam distillation) and upon the type and construction of the stills used. La Face's data confirm the rule that distillation of bitter orange leaf material should be carried out with direct steam and as quickly as possible to prevent hydrolysis of the linalyl acetate, the principal constituent of petitgrain bigarade oil.

TABLE 1.17

Sample	Specific Gravity at 15°	Optical Rotation at 15°	Ester Content, Calculated as Linalyl Acetate (%)	Free Alcohol Content, Calculated as Linaloöl (%)	Aldehyde Content, Calculated as Citral (%)	Solubility in 70% Alcohol
1 [a]	0.8985	−6°	74.70	10.20	1.43	1:2
2 [a]	0.8980	−6°	72.90	12.75	1.18	1:2.1
3 [b]	0.8940	−3° 36′	62.50	17.30	1.60	1:2.6
4 [b]	0.8950	−2° 24′	57.75	21.20	1.21	1:2.6
5 [b]	0.8928	−2° 24′	56.20	21.60	1.38	1:3.6
6 [b]	0.8945	−4° 48′	64.70	16.30	1.35	1:2.4
7 [b]	0.8932	−3° 36′	60.90	18.20	1.40	1:2.7
8 [c]	0.8930	−2° 24′	52.45	21.45	1.60	1:3.8
9 [c]	0.8924	−2° 0′	51.80	20.35	1.13	1:3.8
10 [c]	0.8924	−2° 12′	52.30	20.25	1.16	1:4

[a] Samples 1 and 2 were distilled from leaf material cut from young (nursery) trees.

[b] Samples 3, 4, 5, 6, and 7 were distilled in steam stills.

[c] Samples 8, 9 and 10 were distilled in directly fired stills.

[7] It seems likely that in Dr. La Face's experiments the stills were not properly insulated, with resultant wetting of the plant charge and undue prolongation of the distillation process (the Author).

Physicochemical Properties.—La Face [8] reported the properties of genuine petitgrain bigarade oils which he distilled in Calabria as given in Table 1.17.

According to Chiris,[9] six lots of petitgrain bigarade oil produced in Sicily and Calabria had these properties:

Specific Gravity at 15°	0.8922 to 0.8974
Optical Rotation	+2° 35′ to −6° 15′
Ester Content, Calculated as Linalyl Acetate	46.8 to 69.5%
Solubility	Soluble in 2 to 4 vol. of 70% alcohol; in some cases with turbidity on further dilution

As these figures indicate, some of the commercial lots of Italian petitgrain oil offered on the market are probably mixtures, having been distilled from the leaves of the true bitter (sour) orange, together with leaves of the sweet orange tree. At least the physicochemical properties and the odor of some Italian oils seem to indicate such mixture.

North African Petitgrain Bigarade Oil

The quantity of petitgrain bigarade oil distilled annually in North Africa up to 1946 was small; production, however, is on the increase. For 1946 the figures read as follows:

	Kilograms
Algeria	150
Tunisia	100
Morocco	50

Distillation is carried out as in France. If distilled from the leaves of the true bitter (sour) orange tree, the North African oils are of excellent quality, closely resembling the French product. In some cases, however, the plant material does not appear to have been properly selected, as can be judged from the physicochemical properties of some North African oils. During the past few years, new groves of the bitter orange tree have been planted, particularly in Morocco, and therefore larger quantities of the oil can be expected.

Physicochemical Properties.—Algerian petitgrain bigarade oils, examined by Chiris,[10] had the following properties:

[8] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **20**, Nos. 4, 5, 6 April–June (1942).
[9] *Parfums France* **8** (1930), 74.
[10] *Ibid.*

Specific Gravity at 15°	0.8868 to 0.8978
Optical Rotation	+2° 3′ to −5° 50′
Ester Content, Calculated as Linalyl Acetate	38.95 to 69.82%
Solubility in 70% Alcohol	Soluble in 1.8 to 4.5 vol., usually with separation of paraffins upon further dilution

French Guinea Petitgrain Bigarade Oil

Several years prior to the outbreak of World War II, plantations of the bitter (sour) orange tree were started in Nadel and in La Sala, near Labé (French Guinea) with a view to producing oil of neroli bigarade and oil of petitgrain bigarade. The oils appear to be of very good quality, resembling the French product, because the plant material is properly selected, and distillation is carried out as in France.

Physicochemical Properties.—Five samples of petitgrain bigarade distilled on the plantations of Nadel and La Sala, near Labé (French Guinea), had the following properties, according to Trabaud.[11]

	I	*II*	*III*	*IV*	*V*
Specific Gravity at 15°	0.8887	0.8897	0.8915	0.8929	0.8937
Optical Rotation	−6° 0′	−6° 4′	−6° 10′	−4° 54′	−5° 44′
Acid Number	0.9	1.0	0.4	1.0	0.5
Ester Number	140.0	143.0	162.4	169.0	186.4
Ester Content, Calculated as Linalyl Acetate	49.0%	50.0%	56.8%	59.1%	65.1%
Solubility in 70% Alcohol	Soluble in 2.75 vol. and more	Soluble in 3 vol. and more	Soluble in 3.2 vol. and more	Soluble in 4 vol. and more	Soluble in 2.4 vol. and more

All oils were soluble with fluorescence. The properties and odor of these oils closely resemble those of the oils produced in Southern France.

Haiti Petitgrain Oil

As far as the production of petitgrain oil in the Republic of Haiti (West Indies) is concerned, its beginning dates back to about 1930, when a French neroli oil distiller arrived in Haiti and, impressed by the abundance of bitter orange trees, started to distill oil of neroli and oil of petitgrain. Originally, the bitter (sour) orange tree was introduced to the island of Hispaniola by the early Spanish explorers and settlers. At first cultivated, the tree has long since escaped cultivation and now grows wild and semi-

[11] *Perfumery Essential Oil Record* **27** (1936), 356.

wild in the south and southwest of Haiti. In the course of centuries, these trees most likely hybridized with the sweet orange, which also had escaped cultivation, and formed a new group which Webber [12] lists as bitter-sweet. Hence along with the true bitter (sour) and the true sweet orange tree, Haiti possesses the bitter-sweet variety, locally called "orange commune." A similar hybridization probably occurred also in Paraguay, but not in Mediterranean countries, where the citrus trees always were kept under strict cultivation. The flowers and leaves of the true bitter (sour) orange tree and those of the bitter-sweet variety are morphologically quite similar and cannot be distinguished readily. As a result, the leaf material collected in Haiti for the distillation of oil of petitgrain may contain substantial quantities of leaves from the bitter-sweet variety. Furthermore, these regions abound in the true sweet orange and the Shaddock (a parent of the grapefruit). These, however, can be distinguished quite easily from the true bitter (sour) and from the bitter-sweet variety, for which reason the leaf material gathered for distillation usually contains only a small percentage (not more than 5 to 10 per cent) of Shaddock and sweet orange leaves.

Producing Regions.—The principal area in which the bitter (sour) orange tree and the other above-mentioned varieties grow abundantly lies south of Port-au-Prince, in the great triangle between Leogane, Petit-Goave and Jacmel, a port on the Caribbean Sea; the centers of production are Jacmel and Trouin. Another area lies further west, near Fond-des-Nègres and L'Asile. Southeast of that section an important producing region lies in the Plaine-des-Cayes and near Port-Salut. In all these regions oil of petitgrain is in actual production. A large area of potential production lies to the north of Port-au-Prince, near Ennery and Grande Rivière. Here, however, actual distillation has not yet been started, but is under consideration.

There are no regular plantations of the bitter (sour) orange tree in Haiti; the plant occurs wild and semiwild all over the island, in gardens, and in hedges dividing small holdings. The natives use the fruit as condiment in flavoring meat, and as feed for hogs. In certain areas, however (for example, in Jacmel, Trouin, Fonds-des-Nègres, Ducis, Maniche, Port-Salut and Grande Rivière du Nord), there is such an abundance of bitter (sour) orange trees that distilleries can be kept in operation throughout most of the year. In these sections the leaves and terminal branches are distilled in large vats of 1 to 3 metric tons capacity. In other parts of Haiti, where the tree grows more scattered, the oil would have to be produced in small field stills. If this were done the total annual output of petitgrain oil in Haiti could be increased to about 20 metric tons.

[12] "The Citrus Industry," Vol. I, 499, Univ. Calif. Press, 1943.

Harvest, Distillation, and Yield of Oil.—In Haiti, the harvest of petitgrain leaf material lasts throughout the year, but the peasants prefer the season from November to May, when they are idle and waiting for the spring rains, to get busy with their own food crops. The best quality of oil is obtained from May to October, after the harvest of the blossoms.

The distillation of one batch of leaves and terminal branches requires from 3 to 3½ hr. One metric ton of plant material yields from 7 to 8 lb. of oil. A steam pressure of 50 to 60 lb. per sq. in. (as measured in the steam boiler) gives good results. Dry steam of high pressure yields an oil with a higher ester content than low pressure steam does, but care has to be exercised not to "burn" the plant material and the volatile oil.

Haitian oil of petitgrain contains up to 80 per cent of linalyl acetate, the highest percentage being obtained in the fall. When young leaves are distilled in the spring, the ester content may occasionally drop to 40 per cent; but this is exceptional. If the leaves are properly selected, the quality of the Haiti petitgrain oil should be good, because frequently the leaves and petioles are distilled together with a small quantity of adhering blossoms. At any rate, the methods of distillation employed in Haiti are far superior to those used in Paraguay, which partly accounts for the better quality of the Haiti oil; the latter, indeed, compares not unfavorably with the true French petitgrain oil and, as a result, has found a ready market in the United States, especially during World War II, when the European and African oils were no longer available.

Total Production.—The development of Haiti's petitgrain oil industry can be seen from the following figures indicating the annual production from 1932–1933 to 1947–1948 inclusive:

Fiscal Year	*Total Oil Production (kg.)*
1932–1933	555
1933–1934	188
1934–1935	348
1935–1936	755
1936–1937	1,103
1937–1938	956
1938–1939	2,158
1939–1940	2,779
1940–1941	1,156
1941–1942	2,284
1942–1943	4,572
1943–1944	1,394
1944–1945	3,082
1945–1946	(Not available)
1946–1947	3,737
1947–1948	8,707

Production could be increased substantially provided demand and prices warrant.

Physicochemical Properties.—Shipments and samples of Haitian petitgrain bigarade oils analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 15°/15°	0.892 to 0.900
Optical Rotation	−1° 26′ to −6° 35′
Refractive Index at 20°	1.4542 to 1.4598
Ester Content, Calculated as Linalyl Acetate	60.3 to 80.4%
Solubility in 70% Alcohol	Soluble in 3 to 4 vol. and more; occasionally opalescent on addition of more alcohol

One lot had an optical rotation of +2° 4′ and an ester content of 57.7 per cent. The plant material from which this oil was distilled probably contained small quantities of unripe fruit.

Chemical Composition and Use of Petitgrain Bigarade Oil

Chemical Composition of Petitgrain Bigarade Oil.—The chemical composition of petitgrain bigarade oil is described below under "Oil of Petitgrain Paraguay."

Use.—True petitgrain bigarade oil has good odor qualities. It possesses strong, yet suave and pleasing, tonalities. The oil can be employed to great advantage in conjunction with the much higher priced oil of neroli bigarade to reduce the cost of the latter in lower priced perfume compounds. Oil of petitgrain bigarade is also employed quite frequently to adulterate oil of neroli bigarade.

Petitgrain Bigarade Water Oil

The distillation water obtained in the production of oil of petitgrain bigarade retains some oil in solution or suspension. It can be extracted from the water with volatile solvents, such as petroleum ether. This is sometimes done in Southern France. Ten kilograms of oil of petitgrain bigarade correspond in yield to about 50 g. of petitgrain bigarade water oil. The product has a dark color and possesses a powerful, somewhat empyreumatic, odor. Petitgrain water oil is occasionally used for adulterating the much more valuable orange flower water oil, which is extracted from the distillation waters of neroli bigarade oil.

According to Naves,[13] a sample of petitgrain water oil had the following properties:

Specific Gravity at 15°	0.8988
Optical Rotation	Too dark
Refractive Index at 20°	1.4682
Acid Number	1.12
Ester Number	4.9
Ester Number after Cold Formylation	286.3
Solubility	Soluble in 2.6 vol. of 60% alcohol

The oil contained traces of methyl anthranilate.

Using petroleum ether or benzene, Igolen [14] extracted the aqueous distillate obtained on direct steam distillation of leaves and petioles from the bitter (sour) orange tree and obtained an oil in which the following compounds were identified:

	Per Cent
Terpenes (Dipentene and Limonene)	17.0
Acids (Isovaleric, Lauric, Myristic, Stearic, and Cinnamic)	0.7
Aldehydes (Benzaldehyde and Lauraldehyde)	1.7
Alcohols (*d*- and *l*-Linaloöl, *d*-α-Terpineol, Geraniol, Citronellol, Nerolidol and Farnesol)	75.0
Phenols (Guaiacol, *p*-Cresol, and Eugenol)	0.5
Basic Compounds (Methyl Anthranilate and Quinoline)	0.2

OIL OF PETITGRAIN PARAGUAY

Essence de Petitgrain Paraguay *Aceite Esencial Petitgrain Paraguay*
Petitgrain Paraguayöl

Introduction.—True petitgrain bigarade oil, distilled in Southern France and other Mediterranean countries, represents the highest quality of petitgrain oil, because the carefully selected leaf material originates exclusively from the true bitter (sour) orange tree, *Citrus aurantium* Linnaeus, subsp. *amara* Linn., and because distillation is carried out in modern steam stills. Since labor costs in Southern France are high, the French oil has always

[13] *Parfums France* **12** (1934), 69.
[14] *Rev. marques parfums France* **17** (1939), 55, 79.

demanded a premium price, with the result that consumption of the French oil has remained restricted. Today the bulk of petitgrain oil comes from Paraguay, where the entire industry is based upon low-cost family production. The stills are primitive, and the plant material is not carefully selected. The Paraguay oil, in consequence, possesses a harsher odor than the French; and it is limited in its use to soaps and cosmetic preparations rather than to delicate perfumes.

A traveler, setting out from Asunción, Paraguay's capital, and riding across the rolling hills and verdant plains covered by dense brush or vast forests, will never forget the poor roads, which turn into mud traps during the rainy season, obliging him to resort to horses or ox-drawn carts that move slowly but steadily through rain and mire. He will never forget the orange trees growing luxuriantly along the roadside, in the gardens of Asunción's mansions or around humble thatched huts far out in the pampas. Golden jets of orange, illumined by the sun's rays, flash through the greenery of dense jungles, and oranges seem to be present everywhere. Much of the fruit goes to waste, falling from the trees and rotting along the roads, in yards and gardens. Paraguay could supply enormous quantities of oranges, if the fruit could only be transported from the interior to a shipping port.

History and Botany.—When Spanish Jesuit padres colonized Paraguay, during the seventeenth and eighteenth centuries, and brought their settlements to great prosperity, they introduced the sweet orange, *Citrus sinensis* (Linn.) Osbeck. The dictator Francisco S. Lopez, who ruled Paraguay from 1862 to 1870, followed the example of the Jesuit missionaries and had orange trees planted along highways and roads. These trees, which can be seen throughout the countryside, have grown to an impressive height and bear abundant fruit.

Besides the sweet orange, the early padres and colonizers very likely brought from Spain the bitter (sour) orange, *Citrus aurantium* Linnaeus, subsp. *amara* Linn., planting the trees around their missions and settlements in Guaira, San Ignacio, Jesús y Trinidad, Santa Rosa, etc. Both the sweet and the bitter (sour) orange soon escaped cultivation and, with favorable soil and climatic conditions, spread wild and semiwild over wide areas in the vast forests and jungles of Paraguay. Undoubtedly they formed many hybrids and produced mutations which are now difficult to classify morphologically.

Both Swingle [1] and Webber [2] list these varieties under the name of Bittersweet oranges. Although they may be hybrids of the true bitter (sour)

[1] H. J. Webber and L. D. Batchelor, "The Citrus Industry," Vol. I, 406, Univ. Calif. Press (1943).
[2] *Ibid.*, 491.

orange, *Citrus aurantium* Linnaeus, subsp. *amara* Linn., with the sweet orange, *Citrus sinensis* (Linn.) Osbeck, it would be just as reasonable to assume that they arose as mutations of the true bitter (sour) orange. The trees, foliage, and general character of the fruit, together with the odor and bitter taste, closely resemble those of the true bitter (sour) orange; the pulp, however, is sweeter. Swingle and Webber classify these orange trees as "Paraguay-Apepú," and note that their fruits differ from those of most bitter (sour) orange varieties in that they lack the reddish blush and they have a fairly sweet pulp. The term bitter-sweet in a strict sense can scarcely be considered as a variety name; it is rather a group name for the type of orange of which the Paraguay-Apepú is one representative. The Apepú orange itself occurs in many forms, which can be distinguished only by the appearance, form, color, and degree of sweetness of the fruit. The Guarani Indians, keen observers of nature, distinguish, for example, between the Apepú-jhaí (jhaí = bitter), the Apepú-jheé (jheé = sweet), and the Apepú-í (í = small). The Indian term Apepú indicates that the peel of the fruit is rough. The Guaranis greatly relish the Apepú-jheé with its sweeter juice. The Apepú-jhaí, however, is inedible, approaching probably the true bitter (sour) orange. The leaves and twiglets of the Apepú-jhaí furnish the best material for the distillation of the Paraguay petitgrain oil, but those of the Apepú-jheé are also used, occasionally, for this purpose, although they give a smaller yield and a lower quality of oil. The leaves of these Apepú forms possess a winged stalk, and have an ovate, smooth, pointed shape, shiny on top.

The Apepú-í is not used, or at least should not be used, for the purpose of distillation. As a matter of fact, the Apepú-í does not belong in the group of the bitter-sweet oranges at all; it is most probably *Citrus aurantium* var. *myrtifolia* Ker-Gawl., the so-called Chinotto orange. It has small leaves. The fruit is mandarin-like, but smaller, and possesses numerous pits. The fruit grows in clusters close to the branches; they are so bitter that they can be used for the making of preserves only. The trees occur singly, seldom in groups.

Development of Paraguay's Petitgrain Oil Industry.—The Paraguayan petitgrain oil industry owes its existence to the French botanist, Benjamin Balansa, who visited Paraguay in 1873 and began production of petitgrain oil near Villa Rica in 1880. Even today, the Balansa family owns extensive petitgrain plantations around Villa Rica. The industry developed, and the Paraguay petitgrain oil became an important raw material for perfumery, especially for the scenting of soap. Its odor is strong and refreshing. More than 100,000 kg. of petitgrain oil were exported from Paraguay in 1938. Production can be increased at any time, if the distillers, instead of using

only plant material from their own plantations, set up movable field stills in the jungles and penetrate the more remote regions where countless wild trees, growing in patches ("manchones"), await exploitation. This happened during the last years of World War II, when attractive prices induced producers to undertake the hardships and cost of organizing distillation posts in the interior. Thus Paraguay produced more than 200,000 kg. of oil during 1944, and more than 250,000 kg. during 1946. A good portion of Paraguay's exports goes to the United States, the rest to Argentina, France, England, and other countries.

Planting.—To start a plantation, the seed is first planted in a nursery. After one year, the young plants are transplanted into rows 3 m. apart, with a distance of 2 m. between each plant, so that one hectare contains about fifteen hundred trees. The root system develops after the second year. After three more years, the tree bears fruit and sufficient leaves to be harvested. If the young plants are not transplanted, the time until the first harvest can be shortened to three years, but the trees will be rather weak. The planting should be weeded out three or four times a year, which procedure assures a much higher yield of leaves. A normal tree yields 10 to 15 kg. of leaves per year. Without hoeing and weeding, the leaves have a tendency to turn yellow.

It is interesting to note that the planted bitter (sour) orange trees of Paraguay are not permitted to grow to full development, with trunk and round crown like the trees in Southern France, Spain, Italy, and Algeria. They are kept in bush form, from which the outer branches and leaves are hacked off with machetes, so that only the skeleton of the bush remains. From the side branches, the leaves and green branchlets are cut off for distillation, and the wooden parts are thrown away or used as fuel. The distillation material should consist only of leaves and should not contain any small fruit, which lowers the solubility of the oil and influences its optical rotation. Oil distilled exclusively from leaf material is laevorotatory; hence dextrorotation indicates the presence of oil distilled from the fruit peel.

When the leaf material is harvested from *wild-growing* trees, the branches are hacked off even more crudely, and the trees are trimmed without any regard for their life. Sometimes the entire tree is felled in order to facilitate cutting of the branches and leaves. In general, there has been such crude exploitation of the wild-growing trees that today the field distillers have to go ever farther inland and deeper into the forests in search of sufficient distillation material; this obviously increases the cost of production. However, there are still vast unexploited sections permitting increased production, should demand warrant it.

Another bad practice consists in the cutting of leaf material, either from

planted or wild-growing trees, during the cold season, when temperatures of −2° to −3° C. are not unusual, and even −5° has been observed on rare occasions. Such frosts kill the tender young shoots developing on freshly cut branches.

The most productive months are September to March–April. The months during which oils of the best quality arrive in Asunción are January to June–July. In the experience of a prominent exporter [3] in Asunción, the oil derived from fresh leaves during Paraguay's spring (August to October) frequently possesses too low an ester content (below 46 per cent, calculated as linalyl acetate) which may be due to immaturity of the leaves. Yet, a fine quality of oil is occasionally obtained in August from trees which have been permitted to rest for some time and which are in bloom, because the distillation material then consists not only of leaves but also of blossoms.

It is not possible to speak of a definite petitgrain oil distillation period in Paraguay, although the government, with a view toward improvement of the quality of the oil, has considered the advisability of prohibiting distillation during the spring months. In Paraguay there exist numerous small plantations of the bitter-sweet orange tree—their number is increasing—aside from a few large plantations. A great part of the total production, however, still originates from the leaves of wild growing trees, although their oil is usually of inferior quality (the result, largely, of a lack of sunlight in the dense forests). The leaves of these wild growing trees are usually cut in a very crude way and often the trees perish after they have been deprived of most or all of their branches and leaves. Frequently the entire tree is felled for the simple purpose of getting at the leaves more easily and quickly. Thus the leaves are collected, no matter whether the tree perishes after the first, second, or third trimming.

Conditions are somewhat different in the plantations, because the owners spend considerable effort and time on their trees and have a certain interest in their survival. But even these trees, which normally should not be trimmed more than once per year, often have to undergo two and even three trimmings. Illogical as this practice may appear, there are sometimes good reasons for it. For instance, during years of very good weather, a tree may support repeated trimmings without suffering permanent damage. There are other considerations, such as a high price of the oil, which may induce producers to cut leaf material regardless of the damage inflicted upon the tree and regardless of the season. If other produce of the soil have failed (because of drought, excessive rains, locusts, etc.) the small operator —who usually lives from hand to mouth—will distill petitgrain oil to profit from at least one source. At the end of 1947 producers in many sections

[3] The author is greatly indebted to Mr. H. Krauch in Asunción for this information.

suddenly started collecting the leaves from their Apepú trees for the simple reason that locusts threatened to devour them after they had already destroyed the other crops.

There may, of course, be factors which will have the opposite effect. For example, if other produce bring sufficiently high profits, the small settler may neglect petitgrain distillation altogether, and production of the oil may be greatly reduced. During prolonged spells of droughts, rivers and wells may dry up, and distillation has to be stopped for lack of water. In Paraguay climatic conditions often deviate from normal, because tropical and subtropical sections overlap: even the weather is thus a most uncertain factor.

Considering everything, it is practically impossible definitely to designate the months most suitable to production, or the period of the year at which the largest quantities of oil and the best qualities are produced. Everything depends upon the individual operator, upon the methods he uses, and upon general conditions prevailing at a given time. And this state of things probably will continue until large plantations are created and until the goverment decides upon, and enforces, a "calendar" of production. To improve the quality of the oil it would be advisable to introduce a simple, inexpensive, but more modern type of still, in which the leaf material can be distilled rapidly, with direct live steam. But even then, there will always remain one uncertain factor, viz., the weather.

Plant Varieties and Producing Regions.—As has been pointed out, there exist in Paraguay two local varieties of the bitter (sour) orange tree, the leaves and twigs of which are distilled for their essential oil:

1. The so-called "Apepú-jhaí," a bittersweet hybrid (sour-bitter) which is not edible. Its leaves have a normal content of essential oil, and the oil has a normal ester content.
2. The so-called "Apepú-jheé," another bittersweet hybrid (semisweet), the juice of which is consumed by the Indians. Its leaves contain much less essential oil than those of the "Apepú-jhaí"; the ester content of the oil, too, is subnormal. The leaves of the "Apepú-jheé" should, therefore, not be used for distillation, although this is occasionally done in certain districts.

The production areas lie to the northeast and to the south of Asunción, between the rivers Paraná and Paraguay, with main centers in Caballero, Itacurubi, San José, Coronel Oviedo, Villa Rica, Caazapa, and Yegros. Orange trees also grow in the state of Matto Grosso in Brazil, but it is said that their yield of leaf oil is inferior, and that the oil is not exported. The

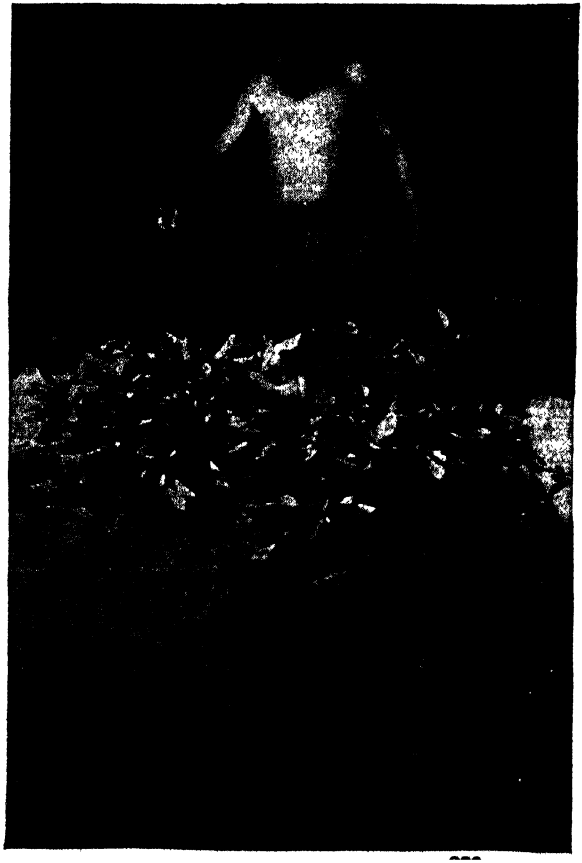
producing centers of Paraguay are located mainly in the Cordilleras, the hilly sections between the above-mentioned rivers. The trees growing in the lower altitudes and plains give an inferior yield, the oil being subnormal also in regard to ester content. Because of the absence of ample sunshine, the same is true of the trees growing wild in the dense jungles.

Distillation.—The producers distill leaf material harvested from their own property or purchased from neighboring settlers, who do not possess their own stills. The harvested leaves should not be stacked up in piles, as this would result in fermentation, the leaves then turning black and losing considerable oil.

A typical still consists of a simple iron vessel or drum, of 200- to 300-liter capacity, which serves as a steam generator (Government regulations prohibit the employment of copper stills, which could be used for the clandestine and illegal production of spirits.) This iron tank is heated by open fire, wood from the nearby forests serving as fuel. The steam thus generated enters at the bottom of a wooden vat of conical shape, holding from 300 to 600 kg. of leaves. The vat is usually not provided with a perforated grid, and the lower leaf material is in direct contact with boiling water condensed from the steam within the still. This practice undoubtedly results in excessive wetting of the charge and in prolonged distillation. Therefore, about 6 hr. are required to distill one charge of leaves. During the height of the season, the producers operate day and night in order to process the accumulating leaf material. A 6-hr. distillation period for one charge of leaf material seems like a long time, but it is necessitated by the high ratio of steam condensed within these crude stills, and even more so by insufficient cooling in the primitive condensers. The long contact of boiling water with the leaf material, in turn, causes considerable hydrolysis of esters. It is a case quite similar to the distillation of oil of lavender as it was carried out thirty years ago in Southern France. Experiments, undertaken in Paraguay in a modern still constructed in Grasse (Southern France), yielded petitgrain oils containing up to 80 per cent linalyl acetate, instead of the usual 46 to 55 per cent. Distillation in this case could be shortened to less than 1 hr.

The yield of oil depends upon many factors, such as the condition of the planting, the leaf material, the season, weather, etc. The amount of leaves required to yield 1 kg. of oil varies from 200 to 400 kg. Young, healthy, and vigorous trees seem to yield more oil than old and ligneous trees. Old leaves contain less oil than young ones. Leaves from a tree which has been trimmed during the preceding year yield more oil. Material cut during the most favorable season of the year and from an airy, sunny, well-kept and weeded planting yields 1 kg. of oil per 200 to 240 kg. of leaves; whereas

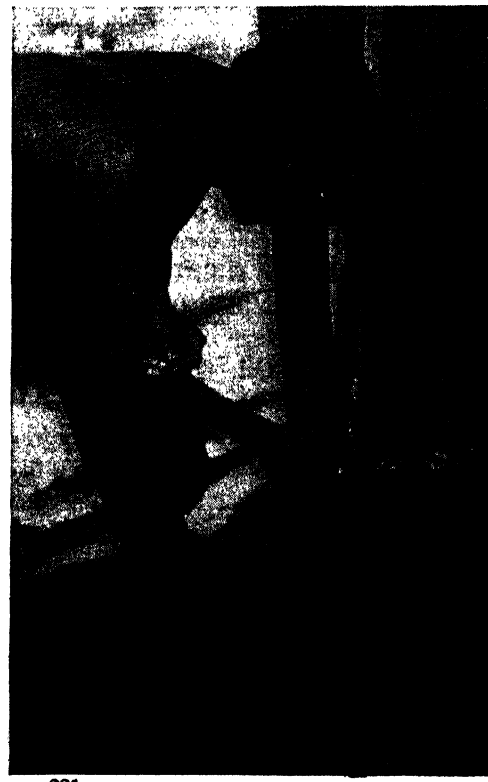




Above: Field still for the distillation of petitgrain leaves in Paraguay.

Left: Charging of still with petitgrain leaf material.





Above: Firing of steam boiler for distillation of petitgrain leaves in Paraguay.

Right: Drawing the oil from the separator.

All photographs courtesy of Fritzsche Brothers, Inc., New York.

material cut from jungles, through which the sun can hardly penetrate, yields 1 kg. of oil per 400 kg. of leaves. There is a direct relationship between yield and quality of oil (ester content and fragrance)—a high yield indicating high quality.

Summarizing, we find that the following factors influence the yield and quality of Paraguay petitgrain oil:

1. Selection of leaf material from the proper trees. "Apepú-jhaí" give better results than "Apepú-jheé." The oil from the latter has a much lower ester content; the yield, too, is inferior.
2. Soil conditions and altitude. Leaves cut from trees growing in the plains give a lower yield and quality of oil than the leaf material from the Cordilleras.
3. The season. Yield and quality of oil are highest from January to June and from then on fall off gradually. From August to October the yield and quality are poorest.
4. Condition of the plant material. Leaves from well-kept, airy, and sunny plantings give a better yield and higher quality of oil than the leaves from dense forests and jungles. The material should be distilled soon after harvesting.
5. Distillation of fresh leaves. This should be carried out as rapidly as possible, and with steam of slightly high pressure. To prevent hydrolysis of the esters, condensed water should not be permitted to accumulate inside the still. The still should be insulated and contain a perforated false bottom (grid) to prevent direct contact of the plant charge with any boiling water condensed within the still. The condenser should be sufficiently large and efficient to permit rapid distillation.

Handling of the Oil.—The producers sell their small lots of oil to field brokers and shop owners, many of them Armenians, in the nearest villages. There the oil is packed into small drums or gasoline cans and transported to the exporters in Asunción. Shipping from the interior usually takes time because of the very poor roads in Paraguay, many of which are only mud tracks, deeply furrowed by the heavy, two-wheeled ox carts. During rainy weather these "roads" frequently become mud traps. For this reason, the exporters in Asunción are sometimes cut off for weeks from their suppliers in the interior and are temporarily prevented from filling their contracts abroad.

Careful exporters examine every small lot of oil for solubility and specific gravity in their "laboratories," which consist of a few bottles, test tubes, and a Westphalian scale. Small lots, found normal by this prelimi-

nary examination, are bulked into larger lots, samples of which are sent to the government analyst of Asunción. Thus, standardized shipments with certain properties are made up, each exporter specializing in his own brand. The bulked oils are finally shipped abroad in wooden cases of eight cans, each can holding 5 kg., or 11 lb., of oil.

Economic Setup.—Years ago, the bulk of Paraguay petitgrain oil was distilled in numerous field stills erected in the vast jungles, the leaves of wild-growing trees serving as distillation material. The relatively high prices of oil prevailing at that time permitted distillers to move their stills and equipment into the forests, carry along supplies for several months, and finally to transport the oil back to the trading centers. The lower prices of the last prewar years eliminated this form of ambulatory distillation. The producers could no longer make a living exclusively from distilling petitgrain oil, and certainly not by distilling in the inaccessible interior, where transportation doubles and triples the cost of food, general supplies, etc. Consequently, the bulk of oil was produced by a great many small settlers, white and half-breed. Cutting and clearing the jungle, they spared the wild-growing orange trees; and between them they planted other crops, such as corn, tobacco, cotton, and cassava. Whenever these settlers were in need of cash and had time on hand, they distilled the leaves of their bitter orange trees. This condition prevailed generally until the outbreak of World War II, when oil prices started to rise and it became again feasible for producers to set up movable field stills in the forests when the demand for oil warranted it.

Physicochemical Properties.—The properties of the shipments exported from Paraguay vary within relatively narrow limits, because all the shipments represent bulkings of many small lots.

The oils should be slightly laevorotatory, dextrorotation indicating the presence of small fruit in the leaf material.

Pure oils are usually soluble in 0.8 vols. of 80% alcohol, and in 2.5 to 3 vols. of 70% alcohol (usually opalescent with more alcohol). A poor solubility may be the result of (*a*) the presence in the distillation material of small fruit, which contains much limonene; or (*b*) contamination of the oil with kerosene.

An oil may be pure, although it contains less than 43 per cent of ester calculated as linalyl acetate; the quality of Paraguay petitgrain oil, however, is evaluated, in general, by its ester content, which ranges in the best oils from 46 to 55 per cent (in some cases up to 59 per cent). The content of free linaloöl ranges between 35 and 55 per cent.

Shipments of genuine oils received and analyzed by Fritzsche Brothers, Inc., varied between the following limits:

Specific Gravity at 15°/15°..	0.887 to 0.893
Optical Rotation.....	−0° 8′ to −2° 33′; some oils show slight dextrorotation up to +2° 13′
Refractive Index at 20°.....	1.4595 to 1.4630
Ester Content, Calculated as Linalyl Acetate	43.0 to 55.5% (a good average is 50%; the minimum ester content of commercial oils is 46%)
Solubility at 20°.....	Soluble in 2.5 to 3 vol. of 70% alcohol, opalescent with more. In isolated cases, hazy in 1 to 10 vol. of 70% alcohol

A shipment of Paraguay petitgrain oil, which contained a very high percentage of esters, had these properties:

Specific Gravity at 15°/15°..	0.901
Optical Rotation.....	−5° 58′
Refractive Index at 20°.....	1.4558
Ester Content, Calculated as Linalyl Acetate.....	80.3%
Solubility.....	Soluble in 3.5 vol. of 70% alcohol; slightly opalescent in 10 vol.

The high ester content of this oil is probably due to the fact that the oil was distilled very rapidly in a modern steam still (see preceding section on "Distillation").

Adulteration.—The original lots of oil arriving from Paraguay are seldom adulterated. Occasionally, however, they do contain small amounts of kerosene, which may be regarded as contamination rather than as willful adulteration.

Use.—Because of its pronounced odor, oil petitgrain Paraguay lends itself especially well to the scenting of soap, or of other preparations, where strength and low price are of prime consideration. However, in handkerchief perfumes, eaux de Cologne, lotions, and cosmetics, where a more delicate note is desired, the regular oil should be replaced by the so-called terpeneless petitgrain oil, which is prepared by eliminating most of the terpenes from the original oil.

Terpeneless Petitgrain Oil.—Terpeneless petitgrain oils prepared by Fritzsche Brothers, Inc., during the past twenty years, had the following properties:

Specific Gravity at 15°/15°..	0.889 to 0.898
Optical Rotation.....	−0° 55′ to −2° 58′
Refractive Index at 20°.....	1.4586 to 1.4619
Ester Content, Calculated as Linalyl Acetate.....	46.1 to 60.4%
Solubility at 20°.....	Soluble in 2 to 3 vol. and more of 70% alcohol

Terpeneless petitgrain oil is one of the most useful perfume raw materials; its scent is rich, smooth, and harmonious. These features, in conjunction with its relatively moderate price, offer a wide range of application in many fields of the perfumer's art. Terpeneless petitgrain oil is a base par excellence of synthetic neroli oils or orange blossom scents.

Chemical Composition of Oil of Petitgrain Bigarade and Petitgrain Paraguay.—The chemistry of "petitgrain oil" has been investigated by a number of workers, but unfortunately in the original publications the source of the oil examined is not always clearly stated. The Schimmel chemists (including Walbaum and Hüthig), von Soden and Zeitschel, Charabot and Pillet, and Naves, investigated Paraguay oils; Semmler and Tiemann used both types of oil, viz., the Paraguay and the bigarade oil; Passy does not mention the origin of his oil; and Erdmann speaks of an oil distilled from unripe fruits (probably of the bigarade tree—the author). The chemical composition of the bigarade oil is apparently closely related to that of the Paraguay oil, but it may be true that some of the constituents of the bigarade oil—pyrrole and furfural, for example—occur in heavier amounts in the Paraguayan product for the simple reason that the latter has a much coarser and more pungent odor.

The presence of the following constituents has been established in petitgrain oil:

Pyrrole and Furfural. Both compounds occur in the foreruns; pyrrole has been detected through color reactions by Erdmann and Erdmann,[4] furfural by Schimmel & Co.[5]

β-Ocimene. More recently Crabalona[6] observed the presence of β-ocimene in the fraction b_7 51°–54°, d_4^{16} 0.815, α_D +13° 30′, n_D^{16} 1.4861 of petitgrain bigarade oil produced in Southern France. The terpene was identified by means of its addition product with maleic anhydride (cf. "Oil of Neroli Bigarade," French, Chemical Composition).

Camphene. Walbaum and Hüthig[7] found that the fraction b. 160°–170°, when treated with a glacial acetic acid–sulfuric acid mixture, developed the typical odor of isoborneol, although crystals of isoborneol could not be obtained.

β-Pinene. When treated with an alkaline solution of potassium permanganate, the fraction b. 167°–170° (d_{15} 0.8474, α_D −7° 10′) yielded the crystalline sodium salt of nopinic acid, which could be converted into free nopinic acid m. 126°–127°, with sulfuric acid. Schimmel & Co.[8] also prepared nopinone from nopinic acid and condensed it with benzaldehyde into the benzylidene compound $C_9H_{12}O{=}CHC_6H_5$, m. 107°.

[4] *Ber.* **32**(1899), 1217.
[5] *Ber. Schimmel & Co.*, October (1902), 66.
[6] *Bull. soc. chim.*, March/April (1948), 388.
[7] *J. prakt. Chem.* [2], **67** (1903), 321.
[8] *Ber. Schimmel & Co.*, April (1914), 77.

Dipentene and Limonene. Walbaum and Hüthig [9] proved the presence of dipentene by preparing its tetrabromide m. 125°. Semmler and Tiemann [10] reported the occurrence of limonene in petitgrain oil; but Charabot and Pillet [11] contended that oils distilled exclusively from leaves and twiglets contain no limonene. The presence of limonene in petitgrain oil, according to these authors, is a proof that the distillation material contained small, unripe fruit.

l-Linaloöl and *l*-Linalyl Acetate. Semmler and Tiemann's [12] discovery that the oil contains linaloöl, free and as ester, was confirmed by Walbaum and Hüthig [13] who prepared the phenylurethane m. 65°.

Investigating the alcohols occurring in petitgrain oil from Paraguay, Naves [14] found that the oil contains laevorotatory linalyl acetate and a slightly laevorotatory mixture of free linaloöls (see also below). The *l*-linaloöl obtained by saponification of the acetate yielded a phenylurethane m. 64°–64.5°, and a xenylurethane m. 90.5°–91°.

α-Terpineol and Terpinyl Acetate. According to the same author,[15] *l*-linaloöl is accompanied by a substantial quantity of free α-terpineol which occurs in the oil as a mixture of approximately equal parts of *d*-α- and *d,l*-α-terpineol. The fractions of petitgrain oil which contain most of the free terpineol are partly racemized. Only very small quantities of terpineol esters are present in the oil. Naves [16] identified terpineol by preparation of its phenylurethane m. 112°–113°, and of its α-naphthylurethane m. 147.5°–148°. That *d*-α-terpineol occurs in petitgrain oil was shown years ago by Walbaum and Hüthig,[17] who prepared the phenylurethane m. 112°.

Nerol and Neryl Acetate. Von Soden and Zeitschel [18] isolated about 2 per cent of nerol from petitgrain oil. Naves [19] obtained only traces of nerol, which he separated from the free alcohols (after they had been separated from terpineol by phthalization) through the allophanate. Very small quantities of neryl acetate, too, are present in the oil.

Geraniol and Geranyl Acetate. According to the same author,[20] oil of petitgrain contains traces of geraniol and small quantities of geranyl acetate. The alcohol was identified by preparation of its allophanate m. 124°–124.5°. Years ago, Passy [21] had already noted the presence of geraniol and of geranyl acetate in petitgrain oil by preparing the diphenylurethane m. 82° and analyzing the silver acetate.

Methyl Anthranilate(?). In the opinion of Walbaum and Hüthig,[22] the bluish fluorescence of petitgrain oil is probably caused by methyl anthranilate.

A Base(?). Shaking the fraction boiling at about 200° with dilute sulfuric acid, these authors also obtained traces of an oily substance which had a strongly basic, characteristic petitgrain odor.

[9] *J. prakt. Chem.* [2], **67** (1903), 321.
[10] *Ber.* **25** (1892), 1186.
[11] *Bull. soc. chim.* [3], **21** (1899), 74.
[12] *Ber.* **25** (1892), 1186.
[13] *J. prakt. Chem.* [2], **67** (1903), 321.
[14] *Helv. Chim. Acta* **29** (1946), 553.
[15] *Ibid.*
[16] *Ibid.*
[17] *J. prakt. Chem.* [2], **67** (1903), 321.
[18] *Ber.* **36** (1903), 265.
[19] *Helv. Chim. Acta* **29** (1946), 557.
[20] *Ibid.*
[21] *Bull. soc. chim.* [3], **17** (1897), 519.
[22] *J. prakt. Chem.* [2], **67** (1903), 321.

Summarizing the recent work of Naves [23] on the terpene alcohols and esters present in Paraguay petitgrain oil, it may be stated that:

1. The free alcohols are represented chiefly by a slightly laevorotatory mixture of *d,l*-linaloöl and of *l*-linaloöl. This mixture of linaloöls is accompanied by a good portion of α-terpineols with an optical rotation of about +40°. Free geraniol and nerol are present in very small quantities only (about 0.2 per cent).

2. The esters occurring in petitgrain oil are those of linaloöl (chiefly), geraniol, and nerol. Esters of terpineol are present in very small quantities only.

3. The *l*-linaloöl (in excess of *d*-linaloöl, as required by optical compensation) seems to have originated, at least in part, in *post-mortem* hydrolysis of the linalyl acetate and perhaps also of other plant constituents.

So far as the sesquiterpenes are concerned, Semmler and Tiemann [24] years ago expressed the opinion that the higher boiling fractions of petitgrain oil contain sesquiterpenes which, however, they did not identify. It was Naves [25] who succeeded in identifying some of these high boiling constituents of Paraguay petitgrain oil:

d-Nerolidol. $b_{2.6}$ 118°–119°, d_4^{20} 0.8786, n_D^{20} 1.47996.
Oxidation of nerolidol with potassium bichromate and 50 per cent sulfuric acid led to farnesal which could be characterized by the preparation of its semicarbazone m. 132°–133° (recrystallized) and of its dinitro-2,4-phenyl-hydrazone m. 83°–84° (recrystallized).

Farnesol. b_3 131°–132°, d_4^{20} 0.8880, n_D^{20} 1.48906; identified by preparation of its di-β-naphthylurethane m. 70°–70.5°, allophanate m. 78°–79°, and diphenylurethane m. 54.5°–55° (all derivatives recrystallized).
Nerolidol and farnesol occur in the oil as traces (about 0.03 per cent) only, and are accompanied by thirty times the quantity of

Tertiary Sesquiterpene Alcohols(?), $C_{15}H_{26}O$. One of these tertiary $C_{15}H_{26}O$ alcohols is apparently tricyclic and yields guaiazulene, whereas the other is monocyclic and may be bisabolol.

Secondary Sesquiterpene Alcohols(?), $C_{15}H_{24}O$. These bicyclic $C_{15}H_{24}O$ alcohols belong to the group of the cadalene derivatives.

Geranyl (Neryl) Oxide, $C_{20}H_{34}O$. The crude fractions b_2 156°–170°, freed from the alcohols by borization, were redistilled over metallic sodium. It was found that the natural oil, and in much larger measure, the saponified oil, contains geranyl or neryl oxide b_2 163°–164°, d_4^{20} 0.8696, n_D^{20} 1.48474, which could have originated from the reactions to which the leaves of the tree and the oil were subjected.

[23] *Helv. Chim. Acta* **29** (1946), 553.
[24] *Ber.* **25** (1892), 1186.
[25] *Helv. Chim. Acta* **29** (1946), 1084.

OIL OF NEROLI BIGARADE

(Bitter Orange Blossom Oil)

Essence de Neroli *Aceite Esencial Neroli* *Neroliöl*
Oleum Florum Aurantii

Botany.—The sour or bitter orange, *Citrus aurantium* Linnaeus, closely resembles the sweet orange, *Citrus sinensis* (Linn.) Osbeck, in general character and appearance of tree and fruit; yet the two represent very distinct botanical species and not merely cultivated varieties of one species. According to Webber,[1] the bitter (sour) orange species contain several subspecies, with such markedly distinct characteristics that some authors would consider them separate species. One of these subspecies is the normal or true sour, true bitter, bigarade, or Seville orange, *Citrus aurantium* Linnaeus, subsp. *amara* Linn. It is distinguished from the sweet orange most readily by its broadly wing-margined leaf petioles, by the commonly hollow axis or core of its fruit, and by the acidity of its pulp. The volatile oils in the leaves, flowers, and fruit of the bitter orange possess an odor different from that in the sweet orange and have a different chemical composition. However, some extreme forms of the true species present overlapping features and are difficult to identify with certainty, the odor of leaves, flowers, and fruit peel being probably the most distinctive characteristics.

The most important commercial use of the peel of the bitter orange is in marmalades. The blossoms contain a volatile oil of delightful fragrance, highly esteemed by perfumers; it can be isolated by steam distillation or by extraction with volatile solvents. The principal value of the bitter (sour) orange tree to the citrus industry as a whole arises from its general use as a root stock. It is quite resistant to the dreaded gummosis (*mal secco* or *mal di gomma*) which on one occasion almost completely destroyed Italy's citrus orchards. Since that time it has been the practice to propagate lemon, sweet orange, mandarin, grapefruit, and bergamot trees on the more resistant stocks of the sour orange.

History.—The sour or bitter orange is, in all probability, a native of Cochin China in southeastern Asia, whence it spread to India and Persia. Unknown to the Romans, even during the period of their greatest imperial expansion, it was introduced to the Mediterranean countries (Syria, Palestine, Egypt, North Africa, Sicily, Sardinia, Spain, and Southern France)

[1] "The Citrus Industry," Vol. I, 485, Univ. Calif. Press (1943).

by the conquering Arabs in the tenth and eleventh centuries A.D. Strangely enough, for about five centuries the bitter (sour) orange was the only orange known to Europeans, the sweet orange appearing at a much later date. After the discovery of the New World by Columbus, the bitter orange was also introduced to the West Indies, and to North, Central and South America, where it escaped cultivation and became feral in many sections—in the interior of Paraguay, for example.

It is not known whether the Moors, experts in the distillation process, worked with bitter orange blossoms. The precious volatile oil from these flowers was first mentioned in 1563 by the Italian naturalist, J. B. della Porta. The designation neroli has been attributed to the Princess of Neroli, a member of the distinguished Italian Orsini family, who toward the close of the seventeenth century introduced this delightful oil as a fashionable perfume into the courts of Europe. Since then oil of neroli has become an invaluable ingredient in perfumes of all types, in toilet waters, and especially in eaux de Cologne.

The bulk of neroli oil and, incidentally, that of the finest quality, is produced today in Southern France, with Tunisia, Algeria, Italy, Andalusia (Spain), and Morocco following. Since the outbreak of World War II Haiti, in the West Indies, has also been producing substantial quantities of neroli oil; the quality, however, has not always been satisfactory for reasons which will be described later. The supremacy of the French oil is due to a combination of several factors—latitude, climate, composition of the soil, methods of planting and cultivation, and absence of the sweet orange tree—and particularly to the careful selection and harvest of the flower material, the long experience and care exercised in the distillation, etc.

French Neroli Bigarade Oil

Producing Regions.—The growing regions of the true bitter (sour) orange tree in Southern France are located in the south of the Département Alpes-Maritimes. This area forms a small triangle, bordered by the Sea-Alpes (Alpes-Maritimes) in the north and by the Mediterranean coast in the south, stretching from Cannes and Grasse in the west toward Menton in the east. The section located on the right bank of the river Var is the center of the whole triangle. This center can again be subdivided into four sections according to importance of production:

Section I—about 55% of the total harvest

Vallauris	Juan-Les-Pins
Golfe-Juan	Antibes

Section II—about 25% of the total harvest

Biot	Vence
Cagnes	Gattières
St. Laurent	St. Jeannet
La Colle	La Gaude
St. Paul	

Section III—about 10% of the total harvest

Le Bar	Gorges du Loup

Section IV—about 10% of the total harvest

Le Cannet	Mouans
Mougins	

Climatic and Soil Conditions.—The bitter orange tree grows at altitudes below 400 m., in a warm climate, with an optimum average yearly temperature of 22°–23° C. The trees are very sensitive to cold weather, particularly when previously weakened by attacks of insects and diseases. A temperature of −4° to −5°, maintained for several days, may cause serious damage, affecting especially the young branches that have not yet lignified. Trees entirely covered with ice may have to be cut down. In some years, late spring frosts destroy a great part of the flower crop. A bitter orange grove should have much sun and air, but must be protected against strong winds, and particularly against the cold mistral of Southern France, which blows off flowers and leaves.

With a favorable climate, the bitter orange tree may be planted in almost any soil, regularly manured and irrigated during the summer, but not in a soil which is too tightly packed or moist, or one containing excessive lime, clay, or silica.

Planting and Cultivating.—According to Hugues,[2] bitter orange trees are propagated in Southern France by seed and grafting, and in Spain by layering. The seeds are planted in seed beds in March or April; transplanting takes place early in their second year, when the weather is warm and bright. The young plants are set out 30 cm. apart, in rows 1 m. apart. After two years they are grafted with slips containing buds, the most favorable time being in May or June, when sap flows freely in the trees and when the bark can be loosened easily from the trunk. All this work is done in commercial nurseries, which subsequently sell the young trees to grove owners.

[2] *Am. Perfumer* **44**, October (1942), 31.

Final planting of the young grafted trees takes place in April–May, at intervals of 4 m. During the first year branch growth must be controlled to keep the foliage sufficiently high above the ground and in well rounded shape, with space between the branches for flower harvesters to reach the center of the tree.

Cultivation consists of hoeing, plowing, manuring, pruning, irrigating, and treating against insects and diseases. The ground should be worked three times each year by fertilizing in spring, hoeing after the harvest, and hoeing during September–October in order to apply slowly decomposing manure. At least two plowings are required each summer. Irrigation is particularly important during the first few years after planting. Undertaken early in the morning or after sunset, or even at night, it varies according to climate, soil, exposure, and atmospheric conditions.

In Southern France the trees are trimmed after the flower harvest. Lower branches, dead branches—in fact, all superfluous branches—are removed. This is done in such a way that the foliage is exposed as much as possible to air, sun, and rain. The leaf material removed can be used for distilling the so-called oil of petitgrain bigarade.

Insect Pests.—The orange tree, according to Hugues,[3] has several enemies, among them *cochineal,* a beetle. A subspecies, *chrysomphalus*, popularly called red flea, does considerable damage. The fight against these pests is difficult because they are well "camouflaged." The trees must be protected by spraying in spring and summer with a powder mixture. Hot liquids offer the advantage of remaining effective much longer. Other species of insects attack the young shoots, leaves, and flowers.

Diseases.—The principal disease is "fumagine," a black dust caused by fungi which form on the surface of the leaves and impede their natural functions. Trunk and branches are often smitten with a kind of flowing resin whereby the bark loosens and swells. The branches then dry out and die. Various explanations have been given for this disease, but nothing is known definitely. It has been attributed to a too tightly packed soil insufficiently aired, to too rich manure, to too much irrigation, and to excessive humidity. The trees may have been trimmed too closely or injured by a cold spell after a warm period.

Yield of Flowers.—The flower yield of each tree depends upon its age, the care taken of it, weather conditions, and injury by insects and diseases. An irrigated orchard begins to produce three or four years after planting; nonirrigated orchards require more time. For the next ten years the orchard produces a medium harvest. The highest yield is obtained in the twentieth to thirtieth years. A ten-year-old tree produces about 6 kg. of flowers

[3] *Ibid.*

yearly, an older tree up to 20 kg., 5 to 10 kg. being the average in Southern France where the trees are smaller than in North Africa.

The bitter orange tree has a long life span; eighty to one hundred years is not exceptional. The farmers consider the groves, usually inherited from their ancestors, as a valuable family possession, which they are loath to abandon even when flower prices fall to unprofitable levels. For this reason the orchards of Southern France have withstood many severe economic crises, except for the very old groves which are left to die out without being renewed.

Flower Harvest.—In Southern France the orange flower harvest takes place from the end of April to late May or early June; depending upon weather conditions, it lasts from three to four weeks. A small harvest can be gathered also in fall, but compared with the spring harvest it is insignificant. Picking is done mostly by women and children, who stand on ladders and drop the flowers on sheets spread on the ground around the trees. The blossoms from one tree are collected and put into a basket, the sheets spread beneath the next tree, the ladders moved, and the picking resumed. Years ago the flowers were picked only in the early morning after the dew had dried, but since World War I the picking has been extended to noon and even into the early afternoon. A skilled worker can harvest daily from 8 to 10 kg. of blossoms.

The blossoms must be picked at the proper stage of development, when just beginning to open. Closed buds give an inferior yield of oil with a somewhat "green" odor. (On the other hand, the orange flower water distilled from closed buds is very strong.) Flowers opened too far are apt to fade and spoil during the transport and storage preceding distillation. The flower material best suited to distillation or extraction consists of buds picked on a warm, sunny day. Flowers collected on cloudy, foggy or rainy days give an inferior yield of oil. Care must be taken to pick only the blossoms, and to exclude leaflets and petioles which, although increasing the weight of the flower material, impart a somewhat harsh petitgrain "by-note" to the distilled neroli oil. Picking the proper blossom material requires considerable labor and is costly. For this reason the flowers are less carefully harvested during years of low oil prices. The producers then frequently resort to a much cruder method—simply shaking the trees or beating down the flowers with sticks, which obviously results in a lower quality of oil.

The day's harvest is transported from the orchards to a field broker (*courtier*) in a neighboring village, who spreads the blossoms on sheets in a thin layer and delivers them early the following morning to the distillers.



Courtesy of M. Pierre Chauvet, Seillans (Var), France.

Harvesting of bitter orange blossoms in southern France.



It is necessary to turn the blossoms over frequently during the overnight storage; otherwise, they develop heat and ferment.

Distillation.—In the nineteenth century the oil was distilled by the growers chiefly in old-fashioned, small stills, heated with direct fire. Some of these are still employed, but today more than nine-tenths of all French neroli oil is produced in modern stills, heated indirectly through steam jackets or steam coils. These stills, which hold about 700 liters, are charged with 250–300 kg. of flowers and 1½ times that amount of water. The blossoms must float freely in boiling water (water distillation), as distillation with direct steam would result in an inferior yield. Orange blossoms, like roses, clog together on treatment with live steam, the steam then forming channels through the agglutinated mass and escaping without coming in contact with all the blossoms. Distillation is usually carried out in such a way that 1 liter (1 kg.) of distillation water[4] ("orange flower water") is obtained per kilogram of charged orange flowers. This method, incidentally, yields on the average about 1 g. of neroli oil. Obviously, the length of distillation depends upon the quantity of water distilled over; in the usual stills it takes about 3 hr. to obtain 1 liter of orange flower water per kilogram of flowers. The oil of neroli floats on top of the distillation water as a yellowish liquid and is easily separated in the Florentine flask. The distillation water retains, in a dissolved state, about one-third of the total amount of volatile oil distilled over and is therefore very fragrant. We shall refer to it later.

Yield of Oil.—As has been said, 1 kg. of orange blossoms yields about 1 g. of neroli oil; but the oil content is affected by many factors, and particularly by atmospheric conditions. Warm weather and ample sunshine increase the yield, because the blossoms then contain less water. A belated flower season is usually favorable to the yield of oil. The yield improves as the season progresses; it is lowest (about 0.07 per cent) at the beginning, and highest (about 0.12 per cent) toward the end of the harvest. Flowers from groves on slopes with southern exposure and protected from cold winds give the best yield.

Total Production in Southern France.—The bulk of the orange blossoms produced in Southern France serves for the distillation of oil of neroli bigarade, with orange flower water as a by-product. A smaller portion—which varies from year to year—is employed for the manufacture of extracted concrete and absolute of orange flower.

The importance of the total annual harvest has varied greatly from 1914 to the present time, fluctuating every year according to atmospheric con-

[4] To be exact, the term distillation water means water that has been distilled over in the course of distillation.

ditions. Late frosts in the early spring may destroy a part of the harvest, and favorable weather may increase the crop considerably. The grove owners in Southern France will always remember those days early in 1929 when an intense and late cold wave ravaged a part of the then magnificent bitter orange plantations. The cold was so intense that the 1929 harvest was almost completely destroyed and, even worse, many trees were killed. It was only due to great effort and care on the part of the growers that the major part of the groves could be saved. Yet, as a consequence of that disaster, the orange flower harvest since 1929 has never exceeded 1,500,000 kg.; prior to that date the crop in some years amounted to 2,500,000 kg. Lately, the average yearly production has varied from 1,100,000 kg. to 1,500,000 kg., averaging about 1,250,000 kg. The table below indicates the importance of the annual harvest according to the various sections; it refers only to the spring harvest and does not include the small quantities of flowers which are gathered in the fall. Neither does the table include the negligible production on the left bank of the River Var, viz., in the region around Menton.

Producing Sections [5]	*Bitter Orange Blossoms* (*kg.*)	
1. Vallauris, Golfe-Juan, Antibes	600,000 to	800,000
2. Biot, Vence, St. Jeannet.....	300,000 to	400,000
3. Le Bar and Gorges du Loup.....	130,000 to	150,000
4. Cannet, Mougins, Mouans.....	130,000 to	150,000
	1,160,000 to	1,500,000

To achieve a better control over flower prices, which depend also upon the quality of the deliveries, and to safeguard their general interests, many growers have joined the Cooperative "Nerolium," which has attained considerable power. This cooperative today controls a large portion of the total orange flower harvest; daily it collects the production of its various members in certain weighing posts, ultimately selling the flowers to the factories around Grasse, Vallauris, Le Bar, and Seillans. In difficult years, the cooperative processes the unsold part of its harvest in its own distilleries, located in Vallauris and in Golfe-Juan.

The harvest of those growers who do not belong to the Cooperative "Nerolium" is called "free flowers" and is handled by flower brokers who collect the blossoms in the same way as the cooperative and supply them also to the factories of the flower oil manufacturers in Grasse, etc.

Due to fluctuations in the quantities harvested and to the fact that two processes of treatment are employed, it is difficult to estimate exactly the

[5] The author is greatly indebted to his friend, Mr. Pierre Chauvet, Seillans, Var, for this information, and other data contained in this section.

Leaves
Cooperative
Brokers
Factories
Distillation
Oil of Petitgrain Bigarade
Petitgrain Water
Absolute from Petitgrain Water
Blossoms
Cooperative
Brokers
Factories
Distillation
Oil of Neroli Bigarade
Orange Flower Water
Extraction
Absolute from Orange Flower Water
Concrete → Absolute of Orange Flowers
Fruits
Cooperative
Brokers
Factories
Bitter Orange Peel
Marmalade

quantity of oil of neroli produced every year in Southern France. In general, it can be said that the area produces yearly a minimum of about 1,000 kg. of distilled oil of neroli, to which quantity must be added a few hundred kilograms of concrete of orange flower (see below). To these two products—oil of neroli bigarade and concrete of orange flower—we must also add the large quantity of orange flower water obtained as a by-product during the distillation of oil of neroli, a part of which is transformed into absolute from orange flower water (see below). A small quantity of flowers is also treated every year by the old-fashioned process of maceration (hot *enfleurage*). It should also be noted in this connection that a small number of orange blossoms at the end of the spring harvest remains on the trees, and that these flowers, during the following fall, develop into fruit. Such fruit serves for the preparation of dried bitter orange peel used in marmalades.

The diagram on page 236 shows how the various products of the bitter orange tree are derived, starting from the leaves, the blossoms, and the fruit.

Cost Calculation.—The cost of neroli oil depends primarily upon the cost of the flowers and the yield of oil, aside from labor and fuel consumption. Since distillation of orange flowers yields two products—oil of neroli and orange flower water—it is possible to charge the cost of production to the two products, or to either one of them, depending upon which of the two the producer can more profitably dispose of.

Physicochemical Properties of French Neroli Bigarade Oils.—Genuine neroli oils distilled under the author's supervision had properties which have varied within the following limits:

Specific Gravity at 25°/25°	0.864 to 0.871
Optical Rotation at 25°	+2° 35′ to +6° 52′
Refractive Index at 20°	1.4707 to 1.4741
Ester Content, Calculated as Linalyl Acetate	6.9 to 21.0%
Solubility	Soluble in 1 to 2 vol. of 80% alcohol, hazy to turbid with more; sometimes separation of paraffins

Gildemeister and Hoffmann [6] give somewhat wider limits:

Specific Gravity at 15°/15°	0.870 to 0.881
Optical Rotation	+1° 30′ to +12° 0′, usually not higher than +7° 0′
Refractive Index at 20°	1.468 to 1.474
Acid Number	Up to 1.8
Ester Number	19 to 69

[6] "Die Ätherischen Öle," 3d Ed., Vol. III, 123.

Methyl Anthranilate Content	0.45 to 1.10%
Solubility	Soluble in 1 to 2 vol. of 80% alcohol; turbid with more alcohol; separation of paraffin crystals upon standing

Methods of determining anthranilic acid methyl ester have been developed by Hesse and Zeitschel,[7] and by Erdmann [8] (see Vol. I of this work, p. 302). A modification of Hesse and Zeitschel's method has been suggested by Laloue.[9]

Chiris [10] some years ago reported the following properties of oil of neroli bigarade distilled in the Grasse region:

Specific Gravity at 15°	0.8696-0.8812
Optical Rotation	+1° 30′ to +10° 15′, usually +4° to +9°
Refractive Index at 20°	1.4680 to 1.4740
Acid Number	Up to 1.4
Ester Number	20 to 70, rarely higher than 45
Ester Content, Calculated as Linalyl Acetate	6.75 to 15.8%
Ester Number after Formylation in the Cold	180 to 200
Methyl Anthranilate Content (Method of Hesse)	0.5 to 1.2%
Solubility	Soluble in 1 to 2.5 vol. of 80% alcohol. Usually separation of paraffins on further dilution

More recently Igolen [11] reported these properties for oil of neroli bigarade produced in the Grasse region:

Specific Gravity at 15°	0.8696–0.8812
Optical Rotation at 20°	+0° 20′ to +6° 50′
Refractive Index at 20°	1.4710 to 1.4740
Acid Number	Up to 1.8
Ester Number	20 to 46.2

Adulteration.—Because of its very high price, oil of neroli is frequently adulterated with lower priced volatile oils, aromatic isolates, and synthetics. The most common adulterant is oil of petitgrain bigarade, natural, and terpeneless. Any addition of these oils increases the ester number of the neroli oil, oil of petitgrain containing much more linalyl acetate. To coun-

[7] *Ber.* **34** (1901), 296; **35** (1902), 2355. *J. prakt. Chem.* [2], **64** (1901), 246.
[8] *Ber.* **35** (1902), 24.
[9] *Bull. soc. chim.* [4] **7** (1910), 1101.
[10] *Parfums France* **9** (1931), 152.
[11] *Industrie de la Parfumerie* **1**, No. 7 (1946), 218.

teract this increase, linaloöl is sometimes added. Oil of neroli is also sophisticated with compounds which have been found to occur naturally in it—e.g., linalyl acetate, linaloöl, nerol, geraniol, geranyl acetate, terpineol, methyl anthranilate, and indole. Oil of neroli, therefore, must be submitted to a very careful organoleptic examination, since chemical routine analysis alone is inadequate for proper evaluation.

In the opinion of Naves,[12] a thorough analysis of oil of neroli bigarade (as well as of oil of petitgrain bigarade) should include a determination of the composition of the free alcohol fraction, and that of the alcohol fraction isolated by the saponification of the esters.

Examining commercial neroli bigarade and petitgrain oils, which in the course of distillation of the plant material had undergone partial hydrolysis, Naves was able to establish that:

1. The proportion of optically active linaloöl in the free alcohols depends upon the extent of the hydrolytic reactions that take place during the distillation of the plant material. The content of free linaloöl increases in direct proportion to the decrease in the content of esters.
2. Esterified linaloöl occurs in the oil to a great extent in laevorotatory and stereochemically pure form.
3. Free geraniol and nerol occur together.

An examination of the free alcohols contained in pure oils will indicate to what extent the esters have undergone hydrolysis in the course of the distillation of the plant material. In the case of products of doubtful purity, an investigation of the free alcohols will reveal whether alcohol fractions of foreign origin have been incorporated into the oil. Thus, an examination of the alcohols resulting from analytical saponification may indicate the addition of artificial linalyl acetate (partly racemized linaloöl) or of products containing terpinyl acetate. The isolation of the free alcohols from saponification products of mixtures that contain esters can be carried out by preparation of boric esters (cf. Vol. II of this work, p. 793). It is then possible to distinguish the constituents of the alcoholic mixture by fractional distillation and to identify them perhaps by phthalization.

Chemical Composition.—The chemical composition of French neroli bigarade oil, obtained by distillation of the blossoms, was elucidated by Walbaum and Hüthig,[13] and by Hesse and Zeitschel[14] in the course of investigations which were almost simultaneously, but independently, carried out

[12] *Soap, Perfumery & Cosmetics* **21** (1948), 797. Cf. *Helv. Chim. Acta* **29** (1946), 553.
[13] *J. prakt. Chem.* [2] **67** (1903), 315.
[14] *Ibid.* [2] **64** (1901), 245; [2] **66** (1902), 481.

at the turn of the century. Several years earlier Tiemann and Semmler,[15] too, had worked on this valuable oil. The results of these classical works proved for the first time the presence of nitrogen-containing, highly aromatic, compounds in an essential oil.

The following constituents have been identified:

β-Ocimene. Crabalona [16] more recently observed the presence of *β*-ocimene in the fraction b_7 50°–55°, d_{15}^{19} 0.811, α_D +10° 30′; n_D^{16} 1.4859 of French neroli bigarade oil. Compared with the other low boiling fractions, this fraction possesses the highest refractive index and the lowest specific gravity. The *β*-ocimene was identified by means of its addition product with maleic anhydride which on hydration yielded an acid m. 163°. This acid was identical with the acid of the tetrahydro-*o*-phthalic series which Crabalona [17] had obtained from *β*-ocimene occurring in lavender oil. Crabalona attributes the pronounced tendency of neroli oil toward autoxidation to the presence of *β*-ocimene. In his opinion, *β*-ocimene occurs probably in many more essential oils (particularly in oils which contain linaloöl and linalyl acetate) than has been heretofore supposed. From a study of the structural formula of *β*-ocimene we may conclude that this aliphatic terpene is closely related to linaloöl and linalyl acetate, and differs from them merely by the absence of 1 mol of water and acetic acid, respectively. Such processes as the elimination or addition of water or acetic acid take place, perhaps, in the living plant; whence the simultaneous occurrence of *β*-ocimene, linaloöl, and linalyl acetate in certain essential oils.

l-*α*-Pinene. Identified by Walbaum and Hüthig [18] as pinene nitrolbenzylamine m. 122°–123°.

l-Camphene. Treating the fraction b. 168°–170° with a glacial acetic acid–sulfuric acid mixture, the same authors obtained isoborneol which, however, melted at 195°, instead of at 212°. Hesse and Zeitschel [19] purified the isoborneol over the phthalic ester compound but were not able to raise the melting point of the isoborneol above 200°.

Dipentene. Walbaum and Hüthig [20] identified dipentene in the fraction b. 175°–179° (α_D −1° 6′) as tetrabromide m. 125°. Tiemann and Semmler's [21] earlier conclusion that the oil contains limonene does not seem to hold true; their tetrabromide m. 105° was either not sufficiently purified or perhaps their oil was adulterated with sweet orange oil.

Decyl Aldehyde (Probably). Shaking the fraction b_{7-8} 70°–82° with bisulfite solution, Walbaum and Hüthig [22] obtained a solid compound which, after decomposition with alkali carbonate, showed the typical odor of decyl aldehyde; derivatives for definite identification could not be obtained.

l-Linaloöl. The presence of *l*-linaloöl was first reported by Tiemann and Semmler [23] and later proved by Walbaum and Hüthig.[24] Identified as phenylurethane m.

[15] *Ber.* **26** (1893), 853, 2711.
[16] *Bull. soc. chim.*, March/April (1948), 388.
[17] *Recherches* **8** (1938), 155.
[18] *J. prakt. Chem.* [2] **67** (1903), 315.
[19] *Ibid.* [2] **66** (1902), 481.
[20] *Ibid.* [2] **67** (1903), 316.
[21] *Ber.* **26** (1893), 2711 footnote.
[22] *J. prakt. Chem.* [2] **67** (1903), 317.
[23] *Ber.* **26** (1893), 853.
[24] *J. prakt. Chem.* [2] **67** (1903), 318.

65°. According to Hesse and Zeitschel,[25] the oil contains about 30 per cent of linaloöl, partly in ester form.

l-Linalyl Acetate. Tiemann and Semmler [26] found that the fraction b_{15} 97°–104° (d_{20} 0.8972) consisted of linalyl acetate. The presence of this ester in pure neroli oil was later confirmed by Hesse and Zeitschel.[27]

Phenylethyl Alcohol. The last-named authors established the presence of this alcohol in the water oil obtained by extracting the distillation waters of bitter orange flowers with ether. Walbaum and Hüthig [28] characterized phenylethyl alcohol also in regular neroli bigarade oil by oxidation to phenylacetic acid.

α-Terpineol. M. above 33°; identified as phenylurethane m. 112° by Walbaum and Hüthig,[29] and Hesse and Zeitschel.[30]

Nerol and Neryl Acetate. Discovered by Hesse and Zeitschel [31] in neroli oil where it occurs in free form and as acetate. Boiling somewhat lower than geraniol, this alcohol does not form a calcium chloride compound and can thus be separated from geraniol. Preparation of the diphenylurethane m. 52°–53°, not 73°–75°, as reported by Hesse and Zeitschel.[32]

Geraniol. Noticed first by Tiemann and Semmler [33] and identified later by Hesse and Zeitschel [34] through oxidation to citral; preparation of citrylidene cyanacetic acid m. 122°.

Jasmone (Probably). According to Schimmel & Co.[35] the presence of this ketone in neroli oil is probable, as the corresponding fraction yields a semicarbazone m. 200°–204°.

Nerolidol. According to Hesse and Zeitschel,[36] the high boiling constituents of neroli oil contain a sesquiterpene alcohol, $C_{15}H_{26}O$, which they named nerolidol. The phenylurethane m. 37°–38° formed only after standing with phenylisocyanate for several weeks.

Farnesol. Isolated by Schimmel & Co.[37] in the fraction following nerolidol (b_{4-5} above 127°), on treatment with phthalic anhydride. Identified through its constants and through conversion into farnesal; semicarbazone m. 127°–132°, instead of 133°–135°, as reported by Kerschbaum.[38]

Acetic Acid, Phenylacetic Acid, Benzoic Acid, and Palmitic Acid (Traces). All these acids are present probably in esterified form. The water oil contains considerable amounts of phenylacetic acid.

Phenols(?). According to Hesse and Zeitschel,[39] neroli bigarade oil contains traces of phenols.

[25] *Ibid.* [2] **64** (1901), 245.
[26] *Ber.* **26** (1893), 853.
[27] *J. prakt. Chem.* [2] **64** (1901), 254.
[28] *Ibid.* [2] **67** (1903), 318.
[29] *Ibid.*
[30] *Ibid.* [2] **66** (1902), 497.
[31] *Ibid.*, 502. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 129.
[32] *Ibid.*
[33] Ber. **26** (1893), 853.
[34] *J. prakt. Chem.* [2] **66** (1902), 500.
[35] *Ber. Schimmel & Co.*, April (1903), 56.
[36] *J. prakt. Chem.* [2] **66** (1902), 503.
[37] *Ber. Schimmel & Co.*, April (1914), 71.
[38] *Ber.* **46** (1913), 1732.
[39] *J. prakt. Chem.* [2] **66** (1902), 481.

Methyl Anthranilate. This important ester which exerts a considerable influence upon the odor of neroli bigarade oil was first discovered by Walbaum.[40] It causes the characteristic fluorescence of neroli oil. The odor of this compound is agreeable only in strong dilution; b_{14} 132°; m. 25°.

Indole. Another important constituent, so far as the odor is concerned, was first noticed in orange flower pomades by Engels, and later identified in distilled neroli bigarade oil by Hesse and Zeitschel.[41]

Paraffins. The stearoptene or "neroli camphor" or "aurade" first noticed in neroli bigarade oil by Boullay [42] is, in reality, nothing more than one of the many paraffins which occur in almost all flower oils. In pure form it is odorless; m. 55°, according to Erdmann and Erdmann.[43]

The same authors mention the occurrence of pyrrole and pyrrole derivatives in neroli oil, but Walbaum and Hüthig,[44] as well as Hesse and Zeitschel, deny the presence of these compounds in pure neroli bigarade oil. The neroli oil of Erdmann was possibly adulterated with petitgrain oil.

After completing their investigation Hesse and Zeitschel [45] suggested the quantitative composition of neroli bigarade oil given in Table 1.18.

Use.—Oil of neroli bigarade represents one of the oldest, most valuable and useful perfumers' raw materials and is employed in almost all high-grade perfumes, of oriental, as well as of floral, type. Oil of neroli imparts suave, flowery notes to a composition.

Suggested Additional Literature

Y. R. Naves, "Petitgrain and Neroli Bigarade," *Soap, Perfumery & Cosmetics* **21** (1948), 797.

A. Maurel, "Contribution à l'Étude du Bigaradier et de l'Essence de Néroli," *Ind. parfum.* **4** (1949), 4.

Italian Neroli Bigarade Oil

Italy, also, has become an important producer of neroli bigarade oil, the plantations of bitter (sour) orange trees being located in Sicily, and in Calabria, on the southern tip of the Italian peninsula. Details will be found in the section on "Bitter Orange Oil" (Italian). The distilleries of neroli bigarade oil in Calabria are in and near Reggio Calabria, Melito, Brancaleone, and Rocella Jonica.

The bitter orange plantations in Sicily and Calabria could produce about 350 kg. of neroli bigarade oil annually, but actual production varies from 100 to 150 kg. This difference between potential and actual production is due to the fact that a substantial number of the blossoms are not picked at all, but are left on the trees to develop into fruit. Part of the bitter

[40] *Ibid.* [2] **59** (1899), 350.
[41] *Ibid.* [2] **66** (1902), 504.
[42] *J. Pharm.* **14** (1828), 497.
[43] *Ber.* **32** (1899), 1214.
[44] *Ber. Schimmel & Co.*, October (1902), 60.
[45] *J. prakt. Chem.* [2] **66** (1902), 505.

TABLE 1.18. COMPOSITION OF NEROLI OIL

	Constituents	Approximate Amount in Percentage
Hydrocarbons, 35%	1. Pinene 2. Camphene 3. Dipentene 4. Paraffin C_{27}	35
Terpene Alcohols and Their Acetates, 47%	5. *l*-Linaloöl 6. *l*-Linalyl acetate 7. *d*-α-Terpineol 8 and 9. Geraniol and Nerol 10 and 11. Geranyl acetate and Neryl acetate	30 7 2 4 4
Sesquiterpene Derivatives, 6%	12. *d*-Nerolidol	6
Nitrogenous Compounds, 0.7%	13. Anthranilic acid methyl ester 14. Indole	0.6 Less than 0.1
Acids and Phenols, 0.1%	15. Acetic acid 16. Palmitic acid	0.1
Other Constituents, Resinous Products and Loss	Decyl aldehyde(?); esters of phenylacetic acid and benzoic acid, jasmone and farnesol	11.2

orange crop is processed for dried peel and the balance is treated to recover the essential oil from the peel and to brine the residual peel for export, which represents the most lucrative aspect of the whole Italian bitter orange industry. In the province of Calabria the annual harvest of bitter orange blossoms varies from 500 to 600 quintals,[46] although it could readily amount to 1,000 quintals if the entire quantity of blossoms available were utilized. The bulk of the flower harvest is distilled (oil of neroli bigarade); the balance is extracted with volatile solvents (petroleum ether), which process yields concrete and absolute of orange flowers. Much of the Italian neroli bigarade oil and concrete and absolute is shipped to Grasse (A.M.) in France, where it is occasionally mixed with the French product and exported under a French label. Other lots are exported as Italian products from Sicily and Calabria directly to other European countries, to the United States, and to other parts of the world.

[46] One quintal = one hundred kilograms.

The bitter orange is one of the earliest flowering citrus trees, and incidentally one of the most sensitive to cold. The flowering period varies with the weather and with the prevailing temperature. In Sicily and Calabria it usually begins in the early part of April and continues until about May 10th. As in Southern France, there may be another, but much smaller crop in the fall, provided the weather has been favorable.

The stills used in Italy for the distillation of neroli bigarade oil closely resemble those used in the Grasse and Vallauris region of Southern France. Distillation is carried out with indirect steam (water distillation), 1,000 kg. of fresh blossoms yielding on the average 1 kg. of oil of neroli bigarade. A few producers in Sicily and Calabria have also installed batteries for extraction with volatile solvents. Some Italian manufacturers have arrangements with essential oil houses in Grasse to sell them their output in the years when there is a small bitter orange flower harvest in Southern France.

The distillers in Italy, like those in France, insist that the flower material be gathered exclusively from bitter orange trees and not from sweet orange trees—an important point in Sicily and Calabria, where the sweet orange tree abounds. Whether this precaution is always strictly adhered to appears doubtful, as the properties of some Italian oils occasionally indicate the presence of sweet orange blossom material. For this reason connoisseurs do not value the Italian oil quite so highly as the French product. The properties of strictly pure Italian oil of neroli bigarade resemble those of the French oil; however, the specific gravity of the former is occasionally slightly higher. A too high specific gravity and ester content indicate the presence of petitgrain bigarade oil, whereas a high optical rotation indicates the presence of sweet orange blossom oil (oil of neroli Portugal).

Examining Calabrian neroli bigarade oils distilled in 1937 and 1938, Sorgona Luisi [47] reported the following limits:

1937

Specific Gravity at 20°	0.8704 to 0.8747
Optical Rotation at 20°	+5° 0′ to +6° 36′
Refractive Index at 20°	1.4720 to 1.4725
Acid Number	0.63 to 0.68
Ester Content, Calculated as Linalyl Acetate	7.29 to 11.28%
Free Alcohol Content, Calculated as Linaloöl	54.30 to 67.51%
Methyl Anthranilate Content	0.60 to 0.89%
Solubility	Soluble in 0.9 to 1.2 vol. of 80% alcohol

[47] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **12,** March–April (1937), 40; **13,** March–April (1938), 43. *Chem. Zentr.* II (1937), 3539. *Revue des Marques, Parfums France* **16,** September (1938), 84.

1938

Specific Gravity at 25°	0.8700 to 0.8733
Optical Rotation at 26°	+4° 0′ to +5° 50′
Refractive Index at 25°	1.4695 to 1.4710
Acid Number	2.64 to 6.21
Ester Content, Calculated as Linalyl Acetate	9.9 to 11.6%
Total Alcohol Content, Calculated as Linaloöl	58.5 to 64.5%
Free Alcohol Content, Calculated as Linaloöl	49.9 to 55.9%
Methyl Anthranilate Content	0.7 to 1.1%
Solubility	Soluble in 0.9 to 1.3 vol. of 80% alcohol

The same author [48] reported these limits for Calabrian neroli bigarade oil produced in 1939:

Specific Gravity at 20°	0.8704 to 0.8779
Optical Rotation at 23°	+2° 36′ to +6° 18′
Refractive Index at 20°	1.4700 to 1.4740
Acid Number	0 to 1.35
Ester Number, Calculated as Linalyl Acetate	7.71 to 14.70%
Total Alcohol Content, Calculated as Linaloöl	57.14 to 63.19%
Methyl Anthranilate Content	0.71 to 1.37%
Solubility	Soluble in 1.1 to 1.8 vol. of 80% alcohol

A Calabrian neroli oil examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 15°/15°	0.875
Optical Rotation	+10° 24′
Refractive Index at 20°	1.4711
Ester Content, Calculated as Linalyl Acetate	12.4%
Solubility	Soluble in 1 vol. and more of 80% alcohol

The odor of this Italian oil was not quite so fine as that of pure French oils.

Igolen [49] reported the following properties for Italian neroli oil:

Specific Gravity at 15°	0.8699 to 0.8784
Optical Rotation at 20°	+4° 45′ to +10° 28′

[48] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **14**, March–April (1939), 42.

[49] *Industrie de la Parfumerie* **1**, No. 7 (1946), 218.

Refractive Index at 20°	1.4690 to 1.4718
Acid Number	Up to 1
Ester Number	35 to 42.7

Suggested Additional Literature

G. Rovesti, "Bitter Orange and Its Products," *Rivista ital. essenze profumi* **13** (1931), 35. *Chem. Abstracts* **25** (1931), 2522.

Spanish Neroli Bigarade Oil

The center of the Spanish bitter (sour) orange production lies around Seville in Andalusia, former seat of the Moorish caliphs, who originally introduced the tree from Asia Minor. Total production of neroli bigarade oil in Andalusia varies from year to year but averages about 200 kg.

Harvest of the blossoms lasts from the end of April to early May. The quality of the Spanish neroli oil is affected by the fact that (1) the flower material frequently contains blossoms from sweet orange trees, which in the gardens and groves of Andalusia are cultivated side by side with bitter (sour) orange trees; (2) the blossoms are not picked carefully by hand, but simply shaken or beaten down with sticks and collected on sheets spread around the trees, or only those blossoms are gathered which have dropped to the ground spontaneously. It must be kept in mind that the Spanish growers are interested primarily in the sale of the fruit, which fetches good prices, and are not willing to denude the trees of vigorous blossoms. Often the flower material is contaminated with leaflets, petioles, unopened buds, and with dust or earth. All these factors affect the yield and quality of the Spanish neroli oil.

Distillation is carried out as in France. One thousand kilograms of flower material yield about 800 g. of oil and 1,000 liters of orange flower water. The bulk (about 80 per cent) of Spanish neroli bigarade oil has been produced in Seville by a prominent firm which enjoys a nation-wide reputation for the retail sale of orange flower water. Spanish neroli oil is thus more or less a by-product in the production of the water, the sale of which seems to be very profitable.

The physicochemical properties of Spanish neroli bigarade oil resemble those of the French oil, except, perhaps, for the specific gravity, which in some instances is higher, due probably to the presence of leaflets and twiglets in carelessly collected flower material. An abnormally high optical rotation, occasionally found in Spanish oils, may be caused by the presence of sweet orange blossoms in the distillation material, or by the admix-

ture of oil of neroli Portugal, obtained from the distillation of sweet orange blossoms.

Spanish neroli bigarade oil is less esteemed than that of France or Algeria. It has found an outlet mainly on the local Spanish market.

Samples of Spanish neroli bigarade oil, procured from reliable sources in Seville and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 25°/25°	0.864 to 0.872
Optical Rotation	+7° 50′ to +11° 40′
Ester Content, Calculated as Linalyl Acetate	12.3 to 32.3%
Solubility at 20°	Soluble in 1 to 1.5 vol. of 80% alcohol, turbid with more; in some cases separation of paraffins

The ester content of some of these oils was unusually high, indicating the presence of leaflets in the distillation material.

Tunisian Neroli Bigarade Oil

The beginning of this industry dates back to the days when the natives first harvested bitter orange flowers in their own gardens or bought them on the markets and distilled the flowers in a rather crude way, to prepare orange flower water (which in North Africa is very popular as a flavoring agent of baked goods). The minute quantities of oil of neroli recovered in the course of this simple distillation were then sold as perfume in the bazaars of Tunisia. Prior to the outbreak of World War II, several European operators had organized and modernized the distillation of the oil to such an extent that in 1938 the production of oil of neroli in Tunisia reached about 150 kg.

The bitter (sour) orange trees are cultivated in groves located along the northeast and east coast, the main center of production being on Cap Bon and especially around Nabeul, forty-two miles from the city of Tunis. In this section the plantations of bitter oranges, however, form only a small part of the citrus crop. All these orange groves (bitter and sweet orange trees) are surrounded by cypress trees, which grow rapidly and protect the citrus groves against the strong winds prevailing in that section.

During World War II, the crop of bitter orange flowers fell off considerably and reached the vanishing point during the battle of Tunisia. Since then, however, the industry has recovered, and during 1945 the harvest of bitter orange blossoms amounted to about 200,000 kg. As there exist no factories in Tunisia for the extraction of the flowers with volatile solvents,

the whole crop is distilled and, therefore, one can estimate the actual production of Tunisian oil of neroli at about 200 kg. The following figures give an idea of the production of this oil from 1938 to 1947:

	Kilograms		*Kilograms*
1938	180	1943	0 [a]
1939	180	1944	80
1940	130	1945	120
1941	100	1946	200
1942	50	1947	200

[a] Battle of Tunisia.

Harvesting takes place somewhat earlier than in France, the bulk of the crop being collected at the end of April.

A certain quantity of the picked flowers is transported directly to the distilleries; but frequently the blossoms are brought to the markets and sold there to the highest bidder—a procedure contrary to that employed in Southern France, where a definite price is established for the entire crop.

In the producing region mentioned above there exists one modern distillery equipped very much along the lines of distilleries in Southern France.

Algerian Neroli Bigarade Oil

Algeria's climate is most favorable to the growth of bitter orange trees; the temperature never falls below the freezing point and the blossoms are not exposed to the destructive frosts that have done so much damage in Southern France. Algeria has therefore become an important producer of neroli bigarade oil, plantations being located chiefly in the Mitidja Plain, around Boufarik.

The properties of the Algerian oil resemble those of the French oil, with the exception that the optical rotation and the refractive index are sometimes slightly higher. Algerian oils examined in the laboratories of Antoine Chiris [50] had properties which fell within the following limits:

Specific Gravity at 15°	0.8726 to 0.8783
Optical Rotation	+5° 45′ to +10° 24′; usually between +7° 15′ and +10° 24′
Refractive Index at 20°	1.4700 to 1.4730
Acid Number	Up to 1.40
Saponification Number	30.0 to 43.5, seldom higher
Saponification Number after Formylation in the Cold	178.5 to 202.4
Solubility	Soluble in 1.5 to 4 vol. of 80% alcohol, separation of paraffins upon addition of more alcohol

[50] *Parfums France* **10** (1932), 313.

The odor of Algerian oils is very fine, although connoisseurs prefer the French product.

During World War II, and especially during the landing operations on the part of the Allied forces, Algeria was for a long time separated from Continental France. The production of oil of neroli fell off considerably. Small lots of oil of neroli bigarade produced in the course of those years were used locally by the manufacturers of eaux de Cologne, which Algeria then could no longer import from France.

In 1945 and 1946 the production of neroli bigarade oil in Algeria approached 150 kg.; in 1947 it was 170 kg. The orange flower water obtained as by-product in the course of the distillation is used locally, just as in Tunisia, for the flavoring of all kinds of baked goods, confectionery, and beverages.

Since the white settlers in Algeria tend more and more to concentrate on the production of fresh fruit, one cannot, at least not for the next few years, count on any substantial increase in the production of Algerian oil of neroli.

Moroccan Neroli Bigarade Oil

Morocco, like her two North African sisters, Algeria and Tunisia, has potentialities for producing a substantial quantity of oil of neroli bigarade. Just as they do in Algeria and Tunisia, the Arabs have been distilling small quantities of bitter orange blossoms for centuries, primarily to obtain the orange flower water, which they require for flavoring purposes.

Industrial production of oil of neroli bigarade by Europeans, however, was started only in 1930, by a Frenchman, a native of Southern France. His plantings are located about 50 km. from the Atlantic seacoast, in that fertile plain, Rgarb, near the important dam and artificial lake of El Kansera. Other growing experiments have been made in the region of Marrakech, and nurseries to supply an important plantation are underway in Khemisset, between Rabat and Meknes.

As with the Algerian oil, the oil of neroli bigarade produced in Morocco during World War II was employed locally for the preparation of eau de Cologne and perfume. During these years it was customary to pick only a part of the flower growth, leaving most blossoms to develop into fruit (bitter orange), which was then exported to England.

The soil and the climate in Morocco are even more favorable to the development of the orange tree than they are in Algeria and Tunisia, and the bitter orange tree in Morocco reaches the producing stage more rapidly than in Algeria. The quality of the oil obtained from the blossoms, although

not so fine as the French oil, is good, and equals that of the Algerian and Tunisian oils.

The production of Moroccan oil of neroli bigarade in 1945 was 80 kg., in 1946, 100 kg., and in 1947, 120 kg. Because new plantations have been started, this figure will increase during the years to come and ought finally to equal that of production in Tunisia.

Haiti Neroli Oil

When Columbus, after discovering the New World, returned to Hispaniola on his second voyage to the West Indies, he brought along the seeds of many plants, among them the true bitter (sour) orange and the true sweet orange. These were planted and cultivated but, in the course of time, both species escaped cultivation and began to grow at first semiwild, but finally wild, over wide areas of Hispaniola, the western part of which island is now the Republic of Haiti. Gradually the two orange species hybridized and perhaps formed what Webber [51] calls the bitter-sweet or Paraguay variety. (A similar development seems to have taken place in Paraguay. See "Oil of Petitgrain Paraguay.") Since then the bitter (sour), the sweet, and the bitter-sweet orange trees have grown wild and abundantly in the southwestern part of the island, around Fond-des-Nègres and L'Asile in the Département de Sud of Haiti, and near Jacmel and Trouin in the Département d'Ouest. The same sections abound also with the Shaddock tree, a parent of the grapefruit. The Shaddock is readily distinguished from other citrus varieties by its leaves and flowers, which are considerably larger and thicker than those of other varieties. In Haiti the bitter (sour) orange tree can be distinguished from the sweet orange by the lighter color on the underside of its leaf, and by the fact that it bears thorns 2 to 3 in. long, whereas the sweet orange tree bears no thorns, or only very short ones. (In this connection it should be mentioned that the true bitter [sour] orange tree of Southern France and Spain is thornless; the Haiti bitter [sour] orange may, therefore, be a variety of the European plant, although undoubtedly belonging to the same species.) As far as Haiti's bitter-sweet orange, locally called "orange commune," is concerned, it cannot easily be distinguished from the true bitter (sour) variety. Since all these trees grow profusely, semiwild, and wild in the same localities, the natives who gather the blossoms for the distillation of neroli oil are likely to bring into the distilleries a mixture derived from several orange species and varieties, and blossoms of the Shaddock. This fact, obviously, has a definite influence upon the physicochemical properties, and the odor quality of the neroli oil

[51] "The Citrus Industry," Vol. I, 485, Univ. Calif. Press (1943).

distilled from such flower material. Furthermore, the natives are rather careless in the picking of blossoms, and frequently include green buds, stems, small leaves, and other extraneous material. During the long trip to the distilleries, and in the hot climate of Haiti, the blossoms, which have often been picked the night before, are likely to ferment and start to turn brown; another reason why the quality of the Haiti neroli oil cannot compare with that of the French product.[52]

Haiti's neroli oil production dates back to about 1930 when a neroli oil distiller from Southern France visited Haiti and, impressed by the abundance of bitter orange trees growing wild in Haiti, conceived the idea of extracting the oil. The new industry experienced its greatest development during World War II when the European and North African neroli oils were no longer available on the American market, and the consuming industries in the United States eagerly absorbed the Haiti product. Haiti could produce about 600 kg. of neroli oil per year, provided the demand warranted such heavy production. This, however, would be of the regular Haiti quality, viz., an oil distilled from bitter orange blossoms, together with some bitter-sweet and sweet orange, and some Shaddock blossoms. There is one section in the south of Haiti, near Port-Salut where the bitter (sour) orange tree grows exclusively, and no other citrus variety. Here, a small quantity of neroli bigarade oil could be produced.

TABLE 1.19

Properties	I	II	III	IV	V
Specific Gravity at 25°/25°	0.863	0.863	0.860	0.862	0.859
Optical Rotation at 25°	+18° 57′	+19° 25′	+27° 10′	+24° 53′	+26° 50′
Refractive Index at 20°	1.4740	1.4728	1.4728	1.4758	1.4770
Ester Content, Calculated as Linalyl Acetate	18.5%	18.7%	17.6%	11.9%	8.7%
Solubility at 25°	Soluble in 1 vol. of 80% alcohol, cloudy in 3 vol. Turbid in 10 vol. Separation of paraffins		Hazy in 8 vol. and more of 80% alcohol; separation of paraffins	Soluble in 0.5 vol. of 90% alcohol	Cloudy in 10 vol. of 80% alcohol

[52] In the opinion of Senator Louis Dejoie, Port-au-Prince, Haiti, the difference in the quality between the French and the Haitian neroli oils cannot be attributed to any morphological factor, as the French and the Haitian plants appear to belong to the same variety (with the exception that the latter variety is thorny). The inferior odor of the Haitian neroli oil is a result chiefly of the admixture of shaddock blossoms to the bitter orange blossoms, the careless handling of the harvested blossoms, and of the long transport in the hot climate of Haiti, with consequent fermentation in the tightly packed baskets.

The present distilleries of Haiti neroli oil are located in Fond-des-Nègres and in Trouin. The flower harvest coincides with the rainy season, starting usually at the beginning of April and lasting until the end of May. Distillation is carried out as in Southern France, 1 metric ton of blossoms yielding about 2 lb. of oil.

Physicochemical Properties.—Five Haitian neroli oils analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the properties given in Table 1.19.

ORANGE FLOWER WATER

As has been mentioned, it is usual to distill orange blossoms until about 1 liter of distillation water has been collected per kilogram of flower material; this coincides with a yield of about 1 g. of neroli oil. Some distillers prefer to produce a more concentrated and stronger orange flower water by collecting only 800 g. or even only 500 g. of water per kilogram of flowers. These more concentrated flower waters possess a correspondingly stronger odor. According to Harmel,[53] the European trade distinguishes between several types of orange flower water:

(a) *"Eau double"*

This water is obtained by collecting two parts of water per one part of flower material. Diluting it with the same volume of distilled water gives *"Eau simple."*

(b) *"Eau triple"*

Obtained by distilling three parts of water per two parts of flowers.

(c) *"Eau quadruple"* or "kilogram-kilogram."

Obtained by collecting 1 kg. (one liter) of flower water per 1 kg. of flowers.

The production of a more concentrated water (the so-called "80 per cent") is coming more and more into vogue, as it permits a considerable saving of fuel. In this case 800 g. of orange flower water are collected per kilogram of flowers.

(d) *"Eau deux kilograms"* ("two kilogram water").

Obtained by collecting only 1 liter of water per 2 kg. of flowers (equal to 500 g. of water per kilogram of flowers). Obviously this is the most concentrated product.

These specifications appear somewhat obsolete, at least for France, as French laws now require that orange flower water sold in France conform

[53] "Contribution à l'Etude des Eaux Distillées des Hesperidées des Alpes-Maritimes," Doctor Thesis, Faculté de Medicine et Pharmacie, Marseille (1939).

to a certain minimum standard. To comply with these rules the more reliable (but not all) French producers now distill 1,000 kg. of blossoms with 800 liters of water, and collect 700 liters of orange flower water, which in the trade is called "Eau 70 per cent." This orange flower water must assay 0.350 g. of oil (extracted with pentane) per liter of water.

Quality of orange flower waters is judged chiefly by organoleptic and a few chemical tests, which consist of extracting the water with ether and evaporating the ether from the extract. According to Kling and Florentin,[54] the ether extract of a good orange flower water is 0.025 to 0.035 per cent, the acid content, calculated as acetic acid (phenolphthalein as indicator), about 0.05 per cent, and the content of methyl anthranilate 0.02 to 0.05 per cent. Further details may be found in the above-cited paper of Harmel and in a later study by Maurel.[55]

Rapid Test of Orange Flower Water.—In describing a rapid procedure for the examination of orange flower water, Danet [56] suggested a method depending on the colorimetric determination of the methyl ester of anthranilic acid by diazotization and coupling with 2-naphthol. The method may be carried out as follows:

Treat 5 cc. of the orange flower water with 0.25 cc. of a 10 per cent sodium nitrite solution and 0.25 cc. of acetic acid, couple with 0.5 cc. of a saturated solution of 2-naphthol in ammonia, and dissolve the precipitate with 4 cc. of acetone. A standard solution is prepared by using the methyl ester.

Adulteration of Orange Flower Water.—Orange flower water is occasionally adulterated by adding minute quantities of synthetic compounds which occur naturally in the water—methyl anthranilate, phenylethyl alcohol, and indole, for example. No reliable analysis existing, the organoleptic test and comparison with a genuine standard sample are still the best methods of evaluation.

Storage of Orange Flower Water.—In his study of orange flower water Maurel [57] observed—

1. That the fluorescence displayed by orange flower water is not due exclusively to the presence of methyl anthranilate.
2. That the indole, although a normal constituent of orange flower water, seems to disappear quite rapidly after distillation.
3. That the content of (extractive) oil diminishes quite rapidly with time. Generally this loss is clearly noticeable during the first six months

[54] *Ann. fals.* **18** (1925), 22. *J. pharm. chim.* [8] **4** (1926), 265.
[55] *Ann. chim. anal.* **27**, No. 7–8 (1945), 1, 124, 150. Cf. Tombarel Frères, *ibid.* **28** (1946), 153. *Chem. Abstracts* **40** (1946), 6210.
[56] *J. pharm. chim.* **1** (1941), 434. *Chem. Abstracts* **38** (1944), 2163.
[57] *Ann. chim. anal.* **27**, No. 7–8 (1945), 1.

following distillation. An orange flower water, in the course of one year loses not only a part (on the average 25 per cent) of its oil, but its aroma also diminishes, due largely to the formation of mycelium, and occasionally to bacteria growth, which may make the water unfit for consumption and may develop a foreign odor.

Orange flower water must, therefore, be handled and stored very carefully in scrupulously clean containers, made of glass or tinned copper, and kept at low temperature. Utmost cleanliness is essential as the above-mentioned growth of bacteria will cause an ugly green deposit. Harmel [58] recommended sterilization. Danger of deterioration is the main reason why small distillers are not always in a position to handle this delicate product properly.

Use of Orange Flower Water.—The fragrant and aromatic orange flower water is very popular in France, Italy, Spain, and other Mediterranean countries, including North Africa, for the flavoring of beverages (teas, infusions, liquors), baked goods, confectionery, and pharmaceutical preparations. Like rose water, it finds wide application in the households of these countries. It is a well-known remedy for insomnia. Part of the orange flower water produced in Southern France is converted into the so-called "absolute of orange flower water."

Absolute of Orange Flower Water.—Before World War I, orange flower water was shipped all over Europe and overseas. Since then increased freight rates and high custom duties have raised barriers to the shipping of this bulky product. A method has, therefore, been developed to isolate the odoriferous principles from the water in highest concentration. The resulting so-called "absolute of orange flower water" is prepared by extracting freshly distilled orange flower water several times with highly rectified petroleum ether, by distilling off the solvent and purifying the concentrate. The concrete thus obtained is then transformed into alcohol soluble absolute by the usual method (see "Natural Flower Oils," Vol. I of this work, p. 211). From 3,000 to 3,500 kg. of water are required to produce 1 kg. of absolute from orange flower water. This yield conforms with the figures stated for the distillation of neroli oil; namely, that 1,000 kg. of orange flowers, upon distillation, yield 1 kg. of neroli oil and 1,000 kg. (or liters) of orange flower water, in which one-third (about 330 g.) of the total volatile oil of the orange blossoms remains in solution. When preparing this absolute it is necessary to extract the water as soon as possible after distillation, since the yield diminishes considerably as the water ages. Absolute of orange flower water is a yellow-brown liquid of extremely powerful odor.

[58] "Contribution à l'Etude des Eaux Distillées des Hesperidées des Alpes-Maritimes," Doctor Thesis, Faculté de Medicine et Pharmacie, Marseille (1939).

According to Hesse and Zeitschel,[59] orange flower water oil has the following properties:

Specific Gravity at 15°	0.945 to 0.968
Optical Rotation	+1° 47′ to +2° 30′
Saponification Number	49 to 100
Methyl Anthranilate Content	11.6 to 16.0%

Steam distilling 100 g. of absolute of orange flower water, which he had prepared in Southern France, the author obtained a volatile oil which was united with the ether extract from the distillation water of this oil. A total of 90 g. of oil was obtained which had the following properties:

Specific Gravity at 15°/15°	0.921
Optical Rotation	+1° 10′
Refractive Index at 20°	1.4814
Acid Number	3.3
Saponification Number	36.9
Saponification Number after Acetylation	212.8
Solubility	Soluble in 2.5 vol. and more of 60% alcohol

The great advantage of the absolute from orange flower water lies in the fact that it represents the odoriferous principles of the water in a very concentrated and pure form. Considerable expense in freight can be saved because, instead of 3,000 to 3,500 liters of orange flower water, only 1 kg. of the absolute need be shipped. By adding the absolute in the above indicated ratio to distilled water, a product not quite identical with, but similar to, the original orange flower water can thus be obtained. If complete solution is not achieved, water is put into a still, the calculated amount of absolute added, and the mixture distilled until the theoretical quantity of reconstituted orange flower water has been collected.

Chemical Composition of Orange Flower Water Oil.—Bitter orange flower water oil contains all the constituents of the normal (direct) oil, but in different proportions. The more water soluble compounds, such as alcohols and methyl anthranilate, predominate in the water oil, whereas the less soluble compounds, such as the terpenes, sesquiterpenes, and esters, are less predominant. The water oil probably also contains phenylacetic acid nitrile, and, according to Hesse and Zeitschel,[60] a nitrogenous compound, m. 159°.

Naves [61] studied the chemical composition of two types of orange flower water oil, the one ("two kilograms") representing 500 liters of distillation

[59] *J. prakt. Chem.* [2] **64** (1901), 250, 258; **66** (1902), 506. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 124.
[60] *J. prakt. Chem.* [2] **66** (1902), 507.
[61] *Parfums France* **12** (1934), 61.

water per thousand kilograms of flowers, and the other ("Kg/Kg") representing a thousand liters of distillation water per thousand kilograms of flower material.

It is interesting to compare the chemical composition of these types of water oil with that of regular neroli bigarade oil as established by Hesse and Zeitschel.

TABLE 1.20

	Water Oil "Two Kg."	Water Oil "Kg/Kg"	Distilled Neroli Oil (Hesse and Zeitschel)
Hydrocarbons (Pinene, Camphene, Dipentene, Paraffin C_{27})	Traces	Traces	35%
l-Linaloöl	32%	54%	30%
l-Linalyl Acetate	Traces	Traces	7%
d-α-Terpineol	13%	18%	2%
Geraniol + Nerol	8%	6%	4%
Geranyl + Neryl Acetate	Traces	Traces	4%
d-Nerolidol	1%	1%	6%
Methyl Anthranilate	22%	8%	0.6%
Indole	Traces	Traces	Below 0.1%
Free Acids and Phenols	1%	Traces	0.1%
Phenylethyl Alcohol Esterified with Phenylacetic Acid	8–10%	1–2%	...
Benzyl Alcohol	2%	Traces	...

Naves,[62] furthermore, identified in the water oil "two kilograms" the following constituents:

Eugenol	Bisabol(?)
Benzaldehyde	Palmitic acid
Jasmone	Myristic acid

SUGGESTED ADDITIONAL LITERATURE

J. Deshusses, "The Analysis and Evaluation of Orange Flower Water," *Pharm. Acta Helv.* **22** (1947), 208 (in French). *Chem. Abstracts* **43** (1949), 1152.

ORANGE FLOWER OIL BY EXTRACTION (ABSOLUTE OF ORANGE FLOWER)

Distilled oil of neroli bigarade does not represent the true perfume of the living flower. In order to isolate the complete natural perfume of the

[62] *Ibid.*

orange blossom by the method of distillation, it would be necessary to add the oil dissolved in the distillation water (absolute of orange flower water) to the direct oil (oil of neroli bigarade). However, even this combined oil would not be identical with the flower oil as it exists in the living blossoms. Some of the constituents of the natural perfume are altered by distillation; esters are hydrolized, polymerization takes place, and the highest boiling compounds are not distilled over at all and are therefore lacking in the distilled product.

The modern process of extracting orange blossoms with volatile solvents overcomes this disadvantage. The so-called absolute of orange flowers obtained by this method represents the natural flower oil of the blossoms in a perfect way. To produce this absolute, the fresh blossoms are extracted several times with highly purified petroleum ether, the ethereal solutions are concentrated, and the concrete thus obtained is freed from waxes in the usual way, yielding the absolute. (See "Natural Flower Oils," Vol. I of this work, pp. 200 ff.)

Four hundred to 530 kg. of orange blossoms yield 1 kg. of concrete; the latter, in turn, yields from 48 to 58 per cent, on the average 53 per cent of alcohol soluble absolute.

Absolute of orange flowers is one of the most valuable and useful perfumers' raw materials. It possesses a rather heavy and powerful, yet delicate, suave note, which blends into all kinds of scents, particularly those of oriental type. The product also possesses good lasting qualities.

Absolute of orange flowers is produced principally in the Grasse region of Southern France, lately also in Calabria and Sicily.

The properties of orange flower absolute vary considerably according to the process of extraction, the solvent used, the method of purification, and other factors. Indeed, there are no generally accepted limits, each manufacturer following his own methods. The data indicated in literature are not based upon scientific standards and hence have no practical significance, until definite specifications are agreed upon.

Like all high-priced natural flower oils, absolute of orange blossoms is frequently sophisticated. In order to detect adulteration, it is advisable to submit a sample to co-distillation with glycol, according to the method of Sabetay.[63] Gildemeister and Hoffmann [64] indicated the following properties for the volatile oil, distilled with steam from the absolute (evidently it is necessary to add the oil extracted from the distillation waters to the direct oil):

Specific Gravity at 15°	0.889 to 0.929
Optical Rotation	−0° 48′ to −4° 6′

[63] *Ann. chim. anal. chim. appl.* **21** (1939), 173. *Chem. Abstracts* **34** (1940), 3018. Cf. Vol. I of this work, p. 215.

[64] "Die Ätherischen Öle," 3d Ed., Vol. III, 125.

Saponification Number	55 to 118
Methyl Anthranilate Content	2.7 to 15.0%

An oil distilled in the New York laboratories of Fritzsche Brothers, Inc., from bitter orange flower absolute of their own manufacture had the following properties:

Specific Gravity at 25°/25°	0.906
Optical Rotation	−3° 36′
Refractive Index at 20°	1.4819
Acid Number	1.4
Saponification Number	95.2
Saponification Number after Acetylation	200.7
Solubility	Soluble in 2.5 vol. and more of 60% alcohol

It should be mentioned here that the volatile oil obtained by steam distillation of the absolute of orange flower is not an article of commerce, and not used in perfumery.

Chemical Composition of Orange Flower Extracts (Concrete and Absolute).—The concrete or absolute oil obtained by extracting bitter orange blossoms with volatile solvents contains not only the constituents identified in the distilled oil (oil of neroli bigarade) but also the following, according to the Schimmel chemists: [65]

Benzaldehyde. Identified as semicarbazone m. 214°.

A Basic Compound(?). Of strong, nicotine-like odor; b_6 above 110°.

Nitrile of Phenylacetic Acid (Very Probably). When hydrolyzed this nitrogenous compound is decomposed into ammonia and phenylacetic acid.

A Nitrogenous Compound(?). The same compound, m. 159°, had already been observed in the water oil by Hesse and Zeitschel.

Jasmone (Probably). The extract oil also contains a ketone of typical jasmine-like odor; it is probably jasmone. The semicarbazone melts at 204°–205°.

Absolute from Orange Flower Pomade.—In the past, before the introduction of the modern process of extraction with volatile solvents, bitter orange blossoms in Southern France were treated also by maceration (hot *enfleurage*, see "Natural Flower Oils," Vol. I of this work, p. 198). In the course of the orange blossom harvest a batch of 300 kg. of fat *corps* is gradually macerated with 1,500 kg. of orange flowers by heating the 300 kg. of fat with 60 kg. of blossoms at a time. Each operation lasts 2 hr.; the exhausted blossoms are then strained off the heated liquid fat and replaced by 60 kg. of fresh blossoms. At the end of the harvest only 275 kg. remain from the

[65] *Ber. Schimmel & Co.*, October (1903), 52.

original 300 kg. of fat, the loss being due to shrinkage. The resulting *pommade de fleur d'oranger* is a white mass of delicate orange blossom odor. During the winter months it is extracted systematically with strong alcohol in *batteuses*. The resulting *extrait de fleur d'oranger,* after freezing and filtering, is an alcoholic extract of delicate odor which in years past found extensive application in fine French perfumes. By concentrating the alcoholic *extraits,* about 3.5 kg. of a semisolid dark mass, the so-called "absolute of orange flower maceration" is obtained. It possesses the typical odor of orange blossoms with a slight "by-note" of fat and benzoin; the latter, originally added to protect the *corps* against rancidity, dissolves in the alcohol during the process of extracting the pomade.

Absolute of orange flower maceration contains a relatively small amount of volatile oil (8 to 12 per cent), which can be isolated by steam distilling the absolute. To make matters clear this volatile oil is not employed in perfumery but is sometimes prepared in the laboratory in order to check the purity of an absolute of maceration. An oil thus distilled from absolute of orange flower maceration produced by the author in Southern France had these properties:

Specific Gravity at 15°/15°	0.8918
Optical Rotation	−7° 20′
Refractive Index at 20°	1.4718
Acid Number	30.2
Saponification Number	63.2
Saponification Number after Acetylation	198
Solubility	Soluble in 2 to 2.5 vol. of 70% alcohol, cloudy with more; soluble in 1 to 2.5 vol. of 80% alcohol, turbid with more

Hesse and Zeitschel [66] gave the following properties for the volatile oil from the pomade:

Specific Gravity at 15°	0.913
Optical Rotation	−5° 0′
Saponification Number	78.1
Methyl Anthranilate Content	9.2%

As has been mentioned, the absolute of maceration as well as the *extraits* from the pomade are used very little today; they have been replaced by the absolute obtained by extracting the flowers with volatile solvents.

Hesse and Zeitschel, studying the yields of volatile oil obtained by the various methods of processing bitter orange flowers, found that maceration (hot *enfleurage*) yields only one-third, and cold *enfleurage* only one-fif-

[66] *J. prakt. Chem.* [2] **64** (1901), 250.

teenth, the yield of oil obtained by steam distilling the blossoms. These facts led Hesse and Zeitschel to the conclusion that orange blossoms contain their volatile oil ready formed in the cells and do not develop additional oil during the process of *enfleurage,* unlike jasmine and tuberose flowers.

According to the same authors, 1,000 kg. of orange blossoms, upon distillation, yield about 1,000 g. of neroli bigarade oil, and 300 to 330 g. of orange flower water oil; altogether 1,300 to 1,330 g. of volatile orange blossom oil. One thousand kilograms of orange blossoms, upon extraction with volatile solvents, yield from 1,000 to 1,300 g. of absolute, and upon steam distillation of the absolute, from 450 to 580 g. of volatile orange blossom oil. The nonvolatile constituents of the absolute are composed of alcohol-soluble flower waxes and other odorless matter. These figures show that distillation of the orange blossoms yields more than twice as much *volatile* oil as does extraction with volatile solvents. A satisfactory explanation for this rather surprising fact has not yet been given.

SUGGESTED ADDITIONAL LITERATURE

Louis Girard, "Present Status of the Question of Concretes and Concrete Absolutes," *Ind. parfum.* **2** (1947), 183, 217, 257. *Chem. Abstracts* **41** (1947), 7671.

OIL OF BERGAMOT

Essence de Bergamote *Aceite Esencial Bergamota* *Bergamottöl*
Oleum Bergamottae

History.—The origin of the word bergamot is obscure. It might have been derived from the shape of the fruit, which resembles the bergamot pear. Engler and Prantl[1] trace the name bergamot to the small Asiatic city of Bergamia in northern Smyrna. Another account, quoted by Mottareale,[2] has it that the bergamot orange was brought by Columbus from the Canary Islands to the city of Berga, in the Province of Barcelona, Spain, and was introduced from there to Calabria in Southern Italy, the present principal growing region. The planting and cultivation of the bergamot in Calabria

[1] "Die Natürlichen Pflanzenfamilien," 2d Ed. (1931), *Rutaceae,* 19a, 344.
[2] *Italia Agric.* **65** (1928), 1043. H. J. Webber and L. D. Batchelor, "The Citrus Industry," Vol. I, 489, Univ. Calif. Press (1943).

commenced probably during the first quarter of the eighteenth century. At the same time, the oil, obtained by expression of the rind, became known as a very fine "essence"; by 1725 its use was well established in Florence.

Botany and Description.—The botanical origin of the bergamot group, too, is doubtful. Webber [3] lists the bergamot oranges (*Citrus aurantium* Linnaeus, subsp. *bergamia* [Risso and Poit.] Wright and Arn.) as subspecies of the sour (bitter) orange species (*Citrus aurantium* Linnaeus), but mentions that between certain subspecies there are such marked differences that some authorities class these as distinct species. According to Swingle,[4] opinions differ as to whether the variety bergamot is a mutation of the sour orange, or a hybrid. Swingle believes that this question could be settled by experimental hybridization.

The bergamot tree is rather small, attaining a height of about 4 m. The deep green leaves are long and glabrate, remain on the tree throughout the year, and contain a volatile oil which may be obtained by steam distillation. However, this oil (oil of petitgrain bergamot) is only seldom produced; commercially it is thus much less important than the oil expressed from the peel of the fruit. The fragrant flowers are white, a little smaller than those of the orange. They bloom from March to May, and a second time toward the end of Calabria's long dry summer, thus producing late fruits which are called "bastardi." The globose to pyriform fruits contain a sour pulp. A little smaller than the sweet orange, they frequently attain a diameter of almost 3 in. The rind of the ripe fruit possesses a lemon-yellow color; depending upon the variety, it may be smooth or rough. The peel is thin and quite tough; in the flavedo numerous oil glands are embedded from which a very pleasant essential oil—the so-called oil of bergamot—may be expressed. The spherical shape of the fruits of the cultivated varieties facilitates mechanical extraction of the oil by rasping.

Producing Regions.—Although it would seem that the bergamot tree could be raised in all mild climates and on all soils suited for citrus growth, it is restricted to a narrow coastal strip in Calabria, on the southwestern tip of the Italian peninsula, opposite Messina. The producing regions are confined to a small zone, with Reggio Calabria as its center, beginning at the northern entrance to the Strait of Messina and extending south to Brancaleone. Small plantings may be found north of Brancaleone, as far as Siderno. This narrow belt, supplying the world with bergamot oil, is only about 100 km. long. The bergamot groves there cover a total area of about 2,400 hectares, being divided into more than 2,500 properties of variable size and producing from a minimum of 20 quintals (1 quintal = 100 kg.)

[3] "The Citrus Industry," Vol. I, 488, Univ. Calif. Press (1943).
[4] *Ibid.*, 406.

of fruit to a maximum of 6,000 quintals. According to La Face,[5] the bergamot orchards are divided as follows:

1. Properties of small production, about 30 kg. of oil	1,295
2. Properties of small production, between 30 and 60 kg. of oil	489
3. Properties of small production, between 60 and 100 kg. of oil	289
4. Properties of small production, between 200 and 300 kg. of oil	353
5. Properties of larger production, from 300 kg. of oil upward	99

These figures show that oil of bergamot is produced almost exclusively by small farmers, except for a few landed proprietors who produce as much as 5,000 Sicilian lb.[6] yearly. The expressing of bergamot oil in Calabria is thus a small home industry; entire families engage in it, processing their own fruit, and selling the oil through official channels to the exporters in Reggio and Messina. The Consorzio del Bergamotto in Reggio Calabria examines every lot of oil submitted to it. If the quality is approved, the Consorzio's seal is placed upon the can. In this condition it reaches the trade.

Climatic and Soil Conditions.—The bergamot tree, most delicate of all citrus plants, demands a special climate and soil. Easily damaged by frost, any inclemency of weather may seriously affect the entire crop within a few days. Bergamot prefers a mild and equable climate, with a temperature ranging from 2° to 37° C. The lowest average monthly temperature (January and February) in Reggio's bergamot growing regions is 12°. The exposure should be toward the south, the soil well drained. The trees are best grown on well irrigated, low-lying lands, on alluvial soils bordering rivers. Calabria enjoys a warm climate, generally free of frost, but its soil is of rather mediocre quality and requires irrigation. Since the annual rainfalls average only 500 to 700 mm., 150 mm. of which fall during April–September, it is necessary to supply water by irrigation during the summer months. The groves are usually located in the low-lying parts of Calabria, but follow the valleys to an altitude of 400 to 500 m. Since Calabria does not provide uniform conditions of soil, exposure, and temperature, one might be inclined to conclude that bergamot prospers under variant conditions. Nevertheless, repeated attempts to raise bergamot commercially in Sicily have failed, although conditions there are quite similar to those in Calabria, only a few miles across the Strait. The explanation may be sought in some special characteristics of the soil which, however, have not yet been clarified. Attempts to raise bergamot outside of Italy have generally failed, with the exception of a large plantation near Labé in the highlands of

[5] "The Application of Modern Methods in the Production of Bergamot Oil," *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **13**, No. 1-2 (Jan.–Feb. 1938), 3.

[6] A Sicilian pound contains 317.621 g., whereas the American pound contains 453.590 g. This makes the Sicilian pound about 12 oz., as compared to the American 16 oz.



Courtesy of Dr. Francesco La Face, Reggio Calabria, Italy.

Young and older bergamot plantations at Reggio Calabria.

French Guinea in West Africa.[7] It cannot yet be said with certainty, however, that the bergamot tree can grow outside of Calabria, most of the attempts to this effect having so far been only half-hearted. On the other hand, the bergamot oil industry in Calabria has been firmly established for centuries; it would be difficult to compete with Calabria's low cost of production, based upon cheap family labor and long experience.

Planting.—Until the middle of the last century, bergamot was grown from seeds or cuttings. In 1862, however, root-rot and gum disease all but destroyed the citrus orchards, only the sour (bitter) orange tree resisting. Since then, growers in Sicily and Calabria have grown all citrus trees, including the bergamot, by raising sour orange stock and grafting the other citrus upon it. This is particularly true of the delicate bergamot. The sour orange tree seems best suited as stock, because it possesses a long life (70 to 80 years) and is most resistant to diseases, insects, and inclemencies of weather. The sour orange stock itself is raised from seed and budded after two to three years, when it reaches a height of at least 1.5 m. The trees are planted 3.5 to 4.5 m. apart on terraces, and 4.0 to 6.0 m. apart on level ground. The number of trees per hectare varies from 400 to 450.

Cultivation begins in February, after the harvest of the fruit. The trees are pruned lightly but frequently, usually in March or April. Irrigation starts in May or June and is continued for one to two weeks, depending upon the nature of the soil. La Face [8] suggested the use of 35 to 70 kg. of stable manure per tree, plus 3 to 5 kg. of chemical fertilizers (lime, superphosphate, potassium sulfate, ammonium sulfate) every two years.

Strong sea winds, cold spells in spring, excessive heat in June, and "sunstroke" in summer may easily affect the fruit and cause much to fall during the formative period. The most serious biological disease is root-rot (*Marciume radicale*) which causes the roots to decay and the trees to wither and die. It develops especially in trees planted in heavy and poorly drained soil, but may be avoided by drainage and deep cultivation. Rovesti [9] attributes it to *Agaricus citri.*

A somewhat similar disease, "lymphatic apoplexy," exhausts the trees in a few days. It is ascribed to putrefaction and gumosis of the roots. Another very dangerous disease, "honeydew" or "melata," occurs during periods of great summer heat. "Gumosis" or "citrus pestilence" attacks the bark, branches, the trunk, even the roots, and causes deep changes in the wood and shedding of the leaves. This infection may be carried from one part of the tree to another, and from tree to tree. It is due to a generally lowered vitality, resulting particularly from stagnant water.

[7] Cf. Trabaud, *Riechstoff Ind.* **13** (1938), 124.
[8] *Parfumerie moderne* **19** (1926), 49.
[9] *Rivista ital. essenze profumi* **11** (1929), 215. *Ber. Schimmel & Co.* (1930), 35.

Harvesting.—Three years after grafting, in other words when the tree is six to seven years old, it bears 20 to 30 fruits, which number increases until the tree reaches full maturity twelve years after grafting. It then produces about 300 fruits. The yield of oil reaches its maximum (1 kg. or 2.2 lb. of oil per tree) when the trees are fifteen to forty years old. The productive life of a tree ranges from seventy to eighty years.

The harvest usually begins the first of December and is completed toward the middle or end of March. Unlike other citrus fruit, the bergamot is gathered while approaching maturity.

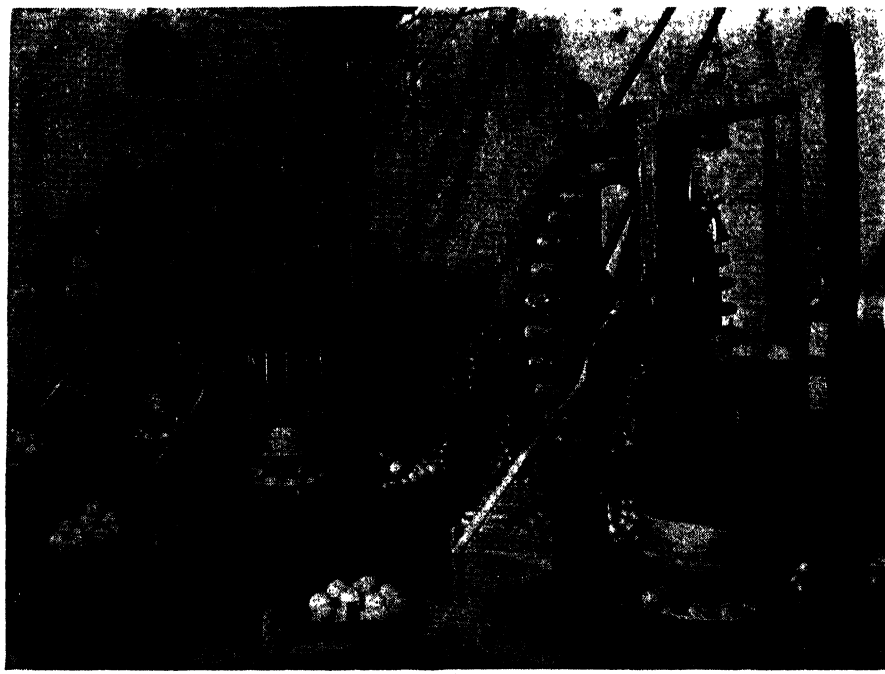
Expression of the Oil.—Expressed bergamot oil is obtained solely by rasping the fruit. The oil occurs in sacs, or glands, distributed throughout the outer, colored stratum (flavedo) of the maturing and mature peel. When the walls of these oil reservoirs are punctured, the oil is forced out. The force of ejection is very important in the processing of the fruit and depends in great measure upon the tension of the skin which, in turn, is an index of the fruit's maturity and freshness. A part of the oil evidently adheres to the cell tissue, thereby causing losses and complicating the problem of expression. As the bergamot fruit is of approximately spherical form, it is possible to extract the oil by machine-rasping. Around 1840, Nicola Barilla invented a machine which became known as the bergamot, Calabrese, or Gangeri machine. Originally rather clumsy, it has been improved several times in the course of years and is currently being offered in a more modern design. Formerly hand operated, the machine is now usually powered by electricity, each machine requiring about 0.5 to 1.0 h.p.

According to Donovan,[10] the bergamot fruit is first allowed to dry and harden somewhat over a period of several days before processing. The fruits are then graded to about the same size, fed into the machine one by one, and rotated by an upper ribbed cup over a lower fixed one fitted with a number of points, for about 120 to 240 revolutions. No sprays of water are used, but when the fruit has been overdried, it must first be placed in water for 15 to 30 min. to facilitate ejection of the oil. This, however, is said to affect the yield and the quality of the oil to some degree. The processed (rasped) fruits are carefully wiped with a sponge to recover any adhering oil. The emulsion and cell detritus are collected from the decantation vessels, pressed with increasing force in wool or hair bags, which causes the mass of aqueous cell liquid, oil, and detritus to separate, the essential oil slowly filtering through the bag after the aqueous phase. This oil, after further clarification, filtering, etc., represents the well-known expressed oil of bergamot. The thick residue is dispersed in warm water and the pulp repeatedly treated as above. The final residue may be steam distilled,

[10] *Perfumery Essential Oil Record,* Special Issue (1937), 18.

yielding a secondary oil, the so-called *distillato di feccia di bergamotto,* the properties of which will be described later.

Yield of Oil.—The quality and quantity of the oil vary considerably in the different districts from year to year, and even among individual trees. On the average, the yield of expressed oil is about 480 g. per 100 kg. of fruit (0.48 per cent). The Calabrese machine, when hand driven, produces about



Courtesy of Fritzsche Brothers, Inc., New York.

Calabrese Macchina, used in Calabria for the extraction of bergamot oil.

9 Sicilian lb. (1 Sicilian lb. equals about 12 oz.) of oil in eight hours; but when motor driven, about 15 lb. It has been estimated that about 14 per cent of the oil remains in the peel and is lost unless the fruit is steam distilled, yielding thereby *distillato di feccia di bergamotto.*

As a result of the rather crude method of expression provided by the Calabrese machine, the yield obtained is thus considerably lower than the actual oil content of the fruit. For this reason, La Face [11] suggested the use of some of the latest *pellatrici,* e.g., the Avena, which are used for processing lemon fruit in Sicily. These more practical and efficient rotary rasping machines have been described in a previous chapter.

[11] *Parfumerie moderne* **19** (1926), 49.

The modern rotary machines offer the following advantages over the Calabrese:

1. No grading of fruit according to size, previous to pressing, is required.
2. A nine to ten times larger working capacity.
3. A higher yield of oil.
4. Large lots of fruit can be processed daily, thus recommending these machines for large-scale producers or cooperatives.
5. The oil yield is higher with fully ripened fruit, toward the end of the harvest, when the Calabrese machine becomes rather ineffective.
6. The *pellatrici* are simple to work; whereas the success of the Calabrese depends upon several factors, for instance, storage of the fruit after harvesting, proper duration of the rasping, proper pressure, and experience of the operators.

The *pellatrici* require merely a sufficient amount of spraying water. It is, however, advisable not to permit the expressed oil to remain too long in contact with the water in the separation tanks, as the accumulating colloidal matter would prevent the separation of oil and aqueous liquid. In actual practice, the pulpy peel detritus is often separated in woolen bags.

Following the advice of the Stazione Sperimentale in Reggio Calabria, a few large-scale producers have with good success adopted *pellatrici* for the pressing of bergamot fruit. Obviously the *pellatrici* are too costly for the small operators.

Physicochemical Properties of Expressed Bergamot Oil.—The main constituent of expressed bergamot oil is linalyl acetate, the percentage of which, according to accepted trade practice, determines the quality of the oil. The content of free linaloöl varies from 20 to 30 per cent. As the season progresses the ester (mainly linalyl acetate) content increases. Oils obtained from green fruits may contain only 30 to 32 per cent of esters; normal oils produced during December, as a rule, contain about 34 per cent, during January 38 per cent, during February 40 to 41 per cent and during March 42 per cent of ester. There are certain regions in which oils containing 43 and even 45 per cent of ester are produced, but this may be due to exceptional weather conditions. A dry season increases the ester content. Some seasons produce a much larger proportion of oils with a higher ester content than others. Such may be the situation two years in succession, often followed by two or three years in which high-grade oils are rare.

La Face [12] expressed the belief that the character of bergamot oil is influenced by:

[12] *Parfumerie moderne* **19** (1926), 49.

1. *The soil, its cultivation, irrigation, etc.*
   A too abundant water supply results in the formation of excessive amounts of terpenes, and of less oxygenated compounds.
2. *Morphological conditions.*
   Hot, dry summers bring about a higher ester content.
3. *The age and variety of the trees.*
   Two varieties growing in the same soil yield oils of different ester content and rotation.
4. *The time of flowering.*
   Fruits from April flowers give oils containing less terpenes than fruit from May flowers.

The same author [13] indicated the following limits for expressed bergamot oils:

Specific Gravity at 15°	0.880 to 0.887
Optical Rotation	+8° 0′ to +24° 0′
Acid Number	1.0 to 3.5
Ester Content, Calculated as Linalyl Acetate	35.0 to 45.0%
Evaporation Residue	4.5 to 6.5%
Solubility	Soluble in 0.5 vol. of 90% alcohol

Gildemeister and Hoffmann [14] give these limits for bergamot oils:

Specific Gravity at 15°	0.881 to 0.886; very rarely up to 0.888
Optical Rotation	+8° 0′ to +22° 0′; in some cases +5° 24′ to +24° 0′
Refractive Index	1.464 to 1.468
Acid Number	1.0 to 3.5
Ester Content, Calculated as Linalyl Acetate	34.0 to 40.0%; rarely up to 45.0%
Evaporation Residue	4.5 to 6.0%; often as low as 4.0%
Acid Number of the Evaporation Residue	19 to 30
Saponification Number of the Evaporation Residue	117 to 173
Solubility	Soluble in 1 vol. of 90% alcohol, seldom with opalescence. Some oils are soluble in 1–2 vol. of 80% alcohol, turbid with more

Genuine expressed bergamot oils imported from Calabria, and analyzed in the New York laboratories of Fritzsche Brothers, Inc., during the past years, had properties which varied within the following limits:

[13] *Ibid.*
[14] "Die Ätherischen Öle," 3d. Ed., Vol. III, 93.

Specific Gravity at 25°/25°	0.875 to 0.881
Optical Rotation	+11° 12′ to +24° 16′
Refractive Index at 20°	1.4650 to 1.4675
Ester Content, Calculated as Linalyl Acetate	36.0 to 42.0%
Evaporation Residue	4.5 to 6.0%, usually above 5%
Solubility at 25°	Soluble in 0.5 vol. and more of 90% alcohol

According to La Face,[15] the optical rotation of pure bergamot oil is occasionally higher than +24°; it may be as high as +30°. The ester content varies from 35 to 45 per cent; many lots of oil dissolve in 1 to 1.5 volumes of 85 per cent alcohol.

As regards the harvest of 1947–1948, Albricci[16] reported the following properties:

Specific Gravity at 15°	0.8800 to 0.8855, in most cases 0.8810 to 0.8840
Optical Rotation at 15°	+6° 36′ to +24° 36′, in most cases +14° 0′ to +22° 0′
Ester Content, Calculated as Linalyl Acetate	33.58 to 44.18%, in most cases 38 to 44%
Free Alcohol Content, Calculated as Linaloöl	16.29 to 34.60%, in most cases 21 to 30%
Alcohol and Ester Content, Combined	56.52 to 72.91%, in most cases 63 to 70%
Evaporation Residue	4.30 to 6.05%
Solubility	Soluble in 1 vol. of 82% alcohol to 0.4 vol. of 90% alcohol

The bergamot oils of the 1947–1948 harvest in general had an elevated content of oxygenated compounds.

Adulteration.—As a widely used and highly competitive article, oil of bergamot is frequently adulterated. The blame for this abuse cannot always be laid at the door of the producer and exporter, as unreasonable demands on the part of the buyer frequently invite (if not force) the seller to resort to this means, as the only way of getting orders.

In past years, bergamot oil was adulterated mostly by the producers and exporters in Calabria and Sicily; this practice gradually created considerable resentment and distrust abroad, with the result that the Italian government had to take energetic measures to safeguard the reputation of Italy's citrus oil industry. The strict control laws promulgated by Italy, in the years prior to World War II, did a great deal to restore weakened

[15] Recent private communication by Dr. F. La Face, Director of the Stazione Sperimentale, Reggio Calabria.

[16] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **18** (January-March 1948), No. 1, 13.

confidence in the quality of Calabrian and Sicilian citrus oils. No lot of bergamot oil could be exported without a Certificate of Purity granted by the Government Control Laboratories. Synthetics or isolates which might be used for adulteration purposes could no longer be imported and the producers of terpeneless oils had to give strict account of their terpenes. These drastic steps brought about a considerable improvement in the quality of bergamot oil, but were powerless to stop adulteration outside of the frontiers of Italy.

Because of the great variety of natural isolates and terpenes from other citrus oils, it is relatively simple to sophisticate oil of bergamot in such a way that moderate additions of these products cannot be detected in the course of routine analysis. Linaloöl and linalyl acetate are the main constituents of bergamot oil, but they can also be obtained cheaply from low-priced oil of bois de rose and Japanese ho oil (oil of shiu). Deviations of specific gravity and optical rotation resulting from such adulteration can easily be corrected by proper employment of terpenes; and a lowered evaporation residue can be brought up again by additions of residues and waxes from the preparation of sesquiterpeneless citrus oils. It is a difficult task to prove such additions to bergamot oil, even experts being occasionally puzzled. When doubtful of purity, the expert should resort to thorough odor and flavor tests, which usually are more indicative of the quality than mere chemical analysis.

In years past, some of the current adulterants of bergamot oil were high boiling synthetic esters, such as acetins, esters of oxalic, succinic, citric, lauric, and phthalic acid. As in the case of lavender oil, the main constituent of which is also linalyl acetate, such additions simulate a high ester value which the analyst may mistake for linalyl acetate. Special tests for such esters were developed in the laboratories of Schimmel & Co.[17] One of these tests is the determination of the difference between saponification number and acid number II which varies from 0 to 10 in normal bergamot oils (cf. "Oil of Lavender," Adulteration, in the present volume, and Vol. I of this work, pp. 338, 340, and 342).

Bennett and Garrett[18] suggested a very simple test for the presence of esters of certain nonvolatile acids. Their test is based upon the insolubility, in absolute alcohol, of the potassium salts of these acids. A mixture of 10 cc. of oil and 3 cc. of absolute alcoholic potassium hydroxide is prepared in a test tube, kept in a water bath for a few minutes and then cooled. If

[17] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 792.

[18] *Perfumery Essential Oil Record* **14** (1923), 359. See in this connection the excellent study of Mossman and Bogert entitled "Bergamot Oil," p. 87, A.Ph.A. Monograph No. 2 (1941), The American Pharmaceutical Association, Washington, D. C.

no precipitate forms in an hour, adulteration of this type is absent. Bennett and Garrett observed these results:

Phthalate	1%	Crystalline precipitate almost at once
Cinnamate	1%	Crystals after some time
Cinnamate	2.5%	Crystals appear quickly
Succinate	1%	Crystalline precipitate
Succinate	2.5%	Gelatinous precipitate
Citrate	1%	Crystalline precipitate on standing
Tartrate	1%	Ditto
Benzoate	2.5%	Ditto

Ogsten and Moore [19] found the method both trustworthy and convenient. The precipitates may be cooled, filtered, dried, and weighed; and the original ester calculated.

Kleber [20] detected ethyl laurate and other esters of high fatty acids in bergamot oil by the jelly-like mass that formed upon saponification. Neutralizing with hydrochloric acid and adding calcium chloride solution, he obtained an abundant crystalline precipitate. Acidification of the precipitate gave a layer of fatty acids which congealed on cooling.

Another synthetic ester occasionally used for the adulteration of bergamot oil is terpinyl acetate; it possesses an odor somewhat resembling this oil. The test for the detection of terpinyl acetate and other esters, which are difficult to saponify, consists in the determination of the difference in the ester numbers of the fractional saponification which, in the case of genuine bergamot oils, ranges from 0 to 5. For details of procedure, see Vol. I of this work, p. 336.

Chemical Composition.—The first investigations of the chemistry of bergamot oil date back more than one hundred years, to the time when Soubeiran and Capitaine [21] showed that the oil contained various terpenes. Linalyl acetate, the main constituent of bergamot oil, was discovered almost simultaneously, but independently, by Bertram and Walbaum,[22] and by Semmler and Tiemann.[23] So far, quite a number of compounds have been identified in bergamot oil, but it is possible that the oil contains also small quantities of other constituents which have not, as yet, been isolated.

Octylene(?). Burgess and Page [24] reported the occurrence of this olefinic terpene in the lowest fraction of bergamot oil. As proof, these authors cite the fact that the fraction b_{764} 150°–155° possessed a very low specific gravity and a low refractive index, furthermore that oxidation with potassium permanganate gave butyric acid. The latter, however, was identified only by odor and not chemically.

[19] *Perfumery Essential Oil Record* **16** (1925), 114. Cf. Sabetay, *Ann. fals.* **28** (1935), 100.
[20] *Am. Perfumer* **21** (1926), 263.
[21] *Liebigs Ann.* **35** (1840), 313.
[22] *J. prakt. Chem.* [2] **45** (1892), 602.
[23] *Ber.* **25** (1892), 1182.
[24] *J. Chem. Soc.* **85** (1904), 1327.

Burgess and Page, furthermore, reported the occurrence of the following compounds:

α-Pinene(?). In the fraction b_{764} 157°–158°; $[\alpha]_D$ −8° 18′; identified as hydrochloride m. 125°.

Camphene(?). In the fraction b_{764} 164°–165°; $[\alpha]_D$ −22° 48′; conversion into isoborneol m. 203°.

Bisabolene(?). In the higher boiling fractions; identified as hydrochloride m. 79°.

Whether or not these compounds actually occur in genuine bergamot oil is still open to doubt, as the oil investigated by these authors possessed somewhat abnormal properties.

The oil investigated by Burgess and Page, despite their assertion to the contrary, may therefore not have been pure.

Bornylene(?). Parry [25] mentioned the presence of bornylene m. 97.5°–98°, without giving further proof.

d-Limonene. Identified by Wallach [26] in the fraction b. 175°–180°.

Dipentene(?). According to Wallach,[27] the fraction b. 180°–190° absorbed bromine but did not yield a crystalline bromide. Continued heating of the same fraction resulted in the formation of high boiling condensation products; after repeated fractionating the fraction boiling up to 190° at 760 mm. gave dipentene tetrabromide m. 124°–125°.

This fact, however, cannot be taken as proof that dipentene is an actual constituent of bergamot oil as dipentene might have been formed from the linaloöl contained in the fraction b. 180°–190°.

The same holds true of Semmler and Tiemann's observation [28] that the fraction boiling 17° higher than limonene gave dipentene tetrabromide.

l-Linalyl Acetate. The main constituent of bergamot oil, found by Semmler and Tiemann,[29] and by Bertram and Walbaum.[30]

Identified by saponification, oxidation of linaloöl to citral, and análysis of silver acetate.

l-Linaloöl. The oil contains linaloöl not only as ester but also in free form.

Dihydrocuminyl Alcohol. Preparing terpeneless bergamot oil, Elze [31] investigated a fraction which represented about 25 per cent of the total oil. Saponification, steam distillation, and fractionation resulted in an oil: d_{15} 0.890; α_D −10° 0′.

By treating this fraction with phthalic anhydride, Elze isolated a small quantity of an alcohol which proved to be dihydrocuminyl alcohol; identified as naphthylurethane m. 146°–147°. Oxidation of the alcohol with Beckmann's chromic acid mixture gave an aldehyde of cumin-like odor, b. 235°; semicarbazone m. 198°–199°. After regeneration from the semicarbazone, the aldehyde had the properties: d_{15} 0.970; α_D −39° 0′.

[25] "Chemistry Essential Oils," 4th Revised Ed., Vol. I (1921), 450.
[26] *Liebigs Ann.* **227** (1885), 290.
[27] *Ibid.*
[28] *Ber.* **25** (1892), 1182.
[29] *Ibid.*
[30] *J. prakt. Chem.* [2], **45** (1892), 602.
[31] *Chem. Ztg.* **34** (1910), 538.

Nerol. The main portion of the alcohol mixture, as isolated with phthalic anhydride by Elze,[32] consisted of nerol: d_{15} 0.880; tetrabromide m. 118°; diphenylurethane m. 50°.

Geraniol(?). Also present, according to Elze.

Terpineol(?). Among the alcoholic compounds which did not react with phthalic anhydride, Elze identified terpineol m. 35° by its phenylurethane m. 110°. It should be pointed out, in this connection, that terpinyl acetate is frequently added to bergamot oil as adulterant. Without proof that Elze's bergamot oil was absolutely genuine it is very doubtful that pure bergamot oil actually contains terpineol.

Aldehydes(?). The presence of aldehydes, probably citral, has been reported but they were not further identified.[33]

Bergaptene, $C_{12}H_8O_4$. Bergamot oil contains about 5 per cent of this odorless compound which crystallizes in the form of soft, white, silky needles m. 188°. According to Pomeranz,[34] bergaptene, when heated, emits vapors of aromatic odor.

Bergaptol, $C_{11}H_6O_4$. Späth and Socias [35] obtained from bergamot oil by fractional distillation a compound $C_{11}H_6O_4$, viz., bergaptol m. 280°–282°, which Späth et al.[36] had already isolated from masterwort as product of saponification.

Limettin (Citroptene). Aside from bergaptene and bergaptol, bergamot oil contains still other coumarin derivatives. Späth and Kainrath [37] proved the presence of limettin m. 146°–147°, which occurs also in oil of lemon and oil of lime.

Bergamottin,[38] $C_{21}H_{22}O_4$. The same authors isolated from oil of bergamot a new compound, viz., bergamottin m. 59°–61°, which is the geranyl ether of bergaptol. When heated with glacial acetic acid, bergamottin is split into bergaptol and geraniol.

Sethna and Shah [39] suggested a general method of isolating coumarins from plant material; it is described in the section on Coumarins in Vol. II of this work, p. 662.

Summary

A search of the literature on bergamot oil shows that in many cases the evidence presented for certain statements is fragmentary and inconclusive. This is rather surprising, in view of the importance of bergamot oil; but no investigation on the quantitative composition of this oil has been undertaken, except with reference to the ester and alcohol content.

[32] *Ibid.*
[33] Donald A. Mossman, "Bergamot Oils," Dissertation, New York (1932), 49.
[34] *Monatsh.* **12** (1891), 379; **14** (1893), 28.
[35] *Ber.* **67** (1934), 59.
[36] *Ibid.* **66** (1933), 914 and 1146.
[37] *Ber.* **70** (1937), 2272.
[38] Bergamottin is probably identical with bergaptin m. 59.5° described earlier by von Soden and Rojahn, *Pharm. Ztg.* **46** (1901), 778. Cf. Vol. II of this work, p. 685.
[39] *Chem. Rev.* **36** (1945), 1.

The list of components claimed to be present in bergamot oil follows:

Hydrocarbons

octylene(?)	camphene(?)
d-limonene	bornylene(?)
dipentene(?)	bisabolene(?)
α-pinene(?)	

Alcohols and acetic esters

l-linaloöl	α-terpineol(?)
geraniol(?)	dihydrocuminyl alcohol
nerol	

Aldehydes

citral(?)

Coumarin derivatives

bergaptene	limettin
bergaptol	bergamottin

Terpeneless Bergamot Oil.—Romeo [40] reported the following physicochemical properties of terpeneless bergamot oil:

Specific Gravity at 15°	0.890 to 0.898
Optical Rotation at 20°	−3° 0′ to −10° 0′
Ester Content, Calculated as Linalyl Acetate	60% to 70%
Solubility	Soluble in 2 vol. of 70% alcohol

Terpeneless bergamot oils, prepared by Fritzsche Brothers, Inc., New York, in the course of many years, displayed properties which varied within these limits:

Specific Gravity at 15°	0.887 to 0.895
Optical Rotation	−4° 27′ to −9° 50′
Refractive Index at 20°	1.4550 to 1.4570
Ester Content, Calculated as Linalyl Acetate	59.5 to 67.0%
Solubility	Soluble in 2.5 to 3.5 and more volumes of 70% alcohol

The chief advantage of terpeneless bergamot oil consists in its better solubility in dilute alcohol.

Use.—Oil of bergamot is one of the most important, indeed classic, perfume materials. Its pleasant, refreshing scent blends into almost any perfume composition, so that, today, there exists hardly a perfume which does

[40] *Atti congresso naz. chim. pura applicata* **2** (1926), 870. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 31.

not contain some oil of bergamot. It imparts delicate top notes, and at the same time strength and "body." For the same quality, the oil is widely used in lotions, creams, powders and soaps; in eaux de Cologne bergamot oil forms a main constituent.

In a few isolated cases, however, oil of bergamot has been found to cause pigmentation when applied to the skin, in the form of alcoholic lotions, eaux de Cologne, or perfumes, and *when exposed to sunlight.*

This fact was first mentioned by Freund [41] in 1916, who reported several cases of dermatitis caused by application of eau de Cologne; Freund proved that bergamot oil was the factor creating this condition. Hoffman and Schmidtz,[42] in 1925, reported cases of pigmentation of the skin after application of eau de Cologne and exposure to sunlight. Zurhelle [43] found the inflammation preceding the pigmentation strongest in blondes, but occurring pigmentation greater in brunettes. Uhlmann [44] proved by experiments that bergamot oil alone does not produce pigmentation; only when applied in the form of an alcoholic solution was this result obtained. Lane and Strauss [45] reported a case of dermatitis developing after application of a toilet water with bergamot oil as main constituent, followed by pigmentation without exposure to sunlight. The pigmentation disappeared after a month or two. (See in this connection also "Oil of Lime," Use.)

Total Production.—Prior to World War II, Calabria produced annually from 300,000 to 450,000 lb. (American) of expressed bergamot oil. About 100,000 lb. used to be imported yearly to the United States. Part of these imports were shipped to the United States not directly from Calabria or Sicily, but via European ports outside of Italy.

During the years 1940 to 1942 the average annual production of bergamot oil was 174,000 kg.; from 1943 to 1944, 114,000 kg.; whereas in 1945 and 1946 the average annual production was 116,500 kg. In 1947, 145,000 kg. of bergamot oil were produced in Italy.

Other Oils from Bergamot Fruit.—Aside from the normal bergamot oil expressed from the peel of fresh, sound fruit, Calabria produces also small quantities of various types of oil made from windfalls, damaged fruit, or fruit too small to be processed in the Calabrese machine. These oils are of inferior quality, but have a limited use for the isolation of linaloöl and for other purposes; in former years, they were occasionally used for adulterating the genuine, expressed bergamot oil.

[41] *Dermatologische Wochenschrift* **63** (1916), 931.
[42] *Münchener Medizinische Wochenschrift* **72** (1925), 1414.
[43] *Zentralblatt für Haut-Geschlechtskrankheiten* **27** (1928), 738.
[44] *Medizinische Klinik* **23** (1927), 279.
[45] *J. Amer. Med. Assocn.* **95** (1930), 717.

1. *Nero di bergamotto.*—As a result of unfavorable weather conditions in summer and fall, some fruit drops to the ground and, lying there, turns dark. When processed in the Calabrese machine, such fruit yields a dark oil possessing a low ester content, a high content of free alcohols, and a high evaporation residue. Two samples collected by the writer during a visit to Calabria had the following properties:

	A	*B*
Specific Gravity at 25°/25°.	0.893	0.890
Optical Rotation.....	Too dark [46]	Too dark [46]
Solubility at 25°.....	Soluble in 1 vol. of 80% alcohol; cloudy with more	
Ester Content, Calculated as Linalyl Acetate (1 Hr. Saponification).....	25.4%	25.3%
Ester Content, Calculated as Linalyl Acetate (2 Hr. Saponification).....	26.2%	25.6%
Total Alcohol Content, Calculated as Linaloöl.....	52.8%	55.0%
Evaporation Residue.....	14.6%	13.7%

When decolorized and partly acetylized, the reconstituted oil forms a useful base for artificial bergamot compounds.

2. *Distillato di bergamotto* and *distillato di bergamottella.*—Instead of being expressed, dropped mature fruit is sometimes submitted to steam distillation, yielding an oil called *distillato di bergamotto.*

A similar oil may be obtained by steam distilling fruit which is too small to be processed in the Calabrese machine, or by distilling fruit dropped to the ground during the early stages of development from July to early September because of unfavorable weather, storms, or excessive heat. The oil content of such small fruit (*bergamottella*) depends upon its size and the ratio between weight and peel surface. Thus, small fruit contains relatively more oil than larger fruit. According to La Face,[47] small fruit, collected in the middle of June, averaged 5.25 g. each and contained 2.03 per cent of oil; the weight of the fruit increased as the season advanced with a corresponding decrease in the oil content, until mid-September the fruit weighed 80.0 g. and yielded only 0.86 per cent of distilled oil. The oil obtained by steam distillation of the small, unripe, dropped fruit is called *distillato di bergamottella.*

[46] Too dark for determination in tube of 2.5 cm. length.

[47] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **14** (January–February 1939), 12.

Two samples of *distillato di bergamottella,* obtained by the author in Calabria, had these properties:

	A	*B*
Specific Gravity at 25°/25°	0.866	0.867
Optical Rotation	+15° 48′	+12° 10′
Ester Content, Calculated as Linalyl Acetate (1 Hr. Saponification)	4.1%	3.9%
Ester Content, Calculated as Linalyl Acetate (2 Hr. Saponification)	6.7%	4.5%
Total Alcohol Content, Calculated as Linaloöl	47.5%	49.3%
Evaporation Residue	1.0%	1.4%
Solubility at 25°	Soluble in 1 vol. and more of 80% alcohol	Soluble in 2.5 to 5 vol. of 70% alcohol; opalescent with more

La Face [48] reported the following properties for *distillati di bergamottella:*

Specific Gravity at 15°	0.8700 to 0.8730
Optical Rotation	−2° 12′ to +12° 12′
Ester Number	7.47 to 12.82
Total Alcohol Content, Calculated as Linaloöl	56.55% to 66.60%
Total Content of Nontertiary Alcohols, Calculated as Geraniol	6.30% to 8.04%

The advantage of this oil lies in its good solubility. Acetylation yields oils which form a good base for artificial bergamot oil.

It may be interesting to record here the results obtained by Donovan [49] who, instead of distilling, applied a rotary rasping machine (Avena) and the Bennett-Cusmano process of separating the oil and water emulsion to obtain an expressed oil of *bergamottella.* The fruit treated by Donovan averaged 4.15 g. each. Seven lots of 2.15 kg. each were treated in a small Avena machine with a solution of sodium bicarbonate and sodium sulfate, a small Alfa-Laval centrifugal separator being used for oil recovery. The results, including typical analytical data for the usual distilled *bergamottella,* are given in Table 1.21.

It will be seen that the process gave a high yield of a product approaching a high-grade bergamot oil, with which its appearance and fragrance were in accord. It had nothing in common with the usual distilled oils; indeed, the results show that the high alcohol content of the distilled oil does not pre-

[48] *Ibid.*

[49] *Perfumery Essential Oil Record,* Special Issue (1937), 30.

TABLE 1.21

Trial	Yield of Oil from Centrifuge (cc)	Oil Distilled from Centrifuge Emulsion (cc)	Composition of Oil: Non-volatile Residue (%)	Esters as Linalyl Acetate (%)	Free Alcohols as Linaloöl (%)	Optical Rotation at 15.5°	Specific Gravity at 15.5°
1	130	. .	8.52	44.65	27.20	+3° 0′	0.8971
	...	50	...	37.35	...	+5° 45′	0.8764
2	145	...	8.74	43.80	28.70	+2° 24′	0.8968
		(Not distilled)	.	...	...	...	...
Distilled *Bergamottella:*			. .	3.30	62.0	+7° 15′	0.8707
			...	3.40	61.0	+7° 15′	0.8711

exist in the oil while in the fruit, but must derive from hydrolysis of esters during distillation.

3. *Distillato di feccia di bergamotto.*—This oil is a by-product of the expression of normal bergamot fruit in the Calabrese machine. The processed fruit, leaving the machine, retains some essential oil which may be recovered by steam distillation. A similar oil is obtained by distilling the press residue or filter cake (*feccia*) remaining in the separation of expressed oil from peel detritus and mucilaginous matter.

La Face [50] reported the yields given in Table 1.22.

TABLE 1.22

Weight of Processed Fruit (*kg.*)	Yield of Expressed Oil (*kg.*)	Press Residue (*kg.*)	Yield of Distilled Oil (*kg.*)	Percentage of Yield of Distilled Oil
6200	31.31	142.6	0.648	2.07
6300	29.10	124.0	0.610	2.33
8400	42.20	171.6	0.785	1.86

[50] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **14** (January–February 1939), 8.

According to the same author, the properties of this oil vary within these limits:

Specific Gravity at 15°	0.8630 to 0.8670
Optical Rotation	+13° 48′ to +26° 30′
Ester Number	3.73 to 13.07
Total Alcohol Content, Calculated as Linaloöl	46.40 to 55.98%
Nontertiary Alcohol Content, Calculated as Geraniol	5.47 to 7.96%

A sample of *distillato di feccia*, obtained by the author during a visit to Calabria, had the following properties:

Specific Gravity at 25°/25°	0.867
Optical Rotation	+17° 20′
Ester Content, Calculated as Linalyl Acetate (1 Hr. Saponification)	24.1%
Ester Content, Calculated as Linalyl Acetate (2 Hr. Saponification)	23.8%
Saponification Number (I)	67.9
Saponification Number (II)	67.9
Total Alcohol Content, Calculated as Linaloöl	46.5%
Evaporation Residue	1.1%
Solubility at 25°	Soluble in 1.25 to 4 vol. of 80% alcohol; opalescent with more

The chemical composition of these oils is similar to that of the *distillati di bergamottella*, except that they contain a somewhat higher percentage of terpenes and about 20 per cent less linaloöl. By acetylation, the ester content can be increased, the resulting oil suggesting a base for artificial bergamot oils.

4. *Distillato di fabbrica.*—As mentioned, the bergamot fruit, after processing in the Calabrese machine, still contains some oil. Part of this oil goes into the juice if the whole fruit is crushed for the purpose of extracting citric acid from the juice. When the amount of oil seems to warrant it, the juice is distilled, yielding a colorless oil. As the juice often undergoes fermentation, the oil, too, will be affected. Therefore, its odor is quite different from that of expressed bergamot oil.

La Face reported the following properties for *distillati di fabbrica:*

Specific Gravity at 15°	0.8560 to 0.8756
Optical Rotation	+6° 48′ to +47° 0′
Ester Number	3.23 to 8.20
Total Alcohol Content, Calculated as Linaloöl	21.25 to 61.09%

Nontertiary Alcohol Content, Calculated as Geraniol..... 10.07 to 13.76%

The chemical composition of this oil shows a still lower content of linaloöl than that of *distillato di bergamottella* and *distillato di feccia,* but the content of nontertiary alcohols is higher.

Use of the "Distillati."—La Face recommended employing all these secondary bergamot oils for the isolation of linaloöl by fractional distillation *in vacuo.* He obtained the yields given in Table 1.23.

TABLE 1.23

Raw Material	Quantity Employed (kg.)	Linaloöl (kg.)	Yield (%)	Terpenes (kg.)	Yield (%)	Residue and Losses (kg.)	Residue and Losses (%)
Distillato di bergamottella	350	178	51.00	152.8	43.6	19.2	5.40
Distillato di feccia	350	143	40.57	196.7	56.2	10.4	3.23
Distillato di fabbrica	100	32	32.00	61.2	61.2	6.8	6.80

The fractionation products obtained had the properties shown in Table 1.24.

TABLE 1.24

Product	Specific Gravity at 15°	Optical Rotation	Ester Number	Total Alcohol Content (%)	Solubility
Linaloöl from *bergamottella*	0.8707	−12° 30′	...	98.68	1 in 3.6 vol. of 65% alcohol
Terpenes [a] from *bergamottella*	0.8714	+26° 30′	14.38	45.64	1 in 1.4 vol. of 80% alcohol
Linaloöl from *feccia*	0.8730	−12° 0′	...	95.84	1 in 3.8 vol. of 65% alcohol
Terpenes [a] from *feccia*	0.8582	+41° 30′	4.48	31.12	1 in 1.0 vol. of 90% alcohol
Linaloöl from *fabbrica*	0.8698	−9° 36′	...	94.90	1 in 3 vol. of 65% alcohol
Terpenes [a] from *fabbrica*	0.8738	+18° 0′	7.78	54.20	1 in 2.5 vol. of 75% alcohol

[a] These fractions contain not only terpenes, but also some oxygenated compounds.

La Face claimed that Calabria could produce yearly about 4,000 to 5,000 kg. of *distillato di bergamottella,* 8,000 to 10,000 kg. of *distillato di feccia,* and 3,000 to 4,000 kg. of *distillato di fabbrica.* This would represent a yield of approximately 7,000 kg. of linaloöl and 10,000 kg. of terpenes. Therefore, the various *distillati* should be employed, according to La Face's suggestion, for the manufacture of linaloöl, a product which otherwise has to be imported to Italy.

Brazilian and Mexican So-Called Bergamot Oils

During World War II, when the United States was cut off from the old source of supply in Calabria, several types of Central and South American so-called bergamot oils were offered on the North American market. Their physicochemical properties differed considerably from those of normal Calabrian oils, the ester content was usually abnormally low, and the odor was quite different. Experts doubted the authenticity of these oils. Under pressure on the part of the United States custom officials, the Brazilian exporters declared that their bergamot oil consisted of a mixture of several citrus oils, said to be produced in southern Brazil. A personal investigation by the author in São Paulo (Brazil) revealed that the so-called Brazilian bergamot oil was in reality a composition consisting of acetylated oil of bois de rose, oil of orange, lemon, etc.

The Mexican bergamot oils, on the other hand, were found by the author to be oils expressed from the sweet lime fruit, similar to that described by Gildemeister and Hoffmann,[51] under Italian lime oil (*Citrus limetta,* Risso, syn. *Citrus limetta vulgaris,* syn. *Lima dulcis,* syn. *Lima di Spagna dolce*). The ester content of these Italian oils, which however are not produced commercially, is low. For details see "Oil of Sweet Lime," p. 331.

Suggested Additional Literature

Donald D. Mossman and Marston T. Bogert, "Bergamot Oil," A.Ph.A. Monograph No. 2 (1941), The American Pharmaceutical Association, Washington, D. C.

Francesco La Face, "Macchine Pellatrici nell'Industria del Bergamotto," *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **18** (January–March 1948), No. 1, 3.

Bartolo Gandalino, "Le Vicende Della Cultura del Bergamotto," *ibid.,* No. 1, 10.

[51] "Die Ätherischen Öle," 3d Ed., Vol. III, 109.

OIL OF PETITGRAIN BERGAMOT
(Bergamot Leaf Oil)

Essence de Petitgrain Bergamote *Aceite Esencial Petitgrain Bergamota*
Petitgrain Bergamottöl

The leaves gathered in the process of trimming the bergamot tree, *Citrus aurantium* L., subsp. *bergamia* (Risso and Poit.) Wright and Arn., are occasionally steam distilled and yield the so-called oil of petitgrain bergamot (cf. section on "Oil of Petitgrain Bigarade"). The oil is produced in Calabria (Italy), the annual production amounting to only a few hundred kilograms of oil. Larger quantities could, however, be produced if the demand warranted it.

The yield of oil depends upon several factors, viz., the age of the trees, the condition of the leaves, the month of the harvest, and the method of distillation.

La Face [1] proved that the foliage of young bergamot trees (which have just begun to bear fruit) yields 0.403 per cent, that of older trees 0.328 per cent of oil. Freshly trimmed foliage yields 0.380 per cent; after three days of storage the foliage yields 0.290 per cent; after ten days, 0.195 per cent of oil. The yield of oil decreases as the season advances; La Face thus reported a yield of 0.352 per cent for February, 0.333 per cent for March, and 0.228 per cent for April, the three months during which the bergamot trees are trimmed in Calabria. So far as the method of distillation is concerned, bergamot leaves should be distilled as rapidly as possible, and with direct steam, to prevent hydrolysis of linalyl acetate, the principal constituent of petitgrain bergamot oil (cf. section on "Oil of Petitgrain Bigarade Italian").

Oil of petitgrain bergamot has a petitgrain bigarade-like odor with a strong suggestion of bergamot.

Physicochemical Properties.—An oil examined by Gulli [2] had the following properties:

Specific Gravity	0.870 to 0.873
Optical Rotation	+25° 0′ to +26° 0′
Ester Content, Calculated as Linalyl Acetate	32.0 to 34.0%
Solubility	Soluble in 1 vol. of 90% alcohol

[1] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* No. 4–6 (1942), 5.
[2] *Chemist Druggist* **60** (1902), 995. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 102.

The oil contained some methyl anthranilate.

Another oil of bergamot petitgrain, with properties quite different from that above, was described by Giuffré: [3]

Specific Gravity at 15°	0.8915
Optical Rotation at 15°	−2° 30′
Refractive Index at 20°	1.4603
Ester Content, Calculated as Linalyl Acetate	58.39%
Citral Content (Romeo Method)	2.21%
Evaporation Residue	1.70%
Solubility	Soluble in 2 vol. of 70% alcohol

On still another oil Albricci [4] reported these properties:

Specific Gravity at 15°	0.8991
Optical Rotation	−5° 0′
Saponification Number	199.73
Ester Number after Acetylation	213.69
Citral Content	2.10%
Solubility	Soluble in 3 vol. of 70% alcohol

Glichitch and Naves [5] investigated a bergamot leaf oil of the following properties:

Specific Gravity at 15°	0.8938
Optical Rotation	+4° 26′
Refractive Index at 20°	1.4655
Acid Number	1.96
Ester Number	120.75
Ester Number after Cold Formylation	247.45
Solubility	Soluble in 2.8 vol. and more of 70% alcohol

Chemical Composition.—According to Glichitch and Naves,[6] the oil described above contained the following constituents:

Citral. About 2.8 per cent. Identified as naphthocinchoninic acid compound m. 200°.

Decyl Aldehyde. Very small quantities. Semicarbazone m. 102°.

Furfural. Reaction with aniline hydrochloride.

[3] *Rivista ital. essenze profumi* **6** (1924), 25. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 102.

[4] *Parfumerie moderne* **19** (1926), 252.

[5] *Parfums France* **7** (1929), 252.

[6] *Ibid.*

d-Limonene. β-Nitrolpiperidine m. 110°.

Dipentene. β-Nitrolpiperidine m. 152°–153°.

An Aliphatic Terpene(?). Traces only. The oil contained altogether 13 per cent terpenes.

l-Linaloöl. About 55 per cent, free and esterified; α-naphthylurethane m. 52°.

d-α-Terpineol. About 6 per cent, free and esterified. Phenylurethane m. 110°–111°.

Geraniol and Nerol. About 6 per cent, free and esterified. Diphenylurethane m. 81°–82° and 52°–53°, respectively.

Sesquiterpenes(?). About 0.5 per cent.

Sesquiterpene Alcohols(?). About 0.3 per cent.

Acetic Acid. In combined form.

Higher Molecular Acids(?). Traces only; in combined form.

Phenols(?). Traces only.

Free Acids(?). Traces only.

Methyl Anthranilate. Traces only; picrate m. 104°.

Pyrrole. Traces only.

Other Basic Compounds(?). Traces only.

The composition of bergamot petitgrain (bergamot leaf) oil thus resembles that of petitgrain bigarade oil.

Use.—Oil of petitgrain bergamot is used in a few types of eaux de Cologne, perfumes, and soaps to which it imparts a strong and refreshing petitgrain and bergamot note.

OIL OF CITRON

Essence de Cédrat *Aceite Esencial de Cedrato (Cidra)* *Cedratöl*

History and Description.—The citron, *Citrus medica* Linn., has a very thick peel which enables it to last an exceptionally long time. In the earliest days of navigation this keeping quality was of prime importance, and quite likely the Phoenicians carried this hardy fruit on their boats during their long voyages. Thus, the citron was the first citrus fruit to reach all Mediterranean shores and was for a long time the only one known to Europeans. Although probably a native of East India, it has been grown

since time immemorial in China, and reached Mesopotamia in remote antiquity; from there it became known finally to the Phoenicians, Greeks, and Romans. Together with the other citrus fruits, the citron was introduced to the New World immediately after the discovery by Columbus. However, Southern Italy remains to this day the center of citron production.

Only a small part of the crop is sold as fresh fruit, the bulk being prepared as peel in brine and shipped in barrels. Candied citron peel, for which the fruit is mainly employed, has almost completely supplanted the use of fresh peel.

The essential oil of citron is almost never produced and has, therefore, no commercial importance.

Physicochemical Properties.—The physicochemical properties of the oils described in literature are not well defined, probably because authentic oils have seldom been examined; or the botanical origin was not stated properly, due to confusion and contradiction regarding the local names of the citron varieties grown in Italy, i.e., the acid citron, the sweet citron, and perhaps even the sweet variety of lemon.

Chemical Composition.—The same uncertainty applies to the chemistry of this oil, which has not been thoroughly investigated.

The Schimmel chemists [1] established the presence of *citral;* whereas Burgess [2] reported the occurrence of *limonene,* some *dipentene,* and about 6 per cent of citral in an oil, the authenticity of which was later assailed by Gulli.[3]

OIL OF PETITGRAIN CITRON
(Citron Leaf Oil)

Literature describes several specimens of an oil derived (by steam distillation) from the leaves and twigs of the citron tree, *Citrus medica* L. Commercially, the oil is almost unknown.

Physicochemical Properties and Chemical Composition.—Trabaud [1] reported on an oil of petitgrain citron distilled in 1938 in the highlands of French Guinea (West Africa):

Specific Gravity at 15°	0.8730
Optical Rotation	+47° 20′

[1] *Ber. Schimmel & Co.,* October (1895), 18.
[2] *Analyst* **26** (1901), 260.
[3] *Chemist Druggist* **62** (1903), 22.
[1] *Riechstoff Ind.* **13,** No. 6 (1938), 124.

Refractive Index at 20°	1.4799
Acid Number	1.2
Ester Number	14.9
Ester Content	5.2%
Aldehyde Content (by Oximation, Calculated as Citral)	29%
Solubility	Soluble in 1 vol. of 85% alcohol and more

According to Dumont,[2] the properties of oil of petitgrain citron produced in French Guinea vary within these limits:

Specific Gravity at 15°	0.8645 to 0.8655
Optical Rotation	+55° 0′ to +56° 30′
Refractive Index at 20°	1.4772
Acid Number	0.9 to 1.0
Ester Number	22.4 to 24.2
Ester Content	7.8 to 8.5%
Ester Number after Acetylation	133
Solubility	Soluble in 2.4 to 5.5 and more volumes of 85% alcohol

The oil contains 29.5 to 33.5 per cent of aldehydes (calculated as citral), and 40.7 per cent of total alcohols.

The odor of the oil is pleasant, fresh, floral, and somewhat reminiscent of lemon.

Hosking[3] described an oil of petitgrain citron (yield 0.24 per cent) distilled in Samoa from the leaves and twigs of *Citrus medica* L., locally called "Tipolo Patupatu":

Specific Gravity at 19°/19°	0.8559
Optical Rotation	+52° 5′
Refractive Index at 12°	1.4770
Acid Number	1.4
Ester Number	10.1
Aldehyde Content (Bisulfite Method)	40%
Solubility	Not soluble in 10 vol. of 70% alcohol

Use.—The oil has been suggested for use in eaux de Cologne and in certain perfume compositions to which it imparts a refreshing top note.

[2] *Soap, Perfumery & Cosmetics* **13** (1940), 127.
[3] *Perfumery Essential Oil Record* **24** (1933), 2.

OIL OF LIME

Essence de Limette *Aceite Esencial de Lima* *Limettöl*
Oleum Limettae

Introduction.—The varieties of the lime fruit have been little studied, and but a few have been named. They fall into two distinct groups, the acid limes and the sweet limes, the latter being insignificant so far as oil production is concerned.

According to Swingle,[1] the lime is a distinct species, *Citrus aurantifolia* Swingle, not closely related to any other species of *Citrus*. However, limes hybridize freely with other species of *Citrus*, and many such hybrids are found in the East Indies.

History.—Very probably the lime is a native of the East Indian Archipelago, whence it was brought to the Asiatic mainland and to many tropical and subtropical regions of the world. In the author's own opinion, it is even possible that the lime reached the western coast of central and northern South America (Colombia, Ecuador) via the Pacific islands, carried by the Polynesians, those great navigators who sailed the Pacific probably as far as the American west coast, using the South Sea islands as stepping stones. This hypothesis would account for the great abundance of wild limes in the jungles and little known areas of tropical central and northern South America, particularly on the Pacific coast.

So far as the lime in Europe is concerned, it was apparently brought from India to Persia, Palestine, Egypt, and Europe by the Arabs, at about the same time as the sour orange and the lemon. It was first mentioned in Arabian literature of the thirteenth century. Sir Thomas Herbert noticed the lime on the island Mohéli in the Comoro group in the course of a voyage begun in 1626. Most botanists today agree that the lime was brought to the Americas by Spanish and Portuguese explorers in the early part of the sixteenth century. It escaped from cultivation in the West Indies, in Central America, and in southern Florida, and now grows wild, semiwild and cultivated over large areas.

The Acid Limes

The acid varieties of lime fruit are subdivided into several distinct groups, the most important being the Mexican, or West Indian, or Key group, and the Tahitian group.

[1] H. J. Webber and L. D. Batchelor, "The Citrus Industry," Vol. I, 402, Univ. Calif. Press (1943).

The true acid, Mexican, West Indian, or Key lime is considered the type of the species *Citrus aurantifolia* Swingle. Formerly, it had been classified as *Citrus medica* L., var. *acida* Brandis. The trees are small, bushy, thorny, frost-tender, with fine twigs and small leaves, all producing small acid fruit with very thin rinds. The tree is very susceptible to the withertip fungus (*Gloeosporium limetticolum*) but nearly immune to the citrus scab (*Elsinoë fawcetti*). It is the older type, which was much in demand during the days of sailing ships. These vessels were often called "lime juicers," because the crews depended on this fruit, or rather its juice, to prevent scurvy.

The lime fruit and juice industry originated in the West Indies, largely on the British islands of Antigua and Barbados, both heavy sugar producers with large slave populations. In the first decades of the nineteenth century the lime tree was cultivated in Dominica on only a small scale. However, about 1850 more intense cultivation was begun on the island of Montserrat, which in time became the headquarters of the lime industry, remaining so until superseded by Dominica.

The large-fruited, acid, Tahitian, Persian, or seedless lime: These trees are larger, more spreading, more cold resistant than the above variety; the twigs are coarser, nearly thornless, the leaves much larger and of different shape, the fruit also larger (from 2 to 2½ in. in diameter and 2½ to 3 in. in length), and almost totally seedless. The rind is thin, smooth, and glossy; the pulp, fine-grained and juicy. The odor, although resembling that of the Mexican fruit, is less pronounced; the flavor, although fully as acid and with no disagreeable after taste, does not have the same pronounced lime bouquet. Nevertheless, its flavor and greenish pulp make it easily distinguishable from the lemon. The Tahitian lime is almost immune to the withertip fungus, but somewhat susceptible to the citrus scab.

According to Webber,[2] the varieties of the Tahitian group differ from the true, Mexican, West Indian, or Key limes in that the former approach the characteristics of the lemon. It thus appears possible that the Tahitian group may have arisen through hybridization of the lime and the lemon. If this theory is correct, the Tahitian lime should strictly be classified as lemonime.

Commercial plantings of the Tahitian lime are located chiefly in southern Florida, where it is propagated principally on rough lemon stocks. Plantings have been greatly extended in the past few years, as the consuming public is becoming gradually educated to accepting a large fruit, instead of the smaller West Indian lime.

In Mexico practically all lime trees are of the true acid, spiny type, but in the West Indies there exists also the spineless Persian or Tahitian lime.

[2] "The Citrus Industry," Vol. I, 619, Univ. Calif. Press (1943).

The latter was first noticed in Dominica and grown from seedlings by H. F. Green, Curator of the Botanical Station. From there it was later distributed in Dominica and to other islands—Trinidad and Montserrat among them. About 75 per cent of the seedlings come true to type.[3]

The Persian variety is said to be suitable more for cultivation in dry localities near the coast than in the elevated, humid districts. Strength of growth combined with good fruiting qualities are important factors. An experimental plot of the spineless variety yielded per tree and year slightly more than one barrel of fruit (160 lb.) over a period of six years, an excellent return considering that the trees were planted as close as 12 by 12 ft.

The lime trees in the West Indies have been, in the past, propagated mainly from seedlings. Within recent years, however, comparatively large areas of mature seedling trees have died, from still undetermined causes. The usual symptom is the death of sections of the root system, followed by the death of corresponding sections of the stem and branches. To prevent premature death, attempts have been made to bud the trees on rootstocks of the sour (bitter) orange tree. Such budded trees seemed to promise a more satisfactory growth, as well as resistance to root diseases and pests. In addition, the stronger root system affords better support for the trees during hurricanes. However, Fennah [4] reports that West Indian lime trees budded on sour orange root show marked signs of physiological maladjustment of scion and stock. He attributes the slow growth and the generally lower yields of budded trees to some incompatibility of stock and bud. Budding on sour orange stock now is condemned on the island of St. Lucia, and the local department of agriculture advises using wild grapefruit stock of a certain type. To Trinidad growers, faced with the immediate problem of how to replace dead trees, the use of two stocks simultaneously has been suggested.[5] With such an arrangement the stocks should be planted alternately in the rows.

It should be mentioned in this connection that the yield of fruit per acre from seedling lime trees is much higher than that from budded trees. Details will be found in the section "Yield of Fruit per Acre." The yield of lime oil per barrel of fruit from seedling and budded trees is the same.

In Mexico (as we shall see later) the lime tree has been propagated only recently, and chiefly from seedlings.

[3] "Lime Cultivation in the West Indies," *Great Britain, Dept. Agr. for the West Indies, Pamphlet Series* No. 72 (1913).

[4] Report of the First Annual General Meeting of the West Indian Limes Association, Trinidad (1941).

[5] *Ibid.*

The West Indian Lime Industry

Planting and Cultivating.—Flat or gently undulating lands are considered most suitable for lime cultivation; they may extend a considerable distance from the coast up into the valleys. It is quite possible to cultivate limes even on fairly steep slopes, provided the soil is braced by numerous boulders and the trees are carefully terraced and manured. Of course, lime trees raised on steeply sloping, former jungle, land, fed with vegetable matter from forests above the plantings, cannot be expected to bear as good crops as trees grown under more normal conditions. At any rate, if planted on the slopes of valleys, the plantings should be exposed to the sun and well protected from winds. The best crops are obtained in rich soil and sheltered locations, at altitudes ranging from sea level to 800 ft., with well distributed rainfall varying from 80 to 160 in. yearly, about 60 in. being the minimum. Limes can be grown under diverse conditions, provided the rainfall is sufficient and the dry season not too prolonged. In districts with very heavy rains, the terrain must be drained effectively. The average temperature should be about 80° F. in the shade.

So far as soil is concerned, the rich coastal plains and valleys with light, black soil offer ideal conditions; but the red soils of the uplands also are suitable. The lime tree, a surface feeder, flourishes in comparatively shallow soil overlying heavy clay. It prefers to grow amid bushes or in thickets without large shade trees. According to Hanson,[6] surrounding vegetation, such as cassava, protects the trees from scale insects during the critical period of their growth and affords necessary shade.

The seed beds should be laid out in a sheltered corner on well-drained, thoroughly tilled soil. They are 4 to 5 ft. wide with paths 2 to 3 ft. wide running between them. Before being sown, the seed must be carefully washed to remove the enveloping mucilage; this is done for protection from rats. The seed is then dried in the shade and sown before losing its vitality. The seeds are sown thinly, about 1 in. deep and 8 to 9 in. apart. When the seedlings are 4 to 6 in. high they may be transplanted to nursery beds prepared like the seed beds. For this purpose the young plants are carefully lifted with forks, the rootlets trimmed, and the stems topped. The roots are kept moist and covered while out of the ground. In the nursery beds the seedlings are spaced about 8 to 9 in. apart, so that a bed 5 ft. wide and 100 ft. long produces approximately one thousand strong plants for setting out in the fields.

[6] "The Cultivation of Lime Trees," *J. Jamaica Agr. Soc.* **41**, No. 7–8, July–August (1937), 427–433.

The lime tree is a relatively hardy plant which requires no protection from the sun. The young seedlings, however, must be treated very carefully to grow into vigorous plants with a strong root system. In order to assure such a root system, the soil of the nursery beds must be thoroughly broken up; otherwise, the young plants cannot be lifted and transplanted without damage to the roots and heavy losses. The young plants are raised in the nurseries until they are about 16 or 18 in. tall; they are then planted out in the fields. From ten to twelve months are required between the sowing of the seed and the time of setting out. Since the young seedlings speedily absorb available nitrogen from the soil, it is impossible to raise several crops in the same nursery beds unless heavy dressings of organic matter are added. For this reason, the nursery is transferred to a new location from time to time.

The seedlings should be planted in the fields between June and December, and preferably in June or July, to assure satisfactory growth before the dry season commences. For this purpose the seedlings are lifted from the nursery beds with forks, and the ends of the branches cut back 3 or 4 in. Any damaged or torn roots should be trimmed carefully with a sharp knife. The plants are then bundled, placed in baskets, and carried to the fields. The roots are kept moist continuously; they must never be permitted to become dry or exposed.

On land previously cultivated, small, very slightly raised beds are forked; but on newly cleared jungle land, holes about 18 in. deep and 12 to 15 in. square should be dug before planting out. In very heavy soil, however, the system of holes is not advisable, because they easily form water traps during the rainy season, causing root decay and growth arrest, if not death. The depth of the planting should be about the same as that at which the seedlings grew in the nursery beds, this depth being clearly indicated by the color of the stems. Too deep planting should be avoided. After planting, the space around each plant is kept clean and tilled. Brush and grass springing up are cutlassed. Any trenching necessary to drain the soil or prevent washing away should be done before planting, as it may be injurious to the young trees.

Spacing the plants properly is very important, and has much bearing upon the future growth of the crops. Although the lime tree develops a tap root, most of the feeding is done through a very wide system of fine rootlets close to the surface of the soil. Crowding of the trees causes crowding of the tops, many branches then becoming so interlaced that they die. Trees attain a greater size in hot valleys near the coast than in the hills. On steep slopes where conditions of growth are not so favorable, a distance of 12 by 12 ft. or 12 by 14 ft. may be sufficient, but on fairly good land

15 by 15 ft. or 16 by 16 ft. is the usual distance. In localities of very good soil and abundant rainfall, 20 by 20 ft. is preferable; whereas on exceptionally rich soil 25 by 25 ft. is not too wide. It has been a common mistake to plant the trees too close rather than too far apart. Adequate provision should be made for roads, drainage, and windbreaks. The trees must be planted in straight rows to allow for drainage. Exposure to wind has a dwarfing effect upon the lime tree and causes the flowers to fall off easily. Therefore, hedges should be planted as windbreaks, if the higher surrounding land does not afford protection. *Calophyllum calaba* and *Inga laurina* may be used as permanent windbreaks, and sugar cane and *Glyricidia maculata* make good temporary shelters. The weeds around the young plants are kept down by cutlassing. During growth of the trees a great deal of spraying is necessary.

Since the root system of the lime tree feeds on the surface, tillage must be performed very carefully. It is necessary to maintain the humus by careful green dressing, mulching, and green (perhaps artificial) fertilizing.

Soil, climate, and method of planting are the main factors influencing growth of the trees and bearing of fruit. Under favorable conditions the trees may yield small crops in the third year after planting, but in general they require eight to ten years to reach the full bearing stage. If grown under suitable conditions and undamaged by withertip diseases, root rot, insect pests, or hurricanes, the trees reach a considerable age without losing their vitality. Plantings are in existence which are forty years of age (and older) and which still exhibit no diminution of fruit bearing capacity. The trees require little pruning, except that all water suckers and dead branches must be removed, because they tend to choke the bearing branches and cause them to die. If a tree loses a main branch, the wounded surface is smoothed and tarred, and fresh growth is trained. When the main branches are formed, the weak under branches are cut off.

Harvesting.—An interesting fact about the lime tree is that it bears flowers and fruit simultaneously and all year around. Hence, small quantities of fruit may be collected throughout the year. The main harvest, however, extends from June–July to November–December, during which period the trees are in full bearing. (The date of harvest is frequently dictated by the demand for fresh lime fruit.) Four to six months are required for development of the fruit, i.e., from flowering to ripening. Fruit which ripens between June and December is developed from flowers appearing between February and June.

The produce of a lime plantation is marketed either in the form of fresh edible fruit or in the form of by-products, such as clear juice, concentrated juice, distilled and coldpressed oil, and citric acid. As the fruit ripens on

the trees it turns from green to yellow; when fully ripened it drops to the ground. For shipment as fresh limes, the fruit must be picked as it reaches full development, just before the process of ripening begins. Fresh limes are generally green limes; in other words, they are green in the sense of not being fully ripened. They must be green to be accepted on the market. No native of the West Indies would ever think of using a fully matured yellow lime for making a beverage. By the time the originally green fruit reaches consumers in America and England, it may already have begun to turn yellow and ripen.

In practice, the harvesters go through the orchards and pick both green and yellow fruit, including windfalls and over-ripened fruit which has dropped to the ground. On some islands ladders are used in picking the fruit that cannot be reached by hand, or the harvesters employ long hooked staffs to reach and pull down the limes, which are collected in baskets. Obviously, it is much cheaper to harvest green and yellow fruit simultaneously. The value of the green fruit is perhaps three times that of the yellow, much of which may be picked up from the ground.

The harvested fruit is transported to packing houses and carefully assorted. Green fruit is wrapped in paper and packed for export in barrels; whereas the riper yellow fruit is trucked to the processing plants for conversion into juice, oil of lime, and citric acid, as we shall describe later. Whenever the market demand for green, edible fruit slackens, the portion which cannot be shipped is also used for processing. In fact, green fruit would be preferable, as it gives a higher yield and a much better quality of juice, as well as a higher yield of oil; but under normal marketing conditions green fruit is too expensive, and the better yield does not always justify the increase in cost. In most cases, the fruit employed for conversion into by-products consists of a mixture of green and yellow limes, the latter usually predominating.

Yield of Fruit per Acre.—Depending upon conditions of soil, climate, and cultivation, the yield of fruit varies greatly. Under favorable conditions it may be 150 barrels (one barrel holding 160 lb.), or even higher, in exceptional cases. For an ordinary planting, 80 to 100 barrels per acre may be considered a fair average.

According to Pereira,[7] in the original plantations of West Indian seedling lime trees, the average yield of fruit in St. Lucia was about 75 barrels per acre. However, these seedling plantations were wiped out by disease between 1934 and 1940, and some of the estates were replanted with budded lime trees. The yield of limes per acre from budded trees is only about 30 barrels.

[7] Private communication of Mr. Charles Pereira, Port-of-Spain, Trinidad, B.W.I.

Diseases, Insect Pests, and Hurricanes.—In the last twenty-five years the West Indian lime industry has suffered tremendous losses as a result of diseases, insect pests, and hurricanes, and on some islands entire plantations have been wiped out. Great efforts on the part of growers and the government are required to save the once prosperous lime industry.

1. Withertip Disease.—This is a very destructive disease of lime trees, caused by the fungus *Gloeosporium limetticolum* Clausen. Visible symptoms are ringing and tip-wither of new shoots, infection and curling of tender leaves, blighting of buds and flowers, loss of newly set fruit, and development of cankers on the fruit remaining on the tree. The withertip disease does not kill the tree. It occurs primarily in the higher altitudes where the atmosphere, due to monsoon clouds, is generally moist. In St. Lucia, for example, growing of limes in the high rainfall areas has been impossible since the first setback in 1927. Dominica suffered its worst attack in May, 1922.

2. Dieback Disease.—The general term "dying out" includes such phenomena as root disease, dieback, and dying out.

The visible symptom of this disease is a rapid drying out of the branches. Only a twig, here and there, may be affected, or whole sections of the tree, or even the whole tree itself may suddenly become dry. The more exposed branches usually show the first symptoms. Healthy and vigorous green leaves turn yellow, dry in a few days, and are shed; twigs lose their green color, become bleached, and the twig or branch dies back to the union with a larger living branch. This trouble is particularly noticeable when drought occurs.

Since about 1943 the disease has made such disastrous strides in Trinidad that production of limes on that island has already been diminished by half. Despite all the efforts by scientists of the Department of Agriculture and the Imperial College of Tropical Agriculture, both of Trinidad, to trace the cause of this disease, no effective remedy has been found.

Withertip and dieback are two entirely different diseases.

3. Red root fungus (*Sphaerostilbe repens*) grows on the underground roots and prevents them from feeding, thus killing the tree. Dominica experienced one outbreak in 1926 and a worse one in 1931.

4. Attacks by the Citrus Weevil and the Fiddler Beetle.—The lime roots are attacked by larvae of weevils of the genus *diaprepes* (root grubs) and *prepodes*. The roots are girdled or channeled by the larvae, and the tree may succumb under extremely heavy attacks. St. Lucia, Dominica, and Montserrat suffered from this blight in 1933. Fennah [8] recommends as

[8] Report of the First Annual General Meeting of the West Indian Limes Association, Trinidad (1941).

protection the baring of the crown roots and the application of lead arsenate to the soil, either as a layer on the surface, or mixed with the soil along the larger roots. The cultivation between the trees of the cover crop *Tephrosia candida,* repellent to the weevils, has been suggested. Another treatment of the problem is to select only the most vigorous trees for distribution to estates.

5. Periodical hurricanes have wrought tremendous damage on some of the islands; Dominica, for example, was ravaged in 1926, 1928, and 1930.

If any one of the islands should be exposed to a combination of the above factors within a single year its entire lime industry might be destroyed for several years.

Lime By-Products in the West Indies.—As has been pointed out, surplus limes, which cannot be exported as green, edible fruit, are processed on the spot, before spoiling, into a number of by-products—e.g., lime juice (clear and concentrated), lime oil (distilled and coldpressed), and citric acid.

In the days of sailing ships, no British man-of-war would have ventured on a long cruise without ample supplies of concentrated lime juice. Vitamins were unknown then, but painful experience had shown that lime juice prevented outbreaks of scurvy, the ancient scourge of mariners.

The West Indies prospered from the export of lime juice to North America and Europe. The trade continues to this day, on a smaller scale, because lime juice is used widely in English-speaking countries for refreshing hot weather drinks, alcoholic and nonalcoholic, and for cocktails.

Prior to the discovery of the modern process of making citric acid biologically, it was extracted in the West Indies from lime juice by precipitating the acid as calcium citrate. There was always a good demand from abroad for lime juice and calcium citrate (citric acid), and prices for these products were so high that distilled lime oil—another by-product—could be sold cheaply. This afforded simply an incidental profit, since the main commerce was in lime juice and calcium citrate.

Changes in the Lime Industry.—Since discovery of the cheaper process of making citric acid and the introduction of numerous vitamin-containing preparations, the whole aspect of the West Indian lime industry has undergone a fundamental change. Citric acid made from lime juice can no longer compete with the synthetic (biological) product, and the demand for concentrated lime juice is so limited that many factories discard the lees, since the price hardly covers the cost of production. The main product today is oil of lime, the selling price of which must be adjusted to bear almost the entire cost of production.

Clarified lime juice has for some time been coming back into favor for lime juice cordials, and for syruped juices, which by the addition of water

may be converted into nonalcoholic, refreshing hot weather drinks, during World War II very popular with the armies and navies of the Allied Nations.

Chief Use of Lime Oil.—Distilled lime oil is the chief flavoring ingredient of carbonated, nonalcoholic beverages of the ginger ale type, as well as of the popular "cola" drinks, and of ice creams, baked goods, confectionery and candy.

There exists also a limited demand for the so-called "coldpressed" or *"écuelled"* oil of lime, which possesses a very fine, true-to-nature odor and flavor. Its high price has always prevented wider application.

Handpressing of Lime Oil.—In the West Indies most of the so-called handpressed or coldpressed lime oil is still manufactured according to the old-fashioned method of *"écuelling"* described in the chapter on "The Expression of Citrus Oils." This oil is ultimately filtered and exported. Prolonged storage often causes separation of a yellowish crystalline deposit, consisting mainly of limettin.

Workers are paid according to the quantity of oil they produce, the individual's daily output depending upon his skill. A skilled operator can extract as much as 3 to 4 oz. of oil per hour, but the usual output is considerably less than this.

Yield of Handpressed Lime Oil.—Yield of oil expressed depends upon the quality and condition of the fruit—fresh, green fruit yielding more oil than yellow fruit. The yield per barrel of fruit (160 lb.) ranges from 1¾ to 4 oz. of oil, the average being 2½ to 3 oz., representing only one-quarter or one-third of the theoretical yield. This poor yield is due to the fact that the spikes of the *écuelle* not only rupture the oil sacs of the peel, but also pierce the white spongy layer of the skin, which absorbs and retains the oil.

The fruit, thus deprived of some of its essential oil, is usually submitted to further processing, but the juice obtained by crushing such fruit is inferior to juice pressed from limes not previously *écuelled.* It is deficient in essential oil and lacks richness of flavor.

Use of Machines Instead of *Écuelling.*—Several attempts have been made to replace the process of *écuelling* by machine processes. Years ago, a large operator in Dominica imported a Vinci machine, used in Sicily for the extraction of lemon oil. However, he ran into considerable difficulties, obtaining heavy emulsions of oil and cell liquid which he was unable to separate. The early Sicilian machines were constructed to treat lemons, which have much tougher and thicker skins than limes. The colloidal (albuminous, pectinous, and waxy) matter present in the lime peel, and in the white spongy layer beneath, easily forms emulsions. Perhaps it might

have been possible to overcome these difficulties by applying the Bennett-Cusmano process, which uses as carrier fluid (for washing the expelled oil from the fruit) a dilute solution of sodium bicarbonate and sodium sulfate. The emulsion is separated by centrifuging, and the aqueous portion is used over and over again (cf. section on "The Expression of Citrus Oils").

In the years preceding World War II, some of the Sicilian machines, especially the Avena machine, were greatly improved by the insertion of specially constructed corrugated metal and glass plates. This alteration made it possible to process even the thin-skinned lime in these machines.

In Mexico, as we shall see later, coldpressed lime oil is made, not by *écuelling*, but by crushing the entire fruit under heavy pressure and running the oil-containing juice through high-speed centrifuges (separators). The disadvantage of this method is that the oil is diluted in a great volume of liquid, which dissolves part of its important oxygenated constituents.

Both coldpressed and *écuelled* lime oils have an odor and flavor quite different from those of the distilled oil. The latter has a peculiar, fresh, "limey" note which makes it particularly popular in candies and especially in soft drinks; whereas the pressed oils are more reminiscent of the fruit peel. As we shall see later, distillation alters the chemical composition of the oil as it occurs in the peel, whereas pressed oils show a considerably higher content of esters and aldehydes and especially citral. However, the lower yield of expressed oil necessitates higher prices; and this factor has always prevented the wider use which the expressed oil, with its true-to-nature character, merits. It is quite possible that the employment of some of the latest Sicilian machines, which produce a good quality of lemon oil, would give a much higher yield of lime oil than the old method of *écuelling* the fruit or of centrifuging the juice.

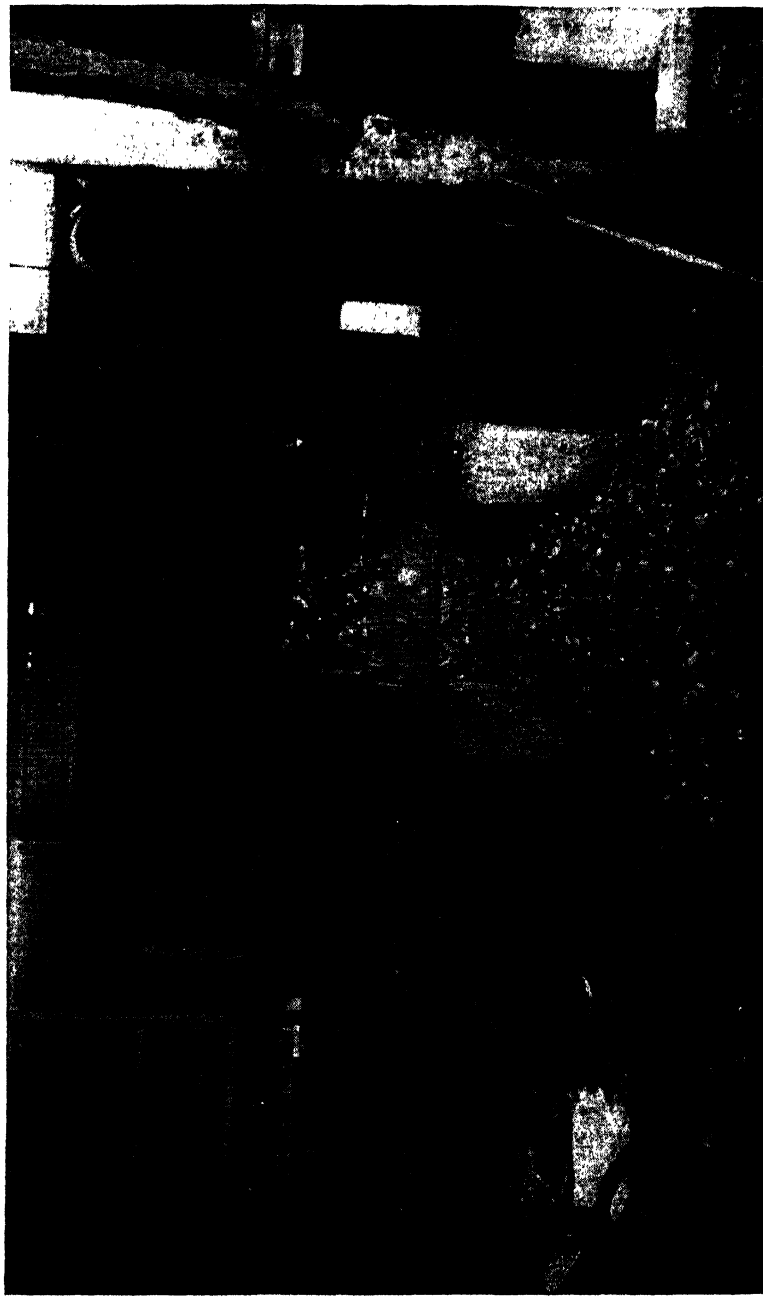
Expression of Lime Juice in the West Indies.—As has been explained, only a very small percentage of the surplus fruit is worked into expressed oil, the bulk being processed for lime juice and distilled lime oil, preparation of these two products usually going hand in hand. It is possible to use for this purpose fruit which previously had been submitted to *écuelling*, but such fruit gives a lower quality of juice and an inferior yield of distilled oil. To obtain richly flavored juice of the highest quality, only sound, fresh limes must be employed.

The surplus fruit arriving from the packing houses is worked up immediately in the processing plants. Any delay causes deterioration of the fruit, with resulting inferior quality of juice and lower yield of oil. Damaged or rotting limes must be eliminated. The sound fruit is washed either by floating in a water tank or by spraying with a hose.

The fruit is then crushed in a mill equipped with two sets of heavy

rollers. In most cases such mills are the old type of sugar cane crushers. One set of rollers is constructed of iron, the other of stone (granite), the latter yielding a lime juice more suitable for edible purposes than that yielded by the iron roller. Each set consists of three heavy cylinders, the two lower ones rotating in one direction, the upper one in an opposite direction. The first cylinder is provided with fine grooves and runs on fixed bearings. The distance between the cylinders is kept as small as possible; during operation it is about one-eighth of an inch. The iron cylinders turn about eight times a minute, and the smaller stone cylinders turn faster. The latter are 24 by 12 in. in size and require 3½ h.p. The larger (iron) ones, 32 by 12 in. or 36 by 16 in., require 5 h.p. and 7½ h.p., respectively. Power is supplied by old-fashioned water wheels or steam; more recently motors have been employed. Beneath each set of cylinders is a wooden box into which juice, pulp, and pits drop. Waste peel ejected at the end of the mill is either fermented and used as cattle feed or simply discarded. The juice, pulp, and pits run from the wooden box into a system of strainers made of brass or copper wire, the first screen being $\frac{3}{16}$ in. mesh, the second $\frac{1}{8}$ in. mesh. Rotary screens are even more effective. They consist of fine mesh, cylindrical, copper sieves, supported and strengthened by a surrounding perforated copper sheet. Brushes attached to a revolving axle in the center pass over the sieve, keeping it clean and pushing the refuse toward the end of the cylinder, where it is ejected.

To replace the above described, old-fashioned sugar cane mill, a novel type of fruit crusher has been introduced. It is small, light in weight, efficient, and relatively inexpensive. If heavy production should require it, several of the machines can be installed, each coupled with a 5 h.p. motor. This apparatus, known as Fruit Press "Sep-Ro-Siv," is manufactured by the Enterprise Manufacturing Company of Philadelphia. The washed fruit runs into the hopper and passes from there to the screw press, a tapered "worm," the recessed part of which continuously diminishes. Tremendous pressure is thus exerted on any material fed into the machine, which is similar to the food grinders of household use, except that the ordinary food grinder is surrounded by a solid casting, whereas the "Sep-Ro-Siv" employs a perforated casting, through which liquids are extruded and solid material passed on. The crushed waste peel is finally ejected, and juice and fine pulp run off through slits in the casing beneath the screw press. The pressure in the apparatus can be adjusted according to the condition of the fruit. The waste peel is practically free of oil; if it is not, however, it can be run through the press again. The juice and pulp flowing from the perforations are strained through metal screens, because thick juice, when distilled, releases the essential oil more slowly than strained



Courtesy of Fritzsche Brothers, Inc., New York.

Crushing of lime fruit prior to distillation of juice, Trinidad, B.W.I.

juice. Thin juice, furthermore, gives less trouble during the process of precipitating calcium citrate. If necessary, the heavy pulp is treated with warm water while being strained, to wash out the essential oil.

Yield of Juice.—The yield of juice varies according to the condition of the fruit; fruit grown in humid districts and during the rainy season contains more moisture than fruit raised in a dry atmosphere. On the average, a 160 lb. barrel of limes yields about 7½ gal. of juice, or about 62 per cent of the total weight of the fruit.

With lower pressure in the mill, a finer quality of juice, more suitable for use in beverages, may be obtained. It is important to adjust the cylinders properly, since under ordinary conditions the amount of juice left in 100 lb. of pressed skins varies from 1.8 to 4.3 gal. Tempany and Weil [9] calculated that one barrel of limes yields about 80 lb. of skins. These authors assume that even with very efficient crushing there is an unavoidable loss of 1½ to 1⅔ gal., sometimes even of 2 gal., of juice per barrel of fruit. Imperfect adjustment of the cylinders may be responsible for a loss of 1 gal. of juice per barrel of fruit, or 12 to 14 per cent of the output. In some instances the ejected lime peel is squeezed in presses similar to the well-known cider presses, to recover any remaining juice and oil.

The mills must be kept very clean, because impurities would cause fermentation and loss of acid in the succeeding batch of lime juice.

Storage of Juice.—The juice flowing from the iron rollers is immediately and without further preparation used for distilling oil. The higher quality of juice running from the stone rollers is pumped into large wooden tanks and stored until ready for export. Time of storage lasts usually one month, but may be shortened, if necessary, to a minimum of sixteen days; it permits the heavier muck to settle at the bottom and the fine, light pulp to rise to the surface. The high acidity and low sugar content of the juice retards fermentation. It is also claimed that the fine film of essential oil forming on the surface of the juice protects it from bacteria in the air, but this contention is unproved.

After a period of storing and settling ranging from sixteen to thirty days, the intermediary layer of juice will be quite clear and can be drawn off through a wooden cock attached to the storage tank. After filtration (simple straining through cloth), the clear juice is filled into wooden casks and protected from fermentation by the addition of sulfur dioxide (350 parts to one million parts of juice) or by sodium benzoate (⅒ of 1 per cent). The choice of preserving agent depends upon the import regulations of the countries to which the juice is shipped.

The wooden casks are made impermeable by pouring in heated wax and

[9] "Lime Cultivation in the West Indies," *Great Britain, Dept. Agr. for the West Indies, Pamphlet Series* No. 72 (1913).

then rolling them. Afterward they are filled with water and kept standing for a few days to check any leakage.

Export of Juice.—There are two types of juice:

1. The clear juice, prepared as described above, and known as "settled" or "racked" juice. It should be clear and sparkling, of typical rich lime flavor and of a certain acid content. An average fresh lime juice contains 12½ to 14 oz. of citric acid per gallon; some juices, however, may contain as much as 16 oz. Rainfalls and moisture-retaining soil have a marked influence upon the acid content, juice of highest acidity being produced from limes grown during the dry season and on well-drained soils. It is said that large fruit yields a juice of lower acidity. Quite possibly abundant moisture results in larger fruit and the two facts may be related. It also appears that fruit grown on older trees yields juice of a higher acidity than fruit grown on young trees. In fact, there is a variation in the acidity even of the fruits of certain trees of the same variety grown under identical conditions.

The "settled" or "racked" juice is sold in wooden casks, so-called "hogsheads," of 50 to 100 imperial gal. The main countries of import are Great Britain, the United States, and Canada.

2. The juice containing light, fine pulp, with the essential oil floating as a thin film on the surface. This is the complete juice of the lime, but free of the heavy muck which settles on the bottom of the storage tanks. Known in the trade as "top juice with pulp and oil," it is exported in hogsheads of 50 to 100 imperial gal. chiefly to Great Britain, the United States, and Canada. Small quantities of this juice are used by essential oil houses in England for distilling lime oil. Most of it, however, is employed in the West Indies for the same purpose, as we shall see later.

One barrel of limes yields about 10 gal. of "top juice with pulp and oil" but only 6 gal. of clear "settled" or "racked" juice.

According to the definition of the West Indian Limes Association, agreed upon at the First Annual General Meeting in Trinidad, April, 1941:

(a) "Top pulp juice" shall be taken to mean the entire juice of the fruit, containing oil.

(b) "Clear, clarified, filtered, racked or settled juice," shall be juice free of oil.

Keeping Qualities of Lime Juice.—The high acidity and the essential oil contained in the juice doubtless enhance the keeping quality of lime juice, and preservatives are added only to make certain that the juice withstands the long transport abroad. Even without preservatives, lime juice keeps

well for quite some time, provided it has been prepared under favorable conditions and stored in clean, sound casks.

Juice derived from unsound fruit is apt to deteriorate rapidly, even though properly stored. Such juice, employed only for making calcium citrate, must be processed as quickly as possible or it will lose a considerable amount of its acid content. Deterioration is caused by molds and aerobic ferments.

Concentrated Lime Juice.—In order to reduce the cost of freight, lime juice is sometimes concentrated to contain at least 64 oz. of citric acid per gallon. The process of concentrating usually brings about loss of acid by heat. This reduction may be as high as 10 per cent when direct fire heating is employed, or as low as 2 per cent if evaporation vats equipped with steam coils are used.

Distillation of Lime Oil.—As has been stated, the preparation of lime juice, distilled lime oil, and calcium citrate usually go hand in hand. Before the introduction of the cheaper biological process of making citric acid, distilled lime oil was considered a by-product, emphasis being placed on the usually quite profitable manufacture of juice and calcium citrate. Today the most important product is distilled lime oil, for which there is great demand from the soft drink, candy, and food industries.

Any type of lime juice may be used for oil recovery (distillation), provided it contains sufficient essential oil. The so-called "top juice with pulp and oil" is particularly adapted to this treatment; but the crude juice, as it runs from the iron rollers, can also be employed. In practice, the manufacturer is guided by the overseas demand for juice and distilled oil, and by prevailing market prices; he would probably submit all surplus juice to distillation rather than have it spoil from fermentation.

The juice running off the presses contains the essential oil of the peels partly in solution, partly in suspension. It is only necessary to recover it by distillation. For this purpose the juice is brought to a boil, the resulting steam and essential oil vapors are reliquefied in a condenser, and the essential oil is recovered in a Florentine flask.

Method of Distillation.—The following describes the actual working process: the juice which runs off the metal cylinders is strained and immediately distilled, this quality not being good enough for export. The juice running from the stone rollers, on the other hand, is first pumped into settling tanks, as described above, and, after sixteen to thirty days of settling, the "top juice with pulp and oil" is distilled. The middle layer, the so-called "settled, clear or racked" juice, is exported on demand. The upper and lower layers are pumped from the settling tank into another wooden tank,

usually located above the stills; from there they flow by gravity into the stills, care being taken to keep out the heavy bottom muck.

Most of the stills are constructed of copper, but wooden stills, too, give good service. In general, they are all simple, some even primitive. A few are heated with direct fire, but the majority by steam, either directly or indirectly or both. Every producer has his own preferences and works according to personal experience. Some distillers prefer steam jackets, others prefer steam coils, by which the juice is brought to a boil. A large producer in Port-of-Spain discarded the indirect steam coils, as sources of too much trouble, especially when the juice contains much pulp. The steam pressure in the jackets or coils varies from 22 to 30 lb. per sq. in. Other distillers prefer direct live steam, which enters the still through a perforated steam coil. In this case the steam pressure in the steam gage needs to be only 2 to 3 lb.

The stills, which usually hold several hundred gallons, are filled with juice and light pulp to about three-quarters of their height. Water is added only if bottom muck from the settling tank has entered the still. The addition of juice running off the iron rollers usually suffices to dilute the still content to the extent that distillation can be carried out without difficulty.

The length of distillation depends upon size of stills, their construction, and efficiency of the condenser system, together with availability of cooling water. Some of the islands occasionally suffer from shortage of water, and distillation then takes longer. The length of distillation depends, furthermore, upon consistency of the juice, a thicker still content requiring more time. Another factor is the ripeness of the fruit, juice from yellow, ripe limes distilling more slowly. Distillation of one batch thus lasts 4 to 16 hr., the average being about 9 hr.

The oil should distill almost water-white, a pronounced yellow color indicating too rapid distillation or too high steam pressure. Premature interruption of distillation gives an inferior oil, consisting mainly of low-boiling terpenes and lacking in oxygenated constituents. During the first hours of operation, oil and water separate easily in a simple Florentine flask. Later the higher boiling constituents, some of them more water soluble, distill over, and slight emulsion may occur. To recover those valuable compounds, it is advisable to connect several sufficiently large Florentine flasks, care being taken to regulate the flow so that oil and water separate completely. Any violent agitation of the oil layer in the oil separator by the inflowing distillate should be avoided as this might cause considerable loss of oil.

Distillation must be carried out very carefully; it should proceed gently

and slowly with steam of low pressure except, perhaps, for the last hours of the process. A too rapid current of live steam or too high temperature might impart a yellow color to the oil and "burn" it. The live steam should bubble gently through the mass, just fast enough to keep the liquid stirred so that it does not burn against the hot walls of the steam jacket. Such is the accepted practice of most distillers for obtaining the quality of lime oil to which the trade has become accustomed. As we shall see later, rapid distillation with steam of higher pressure gives oils of a different chemical constitution containing considerably more citral.

One hundred gallons of juice yield on the average 4 to 5 lb. of distilled lime oil. Of course, if the limes have been *écuelled* previous to crushing, the yield of distilled oil is correspondingly lower.

Yield of Distilled Lime Oil.—Depending upon the condition and size of the fruit, a barrel of limes (160 lb.) yields normally about 8 oz. of distilled oil. Select, green, very fresh limes may give as much as 11 oz. of oil per barrel; and stale, ripe, yellow limes yield only 6 oz., or even less. The yield of oil decreases as the season advances.

According to Pereira,[10] the yield of lime oil per barrel of fruit varies with the different islands, and so does the size of the limes. It seems that a barrel of small limes, running from, say, 1,600 to 1,900 limes per barrel, will yield more oil than a barrel of larger fruit holding 1,300 limes. The plantations and estates on the more fertile islands with a heavy rainfall will produce larger limes and a greater number of barrels of fruit per acre. A more correct method of returns from the estates would be in pounds of lime oil per acre (instead of barrels of fruit per acre), or still better, both should be stated when preparing returns for statistical purposes. The yield of lime oil per barrel from seedling and budded trees is about the same.

The following yields of distilled lime oil have been observed in the various colonies of the British West Indies.

Colony	*Yield*
Dominica	8½ oz. of oil per barrel (160 lb.) of fruit
British Guiana	7.8 oz. of oil per barrel of fruit. On other authority 11 oz. of oil (from very fresh, green limes).
Jamaica	11¾ oz. of oil per barrel of fruit
St. Lucia	8¼ oz. of distilled oil per barrel of fruit. If *écuelled* oil is produced, and if the limes—after *écuelling*—are crushed, the result is 2¼ oz. of *écuelled*, and 4¼ oz. of distilled lime oil, a loss of 1½ oz. of oil being incurred.
Trinidad	9 oz. of distilled oil per barrel of fruit.

As regards Haiti, the author observed a yield of 6 to 8 oz. of distilled oil per barrel of fruit.

[10] Private communication of Mr. Charles Pereira, Port-of-Spain, Trinidad, B.W.I.

Production of a High Quality Oil.—

1. The fruit must be sound. Green limes give a juice of finer, more pronounced flavor, of higher acidity and more sparkling green color. The yield of oil is better. Oil distilled from yellow fruit has a somewhat "flat" and less pronounced odor.

2. The fruit should be crushed immediately after harvesting; otherwise it shrivels up and turns leathery, with resulting inferior yield and quality of oil. Conditions do not usually permit crushing the fruit immediately after harvesting; it must first go to the packing houses for the selection of prime fruit for export. Often several days elapse before the surplus fruit is turned over to the processing plant.

3. For easier distillation, the juice should be free of heavy pulp or muck, which precipitates after several weeks' storage.

4. Distillation should be continued long enough to collect the small quantities of higher boiling oxygenated constituents, without which the oil is not of first quality. Of course, prolonged distillation requires more fuel, and often it may appear that during the last hours practically no more oil is being recovered, for which reason most distillers stop operating. Nevertheless that small percentage of oil which distills over in the sixth and seventh hours contains important constituents, and any oil which contains these is undoubtedly worth a premium. Shorter distillation results in oils of lower specific gravity, higher optical rotation, and lower content of oxygenated compounds. High-grade lime oil should have a specific gravity of not less than 0.864 at 15°.

5. The Florentine flasks must be large enough to permit complete separation of the oil. The oxygenated compounds are more soluble in water than terpenes which distill over in the first hours. By insertion of a funnel with a long neck, into the oil separator, agitation of the oil layer by the inflowing distillate will be prevented.

New Lime Varieties.—The Department of Agriculture of Trinidad some years ago developed through cross-breeding the so-called T-1 Lime, a hybrid of the West Indian and the Philippine lime. It has the great advantage of being hardier than its parent varieties and therefore is more resistant to withertip and other diseases. Furthermore, it bears fruit beyond the normal harvest limit. However, there are several disadvantages connected with the T-1 limes:

1. The flavor of juice and oil is different, resembling that of lemon.
2. The acid content of the juice is low.

3. The essential oil of the T-1 limes does not seem to stand up; upon aging it turns "turpentinic."

The T-1 lime fruit is larger; it resembles the lemon. About 20 per cent of the Trinidad lime crop consists of this hybrid. Dominica and St. Lucia do not raise it. Since the cost of extracting juice and oil from the T-1 limes is the same as that for regular limes, there really is no advantage in producing this oil. Besides, shipments to New York have been rejected; whereas England accepts the oil at prices slightly lower than those paid for regular West Indian oil. The experiment with the T-1 limes cannot be considered successful.

Conditions on the Various Islands.—In the following pages we shall give a short survey of the recent situation prevailing on the various West Indian islands in regard to production of lime fruit and its by-products.

A. Trinidad and Tobago.—Limes are grown on estates which also produce cocoa and coconuts. There are approximately 3,000 to 4,000 acres of lime plantations. In 1916 an acre planted with 150 trees produced 20 to 40 barrels of fruit at four to five years, and 160 to 180 barrels at maturity. The present yield (about 21 barrels) is much lower, probably as a result of poorer soil and cultural conditions and of the widespread withertip disease. The yield of fruit could probably be increased by proper fertilization and manuring.

Within the last few years large areas of mature seedling trees have perished from "dieback," which has had such disastrous consequences that the production of limes on these islands has decreased by 50 per cent.

There are ten lime oil distilleries in Trinidad and one in Tobago. Exports from Trinidad and Tobago of lime oil, distilled and handpressed, during the last years read as follows:

Distilled Oil		*Handpressed Oil*	
Year	*Pounds*	*Year*	*Pounds*
1941	64,798	1938	938
1942	41,039	1939	1,148
1943	35,630	1940	1,505
1944	32,870	1941	515
1945	23,300	1946	288
1946	16,892	1947	...
1947	26,479	1948	306
1948	31,161		

B. Grenada.—In 1939 there were about 730 acres of lime plantations—a decrease of 33 to 40 per cent as compared with previous years.

The following quantities of distilled lime oil have been exported from Grenada in recent years:

Year	*Pounds*	*Year*	*Pounds*
1943	10,455	1946	8,680
1944	5,880	1947	7,687
1945	3,400	1948	10,728

C. St. Lucia.—The industry was firmly established by 1920, and the level of production was maintained until 1927, when the first attack of withertip caused a severe setback, resulting in a considerable curtailment of the areas of production, especially in the regions of high rainfall. Disease again affected the industry in 1933, when the citrus root weevil did a great deal of damage. In the following years many seedling trees died. Since then the growers have replaced dead and dying seedling trees with West Indian limes budded on sour orange stock. In 1940 about 1,500 acres were under cultivation.

The following quantities of distilled lime oil were exported from St. Lucia:

Year	*Pounds*	*Year*	*Pounds*
1943	5,833	1946	2,914
1944	4,348	1947	374
1945	4,175	1948	629

In 1948 St. Lucia exported also 175 lb. of *écuelled* oil.

D. Dominica.—The island of Dominica reached its peak of production in 1921, with over one-half million barrels of fruit, but soon afterward Dominica suffered from a number of adverse events. A severe epidemic of withertip broke out in 1922; the hurricanes of 1926, 1928, and 1930, together with the wholesale death of seedling trees from root diseases, did tremendous damage. On top of all this came the collapse of the market for concentrated lime juice. The area of budded lime trees is now about 1,500 acres and, aside from very small native owned plantings, no considerable extension is anticipated. Since 1926, the Department of Agriculture has distributed nearly 160,000 budded lime plants, mainly on sour orange stock. Wild grapefruit and rough lemon have also been tried. Advances in prices are likely to bring about an upward trend in production, but the effects of frequent hurricanes, withertip, and root rot may retard this movement. Because of the danger of withertip, it may be necessary to concentrate the production of limes within drier areas. There is some hope that the budded trees will prove longer-lived than the old seedling trees of a few years ago. The latter continue to die out. Export figures read:

Distilled Oil		*Écuelled Oil*	
Year	*Pounds*	*Year*	*Pounds*
1942	25,284	1939	18
1943	33,126	1940	...
1944	40,706	1945	3,747
1945	19,745	1946	2,944
1946	31,304	1947	1,503
1947	26,889	1948	...
1948	23,911		

E. Montserrat.—The area under lime cultivation is estimated at about 500 acres, but even this low figure is probably exaggerated, because the groves are very severely thinned, many trees and parts of trees having died. The exports were as follows:

Distilled Oil		*Écuelled Oil*	
Year	*Pounds*	*Year*	*Pounds*
1942	198	1939	2,052
1943	378	1940	981
1944	555	1941	1,165
1945	299	1945	593
1946	487	1946	601
1947	114	1947	304
1948	144	1948	667

The bulk of the crop still comes from seedling trees, but they continue to die out. Efforts are being made to replant with trees budded on sour orange root stock. Much injury has been done by scale insects. The roots of seedling and budded trees are attacked by the grubs of citrus weevils, and the adult weevils feed on the leaves. In most parts of the island it is necessary to shelter the plantings by windbreaks, lime trees being most susceptible to drought, humidity, and wind which easily carries off the flowers.

F. Jamaica.—Lime trees occur mainly on the north coast and in certain portions of the western part of Jamaica. There are a few irregular patches, but the main crop originates from trees scattered through coconut plantations and pastures. No reliable data as to total acreage under lime cultivation can, therefore, be given.

The lime trees of Jamaica have suffered little from withertip disease or from the dying out of seedling trees. The stock seems also to be rather resistant to the citrus weevil, which was once prevalent but did little damage.

Efforts are being made to introduce the seedless or Persian variety of lime which, though less hardy, is expected to find a good market abroad, in competition with Italian and California lemons. Good results were ob-

tained with Persian limes budded on West Indian lime stock. The great majority of trees, however, are still West Indian seedling limes.

The smaller growers sell their fruit to the larger operators; there are four or five lime oil distilleries in Jamaica.

The following quantities of distilled lime oil have been exported from Jamaica in recent years:

Year	*Pounds*	*Year*	*Pounds*
1941	10,788	1945	21,952
1942	12,527	1946	15,035
1943	4,500	1947	12,275
1944	29,051	1948	11,250

G. Antigua.—The island of Antigua exported 952 lb. of distilled lime oil in 1939, about 670 lb. in 1940, 771 lb. in 1941, and nothing in the years from 1942 to 1948.

H. British Guiana.—About 1,000 acres are under lime cultivation. Export figures are as follows:

Year	*Pounds*	*Year*	*Pounds*
1941	6,458	1945	9,012
1942	5,251	1946	8,296
1943	2,997	1947	2,822
1944	4,050	1948	10,550

The total production of distilled lime oil in the British West Indies (including British Guiana) fell from 131,060 lb. in 1941 to 88,373 lb. in 1948. The average figure for six years (1943–1948) was 90,147 lb.

The total yearly production of distilled lime oil in all the West Indies (including British Guiana and Haiti) can be estimated at about 100,000 lb.

I. Haiti.[11]—In Haiti (the former Hispaniola, where Columbus built a fortification on the occasion of his first voyage) the lime tree grows chiefly in the semiwild state, having long ago escaped cultivation. Regular plantations (about 1,000 acres) are located only on the small island of Ile à Vaches, these plantings having been started after 1936. In all the other lime oil producing sections of Haiti the fruit is gathered by the peasants from semiwild and wild growing trees, brought to buying centers near the distilleries, and sold to the oil producers. Years ago (before distillation of the oil was practiced) most of the lime fruit in Haiti was discarded as waste. Today, however, much of it is consumed by the natives.

[11] The author is greatly obliged to Senator Louis Dejoie, Port-au-Prince, Haiti, for much of the information contained in the section on Haitian Lime Oil.

In Haiti the lime tree does not grow well in the mountains. It requires a hot, and rather dry, climate, with about 50 in. of annual rainfall, and a fertile, well-drained soil. It is a surface rooter and, in general, does not lend itself to mechanical cultivation. In the more humid sections of the island the trees are affected by root diseases, withertip, and scale insects.

On the small island of Ile à Vaches the young plants are raised in bamboo pots, in nurseries. Before planting in the field, which takes place during the rainy season in May or October, the bamboo pots are split, and the young plants set out 21 ft. apart, in holes 1 ft. deep and 16 in. wide. Aside from circle weeding, only a minimum of cultivation or pruning is applied. When a tree dies, it is simply replaced by a young plant.

Although the lime tree flowers and bears fruit throughout the year, the real blossoming period starts in spring, with the April showers.

The distilleries are generally located at sea level, in places where fruit is plentiful: Ile à Vaches,* Aux Cayes, Port-Salut,* Fonds-des-Nègres, Miragoane, Trouin, Jacmel,* Petit-Goave, Port-au-Prince,* St. Marc,* Gonaives,* Port de Paix, Cap Haitien, Hinche * and Mirebalais.

Prior to distillation the green or ripe fruit is crushed in small mills such as those commonly used for sugar cane. The juice, which contains most of the essential oil expressed from the peel, is then placed into old-fashioned colonial copper stills of about 300 gal. capacity, and distilled from 4 to 5 hr. The best method of distillation would be with indirect steam (by means of a steam jacket or of heating coils), live steam to be applied for a short time only at the end of distillation. The use of live steam during the entire distillation will result in an oil of abnormally low specific gravity, since heavy condensation of steam within the still will take place. The volume of water to be distilled over will then be unnecessarily large, and the more water-soluble components of the oil in the condensate will be "washed away." In Haiti, the usual method is to distill the juice with direct fire, care being exercised not to overheat the stills, which imparts a slightly "burnt" odor to the oil.

Occasionally a Haitian distilled lime oil of poor quality—which does not meet the usual standards in regard to odor and specific gravity—has appeared on the market. During his last visit to the lime oil producing regions in Haiti, the author concluded that this inferiority is the result of insufficiently long distillation, of too small, and improperly constructed, oil separators, and the use of still necks which are too high, and hence act as reflux condensers, retaining the higher boiling oil constituents in the stills. It should be easy to correct these faults and to produce a very good quality of lime oil in Haiti.

* In actual production. The other distilleries are closed.

The yield of oil depends upon several factors, among them the construction and working condition of the mill in which the fruit is crushed. Other factors include the amount of rainfall, season, degree of maturity, and size of the fruit. Green limes seem to yield more oil per ton of fruit than ripe, yellow limes, but the oil from green fruit sometimes contains less citral and, under tropical conditions, is more difficult to preserve in good condition. According to Dejoie,[12] the average yield of lime oil distilled from juice that had been expressed in sugar cane mills, averages 4 to 5 lb. of oil per metric ton of fruit, provided distillation lasts at least 4 hr. From other sources the author has learned that the yield ranges from 5 to 7 lb. of oil per metric ton of fruit. It is 7 lb. at the beginning of the harvest, but decreases with the arrival of the seasonal rains.

One of the most serious difficulties with which the lime oil producers of Haiti have been confronted, particularly during and after World War II, is the difficulty of procuring galvanized or tin-lined drums. Ordinary, old iron drums (previously used for lubricating oil) have been employed for shipment of lime oil. However, with the high temperature prevailing at sea level, the storage of the delicate lime oil in such drums presents quite a problem. For this reason, producers and exporters in Haiti prefer to ship their oil in one-drum lots, as soon as it is produced.

The production of distilled lime oil in Haiti so far has not been very large and has fluctuated widely, depending primarily upon the market price and the demand on the part of the United States, the sole buyer of the Haitian oil:

Fiscal Year	*Kg. of Oil*
1941–1942	2,396
1942–1943	4,168
1943–1944	5,704
1944–1945	10,078
1945–1946	7,794
1946–1947	5,068
1947–1948	5,963

If properly produced, the Haitian lime oil compares favorably with that from other West Indian islands. It should be kept in mind that in general distilled lime oil is a delicate oil, difficult to produce, and profoundly affected by physiological conditions of the fruit, methods and duration of distillation, and keeping quality of the container.

Quality of West Indian Oil.—The West Indian Lime Oil Sales Co., Ltd., is making considerable efforts toward the improvement and standardization

[12] Private communication of Senator Louis Dejoie, Port-au-Prince, Haiti, who owns and operates thirteen lime oil distilleries in Haiti.

of the quality of (British) West Indian lime oil. According to Lloyd,[13] running the stills too fast, or stopping before the end fractions are entirely over, reduces the specific gravity, and, since the end fractions contain more aromatic elements than the early fractions, the quality of the oil is affected. There is no consistent or standard practice in the West Indies for running stills and making oil. Factories operating small stills run a batch to exhaustion in a couple of hours. Others vary from 6 to 8 hr. in operation and, undoubtedly, when rushed or running to capacity, all hurry the stills along, believing that the minute quantity of oil recovered at the end of the run does not compensate for the fuel expended.

The limits for the specific gravity of good lime oil are as follows:

Temperature, °C.	*Lower Limit*	*Upper Limit*
15	0.864	0.867
25	0.856	0.859
28	0.854	0.857
29	0.853	0.856
30	0.852	0.855
31	0.851	0.854
32	0.850	0.853

It is advisable that the producer check the specific gravity of his distilled lime oil by using a hydrometer graduated from 0.820 to 0.880 and standardized at exactly 15.56°.

Not infrequently the trade has complained that lots of West Indian lime oil reaching the market exhibited wide variations in physicochemical properties. Such variations, of course, are due mainly to the varied climatic and soil conditions of the several islands, to seasonal factors, to the difference in quality of the fruit material employed, and especially to the methods of distillation employed by the numerous producers. On some of the islands the exporters do not carry large bulked lots of oil from which they could draw a uniform quality for export orders. On the contrary, they keep only small lots in stock and purchase from the small producers "from hand to mouth," so to speak, whenever orders from abroad call for certain quantities. This procedure results in much variation in the quality of the lots reaching the consumer. It seems desirable that methods be adopted to assure a more uniform quality of shipment and also that physicochemical properties be standardized to meet certain minimum requirements. The good reputation of the West Indian lime oil would greatly benefit from such measures.

[13] Report of the First Annual General Meeting of the West Indian Limes Association, Inc., Trinidad (1941).

Mexican Lime Oil

History.—In Mexico the lime tree was known in semiwild state on the Atlantic coast before it was regularly planted near Acapulco on the Pacific coast around 1870. Consul Sutter of San Francisco played a pioneer role in this venture.

Lime fruit has been shipped from Acapulco to San Francisco since about 1875. After that date the Mexican lime industry expanded slowly but steadily until 1910, when the Mexican revolution occurred, and American steamers stopped calling on Acapulco. Mexico thus lost practically its entire lime fruit trade with the United States. With the return of more normal conditions in 1917, shipping from Acapulco to the United States was resumed and the Mexican lime industry prospered anew. Between 1915 and 1920 a number of lime plantations were started around Colima and Michoacan, whence the fruit is transported to the United States by rail.

From 1928 to 1935 the lime plantings around Colima were greatly extended, and Colima became Mexico's most important producing center; development of Acapulco and Michoacan was slower.

Producing Regions in Mexico.—One of the largest lime plantations in Mexico today is La Nueva Italia in Michoacan, with La Lombardia following next in size. There are about 100,000 trees on these plantings, but much of the property has been divided. Around Colima there exist about 500,000 lime trees, most of them growing on plantations of about 40,000 trees each; the rest are scattered over several smaller ranches. In the region around Acapulco the number of trees has been increased to approximately 200,000 in 1946, all planted on very small lots, aside from a tremendous number of wild lime trees. There is also a great number of lime trees in the northern part of the state of Vera Cruz, and in the southern part of Tamaulipas around Tampico; but most of these plantings are small and scattered, many of the trees growing semiwild. It is estimated that no less than 300,000 wild trees cover the northeastern part of Tamaulipas. When fruit prices are high, these wild trees will be exploited.

About one-half of the total production of limes is exported as edible fruit, the balance is processed.

Some years ago, Mexican lime oil was generally considered inferior in quality to the West Indian oil, shipments of the former varying in quality and being often unsatisfactory. Indeed, most of the distillation plants were rather primitive and obsolete, and producers knew little about proper working methods which yield high-grade oil. Yet the Mexican lime itself is in no way inferior to the West Indian fruit. In 1939 the picture changed completely, when a large concern, operating in Colima and Acapulco,

erected a modern plant and, following the advice of the author, improved the extraction process. There are now eight distilleries in the neighborhood of Colima, two in Acapulco, three in Apatzingan, five around Tampico, and one in Sayula (Ver.), as well as others under construction, as a result of the growing interest in Mexican lime oil shown by the United States. Five plants supply coldpressed and distilled oil, and the others produce only distilled oil. Five of the existing distilleries are modern—namely, one in Colima, one in Acapulco, one in Michoacan (Apatzingan), one in Sayula (Ver.), and one in Llera (Tamaulipas) located on the highway to Monterrey.

Mexico has been producing from 50,000 to 100,000 lb. of lime oil yearly, but production could be further increased if necessary.

The Mexican lime tree is of the spiny variety. So far only a few Mexican lime trees have been grafted on sour orange stock, but the growers are now starting to follow this West Indian practice.

The most suitable altitudes for lime cultivation range from sea level to about 2,000 ft. and even higher, provided the higher elevations are not subject to frost which destroys the trees. On the Pacific coast of Mexico where lime trees are planted, the soil consists either of volcanic alluvium or sediment. In general, it is dark, loamy, and rich.

Planting.—The seed may be planted in a seed bed at any time of the year, provided ample water is available, either in the form of rainfall or irrigation. After eight to eighteen months, the young plants are transplanted into open fields; this, of course, must be done during the rainy season. The rows are generally spaced at 8 m., and the trees 6 m. apart.

Under ideal conditions, the trees first bear fruit after four years and come into full bearing in the sixth or seventh year. They attain old age, seventy years not being considered exceptional.

Harvesting.—The season for the lime crop is influenced by rain and irrigation. On irrigated plantings the crop continues throughout the year, but has definite peaks during the rainy season. In normal years the rainy season on the west coast lasts from June to October. Colima's main fruiting period is in July–August. Acapulco has two seasons, the first in May and the second in September–October; however, they vary with the rains. The main fruiting period in Tamaulipas and Vera Cruz occurs in January. Generally speaking, the main crop lasts from April to November. One full bearing tree produces normally from 50 to 75 kg. of fruit per year. Some exceptional plantings on the west coat are said to yield as much as 200 kg. of fruit per year, but on a few trees only.

Distillation of Lime Oil.—The process of lime oil distillation as carried out in Mexico is quite similar to that practiced in the West Indies, except

that the West Indian manufacturers lay greater stress on the production of good juice, for which there is a market in Great Britain; whereas Mexico specializes mainly in the production of oil. The fruit is crushed, the pulp strained off the juice, and the latter distilled. For crushing, the Enterprise fruit press, mentioned in the section on West Indian lime oil, is employed.

Eight pounds of distilled oil per metric ton of fruit (0.36 per cent) is considered the average yield.



Courtesy of Fritzsche Brothers, Inc., New York.

Harvesting of lime fruit at Colima, Mexico.

To obtain a very high quality of oil, modern distilleries in Mexico employ as much green fruit as possible, process the fruit immediately after picking, prolong distillation to 7 hr., use Florentine flasks large enough to assure smooth flow of the distillate, and recover the small quantities of oil which are apt to be lost in the distillation water.

Coldpressed Mexican Lime Oil.—In the West Indies coldpressed lime oil is made almost exclusively by the *écuelle* method; the Mexican producers, however, employ the process used formerly in California for lemon and orange oil, but on a modified, much smaller, and simpler basis. The entire fruit is crushed, the pulp strained off, and the mixture of juice and oil separated in high-speed separators. The yield of coldpressed oil in Mexico ranges from 0.28 to 0.35 per cent. It is about 7 lb. of oil per metric ton of fruit.

This process has, of course, certain disadvantages. The oil is very finely distributed in the juice, and parts of the more water soluble oxygenated compounds cannot be recovered.

Prior to the outbreak of World War II, some of the Sicilian machines used for manufacturing citrus oils, especially the Avena machine, were adapted also for the treatment of limes. Undoubtedly these machines could be used to advantage in Mexico.

The quality of Mexican lime oil, coldpressed as well as distilled, will probably undergo some changes in the near future, due to the introduction of new and very modern juice and oil presses by several United States concerns, who are constructing large canneries of lime juice in Mexico (for details see "Florida Lime Oil").

Production of Citric Acid in Mexico.—In Mexico there is a great demand for citric acid, imports from the United States being drastically curtailed during World War II. For this reason, most lime oil distillers in Mexico started to produce calcium citrate in a more or less primitive way. Only two or three plants are equipped for the production of citric acid which is sold on the local market but not exported.

Danger of Insect Pests.—Some years ago there appeared in the Colima region a plague caused by the black fly (*mosca negra*) which affected the entire region and reduced the yield of fruit to about 50 per cent. The plague has been combated with the *avispa de Panama,* a parasite which destroys the eggs of the black fly. This treatment, although not very efficient, has brought about some relief. Up to now the plague has not affected the other lime producing regions, but such a possibility exists and would be quite disastrous for the whole Mexican lime oil industry. During the past few years the plague has been a decisive factor in the production of Mexican lime fruit.

Florida Lime Oil

Of the many varieties and hybrids of lime fruit growing wild or cultivated in Florida, the Key lime (also called West Indian, Dominican, Mexican, or sour lime), and more recently the Persian lime (also called Tahiti or seedless lime) constitute the bulk of commercial production. Today the Persian lime greatly outweighs the Key lime so far as production in Florida is concerned. As a tropical plant the lime tree, especially the Key lime, is severely damaged, if not killed, by frost, and the mainland of Florida does suffer from occasional spells of frost. Practically the entire Florida lime crop was destroyed during the winter of 1939–1940 but, fortunately, most of the trees came through in good condition.

The Key lime is an acid, small (usually less than 2 in. long), almost round, fruit, with a slight nipple. Light greenish to yellow in color, the skin is very smooth. The ten sections are separated by thin walls and usually hold several seeds. Of excellent, very acid flavor, the juice contains 7–8 per cent of citric acid. The trees are bushy, heavily spined, and not more than 10–15 ft. high.

The wild or Key lime was introduced from the West Indies many years ago and has flourished in the Keys since Florida was first settled. It is confined to the Florida Keys, and to the southern tip of the mainland, where it grows on coralline rock soil and seems to get along with little attention. Since the small fruit is difficult to collect from the thorny trees, which either grow wild in almost inaccessible localities, or are planted on scattered, small lots, the harvest of the Key limes offers more difficulties than the collection of any other commercial citrus fruit. Because of sensitiveness to cold and attack by diseases, which disfigure the fruit, the Key lime has not been grown successfully on Florida's mainland north of Miami, and has lately been superseded there by the Persian lime which, according to Mayo,[14] can be grown under favorable conditions and, with proper care for cold protection, as far north as the central part of the state.

According to Camp,[15] the Persian or Tahiti lime cultivated in Florida is a large oval lime, commonly 3 in. long, shaped much like a lemon, with a very smooth skin, green pulp, and almost always seedless. The juice is very acid and of excellent flavor. The Persian limes are picked while still green, since this variety is afflicted with some physiological trouble called stylarend rot which affects the fruit when it starts to turn yellow. The trees are dwarf, 12–15 ft. in height, and somewhat droopy. They are harder to grow than orange or grapefruit trees, being more susceptible to gum disease that may be caused by either of two fungi, viz., *Diplodia* or *Phomopsis*, which cause considerable loss of trees. Despite these handicaps, the Persian type of lime is now cultivated extensively in warm localities on Florida's mainland, the production increasing from year to year.

According to Fleming,[16] the bulk of Persian limes grown in Florida originates from the Redlands district of Dade County, which area begins about 12 miles south of Miami and extends on south to Homestead. However, there are also a good many Persian lime orchards in the Winter Haven section of the state, i.e., in the central part of Florida in the heart of the citrus belt, most plantings located there consisting of top-worked grapefruit groves.

[14] "Limes and Lemons in Florida," *Florida State Dept. Agr., Tallahassee, Florida, Bull.* No. 102, July (1940).
[15] "Citrus Industry of Florida," *Florida State Dept. Agr., Tallahassee, Florida* (1946), 37.
[16] Private communication by Mr. George D. Fleming, Jr., Miami, Florida.

Roughly estimated, the Redlands area produces about 65 per cent of the total crop of Persian limes, the Winter Haven area about 35 per cent. Lime production in the central part of the state has not been as successful as it has been in the south of Florida because of the climate. The climate around Winter Haven is much colder than it is further south, and most of the lime trees bloom at one time, with harvesting restricted to a fairly short season during the summer and early fall. Harvesting in the Redlands area normally continues for 11 or 12 months out of the year, beginning in May with light receipts, increasing to heavy production in July, and continuing with ample supplies throughout the end of the year. January and February production is not very consistent, as sometimes there will be a fair surplus which can be converted into juice, and at other times not much more than is required for local use. March and April production is always light, but usually ample for local requirements.

So far as the production of lime juice and lime oil is concerned, it should be kept in mind that Florida produces a high-grade fruit which in normal times has been readily absorbed by the public in the United States—and at prices attractive to the growers. In past years the growers, therefore, had no interest in converting their lime fruit into juice and oil, and Florida lime oil was not a commercial article. The outbreak of World War II changed the picture, as it caused a tremendous demand for canned juice on the part of the armed forces and lend-lease, and the canners could afford to pay high prices for the fruit. Since then many new groves of Persian limes have been started; fruit production reached 200,000 boxes in 1945 and is still increasing. Canning methods have been perfected and canned lime juice is gaining in popularity. Fruit prices may drop as production increases in years to come. New processes and new machinery, used for the extraction of orange, grapefruit, or lemon juice and oil, are also being adapted to lime fruit, and a substantial production of lime juice and oil in Florida can, therefore, be expected in the coming years.

This whole development will not remain without profound influence upon the future quality of Florida lime oil. For a better understanding of the factors involved, we should remember that the latest and most efficient machines, introduced by the California and Florida citrus canning industry, aim at extracting juice and oil in one operation, and with as little contact of juice and essential oil as possible. The working principles of these machines have been described in previous sections. The oil has become a by-product in the extraction of the juice for canning. Most juice and oil presses separate the oil in some form of emulsion (more or less dense) which is then broken up by supercentrifuging. Such machines and such a procedure should yield a coldpressed lime oil of excellent quality, certainly

better than that obtained by the old-fashioned process in which the whole fruit is crushed (for example in the tapered screw presses used in Mexico), and the entire quantity of juice must be centrifuged in order to separate the oil. In this type of operation, the contact of the minute oil droplets with the large quantity of juice in which these droplets have become suspended undoubtedly affects the physicochemical properties and the quality of the expressed oil. In the new type of operation the oil can be separated without contact of juice and oil.

So far as the distilled oil is concerned, it should be kept in mind that in the old-fashioned distillation process, by which large quantities of oil are produced every year in the West Indies and in Mexico, the oil is distilled from the acid (hot) juice obtained by crushing of the whole fruit. This method of distillation from an acid, hot medium, profoundly affects the chemical constituents, and therefore the odor and flavor, of the oil. Yet, the trade has become accustomed to the flavor of this old-fashioned distilled lime oil and so far seems to prefer it to any other, even to a more natural lime flavor. The new type of distilled lime oil is prepared according to the following general principle: in the course of the juice canning operation, the fresh fruit is washed, assorted according to size, and mechanically conveyed into cutting machines which slice the fruit into halves. These halves are then fed into various types of machines which ream out or express the juice, the essential oil remaining in the skins. These are then submitted to very high pressure (between rotating heavy steel cylinders or in tapered screw presses, etc.) so that the aqueous cell liquid and a part of the essential oil are expressed. After being freed from coarser cellular material by straining through a screen, and after supercentrifuging, this emulsion can be broken up, yielding the "coldpressed oil." The residual skins still contain a good portion of the essential oil, absorbed and retained by the spongy albedo of the skins. After mincing to a thin slurry, followed immediately by steam distillation, the oil remaining in these partly exhausted skins can be obtained as "distilled lime oil." Since this type of oil is distilled from an almost neutral medium (no contact with the acid juice!), its quality will be quite different from the old-fashioned type of distilled oil described under West Indian or Mexican lime oil. Small lots of this new type of distilled lime oil have already been offered on the market, but with the development of the lime juice canning industry in Florida, and also in California, much larger quantities can be expected in the future. To a certain extent, this will apply also to Mexico, as several California canneries are now organizing the production of canned lime juice in Mexico and are installing the most advanced machinery for the extraction of juice and oil in that country.

So far as yield of oil is concerned, one producer[17] in Dunedin, Florida, claimed, in 1941, to have obtained 150 lb. (yield = 0.06 per cent) of cold-pressed oil and 375 lb. (yield = 0.15 per cent) of distilled lime oil from approximately 250,000 lb. of fresh lime fruit, which means a total oil yield of about 0.2 per cent. This producer could not account for the very low yield of expressed oil, but claims to have made such improvement in the machinery during the past years that he has been able to increase the yield of expressed orange oil by about 50 per cent. It is quite possible that he can achieve similar results also with lime oil. In fact, experimenting a few years later at the Citrus Products Station in Winter Haven, Florida, on the recovery of lime oil by coldpressing and centrifuging, Atkins, Wiederholst and Heid,[18] reported average oil yields of 0.10 per cent calculated upon the weight of the whole fruit.

Another producer[19] reported a total yield of about 11 lb. of distilled lime oil (yield = about 0.2 per cent) from 6,600 lb. of whole fruit. This producer did not treat the fruit for expressed oil.

In reference to the quality of lime oil distilled in the West Indies and in Mexico, by the old-fashioned method, compared with that of the oil distilled in Florida, by the new method, the causes for the differences between the two may be summarized as follows:

1. Rapid distillation, and therefore less action of heat in the new process.
2. Absence of citric acid in the still content; thus no action of a highly acid medium upon the citral. Therefore, the new type of oil shows a much higher citral content than the usual distilled lime oils.
3. The new type of oil is distilled from waste peel which had been partly deprived of its oil by coldpressing.

Total Fruit Production.—The reader interested in the latest and more detailed figures on fruit production in the United States is referred to the regularly published Crop Reports of the U. S. Department of Agriculture, Bureau of Agricultural Economics, Crop Reporting Board, Washington, D. C. The following data have been reported for the last few years:

Florida Limes in Thousand Boxes

Average 1935–1944	*1944*	*1945*	*1946*	*1947*
116	250	200	170	200

The net content of one box of limes in Florida is 80 lb.

[17] Private communication by Mr. J. J. R. Bristow, Dunedin.
[18] *Fruit Products J.* **23** (1944), 306.
[19] Private communication of Mr. George D. Fleming, Jr., Miami.

Total Production of Florida Lime Oil.—In past years Florida produced only small quantities of distilled and coldpressed lime oil, amounting from 500 to 1,000 lb. No exact statistical figures are available and nothing is known as to whether this oil was mainly distilled or coldpressed. As has been pointed out, there is hope that the production will be increased considerably during the coming years, as the newly planted lime plantations come into bearing. Of course, the production of oil in Florida will always be limited, because the limes are of high quality and find a ready market as edible fruit in the United States.

East Indian Lime Oil

India, also, produces distilled lime oil, but in limited quantities; the commercial lots offered on the market and exported (chiefly to the United Kingdom) have been very small. Their quality does not compare well with that of West Indian or Mexican oils, probably for the reason that, in India, the distillation of the juice or pulp is not conducted for a sufficient number of hours.

According to Patel,[20] in the Bombay Presidency there are about 1,200 acres devoted to the cultivation of lime. The fruit is harvested abundantly twice a year. The richer harvest begins in the early part of July and ends by the first week of September. Another important collection of fruit is made in December.

For the recovery of the oil the limes are minced in hand operated appliances, and the pulp thus obtained is distilled in steam heated stills, after the addition of water (to the amount of about one-third of the volume of pulp).

Ordinarily 1 (long) ton of Bombay limes yields from 6 to 7 lb. of oil, if the limes are distilled without the recovery of the juice—i.e., when they are minced whole and distilled.

Patel [21] reported on certain properties of three samples of lime oil, which, however, appear quite abnormal (low specific gravity, etc.), and therefore will not be included here.

Physicochemical Properties of Lime Oil.

I. West Indian and Mexican Oils.—During the past years the New York laboratories of Fritzsche Brothers, Inc., have examined a great many

[20] *Perfumery Essential Oil Record* **28** (1937), 358. Cf. *Dept. Ind. Bombay Presidency Bull.* No. 11 (1938).

[21] *Ibid.*

genuine lime oils, expressed and distilled, and established the following limits:

Expressed Lime Oil

Specific Gravity at 15°/15°	0.878 to 0.886 (best oils 0.880 or higher)
Optical Rotation	+35° 0′ to +40° 0′
Refractive Index at 20°	1.4820 to 1.4860
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	4.5 to 8.5%
Evaporation Residue	10.0 to 13.5%

Distilled Lime Oil

Specific Gravity at 15°/15°	0.862 to 0.868 (good oils have a gravity of not less than 0.864)
Optical Rotation	+34° 30′ to +46° 30′
Refractive Index at 20°	1.4750 to 1.4770
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	0.5 to 1.5% (the average citral content of good oils is 1.0%)

In general, a very good quality of oil is characterized by high gravity and low rotation. Such oils are better adapted for making concentrates; they give a better yield. On the other hand, oils of very high terpene content show a low specific gravity and a high rotation. Occasionally oils are observed which have a high specific gravity and a high optical rotation.

II. Florida Oils.—A sample of *expressed* oil made in Dunedin and analyzed in the laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 15°/15°	0.886
Optical Rotation	+41° 26′ (approximately)
Refractive Index	1.4855
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	7.4%
Evaporation Residue	13.0%
Solubility	Because of the presence of waxes, not clearly soluble in 5 vol. of 90% alcohol

The odor and flavor of this oil were good, full, rich, characteristic of the fresh fruit.

A sample of oil *distilled* (new process) in 1940 by J. J. R. Bristow of Dunedin, in the presence of the author, had the following properties:

Specific Gravity at 15°/15°	0.8632
Optical Rotation	+43° 20′

Refractive Index	1.4759
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	5.0%
Solubility	Clearly soluble in 4 vol. and more of 90% alcohol

In regard to odor and flavor, this new type of distilled oil resembled coldpressed lime oil, the citral note being quite pronounced. (For an explanation of the difference between Florida and West Indian or Mexican oils, see section on "Florida Lime Oil.")

In their recent investigation of the properties of Florida citrus oils during the 1947–1948 season, Kesterson and McDuff [22] observed the values in Table 1.25 for six coldpressed and five steam distilled lime oils derived from Persian limes, and one steam distilled lemon oil derived from Meyers lemons.

TABLE 1.25

Properties	Persian Lime				Meyers Lemon
	Coldpressed		Steam Distilled		Steam Distilled
	Maximum	Minimum	Maximum	Minimum	
Specific Gravity at 20°/20°	0.8823	0.8798	0.8579	0.8556	0.8555
Optical Rotation at 20°	+41.80°	+38.60°	+50.52°	+46.84°	+56.00°
Optical Rotation at 20° of 10% Distillate	+49.24°	+47.60°	...	...	...
Difference	9.88°	7.00°	...	...	...
Refractive Index at 20°	1.4853	1.4842	1.4751	1.4743	1.4740
Refractive Index at 20° of 10% Distillate	1.4731	1.4729	...	...	...
Difference	0.0123	0.112	...	...	...
Aldehyde Content, Calculated as Decyl Aldehyde	5.52%	3.66%	2.71%	1.61%	1.19%
Ester Content [a]	8.20%	7.42%	3.49%	2.41%	2.45%
Evaporation Residue	14.67%	12.95%	1.23%	0.18%	0.16%

[a] Seeker and Kirby Method, reported by Poore, *U. S. Dept. Agr., Tech. Bull.* No. 241 (1932), 1–30.

[22] "Florida Citrus Oils," *Univ. Florida, Agr. Expt. Sta., Gainesville, Florida, Tech. Bull.* No. 452 (1948).

The coldpressed Persian lime oil was obtained by passing the peel through a Pipkin Peel Oil Press, after removal of juice. The residual peel, which still contained substantial quantities of oil, was then chopped and steam distilled at atmospheric pressure.

The properties of the Meyers lemon oil indicate that it is predominantly lemon in character, although the Meyers lemon is commonly believed to be a natural hybrid.

Adulteration of Distilled and Expressed Lime Oil.—Distilled lime oil is occasionally adulterated with terpenes resulting from the preparation of terpeneless lime oil. Such common adulteration may be quite easily detected by a resulting diminution of the specific gravity and an increase in the optical rotation. It should be pointed out, however, that a lower gravity and a higher rotation may be the result also of improper distillation—such as occurs when a batch of juice has not been distilled to completion. Additions of lemon and orange terpenes may be detected by similar changes in the physical properties. However, because of their higher optical rotation, only a limited quantity can be added without the adulteration becoming too obvious.

Additions of turpentine oil tend to lower the gravity, but the effect on the optical rotation is dependent upon the type of turpentine oil used. In general, the rotation will be decreased.

The addition of dipentene or terpinolene causes a lowering in the specific gravity and in the optical rotation.

Expressed lime oil is occasionally adulterated by the addition of distilled lime oil. The presence of the latter is difficult to prove and may be detected only by a resultant lowering of the specific gravity and an increase in the optical rotation, accompanied by a weaker and less characteristic flavor. Adulteration with lemon oil has a similar effect on the properties of expressed lime oil; furthermore, a foreign flavor of lemon oil will be noted. All other adulterants listed under distilled lime oil are possible adulterants also of the expressed oil.

Chemical Composition of Expressed Lime Oil.—Relatively little is known about the chemistry of expressed lime oil produced from the fruit of *Citrus aurantifolia* Swingle, the true acid lime.[23]

Analytical data for normal oils indicate the presence of terpenes, aldehydes, esters, free alcohols, and nonvolatile compounds. The low boiling terpenes have not been investigated; nor have the oxygenated constituents been thoroughly studied. *Limonene* and *l-α-terpineol* are probably present in the oil. Gildemeister and Hoffmann[24] state that the most important

[23] The "Limettöl" investigated by Gildemeister was the sweet Italian "lime oil" *Citrus limetta* Risso; this is not the oil of commerce—*Arch. Pharm.* **233** (1895), 175.
[24] "Die Ätherischen Öle," 3d Ed., Vol. III, 107.

aldehydic constituent is *citral.* The *esters,* representing about 10 per cent of the oil, have not been identified; *methyl anthranilate* may possibly be present in small amounts, according to Tempany and Greenhalgh,[25] who separated a substance containing nitrogen. In the higher boiling fractions, the presence of a sesquiterpene, *bisabolene,* was established by Burgess and Page.[26] *Limettin,* a crystalline substance melting at 147.5°, was reported by Tilden,[27] as a nonvolatile constituent of expressed lime oil; it may be found in the evaporation residues or in the sediments which separate when expressed oils are permitted to stand undisturbed for long periods of time. Schmidt [28] later showed limettin to be identical with citroptene, which occurs in lemon oils; it is 5,7-dimethoxycoumarin, $C_{11}H_{10}O_4$. Unquestionably, other nonvolatile compounds, such as waxes, are also normal constituents of expressed lime oil. *Isopimpinellin,* for example, was isolated by Dodge.[29] In a later investigation Caldwell and Jones [30] confirmed the presence of limettin and isopimpinellin in expressed lime oil; furthermore, they proved the occurrence of 2–2.5 per cent of *7-methoxy-5-geranoxycoumarin* and traces of *bergaptol* in this oil. Bergaptol is a natural constituent of bergamot oil.

Studying the nonvolatile constituents of coldpressed lime oil, the New York laboratories of Fritzsche Brothers, Inc., more recently found that the melting points of some of the compounds described in the above cited work of Caldwell and Jones are actually higher. These discrepancies in the melting points perhaps can be explained by the fact that Fritzsche Brothers, Inc., used corrected thermometers.

	Caldwell and Jones	*Fritzsche Brothers, Inc.*
Compound	*M.p.*	*M.p.*
7-Methoxy-5-geranoxycoumarin	86°–87°	87°–88°
5-Hydroxy-7-methoxycoumarin	228°–229°	236.5°
4,6-Dimethoxy-2-geranoxycinnamic acid	98°–99°	98°–100°

Chemical Composition of Distilled Lime Oil.—Little was known concerning the chemical constituents of distilled lime oil prior to an investigation undertaken by the author and E. Langenau.[31]

In 1904, Burgess and Page [32] established the presence of *l*-α-terpineol and bisabolene in lime oil. These investigators also prepared the phenylurethane of a second alcohol, which crystallized in needles and melted at 132°. They suggested that this might be the derivative of an unknown

[25] *West Indian Bull.* **12** (1912), 498.
[26] *J. Chem. Soc.* **85** (1904), 414.
[27] *Ibid.* **61** (1892), 344.
[28] *Arch. Pharm.* **242** (1904), 288.
[29] *Am. Perfumer* **37** Dec. (1938), 34; **41** Nov. (1940), 31.
[30] *J. Chem. Soc.* (1945), 540.
[31] *J. Am. Chem. Soc.* **65** (1943), 959.
[32] *J. Chem. Soc.* **85** (1904), 414, 1329.

isomeric terpineol. In the investigation of Guenther and Langenau, no phenylurethane of such melting point was obtained. Possibly the crystals obtained by Burgess and Page may have been an impure form of bornyl-phenylurethane m. 138°–139°.

Investigating a genuine lime oil of highest quality distilled in Colima (Mexico), from the juice of green, crushed fruit, Guenther and Langenau established the presence of the following constituents:

In Fraction I
b_{14} up to 68°
(75% of the original oil)

α-Pinene. In the fraction b. 150°–160°. Identified as nitrosochloride m. 102°–103°, no depression in a mixed melting point determination.

Furfural. In the fraction b. 160°–170°. Identified as oxime m. 89°–90°, no depression in a mixed melting point determination.

β-Pinene. In the same fraction. Only a small amount of this terpene is present. Oxidation with alkaline potassium permanganate, according to Wallach's method,[33] gave nopinic acid m. 124°–126°.

n-Octyl Aldehyde. The residual 90 per cent of fraction I was treated with a 40 per cent sodium bisulfite solution and the aldehydes regenerated. The mixed melting point of the semicarbazone of *n*-octyl aldehyde was 96.5°–97.5°.

d-Limonene. The aldehyde-free portion was fractionated and *d*-limonene b. 175°–176° identified as tetrabromide m. 103°–104°. No depression in a mixed melting point determination.

Dipentene. Repeated recrystallization of limonene tetrabromide permitted the separation of dipentene tetrabromide. Further recrystallization gave silver-white crystals m. 123.5°–124.5°. No depression in a mixed melting point determination.

The presence of phellandrene, *p*-cymene, or terpinene could not be established in the fractions b. 177°–178°, 178°–179°, and 179°–180°.

In Fraction II
b_{14} 68°, b_{12} 76°
(2.4% of the original oil)

n-Nonyl Aldehyde. The aldehydes were isolated from fraction II by means of the sodium bisulfite method and regenerated. Identified as semicarbazone m. 98°–99°; no depression in a mixed melting point determination.

Borneol (Free). The primary and secondary alcohols were removed from the aldehyde-free portion with phthalic anhydride and freed by saponification with a 50 per cent sodium hydroxide solution. The oil thus obtained had an odor suggestive of borneol and geraniol. Identified as phenylurethane of borneol m. 138°–139°; no depression in a mixed melting point determination.

The presence of *p*-cymene and phellandrene could not be established in the fraction b_{762} 180°–182°.

[33] *Liebigs Ann.* **356** (1907), 228.

In Fraction III
b_{12} 76°–105°
(14.9% of the original oil)

n-Decyl Aldehyde. The aldehydes were removed from this fraction by using a sodium sulfite solution buffered with sodium bicarbonate. The crystals which formed were isolated and the aldehydes regenerated with a 10 per cent sodium carbonate solution. The yellow oil thus obtained was rectified: b_5 80°–81°. Identified as oxime m. 68°–69°, and as semicarbazone of *n*-decyl aldehyde, m. 100°–101°. No depression in a mixed melting point determination.

Citral. The buffered sodium sulfite solution (which contained the soluble labile addition compound of any citral that might have been present in fraction III) was treated with a 20 per cent sodium hydroxide solution and the aldehydes regenerated. A pale yellow oil with a cumin aldehyde-like odor was obtained. To these aldehydes were added the corresponding aldehydes of fraction IV. In an attempt to separate them, these aldehydes were fractionated at 16 mm.; all fractions consisted of pale oils with a similar odor. Doebner's [34] naphthocinchoninic acid derivative of each of the above fractions melted at 187°–195°. The derivatives were combined; repeated recrystallizations from alcohol yielded a small amount of yellow needles m. 200°–201°; a mixed melting point with the naphthocinchoninic acid derivative of citral showed no depression. Attempts to secure crystals of sharp melting point from the mother liquors proved unsuccessful.

An Unidentified Aldehyde(?). The unidentified aldehyde proved very susceptible to polymerization.

The aldehyde-free oil was saponified with alcoholic sodium hydroxide solution, the saponified oil washed with water, and the aqueous washings treated in the manner described under "Acidic Constituents." After saponification, the primary and secondary alcohols were removed with phthalic anhydride.

Geraniol. The recovered primary and secondary alcohols were distilled at 20 mm., and three fractions collected. The first fraction readily yielded crystallized borneol. The second and third fractions, having the odor of geraniol, were combined and purified through the calcium chloride compound. Rectification of the resulting oil yielded pure geraniol. Identified as diphenylurethane m. 81.5°–82.5°; no depression in a mixed melting point determination.

Linaloöl. Thus freed from aldehydes, esters, primary and secondary alcohols, fraction III was fractionated at 20 mm. and rectified at 760 mm. In the fraction b. 196°–200°, a phenylurethane m. 65°–66° was obtained. No depression in a mixed melting point determination.

α-Terpineol. The fraction b. 212°–224° consisted of a viscous, colorless liquid having a pronounced odor of terpineol. It congealed at −5° to a semisolid mass. Identified as phenylurethane m. 111°–112°, and as nitrosochloride m. 121°–122°.

These melting points correspond to the values given by Simonsen [35] for the inactive *dl*-modification. Probably these derivatives were formed because of the relatively small excess of *l*-terpineol over the *d*-modification.

Terpineol was separated as a solid which showed a specific rotation of −11° 0′; m. 34°–35°.

[34] *Ber.* **27** (1894), 2020.
[35] "The Terpenes," Vol. I (1947), 260, 264.

In Fraction IV
b_{12} 105°–129°
(3.8% of the original oil)

Lauric Aldehyde. The aldehydes were removed by the modified method of Tiemann. From the crystalline bisulfite addition compound a yellow oil having the odor of a fatty aldehyde was obtained. The regenerated aldehyde was rectified at 10 mm. Identified as oxime m. 74°–75°, and as semicarbazone m. 100°–101°. No depression of a mixed melting point determination.

Bisabolene. Fraction IV, thus freed of aldehydes, esters, primary and secondary alcohols, was fractionated at 4 mm. and a main fraction b_4 110°–112° obtained. This fraction had properties that approximated the values given by Simonsen [36] for bisabolene. Characterized as trihydrochloride m. 79°–80°. A 10 per cent chloroformic solution of these crystals was optically inactive. Elementary analysis of the trihydrochloride confirmed the presence of bisabolene.

In Residue V
b_{12} above 129°
(3.4% of the original oil)

Lauryl Alcohol as Ester(?). The aldehydes were removed with sodium bisulfite solution and, after saponification of the aldehyde-free oil, the primary and secondary alcohols isolated with phthalic anhydride. After standing at 5° for twelve hours, a white waxy solid separated, m. about 19°. Identified as phenylurethane m. 74°–75°, no depression in a mixed melting point determination. Since this alcohol was not identified in any other fraction, it is likely that it occurs as a high boiling ester.

An Azulenic Compound. Residue V, thus freed of aldehydes, esters, primary and secondary alcohols, was fractionated. Fraction b_4 115°–119° contained some bisabolene but no cadinene. The fraction b_4 120°–145° had an intense blue color; the residue showed the absence of paraffinic hydrocarbons when treated with fuming sulfuric acid. The fraction b_4 120°–145° was then shaken with ice cold phosphoric acid, according to the method of Sherndal.[37] An oil of intense blue color was obtained. A minute amount of this oil dissolved in ether gave a yellow-green color, characteristic of distilled lime oil.

Acidic Constituents. The combined aqueous washings from the saponification of fraction III, fraction IV, and residue V were concentrated and, after washing with ether, the solution was acidified and steam distilled. Sodium carbonate was added until the distillate was alkaline; any phenols that might be present were extracted with ether.

A Phenol(?). Evaporation of the ether yielded an oil with a phenolic carvacrol-like odor. It showed intense yellow color with ferric chloride solution. Phenylurethane m. 134°–137°.

Acetic Acid. The alkaline distillate was concentrated, acidified, and extracted with ether, the free acids distilled. The toluidide of the first fraction melted at 146°–147°; no depression in a mixed melting point determination. The presence of acetic acid was confirmed by elementary analysis of the silver salt.

[36] *Ibid., Vol. II* (1932), 493.
[37] *J. Am. Chem. Soc.* **37** (1915), 167.

n-Octylic Acid. The toluidide of the rectified residue melted at 69°–70°; no depression in a mixed melting point determination.

n-Decylic Acid. The rectified residue deposited a solid acid upon standing. It melted at about 10°. Identified as toluidide m. 74°–75°; no depression in a mixed melting point determination.

Tempany and Greenhalgh,[38] impressed by the great difference in odor between the distilled and expressed oils, suggested that this difference might be due to a loss of the higher and lower boiling constituents upon distillation. In order to test this theory experimentally, these investigators distilled an expressed lime oil; they claimed that the resulting "distilled" oil had the characteristic odor of the commercial distilled oils and lacked its former sweet character. Certain high boiling constituents present in the expressed oil could not be found in this "distilled" oil; e.g., limettin (which is a normal constituent of expressed oils) and methyl anthranilate (which may be a normal constituent of expressed oils).

Schimmel and Co.[39] pointed out that the marked difference in odor of the expressed and the distilled oil might well be due to a degradation of certain constituents by steam in the presence of citric acid rather than to the loss of low and high boiling constituents. Recent experiments, which are described below, support this theory. Furthermore, a normal expressed oil shows an aldehyde content of about 6 per cent and an ester content of about 8 per cent; a distilled oil, on the other hand, has an aldehyde content of only about 1 per cent and an ester content of about 2 per cent. These differences indicate a destruction of these constituents in the presence of heat and acid. Any high boiling constituents which might be lost during distillation would contribute but little to the characteristic odor and flavor of the expressed oil; this is evidenced by the fact that after distillation *in vacuo*, an expressed oil maintains its characteristic odor and flavor.

Less easily explained is the fact that the presence of expected degradation products could not always be established. Citral, reportedly the main aldehydic constituent of the expressed oil, and found only in relatively small amounts in the distilled oil, would be expected to yield *p*-cymene, when heated with dilute acids. Likewise, terpineol would be expected to yield terpinene under such conditions. Yet Guenther and Langenau[40] could not establish the presence of *p*-cymene and terpinene in distilled lime oil. A possible explanation may be that these constituents are present in such small amounts that they have escaped detection.

Effect of Heat and Acid on Lime Oil.—Guenther and Langenau[41] carried out a series of experiments to determine the effect of heat and acid on a

[38] *West Indian Bull.* **12** (1912), 498.
[39] *Ber. Schimmel & Co.*, April (1913), 68.
[40] *Am. Perfumer* **45** April (1943), 44.
[41] *Ibid.*

lime oil. These experiments indicate that steam alone causes very little degradation of the oil. When an aqueous solution of citric acid is permitted to remain in contact with the oil for only short periods of time, relatively little degradation occurs; when it remains in contact with the oil for long periods of time, partial degradation occurs, even in the absence of heat. The combination of heat and acid for long periods of time has by far the most marked effect; there results an oil of low aldehyde content, having the characteristic odor and flavor of the distilled lime oils of commerce.

It must be borne in mind that in the commercial production of distilled lime oil from the juice, the oil is subjected to the action of heat and acid for long hours, while the lime juice is heated at the boiling point. In a commercial distillation supervised by the author, 2½ hr. of heating with steam were required before the actual distillation finally started. Furthermore, the oil is in intimate contact with the acidic juice, in the form of a partial emulsion. In the experiments of Guenther and Langenau, the oil and water layers tended to separate, forming two layers. This probably accounts for the fact that the aldehyde content of the commercial oils is even lower than the values obtained in these experiments. Other factors, such as the action of enzymes, probably also play an important role.

An interesting oil results when the effect of heat and acid is minimized. This is the type of oil produced by J. J. R. Bristow of Dunedin, described in the section on "Florida Lime Oil." It differed considerably from the usual commercial distilled product. The aldehyde content was high (about 5 per cent); the odor and flavor more natural, being more characteristic of the fresh fruit. In these respects, the oil resembled the expressed lime oil.

It is worthy of note that, in the course of time, the trade has adopted the distilled oil of commerce, which possesses a distinctive odor and flavor of its own, not characteristic of the fresh fruit. Indeed, the trade has become so accustomed to this old type of oil (with a low aldehyde content) that it insists upon distilled lime oils having this distinctive, rather unnatural, character.

To conclude, the expressed oil, like all expressed citrus oils, resembles most closely the true, natural odor and flavor of the fresh lime fruit. The distilled oil, however, became popular many years ago, when it was a low-priced by-product in the extraction of lime juice and citric acid. If expressed lime oil could be produced at sufficiently low prices by the employment of modern machines, the flavor industry could probably be induced to use much larger quantities.

Use.—Oil of lime is one of the most popular flavoring ingredients, employed widely in all types of food products, confectionery, and beverages (alcoholic and nonalcoholic), especially of the "cola" type. Because of its superior solubility and pronounced characteristic flavor, the distilled oil is preferred for beverages. The softer, more lasting flavor of the expressed oil is especially suitable in candies, but many manufacturers prefer the distilled oil in hard candies, as it possesses that rather sharp and fresh note, which the public has come to associate with lime.

Expressed lime oil is used quite extensively also in perfumes, toilet waters, cosmetics, and soaps to which it imparts a refreshing citrus note, somewhat similar to bergamot.

Sams [42] reported on cases of occupational dermatitis among the harvesters of lime fruit in Florida. His experiments showed that the oil expressed from West Indian, Mexican, and Persian limes produced dermatitis by topical application on the skin, when followed by exposure of the skin to sunlight. The reaction is similar to that caused by bergamot oil. Sams' experiments prove that the concentration of the photodynamic agent, the length of time of exposure, the subject, the location of the application and previous irradiation determine the intensity of the subsequent dermatitis.

The longer wave lengths of ultraviolet radiation, just below the zone of visible light (3,100 to 3,700 angstrom units), are involved in the production of the dermatitis and subsequent pigmentation.

The chemical nature of the photocatalytic agent remains undetermined. It is probably one of the coumarin derivatives present in the expressed oil.

OIL OF SWEET LIME

Botany.—According to Webber,[1] the sweet limes constitute a separate group, the origin of which remains doubtful. They cannot be classified merely as typical Tahitian-group limes, since they are sweet. The best suggestion that can now be made concerning their relationship is that they are possibly hybrids of lime similar to the Mexican and a type of sweet lemon like the Dorshapo, or a sweet citron like the Corsican. Whatever

[42] *Archives of Dermatology and Syphilology* **44** (1941), 571.

[1] "The Citrus Industry," Vol. I, 619, Univ. Calif. Press (1943).

their origin, it is probably best to consider them as a separate group of the lime (*Citrus aurantifolia* Swingle). This supposition is supported by the fact that the essential oil of the sweet lime differs greatly from that of the acid lime as to odor, flavor, physical properties, and chemical composition.

Several varieties of the sweet lime group grow wild and semiwild in South America (Brazil and Colombia, for example), Central America, and Mexico, where the fruit is relished for its somewhat bergamot and orange-like flavor. The same fruit, however, seems insipid to the public in the United States.

Production.—The oil from the peel of the sweet lime has occasionally been produced in Sicily, probably by the sponge process, but has never attained commercial importance. During the years of World War II, when the United States was completely cut off from the former source of supply of the important Italian bergamot oil, a so-called Mexican bergamot oil appeared on the North American market. Upon closer investigation by the author, this oil proved to be expressed from the rind of the sweet lime, which grows wild and semiwild in certain parts of Mexico. The oil was obtained by crushing the entire fruit and centrifuging the resulting emulsion of juice and oil. The odor, although slightly resembling that of genuine bergamot oil, was far less pronounced, because of a much lower linalyl acetate content. This so-called Mexican bergamot oil, however, aroused little interest in the perfume, cosmetic, soap, and flavor industries, because in 1944 the imported true Italian bergamot oil became available again to the United States.

Physicochemical Properties.—An Italian (Calabria) sweet lime oil, described by Gildemeister and Hoffmann [2] as *Citrus limetta* Risso, syn. *C. limetta vulgaris,* syn. *Lima dulcis,* syn. *L. di Spagna dolce,* had a bergamot-like odor and these properties:

Specific Gravity at 15°/15°	0.872
Optical Rotation	+58° 19′
Saponification Number	75.0

Two coldpressed Mexican oils examined in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	I	*II*
Specific Gravity at 25°/25°	0.849	0.852
Optical Rotation	+76° 50′	+70° 42′
Refractive Index at 20°	1.4721	1.4706
Ester Content, Calculated as Linalyl Acetate	8.5%	15.0%
Evaporation Residue	1.8%	2.0%

[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 109.

Solubility	Turbid in 10 vol. of 90% alcohol, becoming clear upon standing with wax separation	Cloudy in 2 vol. of 90% alcohol; hazy in 10 vol. Clear in 0.5 vol. of 95% alcohol, opalescent in 10 vol. Clearly soluble in glacial acetic acid

Hufenuessler [3] reported about an oil derived from a fruit known as "Lima cheirosa" in the state of São Paulo, Brazil. This oil had a specific gravity of 0.82, ester content of 35–42 per cent, and possessed an odor typical of bergamot. According to Dierberger [4] "Lima cheirosa" belongs to the species *Citrus aurantifolia* Swingle and is probably the sweet lime.

Chemical Composition.—According to Gildemeister and Hoffmann,[5] the Italian sweet lime oil has a chemical composition similar to that of bergamot oil but contains more limonene and less linalyl acetate. Gildemeister [6] established the presence of the following compounds:

d-Limonene. d_{15} 0.848, α_D +81° 45′.
Identified as dihydrochloride m. 50° and as tetrabromide m. 105°.

Linalyl Acetate. The oil contained 26.3 per cent of linalyl acetate b_{13} 101°–103°, d_{15}^{15} 0.898, α_D^{15} −9° 52′.

l-Linaloöl. This alcohol was present in the oil partly esterified with acetic acid, partly in free form, b. 198°–199°, b_{13} 88.3°–89.5°, d_{15}^{15} 0.870, $[\alpha]_D^{15}$ −20° 7′, n_D^{20} 1.4668.

It is quite probable that sweet lime oil contains also limettin, bergaptol, and other coumarin derivatives (cf. "Oil of Bergamot," and "Oil of Lime Expressed," Chemical Composition).

As pointed out, the oil has never attained any commercial importance.

OIL OF MANDARIN AND OIL OF TANGERINE

Essence de Mandarines *Aceite Esencial Mandarina y Tangerina*
Mandarinenöl *Oleum Mandarinae*

Botany.—There has been some confusion regarding the botanical nomenclature of the loose-skinned or kid-glove oranges, as they are frequently

[3] *Rev. chim. ind., Rio de Janeiro* **6** (1938), 24.
[4] Private communication of Mr. Joao Dierberger, São Paulo, Brazil.
[5] "Die Ätherischen Öle," 3d Ed., Vol. III, 109.
[6] *Arch. Pharm.* **233** (1895), 178.

called in the United States. Although they possess many characteristics in common, the familiar cultivated loose-skinned oranges can be separated into several rather distinct groups, viz., the King, Satsuma, Mandarin, and Tangerine group. Certain investigators contend that these groups should be recognized as distinct species.

Of all the loose-skinned or kid-glove oranges, the mandarin seems to be the most highly evolved type, having been developed in China at a very early date and cultivated in Mediterranean countries for many generations. Perhaps the tangerine represents a lower stage in the horticultural development of the mandarin, and might even, with intensive cultivation and after a sufficient period of time, be evolved into a true mandarin. As a corollary to this theory, it may be hazarded that the mandarin, if horticulturally neglected, could retrogress to a lower type of loose-skinned orange.

According to the older classification of Swingle,[1] both the mandarin and the tangerine are horticultural strains of the same botanical variety, *Citrus nobilis* var. *deliciosa* Swingle, and should correctly be written as follows:

Citrus nobilis var. *deliciosa* Swingle "Mandarin," and
Citrus nobilis var. *deliciosa* Swingle "Tangerine."

Later investigations, however, convinced Swingle[2] of the necessity of finding another botanical name for the mandarin and tangerine type of orange. The most appropriate and oldest valid published name for this type of orange, according to Swingle, is *Citrus reticulata* Blanco, because of the irregular network of soft, white fibers found between the loose peel and the juice-filled segments. This name was first published by Blanco in his "Flora of Philippines," 1837, and antedates by three years *C. deliciosa* Tenore, which was based on the so-called Willow-leaf or China mandarin.

According to the latest nomenclature suggested by Swingle, the correct terms for the mandarin and tangerine are:

Citrus reticulata Blanco var. "Mandarin," and
Citrus reticulata Blanco var. "Tangerine."

As far as the colloquial designations mandarin and tangerine are concerned, both names, according to Webber,[3] are frequently used more or less interchangeably: tangerine is applied more strictly to those varieties pro-

[1] "Citrus and Related Genera," *Bailey Standard Cyclopedia of Horticulture* (1914–1917), The Macmillan Co., New York. Cf. Tanaka, "Principal Citrus Fruit of the World," *Kyushu Imp. Univ. Dept. Agr. Bull.* (1924), 1 (1):20. Webber and Batchelor, "Citrus Industry," Vol. I, 999, Univ. Calif. Press (1943).

[2] Webber and Batchelor, "The Citrus Industry," Vol. I, 414, Univ. Calif. Press (1943).

[3] *Ibid.*, 544.

ducing deep orange or scarlet fruits, and the older term mandarin has been reserved for the yellow fruited varieties. Thus, the differential characters separating the so-called tangerines from the other members of the mandarin group are very slight, the main visible difference being the deep orange-red color of the rind. Such differences are usually considered varietal only in magnitude. From the horticultural standpoint, to cite Webber,[4] there is perhaps no longer any need to use the name tangerine.

It is nevertheless a fact, perhaps unknown to some botanists, that there does exist a marked difference in odor and flavor, as well as in physicochemical properties and chemical composition in the essential oils expressed from the peels of the mandarin and the tangerine. Nelson,[5] in his study on the chemical composition of Florida tangerine oil, stated that the oil from the peel of the Florida tangerine must not be confused with the mandarin oil.

The differences between mandarin and tangerine oil cannot be explained merely by the different methods of expressing the oil employed in various countries, because Brazil, where identical methods are used, produces both types of oil, viz., mandarin and tangerine oil, the Brazilian mandarin resembling Italian mandarin oil, and the Brazilian tangerine resembling Florida tangerine oil. The soil, climatic and cultural conditions prevailing in the various producing sections might have a certain, perhaps a fundamental, influence upon the chemical composition and, therefore, upon the physicochemical properties of the oils.

According to Erlanson,[6] there are several cases, which have been authenticated by botanical study, where horticultural strains of the same citrus botanical variety have produced distinctly different oils; it is therefore not unusual that there should be different oils produced in the mandarin-tangerine series. It seems quite possible that we do not grow in the United States the same strain of mandarin that is grown in Sicily; and it could well be that the two strains, both considerably hybridized, have developed differently constituted oils.

That there should be similarity between Brazilian and Floridan oils is understandable, in view of the long-standing close collaboration, and interchange of plant material, between Brazilian and Florida growers. Probably Brazil has also imported the Sicilian strain, which would account for her producing one oil like the Floridan and one like the Sicilian.

[4] *Ibid.*

[5] *Am. Perfumer* **29** (1934), 347.

[6] Private communication by Mr. C. O. Erlanson (U. S. Dept. Agr., Division of Plant Exploration and Introduction, Bureau of Plant Ind., Sta. Beltsville, Md.).

Oil of Mandarin

History and Description.—The mandarin orange (*Citrus reticulata* Blanco, var. "Mandarin," syn. *Citrus nobilis* var. *deliciosa* Swingle "Mandarin"), a native of China and Cochin-China, was known and extensively planted in China and Japan at a very early date, but was not introduced into Europe and America until comparatively modern times. Main producing regions in Europe are in Sicily and Calabria (Southern Italy) along with the sweet orange, in Spain (Andalusia), and on the Mediterranean shores of North Africa. Tanaka [7] believes the Mediterranean mandarin, which he classifies as *C. deliciosa,* to have originated in the Mediterranean region as a chance seedling. His survey of China failed to locate the true mandarin, although it came originally from China.

The Willow-leaf (or China) mandarin was first introduced into the United States by the Italian Consul to New Orleans, La., from Italy, between 1840 and 1850, and was later taken from there to Florida and California.

In Sicily, mandarin groves are scattered quite widely throughout the provinces of Messina, Catania, and Palermo. In Messina the fruit is utilized primarily for domestic consumption as edible fruit, to a lesser extent for export, and in small quantity for the extraction of the essential oil. In Catania almost the entire production serves for export. In Palermo the bulk of the production is consumed locally, the balance being processed for oil. Additional small plantings are to be found in other provinces of Sicily. In the province of Reggio Calabria the cultivation of the mandarin has been increasing constantly; at present the plantings occupy about 140 hectares, the most important ones being located near Rosarno and Radicena and their environs. Mandarin plantations are also located in the bergamot belt. Most of the fruit in Reggio Calabria is sold for consumption; only a small percentage (5–6 per cent) serves for the extraction of oil. The harvest of the mandarin fruit lasts from mid-October to the end of January, but the fruit intended for the expression of the oil is picked from October 25 to November 30—i.e., before full maturity. Fruit gathered in December, or later, serves exclusively for local consumption or export. The oil is recovered from the peel by handpressing (sponge method), and to a small extent by machines of the *sfumatrici* type. One hundred kilograms of whole fruit yield 750–850 g. of oil. The total production of mandarin oil in Sicily and Calabria fluctuates considerably, depending upon the price which the edible

[7] "A monograph of the Satsuma orange, with special reference to the occurrence of new varieties through bud variations." *Taihoku Imp. Univ. Fac. Sci. Agr. Mem.* **4** (1932), 57. Through Webber and Batchelor, "The Citrus Industry," Vol. I, 1000, Univ. Calif. Press (1943).

fruit brings on the local and export market. On the average Sicily produces annually about 8,000 kg. of mandarin oil, and Calabria 1,000–1,500 kg.

Neither Florida, Texas, nor California produces any mandarin oil.

In Brazil mandarins, called locally *Mexerica* because of their pronounced flavor, are grown on small plantations in the Department of Gonzalo (State of Rio de Janeiro) and around Jaraguá do Sul (State of Santa Catarina). The harvest takes place from April to May. The total production of oil amounts to about 1,000 kg. per year, but may be increased if the demand warrants it. Extraction methods are the same as those applied in Brazil for the expressing of sweet orange oil, i.e., in locally constructed types of the Sicilian Avena machine, wherein batches of whole fruit are rasped against rotating corrugated discs and walls within an enclosed drum. The yield of oil is about 2 kg. per metric ton of fruit. Since the mandarins are consumed as fresh fruit in Rio de Janeiro whenever sweet oranges are lacking on the local markets, the mandarins often fetch high prices as fresh fruit, and the oil is usually expensive.

Physicochemical Properties.

A. Italian Mandarin Oil.—The oil has a very agreeable, somewhat peculiar, odor, and shows a bluish fluorescence, especially when diluted with alcohol. Gildemeister and Hoffmann [8] give these properties for Italian mandarin oil:

Specific Gravity at 15°/15°	0.854 to 0.859
Optical Rotation	+65° 0′ to +75° 0′; usually not below +70° 0′
Refractive Index at 20°	1.475 to 1.478
Acid Number	Up to 2.7
Ester Number	5.0 to 11.0; in some cases up to 18.7
Evaporation Residue	2.4 to 3.5%
Solubility	Soluble in 7 to 10 vol. of 90% alcohol, with more or less turbidity; soluble in 1.5 vol. of 95% alcohol but not always clearly

Shipments of genuine Italian mandarin oils, analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within the following limits:

Specific Gravity at 15°/15°	0.855 to 0.857
Optical Rotation (at Room Temperature)	+69° 36′ to +73° 15′
Refractive Index at 20°	1.4750 to 1.4759
Saponification Number	7.5 to 8.8

[8] "Die Ätherischen Öle," 3d Ed., Vol. III, 111.

Evaporation Residue	2.4 to 3.2%
Solubility	Incompletely soluble in 90% alcohol
Color	Light yellow

B. Brazilian Mandarin Oil.—During the years of World War II, when Italian oils were no longer available, Brazil exported limited quantities of mandarin oil to the United States.

Shipments of Brazilian mandarin oils, analyzed by Fritzsche Brothers, Inc., New York, had properties which varied within these limits:

Specific Gravity at 15°/15°	0.854 to 0.858
Optical Rotation (at Room Temperature)	+63° 55′ to +74° 42′
Refractive Index at 20°	1.4745 to 1.4763
Ester Content, Calculated as Linalyl Acetate	1.5 to 3.5%
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	0.4 to 1.5%
Evaporation Residue	3.4 to 4.7%
Solubility	Incompletely soluble in 90% alcohol
Color	Deep green

The evaporation residue of the Brazilian oils is usually higher than that of the Italian oils, because the latter are made by handpressing, the former by machine pressing. The difference is also reflected in the color and quality of the two types of oil, the Italian oil being much lighter and of superior odor and flavor.

Chemical Composition of Mandarin Oil.—The chemical composition of Italian mandarin oil differs from that of the Florida tangerine oil, as investigated by Nelson,[9] mainly by the presence of methyl anthranilic acid methyl ester which imparts to the Italian oil its characteristic fluorescence and odor. The following constituents were identified in Italian mandarin oil:

d-Limonene. According to Gildemeister and Stephan,[10] Italian mandarin oil consists mainly of *d*-limonene b. 175°–177°, α_D +76° 45′. Identified as tetrabromide m. 104°–105°.

Aldehydes(?). When treating the distillation residue with bisulfite solution, a double salt was obtained and an oil regenerated with alkali. Its naphthocinchoninic acid compound did not show a definite melting point. Therefore, it remains doubtful which aldehydes correspond to this compound.

[9] *Am. Perfumer* **29** (1934), 347.
[10] *Arch. Pharm.* **235** (1897), 583.

N-Methyl Anthranilic Acid Methyl Ester. This important constituent of Italian mandarin oil was found by Walbaum.[11] Less than 1 per cent of this ester is present in Italian mandarin oil, yet it is of considerable influence upon the odor of the oil.

It is interesting to note in this connection that the oil distilled from the leaves of the mandarin tree (Mandarin Petitgrain Oil) contains from 50 to 65 per cent of N-methyl anthranilic acid methyl ester.

Use.—Italian mandarin oil has been used principally as a modifier of various types of sweet orange oils, at times quite extensively for this purpose, by manufacturers of beverage extracts. It has also found similar employment in the bouqueting of sweet orange oils for the flavoring of confectionery, including both hard candies and soft centers.

In addition, the oil finds good use in the flavoring of various liqueurs and cordials, especially the well-known mandarin liqueur.

Oil of mandarin is an interesting ingredient also in the production of certain perfume effects, particularly in the French type of bouquets.

Suggested Additional Literature

P. Liotta, "New Polarimetric Data on Oil of Mandarin Oranges," *Riv. ital. essenze profumi* **5** (1923), 104.

K. Kafuku and C. Hata, "Utilization of Unripe Fallen Mandarin," *J. Soc. Chem. Ind. Japan* **29** (1926), 212. *Chem. Abstracts* **20** (1926), 2897.

G. Romero, "Analytical Constants of Deterpenized Essences," *Riv. ital. essenze profumi* **11** (1929), 272.

G. A. Fester, "Some South American Volatile Oils," *Rev. facultad quim. ind. agr. (Univ. nacl. litoral, Santa Fé, Argentina)* **7** (1938), 118. *Chem. Abstracts* **33** (1939), 7958.

Oil of Tangerine

A. History and Description of Florida's Tangerine Industry.—In the United States the best known, most cultivated, and most highly priced of all the loose-skinned oranges is the Dancy tangerine (*Citrus reticulata* Blanco var. "Tangerine," syn. *Citrus nobilis* var. *deliciosa* Swingle var. "Tangerine"), universally shipped under the name of tangerine. The largest plantings are located in Florida, and in approximately the same general sections which produce the orange and grapefruit. How and when the first tangerines reached Florida cannot be determined now but, according to Webber,[12] it is reasonable to assume that the original tangerine type from which the Dancy descended came from China to the United States, prob-

[11] *J. prakt. Chem.* [2], **62** (1900), 135.

[12] "The Citrus Industry," Vol. I, 560, Univ. Calif. Press (1943).

ably by the way of Mediterranean Europe. A very similar form of tangerine is cultivated in China, Formosa, and Japan.

The Dancy originated probably from a seedling grown at Buena Vista, St. Johns County, Florida, in the grove of Colonel George L. Dancy, who introduced this variety into cultivation in 1871 or 1872. Today, about 95 per cent of the tangerines grown in Florida are of the Dancy variety. The fruit ripens from the end of November to March. Tangerine fruit is readily injured by frost while the tree, grown on the very frost resistant *trifoliata* root stock, is quite hardy. Fruit from groves located on the northern edge of Florida's citrus belt must therefore be harvested and shipped before any danger of frost arises. Tangerines, once ripe, decline in quality rather rapidly and have to be shipped within a more limited period of time than oranges or grapefruit. Generally speaking, the bulk of tangerines is shipped from about Thanksgiving to the first of February; a small quantity follows during February, and very few after March first.

Practically all Florida tangerine oil is expressed from the peels of the Dancy.

According to Camp,[13] Florida's Dancy tangerine is oblate in shape, usually 2¾ to 3 in. in lateral diameter, and deep orange red to red in color. It has a nippled base, 11 to 14 sections, and usually about 14 seeds, although their number may vary widely. The skin is very smooth and loose from the pulp. Pulp and juice possess a rich and distinct flavor.

Total Fruit Production.—The reader interested in the latest and more detailed figures on fruit production in the United States is referred to the regularly published Crop Reports of the U. S. Department of Agriculture, Bureau of Agricultural Economics, Crop Reporting Board, Washington, D. C. The following data have been reported for the last few years:

Florida Tangerines in Thousand Boxes

Average 1935–1944	*1944*	*1945*	*1946*	*1947*
2,980	4,000	4,200	4,800	3,900

The net content of one box of tangerines in Florida is 90 lb.

The above cited figures include also fruit not harvested on account of economic conditions, 150,000 boxes in 1944 and 800,000 boxes in 1946.

Methods of Expressing Florida Tangerine Oil.—Although Florida sweet orange and grapefruit oils have always been merely by-products of the canning of juice and fruit segments, the extraction of Florida tangerine oil represented, until recently, an independent, separate industry, for the simple reason that neither juice nor fruit from loose-skinned oranges lends itself

[13] "Citrus Industry of Florida," *Florida State Dept. Agr., Tallahassee, Florida* (1946), 36.

readily to canning. Formerly, therefore, the whole (tangerine) fruit was crushed, the emulsion of juice and oil centrifuged, and the oil separated, the juice being thrown away as useless. Lately, however, efforts toward the production of a good canned tangerine juice by flash pasteurization, and with special precautions, have been successful, and canned tangerine juice has found eager acceptance on the market. Substantial quantities of expressed Florida tangerine oil (up to 10,000 lb. yearly) may, therefore, be expected as a by-product of this new industry.

In the new process of extracting the juice and oil from the tangerines, the washed fruit is first mechanically assorted according to size and sent through a Rotary Juice Extractor, which cuts the fruit into halves and expresses the juice (for details, see section on "Modern, Large-Scale Citrus Juice and Oil Pressing Equipment"). The peel can be expressed for oil either in a tapered screw press of the expeller type or in a Pipkin Peel Oil Press. The resulting effluent, an emulsion of essential oil, aqueous cell liquid and cell detritus, is screened to remove pulpy matter and solid particles, and then broken up by centrifuging, which yields the essential oil. On storage in a refrigerated room, some wax will precipitate, which has to be removed by filtration and renewed centrifuging.

The final oil, expressed by the new process and from the peel only, possesses a deep orange color, and a pleasant, characteristic odor and flavor, which resembles that of true mandarin.

Yield of Expressed Oil.—As in the case of orange oil, only a part of the tangerine oil present in the peel is obtained by the above-described process of expressing the oil, the greater part being retained by the spongy albedo of the peel. The yield of oil obtained by this process is about 2 lb. per U. S. ton of fruit, or 1 lb. from 12 boxes of fruit (1,080 lb.), each box holding 90 lb. of tangerines.

The yield of oil was even less with the old process, in which the whole fruit was crushed and the oil recovered from the expressed juice by centrifuging. In this case, the yield of oil amounted to about 1.3 lb. per ton of juice, or only 0.9 lb. of oil per ton of whole fruit. The quality of oil thus obtained was quite inferior to that of the oil recovered by the new process and from the peel only. As a result of the contact of the oil with large quantities of juice the most characteristic oxygenated constituents of the oil (which incidentally are more water soluble than the terpenes) were undoubtedly lost in the juice.

Total Oil Production.—According to statistics supplied by the Florida Citrus Commission, State of Florida, Lakeland, the following quantities of tangerine oil have been produced in Florida during the past few years:

Year	*Pounds*
1942–1943	5,000
1943–1944	2,986
1944–1945	2,730
1945–1946	10,415
1946–1947	7,708

B. Brazilian Tangerine Oil.—Seedling tangerines of nearly the same type as the Dancy are cultivated in several parts of the world, in Southern Europe, Algeria, South Africa, and especially in Brazil, for example.

In Brazil, tangerines, locally called *Laranja cravo,* are grown on small plantations in the State of São Paulo, in approximately the same sections as the sweet oranges. Since the fruit is sold mainly as edible fruit, it draws high prices, and production of oil is a secondary industry. The harvest takes place from April to June. After that period the peel becomes so loose from the pulp that it comes off easily, thereby making it almost impossible to treat the fruit in the type of Avena machines serving in Brazil for the expressing (rasping) of citrus fruit. Depending upon the type of machinery and the working method, the yield of oil ranges from 2.0 to 2.5 kg.. of oil per metric ton of fruit. The total tangerine oil production in Brazil amounts to about 5 metric tons per year.

Physicochemical Properties.—The physicochemical properties of tangerine oils differ considerably from those of mandarin oils, especially as regards optical rotation, that of tangerine being much higher than that of mandarin, indeed approaching that of sweet orange oil.

A. Florida Tangerine Oil.—Several lots of Florida tangerine oils examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.850 to 0.856
Optical Rotation at 25°	+90° 40′ to +93° 30′
Refractive Index at 20°	1.4732 to 1.4750
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	0.8 to 1.7%
Evaporation Residue	2.3 to 4.7%
Solubility	Incompletely soluble in 95% alcohol
Color	Deep orange to reddish

Kesterson and McDuff[14] investigated two Florida tangerine oils, one coldpressed, the other vacuum steam distilled (the latter obtained in the de-oiling of the juice), and reported these values:

[14] "Florida Citrus Oils," *Univ. Florida, Agr. Expt. Sta., Gainesville, Florida, Tech. Bull.* No. 452 (1948).

	Coldpressed	*Distilled*
Specific Gravity at 25°/25°	0.8456	0.8407
Optical Rotation at 25°	+91.18°	+93.67°
Optical Rotation at 25° of 10% Distillate	+92.68°	...
Difference	1.50°	...
Refractive Index at 20°	1.4734	1.4720
Refractive Index at 20° of 10% Distillate	1.4711	...
Difference	0.0023	...
Aldehyde Content, Calculated as Decyl Aldehyde	1.08%	1.24%
Ester Content [15]	0.34%	0.25%
Evaporation Residue	4.53%	0.20%

B. Brazilian Tangerine Oil.—Two samples of tangerine oil received from Brazil analyzed as follows:

	I	*II*
Specific Gravity at 15°/15°	0.853	0.852
Optical Rotation at 25°	+96° 10′	+94° 40′
Refractive Index at 20°	1.4748	1.4740
Evaporation Residue	3.6%	2.8%
Color	Brownish-green	Dark brown

The odor (and flavor) of these oils differed from that of Italian or Brazilian mandarin oils and resembled that of sweet orange oil. The high optical rotation of the Brazilian tangerine oils also points toward sweet orange oil.

Chemical Composition of Tangerine Oil.—The chemistry of Florida tangerine oil (from Dancy tangerine) was investigated by Nelson [16] who identified the following constituents:

d-Limonene. The principal constituent, amounting to about 95.75 per cent of the total oil. α_D of the purified limonene +94° 30′; identified as tetrabromide m. 104.5°.

Octyl Aldehyde. Isolated as bisulfite compound, and identified as oxime m. 57°–58°. The presence of octyl aldehyde was confirmed by oxidation of the aldehyde to octylic acid and analysis of the silver salt.

Decyl Aldehyde. Isolated as bisulfite compound; oxime m. 66°–67°. Oxidation of the aldehyde to decylic acid and analysis of the silver salt.

Tangerine oil contains much less of octyl and decyl aldehyde than Nelson and Mottern [17] found in Florida grapefruit oil.

[15] Method of Seeker and Kirby as reported by Poore, *U. S. Dept. Agr., Tech. Bull.* No. 241 (1932), 1–30.

[16] *Am. Perfumer* **29** (1934), 347.

[17] *Ind. Eng. Chem.* **26** (1934), 636.

Citral(?). Treating the terpeneless oil with sodium sulfite and sodium bicarbonate, a small quantity of a limpid yellow oil was isolated which possessed a pronounced citral odor. However, no crystallized α-citral semicarbazone could be obtained, probably because some other aldehyde, also forming a labile dihydrodisulfonic acid derivative, was present.

Linaloöl. Identified as phenylurethane m. 61°–62°; no depression of the melting point when mixed with an authentic sample; treatment with a 5 per cent sulfuric acid solution gave terpin hydrate m. 116°–117°.

Oxidation of linaloöl produced an aldehyde with a typical citral odor.

Citronellol(?). An alcohol with a rose-like odor was isolated. The diphenylurethane obtained from it was a liquid which indicated the presence of citronellol rather than geraniol.

Other Unidentified Alcohols(?). The alcohols in tangerine oil are present partly as esters, although the ester content of the oil is low.

Cadinene(?). In the fraction b_{10} 128°-130°. The presence of cadinene was indicated by a blue color on treatment with acetic and sulfuric acids, but no crystalline hydrochloride could be obtained. If cadinene is actually present, it is probably accompanied by other substances which prevent the isolation of cadinene dihydrochloride.

None of the unsaponified fractions showed any fluorescence which indicates the absence of even traces of methyl anthranilate in Florida tangerine oil.

When standing for a long time in a refrigerator, a yellow, partly crystalline material separates from Florida tangerine oil. This substance, named *tangeretin*, was investigated by Nelson.[18] According to Goldsworthy and Robinson,[19] tangeretin, m. 154°, is 3,5,6,7,4′-pentamethoxyflavone.

Use.—In spite of the apparently close botanical relationship of tangerine and mandarin, commercially the oils of tangerine and mandarin must be regarded as quite different products from the standpoint of practical employment. Mandarin oil possesses a very distinctive and characteristic flavor to which it owes its value in flavor and perfume work. Some commercial lots of tangerine oil, on the other hand, are hardly distinguishable from orange oil and bear no resemblance to real mandarin oil. Lately, however, some Florida juice canneries have developed new methods of extracting tangerine juice and oil which have resulted in such an improvement that the odor and flavor of this tangerine oil almost approaches that of true mandarin oil, although the physicochemical properties are still those of tangerine oil. When selecting a lot of Florida tangerine oil, the buyer should therefore pay special attention to odor and flavor tests.

[18] *J. Am. Chem. Soc.* **56** (1934), 1392.
[19] *J. Chem. Soc.* (1937), 46.

SUGGESTED ADDITIONAL LITERATURE

W. S. Tao and C. M. Chu, "Essential Oil in the Ripe Tangerine," *J. Chinese Chem. Soc.* **2** (1934), 282. *Chem. Abstracts* **29** (1935), 543.

P. P. T. Sah and H. Y. Fang, "Studies in Chinese Citrus Fruits. Isolation of Essential Oils from the Tangerine," *J. Chinese Chem. Soc.* **2** (1934), 266. *Chem. Abstracts* **29** (1935), 543.

OIL OF PETITGRAIN MANDARIN

(Mandarin Leaf Oil)

Essence de Petitgrain Mandarines *Aceite Esencial Petitgrain Mandarina*
Petitgrain Mandarinenöl

The leaves trimmed from the mandarin tree, *Citrus reticulata* Blanco, var. "Mandarin," syn. *Citrus nobilis* var. *deliciosa* Swingle "Mandarin," are occasionally steam distilled, like the foliage of the bitter (sour) orange tree (cf. section on "Oil of Petitgrain Bigarade").

The yield of oil increases as the season advances, according to La Face,[1] who reported a yield of 0.289 per cent for February, 0.304 for March, 0.314 for April, and 0.339 for May, during which months the mandarin trees are pruned in Sicily. During distillation, the oil separates in the Florentine flask in two portions, one lighter than water, and one heavier than water, which must be combined. Only insignificant quantities of the oil are annually produced in Sicily, Spain, Algeria and, lately, also in French Guinea. The oil is therefore little known, despite the fact that it offers interesting possibilities in perfume and flavor work.

Physicochemical Properties.—According to Naves,[2] the properties of Algerian mandarin leaf oil vary within these limits:

Specific Gravity at 15°/15°	0.9826 to 1.0140
Optical Rotation	+4° 10′ to +13° 8′
Acid Number	0.52 to 1.12
Ester Number	170.8 to 211.4
Ester Content, Calculated as N-Methyl Anthranilic Acid Methyl Ester	50.3 to 62.3%

[1] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* No. 4-6 (1942), 7.
[2] *Parfums France* **7** (1929), 280.

N-Methyl Anthranilic Acid Methyl Ester Content, According to the Method of Hesse and Zeitschel [3]	59.8 to 63.0%
Solubility	Soluble in 8 to 18 vol. of 80% alcohol, turbid with more; soluble in 3 to 5 vol. and more of 85% alcohol

Trabaud [4] described two "tangerine" leaf oils distilled on the plantations of Nadel and La Sala, near Labé, French Guinea (West Africa) which, however, had properties somewhat different from European mandarin oils. Trabaud, however, is not clear in his differentiation between tangerine and mandarin. (See in this connection also "Florida Tangerine Oil.") Trabaud reported the following properties for his "tangerine" petitgrain oils:

	I	*II*
Specific Gravity at 15°	0.9936	0.9982
Optical Rotation	+21° 28′	+19° 10′
Refractive Index at 20°		1.5284
Acid Number	0.9	0.9
Ester Number	198.6	201.6
Ester Content, Calculated as N-Methyl Anthranilic Acid Methyl Ester	53.48%	54.3%
Solubility in 90% Alcohol	2 and over	1 and over
Solubility in 85% Alcohol	4 and over	3.3 and over

Two samples of Spanish mandarin petitgrain oil examined by Schimmel & Co.[5] showed different properties for the reason that these oils were distilled from small, unripe fruit. The properties of these oils read as follows:

	I	*II*
Specific Gravity at 15°	0.8615	0.8585
Optical Rotation	+57° 27′	+58° 57′
Refractive Index at 20°	1.47867	1.47662
Acid Number	1.5	0.7
Ester Number	11.2	8.4
Solubility	Soluble in 5 vol. and more of 90% alcohol	Soluble in 5.5 vol. and more of 90% alcohol

Chemical Composition.—Charabot [6] found that the main constituent of mandarin leaf oil is methyl anthranilic acid methyl ester. Investigating an oil distilled in Algeria, Naves [7] reported the presence of the following constituents:

[3] *Ber.* **34** (1901), 296. *J. prakt. Chem.* [2], **64** (1901), 246. See also Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 682.
[4] *Perfumery Essential Oil Record* **27** (1936), 356.
[5] *Ber. Schimmel & Co.*, April (1925), 50.
[6] *Compt. rend.* **135** (1902), 580.
[7] *Parfums France* **7** (1929), 279.

α-Pinene. Identified as semicarbazone of the pinonic acid m. 201°–202°.

Camphene(?).

Limonene. Tetrabromide m. 104°.

Dipentene. Tetrabromide m. 124°.

p-Cymene. *p*-Hydroxyisopropyl benzoic acid m. 155°.
According to Naves, the oil contains 42 per cent terpenes.

Linaloöl(?).

Geraniol. Identified as silver salt of the phthalic acid ester m. 133°.
According to Naves, the oil contains about 2 per cent of terpene alcohols $C_{10}H_{18}O$, one-third of which is in ester form.

Sesquiterpene. Traces only.

Anthranilic Acid Methyl Ester. The oil contains 1 per cent of methyl anthranilate, as determined by the method of Erdmann and Scott.[8]

N-Methyl Anthranilic Acid Methyl Ester. In the oil investigated by Naves, 56 per cent of this ester, as determined with 25 per cent sulfuric acid, was present.

Use.—Oil of petitgrain mandarin has so far been only seldom employed in perfumery. Novel possibilities have been suggested by Simonet and Igolen.[9] According to these workers, exposure of the roots of flax and barley seedlings to the vapors of steam distilled petitgrain mandarin oil (from fresh leaves), at room temperature, either stopped cell division in the intermediate stages or produced a marked polyploidism. The effect is due to dimethyl anthranilate of which the oil contains about 60 per cent.

OIL OF GRAPEFRUIT

Essence de Pamplemousse *Aceite Esencial Toranja*
Pompelmusöl

North American Grapefruit Oil

Botany and History.—It is not definitely known whence the grapefruit, *Citrus paradisi* Macfayden, came, or when it was first called grapefruit.

[8] *J. Ind. Eng. Chem.* **15** (1923), 732.
[9] *Compt. rend.* **210** (1940), 510. *Chem. Abstracts* **34** (1940), 4108.

According to Swingle,[1] the grapefruit apparently originated in the West Indies. Careful search has not found it a native of the Old World, where the parent species is largely grown, and where many horticultural varieties are known. Yet, there exists the possibility that the grapefruit actually originated in the Old World and that it was brought to America by that mysterious and elusive Captain Shaddock, who is said to have introduced pummelos (shaddocks) into the West Indies during the eighteenth century. Another alternative, according to Swingle, is that the grapefruit may be a hybrid of the pummelo with the sweet orange. Webber [2] expressed the opinion that the grapefruit is very closely related to the pummelo and was seemingly derived from it or from a common ancestral type. The pummelo had probably arrived in Spain by the middle of the twelfth century, having been brought there by the Arabs from the East over the same path as the orange. In 1750 Griffith Hughes first described the "forbidden fruit" as originating from Barbados, and later, in 1789, Patrick Browne mentioned it under the name "forbidden fruit" or "smaller shaddock" from Jamaica.

According to Webber,[3] the grapefruit varieties which are now cultivated originated for the most part in Florida, where this industry was first commercialized. They came mainly from chance seedlings which were selected and propagated because they supposedly possessed some superior character of fruit or tree. Thus, most of these varieties are known as Florida seedling types and differ from each other in minor character only, their fruit usually being so similar that they cannot be distinguished with certainty.

The original grapefruit varieties planted in Florida were the seedy types, such as the Duncan. In 1895 or 1896 the Marsh Seedless was introduced; since then both the seedless as well as the seedy (Duncan, Walters, McCarty, etc.) varieties have been planted extensively. Today the production of grapefruit in Florida (and in Texas) is so heavy that the fresh fruit market cannot absorb the crop and the bulk of the fruit, therefore, has to be converted into canned juice. The canneries use both the seedy and the seedless varieties, but prefer the former, owing to the much better flavor of the juice.

Years ago, light shipments of fruit arrived from South Africa, but lately the United States has become the world's largest supplier of edible grapefruit, producing about 90 per cent. The utilization of surplus fruit became principally an American industry, comprising the canning of grapefruit segments ("hearts") and juice.

[1] Webber and Batchelor, "The Citrus Industry," Vol. I, 418, Univ. Calif. Press (1943).
[2] *Ibid.*, 570.
[3] *Ibid.*, 571.

Varieties of Grapefruit.—Most grapefruit varieties do not differ so markedly from one another as do orange varieties; indeed a considerable portion of Florida's grapefruit crop is grown on budded trees of unnamed local sorts. In Florida, this fruit, together with that of seedling trees, is usually referred to as Florida Common, which term includes all types of seedy grapefruit. At the present time, new plantings of grapefruit are about evenly divided between the seedy and the seedless varieties.

The Duncan, the original, or seedling grapefruit, is highly flavored and of excellent dessert quality. Although containing a large quantity of seed (30 to 60), it is much preferred to any other variety for canning of the juice. Many packing houses today use the name Duncan to cover all seedy grapefruit. In Florida the Duncan matures early, from November to May, but it is sometimes left on the trees until the beginning of June. The tree grows vigorously, and bears well.

The Marsh, or Marsh's Seedless, is usually oblate, markedly flattened at the ends, with the pith in the center of the fruit slightly opened. Nearly seedless, it contains only 2 to 8 seeds. According to Camp [4] the trees are very rigorous growers, heavy producers, somewhat more resistant to cold and drought than the Duncan, and less susceptible to variations in fertilization and spraying than most varieties of citrus in Florida. The chief advantage of the Marsh on the fresh fruit market is its seedlessness, but in developing this characteristic a great deal of flavor has been sacrificed, as the fruit contains much less acid and sugar than the seedy varieties. For the same reason the Marsh Seedless is not so satisfactory for canning purposes. It matures in mid-spring, but may be held on the trees until later. Years ago, before the advent of the canning industry, and when all fruit was being shipped to the fresh fruit market, the Marsh Seedless was used as a late grapefruit. This practice had no connection with the time of maturity, but was caused by the fact that the seeds in seedy grapefruit tend to sprout in late summer, the fruit as a result developing a bitter flavor. On the other hand, the seeds in Marsh Seedless not only are scarce, but fail to sprout. Most of the seedless grapefruit now going to the fresh fruit market are being shipped just as early as the seedy types.

As has been mentioned above, the canning industry generally prefers the Duncan, and uses it primarily, but toward the end of the season the consumption of canned grapefruit juice increases greatly; at this stage the Marsh Seedless is utilized in almost as large quantities as the Duncan.

[4] "Citrus Industry of Florida," *Florida State Dept. Agr., Tallahassee, Florida* (1946), 35. Also private communications by Dr. A. F. Camp, Lake Alfred, Fla.

Thus large-scale canneries receive the Duncan from the middle of October on, and the Marsh Seedless from the middle of December on. Both types of fruit, however, overlap, and at times are processed together. Both varieties of fruit, on expression, yield the same amount of oil.

There exist other grapefruit varieties of less importance, the Thompson and the Pink Marsh Seedless for example, a description of which will be found in the paper by Vosbury and Robinson,[5] and in the more recent above-named paper by Camp.

Producing Regions.—The grapefruit, even more so than the orange, requires a warm, humid climate. For this reason the grapefruit grows best near the shores of the Gulf of Mexico, viz., between the southern part of the west coast and the center of Florida, and in the warm coastal parts of Texas. In Florida the producing regions of grapefruit are essentially the same as those of the orange, except for the more northern, and colder, sections.

In the lower Rio Grande Valley of Texas, especially in the Brownsville-Mission section, the grapefruit constitutes a very large percentage of the acreage planted with citrus. Scattered grapefruit groves, equally under irrigation, exist also in the orange growing sections of the Texas northern Gulf Coast, particularly in the vicinity of Houston and Beaumont, in Louisiana, in Alabama near Mobile, and in Mississippi along the Gulf Coast.

So far as the grapefruit industry of the Southwest is concerned, its beginning dates back to the introduction of the Marsh Seedless from Florida prior to 1900. This variety was originally chosen primarily because of its better marketability as seedless fruit, also because of its somewhat better resistance to cold and drought. According to Shamel and Caryl,[6] the grapefruit matures very rapidly in the citrus districts of Arizona, and in the San Joaquin, Coachella, and Imperial Valleys of California. Of recent years the picking of the fruit in these sections has been delayed until May, or later, when it is fully ripe, and possesses superior eating qualities.

Total Fruit Production.—The reader interested in the latest and more detailed figures on fruit production in the United States is referred to the regularly published Crop Reports of the U. S. Department of Agriculture, Bureau of Agricultural Economics, Crop Reporting Board, Washington, D. C. The data in Table 1.26 have been reported for the last few years:

[5] "Culture of Citrus Fruits in the Gulf States," *U. S. Dept. Agr., Farmers' Bull.* No. 1343, Revised Ed., September (1929).

[6] "Citrus Fruit Growing in the Southwest," *U. S. Dept. Agr., Farmers' Bull.* No. 1447, Revised, November (1930).

TABLE 1.26. GRAPEFRUIT IN THOUSAND BOXES

State	Average 1935–1944	1944	1945	1946	1947
Florida	20,780	22,300	32,000	30,000	31,000
Texas	14,000	22,300	24,000	25,000	24,000
Arizona	2,800	3,750	4,100	4,100	3,000
California	2,500	3,830	3,450	3,400	2,860
Total	40,080	52,180	63,550	62,500	60,860

The net content of boxes varies in the different producing regions. In California, one box contains from 65 to 68 lb., in Florida and the other states, 80 lb. of grapefruit.

Planting.—The planting of grapefruit resembles that of the orange; this similarity extends also to the practice of budding on sour orange stock or rough lemon stock. The latter is used in the higher and sandy lands, the former in the lower and moister sections. Full details will be found in "Citrus Industry of Florida." [7]

Period of Harvesting.—The time of picking grapefruit coincides approximately with that of oranges, except that the grapefruit harvest is generally completed by the end of June. After that, the only grapefruit available are those known as June Bloom; they are usually the product of a second growth of blossoms on the trees, which happens occasionally as the result of climatic conditions.

Canning of Juice and Fruit Segments.—Today the production of grapefruit greatly exceeds the demand for fresh fruit; therefore the surplus is utilized either for the canning of fruit segments ("hearts") or for the canning of juice. In both processes, the essential oil may be extracted from the residual peel. Of the many canneries in Florida, the Gulf States, and the Southwest, only a few find it worth while to extract the oil; most canneries simply discard the peel as waste. Florida's canneries equipped for the expression of oil are centered in or near Dade City, Winter Haven, Orlando, Tampa, and Dunedin.

(*a*) *Canning of Grapefruit Segments.*—After arrival in the cannery, the fruit is thoroughly washed and scrubbed to remove insects, dirt, soot, and other foreign matter, and carefully inspected on a conveyer belt, any un-

[7] *Florida State Dept. Agr., Tallahassee, Florida* (1946).

sound fruit being eliminated. To facilitate peeling, the fruit then passes through a bath of hot water at a temperature of 196° to 200° F. for about 5 min.; or the fruit is steamed for 2 to 3 min. This procedure dilates the peel, so that it may be readily stripped off by hand, with the use of a stainless steel cobbler's knife. However, the outer membrane of the segments, the so-called "rag," adheres firmly to the fruit, and can be removed only after the peeled fruit has been treated for about 12 sec. in a hot lye bath (containing 2 to 3 per cent of sodium hydroxide). Disintegrated by this treatment, the "rag" is partly detached by passing the fruit beneath sprays of water which wash the fruit thoroughly and at the same time remove the lye solution. Finally the cleaned fruit goes to a sectionizing table, where girls, using stainless steel or aluminum knives, eliminate any adhering rag or section walls, and cut the fruit into sections. The latter, after careful inspection, are canned in sugar syrup.

Most canneries today do not further utilize the peel which has been removed from the fruit after steaming of the latter, or after treatment with hot water, because this process makes it very difficult to obtain a fair yield of oil on expression of the plumped and softened peel. Some of the canneries extracting juice have used this steam method to reduce the amount of oil in the juice; however, it has been found that the extraction of oil from such peel gives only a small yield.

Besides, the total production of canned grapefruit segments is relatively insignificant when compared with the very large quantities of canned juice manufactured yearly; and obviously the same is true of the quantities of essential oil made from peel remaining after the canning of fruit segments.

(*b*) *Canning of Grapefruit Juice.*—On the other hand, the canning of grapefruit juice has reached very large proportions, canned grapefruit juice attaining ever-increasing popularity among the consuming public. As a result of this development, large quantities of expressed grapefruit oil are available nowadays as by-products of the manufacture of canned grapefruit juice. The machines employed today in the United States for the expression of the juice have been described in the section on "Modern, Large-Scale Citrus Juice and Oil Expressing Equipment."

Methods of Expressing Grapefruit Oil and Yield of Oil.—This applies also to the oil presses used for the expression of essential oil from residual grapefruit peel. In the case of grapefruit peel, however, it should be noted that the oil glands are located deeply in the peel, and that, in addition, the peel contains a very thick layer of sponge-like albedo, which has a tendency to absorb the oil as soon as it is expressed from the flavedo, and to retain it despite the application of very high pressure. Compared with that of orange or lemon, the yield of oil expressed from grapefruit is, therefore,

small. Using tapered screw presses, the yield will be, on the average, 1.2 lb. per ton of fruit (22 boxes of grapefruit yield about 1 lb. of oil, one box holding 85 lb. of fruit). To obtain a better yield, it will be necessary to apply a higher pressure than can be obtained in tapered screw presses. The machines most suitable for the expression of grapefruit peel are the Pipkin Peel Oil Press, yielding from 1.3 to 1.8 lb. of oil per U. S. ton of fruit, and the F.M.C. Whole Fruit Extractor which yields on the average 1.25 lb. of oil. This shows that even by the use of the most modern oil presses the actual yield of oil falls far short of the theoretical, as the minced peel of 1 ton of grapefruit on steam distillation is said to give as much as 25 lb., and even more, of oil.

Total Oil Production.—According to statistics supplied by the Florida Citrus Commission, State of Florida, Lakeland, the following quantities of coldpressed grapefruit oil have been produced in Florida during the past few years:

Year	*Pounds*
1942–1943	51,650
1943–1944	53,460
1944–1945	29,106
1945–1946	73,759 [8]
1946–1947	33,944

Aside from small lots of expressed and distilled grapefruit oil regularly produced in California, most commercial expressed grapefruit oil originates in Florida. It has been the endeavor of the Florida canners to keep their production of grapefruit oil in line with actual consumption, which is not yet very large. The oil was not introduced until 1930; and our food, confectionery, and beverage industries have not yet found sufficient employment for grapefruit oil to warrant too heavy a production. The Florida canning houses could readily produce 100,000 lb. of this oil if they would process more of their waste peel, which is so plentiful in their juice canning operation.

There also exists a potentially very heavy production in Texas, where the first experiments of expressing grapefruit oil were made in 1947.

Physicochemical Properties of Grapefruit Oil.—Oil of grapefruit is a light yellow liquid of pleasant odor and flavor, which resembles both orange and lemon oils. On standing or chilling, a yellowish to brown flocculent precipitate forms, which may entirely disappear upon warming. Grapefruit oil differs from coldpressed orange oil in the fact that this sediment seems to precipitate in cold storage for a period of about sixty days; in fact, it continues to precipitate for about two years, but at least 95 per cent of the

[8] This figure appears too high and probably includes distilled grapefruit oil.

sediment separates within the first two months. Although appearing voluminous, the precipitate is of very light weight, amounting to only about 2 per cent of the total weight of the oil.

Shipments of genuine Florida coldpressed grapefruit oils which have been analyzed by Fritzsche Brothers, Inc., New York, since the first days of its introduction about 1930 had properties which varied within these limits:

Specific Gravity at 15°/15°	0.855 to 0.860
Optical Rotation at 25°	+91° 45′ to +94° 36′
Refractive Index at 20°	1.4745 to 1.4778
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	1.4 to 1.6%
Evaporation Residue	5.0 to 8.0%
Solubility	Incompletely soluble in 90% alcohol up to 10 vol. owing to separation of wax

The odor of a grapefruit oil should be characteristic of the fruit; it is a delicate odor which seems to be easily modified by the presence of even very small quantities of orange oil. For this reason grapefruit oil has to be expressed with the greatest of care, and special precaution must be taken that the grapefruit peel to be processed contain no admixed orange peel whatsoever. This is not always easy in the great canneries processing large quantities of fruit and peel, especially when they switch from orange to grapefruit. In this case some orange peel may remain hidden in the long chutes conveying the peel to the oil presses.

Examining fifteen Florida grapefruit oils of the 1947–1948 season, six of them coldpressed, the other nine vacuum steam distilled (the latter obtained in the de-oiling of the juice), Kesterson and McDuff [9] reported these maximum and minimum values:

	Coldpressed Oil		*Distilled Oil*	
	Maximum	*Minimum*	*Maximum*	*Minimum*
Specific Gravity at 25°/25°	0.8532	0.8508	0.8539	0.8415
Optical Rotation at 25°	+92.96°	+91.19°	+96.50°	+91.50°
Optical Rotation at 25° of 10% Distillate	+98.14°	+95.81°	...	...
Difference	6.33°	3.68°	...	...
Refractive Index at 20°	1.4761	1.4746	1.4746	1.4714
Refractive Index at 20° of 10% Distillate	1.4712	1.4698	...	...
Difference	0.0054	0.0038	...	...

[9] "Florida Citrus Oils," *Univ. of Florida, Agr. Expt. Sta., Gainesville, Florida, Tech. Bull.* No. 452 (1948).

	Coldpressed Oil		*Distilled Oil*	
	Maximum	*Minimum*	*Maximum*	*Minimum*
Aldehyde Content, Calculated as Decyl Aldehyde	1.67%	1.49%	4.06%	2.30%
Ester Content [10]	4.20%	2.11%	2.52%	0.08%
Evaporation Residue	8.02%	6.02%	3.66%	0.19%

Interesting is the fact that, compared with the coldpressed oils, the distilled oils exhibit a much higher aldehyde content. This indicates that during the process of expression a considerable proportion of the aldehydes seems to be lost, as a result perhaps of oxidation and reduction by enzymes in the emulsion of essential oil, cell detritus, and mucilaginous matter. Because of hydrolysis during distillation, the steam distilled oils contain a lower percentage of esters than the coldpressed oils.

Chemical Composition.—The investigation undertaken by Zoller [11] on Florida grapefruit oil was based upon only a small quantity (about 100 g.) of oil obtained by steam distillation *in vacuo*. Nelson and Mottern,[12] working with much larger quantities, examined expressed Florida oil.

Distilled Grapefruit Oil.—Zoller [13] established in a *distilled* oil the presence of:

α-Pinene. Identified as nitrosochloride m. 102°–103°; hydrochloride m. 132°.

d-Limonene. In the fraction b. 175°; b_{12} 52°–70°; α_D^{20} +38° 0′; tetrabromide m. 104°.

Linaloöl and Presumably Linalyl Acetate(?). In the fraction b_{12} 70°–85°; treatment with 5 per cent sulfuric acid gave terpin hydrate m. 116°.

Citral. In the fraction b_{12} 85°–115°; semicarbazone m. 165°. According to Zoller, citral is the principal aldehyde occurring in grapefruit oil.

Geraniol(?) and Presumably Geranyl Acetate(?). Geraniol is probably present because the fraction b_{12} 110°–115°, upon treatment with 5 per cent sulfuric acid, gave terpin hydrate m. 116°; the boiling point of this fraction was too high to contain linaloöl.

Expressed Grapefruit Oil.—Nelson and Mottern [14] investigated Florida grapefruit peel oil prepared by *pressing* the peel between rollers (Pipkin Peel Oil Press) and separating the oil in a centrifugal separator. They found that the expressed oil contains approximately 90 per cent of limonene, 2 to 3 per cent of oxygenated volatile constituents and sesquiterpenes, and 7 to 8 per cent of waxy material. The following constituents were identified:

[10] Method of Seeker and Kirby, as reported by Poore, *U. S. Dept. Agr., Tech. Bull.* No. 241 (1932), 1–30.
[11] *Ind. Eng. Chem.* **10** (1918), 364.
[12] *Ibid.* **26** (1934), 634.
[13] *Ibid.* **10** (1918), 369.
[14] *Ibid.* **26** (1934), 634.

Limonene. As tetrabromide m. 104.5°. Limonene is the main constituent (about 90 per cent) of grapefruit oil.

Pinene, according to these authors, is not present in expressed Florida grapefruit oil.

Octyl Aldehyde and Decyl Aldehyde. Isolated as bisulfite compound from the terpeneless oil, and identified by melting points of the corresponding oximes: C_8 = 58°–59°; C_{10} = 69°; also by oxidation with potassium permanganate to the corresponding acids and analysis of the silver salts.

Citral. Small quantities were isolated from a portion of the terpeneless oil with sodium sulfite; semicarbazone m. 160°–162°. No depression when mixed with prepared α-citral semicarbazone.

Acetic Acid, Octylic Acid, and Decylic Acid. Obtained by saponification of the terpeneless aldehyde-free oil, fractional precipitation and analysis of the silver salts. Octylic and decylic acids are present only in small quantities, probably as esters.

n-Octyl Alcohol and *n*-Octyl Acetate. Treating the fraction b_{10} 80°–91° of the saponified, aldehyde-free, terpeneless oil with phenylisocyanate gave a crystalline phenylurethane m. 73°. No depression when mixed with prepared *n*-octyl phenylurethane.

n-Nonyl Alcohol. Treating in the same way the fraction b_{10} 100°–102°, a phenylurethane m. 52°–54° was obtained. No depression when mixed with prepared *n*-nonyl phenylurethane. Only a small quantity of nonyl alcohol can be present.

Geraniol and Geranyl Acetate. Heating the fraction b_{10} 107°–110° with phthalic anhydride, the acid geranyl phthalate was obtained; silver salt m. 135°–137°. Furthermore, the diphenylurethane m. 80°–81° was prepared. No depression when mixed with the corresponding synthetic products.

Methyl Anthranilate. The fraction b_{10} 118°–121° of the unsaponified oil showed blue fluorescence. Diazotization of the isolated product gave a faint reaction with β-naphthol. Hence, the oil contains only small quantities of methyl anthranilate.

d-Cadinene. Positive reaction of the fraction b_{10} 125°–129° with acetic and sulfuric acid; dihydrochloride m. 117°–118.5°. No depression when mixed with *d*-cadinene dihydrochloride.

While from Zoller's work it was assumed that citral is the chief aldehyde occurring in grapefruit oil, Nelson and Mottern showed that citral is a minor constituent, the predominating aldehydes being octyl and decyl aldehydes. They are present in the oil in about equal portions. The relatively high percentages of these compounds characterize grapefruit oil as aldehydic and necessitate protection from oxidation.

So far as the *wax-like constituents* of the expressed oil from the peel of Florida grapefruit are concerned, Markley, Nelson and Sherman[15] found that the nonvolatile residue remaining after distillation contains solid fatty acids of mean molecular weight corresponding to $C_{32}H_{64}O_2$; in addition

[15] *J. Biol. Chem.* **118** (1937), 433.

linolenic, linoleic, and oleic acids; a sapogenic ketone $C_{30}H_{52}CO$; hydrocarbons $C_{29}H_{60}$ and $C_{31}H_{64}$; a phytosterol $C_{28}H_{47}OH$; and *umbelliferone* $C_9H_6O_3$. These substances have their origin in the cuticle wax of the fruit which is dissolved by the oil during the pressing process.

The peel of the grapefruit also contains pectins and naringin. The latter, a glucoside, is the so-called "bitter principle" of grapefruit.

Use.—The odor and flavor of expressed grapefruit oil are soft and pleasant, reminiscent of oranges and lemons.

Since the introduction of this oil, its sales have steadily increased, so that it may be now regarded as having a well-established market.

The most important and regular outlet is the flavor industry, which regularly consumes rather substantial quantities of the natural oil, the terpeneless oil, and the fivefold concentrate. The latter are often used in combination with the expressed oil to produce special effects.

Brazilian Grapefruit Oil

Lately Brazil, too, has started to produce grapefruit oil, the quantities offered so far being small. The producing regions are located in the State of São Paulo and coincide roughly with those of the sweet orange. The method of expressing the oil is the same as that described under "Brazilian Sweet Orange Oil."

A sample of genuine Brazilian grapefruit oil examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°	0.858
Optical Rotation at 25°	+93° 40′
Refractive Index at 20°	1.4755
Aldehyde Content, Calculated as Decyl Aldehyde (Hydroxylamine Hydrochloride Method)	1.0%
Evaporation Residue	6.9%

The properties of this oil were normal, but its odor and flavor showed a slightly spoiled character, due probably to improper storage and oxidation in the hot climate of Brazil.

Suggested Additional Literature

J. Davidsohn, "Citrus Products from Palestine," *Soap Perfumery & Cosmetics* **17** (1944), 337, 356.

W. B. Davis (U. S. Dept. Agr., Los Angeles, Calif.), "Determination of Flavanones in Citrus Fruits," *Anal. Chem.* **19** (1947), 476. *Chem. Abstracts* **41** (1947), 5647.

J. Feigenbaum, "Les Essences de Citrus en Palestine," *Ind. Parf.* **4** (1949), 37.

OIL OF PETITGRAIN GRAPEFRUIT
(Grapefruit Leaf Oil)

Steam distilling the leaves and twigs of the Palestine grapefruit tree, Sabetay and Halasz [1] obtained 0.4 per cent of a volatile oil which had these properties:

Specific Gravity at 15°	0.8607
Optical Rotation	+55° 20′
Refractive Index at 20°	1.4721
Acid Number	2.2
Ester Number	10.6
Aldehyde Content (Calculated as Decyl Aldehyde)	2.81%
Methoxyl Content (Calculated as Methyl Anthranilate)	0.34%

The odor of the oil was duller than that of regular petitgrain oil distilled from the leaves of the bitter orange tree.

OIL OF NEROLI GRAPEFRUIT
(Grapefruit Blossom Oil)

Distilling the blossoms of the Palestine grapefruit tree, Sabetay and Halasz [2] obtained 0.03 per cent of an oil which had these properties:

Specific Gravity at 15°	0.8694
Optical Rotation	+53° 20′
Refractive Index at 20°	1.4761
Acid Number	1.7
Ester Number	10.3
Aldehyde Content (Calculated as Decyl Aldehyde)	4.94%
Methoxyl Content (Calculated as Methyl Anthranilate)	1.60%

The odor of this oil resembled that of oil of neroli bigarade but was more rose and honey-like.

[1] *Ind. Parfum.* **2** (1947), 200. *Chem. Abstracts* **41** (1947), 7676.
[2] *Ibid.*

THE KEEPING QUALITIES OF CITRUS OILS

Citrus oils kept in well-filled, well-stoppered, dark colored bottles and stored in a cool, dark place retain their original delicate flavor for years, but access of air or light, especially in the presence of traces of water, easily spoils citrus oils. They assume an oxidized, acid character, and turpentine-like odor; viscosity and specific gravity greatly increase.

Poore [1] has experimentally proved the effect of air and temperature upon California oils and upon limonene, and he has tabulated the results. He came to the conclusion that at the end of twenty months the limonene was unaffected in the presence of water if air was excluded. Marked changes occurred in the presence of dry air. Water and air together appeared to cause the greatest increase in acid value. As in the lemon and orange oils, all *sealed* samples of limonene remained unchanged.

Practical experience corroborates the findings of Poore. Lemon and orange oils even improve after a year or two of cold storage in that some of the dissolved waxes separate from the oil and may be removed easily by filtration. The resulting oils are more soluble and produce clearer extracts. Neither odor nor flavor is the least impaired if the oils are kept in tin-lined, fully filled drums, at a temperature not higher than 65° F. Citrus oils stored in this manner can be kept safely for three years.

As an added protection, the author suggests using a very simple method, by placing a small quantity of "dry ice" (solid CO_2) in the oil. The solid carbon dioxide rapidly evaporates, drives out the air, and thereby insures the presence of a neutral gas in the container before it is tightly sealed.

[1] *U. S. Dept. Agr., Tech. Bull.* No. 241, March (1932).

B. ESSENTIAL OILS OF OTHER GENERA OF THE PLANT FAMILY *RUTACEAE*

OIL OF ANGOSTURA BARK

Botany and Origin.—The true Angostura bark *Cusparia trifoliata* Engl. (*Galipea cusparia* St. Hil. or *G. officinalis* Hancock), according to Hartwich and Gamper,[1] originates from a tree which grows wild in Venezuela and in certain sections of the upper Orinoco River. It is used widely for the flavoring of bitters, tonics, and liqueurs.

On steam distillation the bark yields 1 to 1.9 per cent of a volatile oil possessing an aromatic odor and flavor.

Physicochemical Properties.—Schimmel & Co.[2] found these properties of the essential oil derived from angostura bark:

Specific Gravity at 15°	0.928 to 0.96
Optical Rotation	−7° 30′ to −50° 0′
Refractive Index at 20°	1.50744
Acid Number	1.8
Ester Number	5.5
Ester Number after Acetylation	35.7
Solubility	Soluble in 9 vol. of 90% alcohol, with turbidity

On standing the originally light yellow color of the oil darkens.

Chemical Composition.—Beckurts and Troeger [3] investigated the composition of the volatile oil contained in the angostura bark and reported the presence of these compounds:

Galipol, $C_{15}H_{26}O$. This sesquiterpene alcohol b. 260°–270°, d_{20} 0.9270, α_D ±0°, appears to be the aromatic principle, the oil containing about 14 per cent of galipol. The alcohol is very unstable and on warming loses water. Nothing is known about the constitution of galipol.

l-Cadinene. An important component of the oil, causing its laevorotation. Identified by means of the crystalline dihydrochloride.

Galipene. This sesquiterpene, of unknown constitution, b. 255°–260°, d_{19} 0.912, α_D ±0°, n_D 1.5051, on treatment with hydrogen chloride, forms liquid hydrochlorides which decompose readily.

Pinene(?). The oil furthermore contains small amounts of a terpene, which is probably pinene.

Use.—The volatile oil of the angostura bark has not attained any commercial importance.

[1] *Arch. Pharm.* **238** (1900), 568.
[2] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 947.
[3] *Arch. Pharm.* **235** (1897), 527, 634; **236** (1898), 392. Cf. Beckurts and Nehring, *ibid.* **229** (1891), 612; Herzog, *ibid.* **143** (1858), 146.

OIL OF *BORONIA MEGASTIGMA*
(Boronia Flower Oil)

Botany and Origin.—About fifteen species of *Boronia* are found in Western Australia. Of these *B. megastigma* Nees is the most common. Because of its graceful form, unusual coloring (the petals are brown on the outside, golden yellow on the inside), and delightful fragrance, the plant is cultivated as an ornamental bush in the hills near Melbourne. In open country *B. megastigma* grows as a wide spreading bush, 1½ to 2 ft. high; under more favorable conditions, however, it may reach 4 to 5 ft. The blooming period lasts about two months, but may be only 3 to 4 weeks in dry years. Usually the plant begins to flower toward the end of July, and flower material is available for extraction purposes until the middle of September.

Boronia megastigma Nees grows wild in moist areas of southwestern Australia, from Collie southward, in the districts of Darling, Stirling, Warren, Mount Barker, Albany, Bridgetown, Greenbushes, southwest of Perth, etc. It prefers swampy lands, and often grows in water, particularly in the paper bark tree thickets of Australia's extreme southwest. For this reason the bush is not destroyed by forest fires. It seems to thrive best in soils where decomposing organic material and waters charged with tannin are to be found. In fact it has been observed that, in the garden cultivation of *B. megastigma*, best results can be obtained by repeatedly dressing the soil with tea leaves and similar tannin-containing material.

Methods of Extraction.—Garner [1] observed that steam distillation of the flowers of *B. megastigma* yields only an extremely small part of the oil actually contained in the flowers, and that the steam-distilled oil possesses an odor quite different from that of the flower itself. The most appropriate method of recovering the natural floral oil from *B. megastigma* is by extraction with volatile solvents (petroleum ether); this method yields a concrete from which the alcohol soluble absolute can be obtained by the usual method (see Vol. I of this work, pp. 200 and 211).

The method employed by the manufacturers of boronia flower oil is to establish agents in charge of centrally located depots in the boronia districts of Australia's extreme southwest. The flower collectors deliver their blossoms daily to these stations. The actual gathering of the blossoms is generally performed by means of combs, whereby the tender stalk of the flowers is easily severed. Impurities, such as leaves and stalks, are removed by shaking the blossoms over blankets stretched at an angle of 20° to 25°.

[1] *Austral. J. Pharm.* (1926), 932.

The blossoms, being round, roll off the blankets and the needle shaped leaves and stalks are retained by the hair of the blankets. After inspection, passing and weighing at the station, the day's harvest is transferred to drums of 60-gal. capacity containing sufficient quantities of volatile solvents (petroleum ether) with which the extraction is carried out. These solvents act at the same time as a preservative while the blossoms are in transit. Thus, the drums, containing the blossoms and the solvent, are transported to the factory where the extraction is completed and the solutions are concentrated *in vacuo*. The resulting concretes consist of the volatile oil and the natural flower waxes which are also extracted by the volatile solvent process.

Yield of Flower Oil.—The yield of concrete and absolute is influenced by seasonal factors and varies considerably. Garner [2] obtained a yield of 0.78 per cent of concrete, which gave 47.6 per cent of absolute. Naves and Mazuyer [3] reported a yield of 0.4 per cent of concrete. By extracting, with benzene, the freshly picked flowering tops of plants gathered in the hills near Melbourne, Naves and Parry [4] obtained a yield of 0.52 per cent; however, on extracting a small quantity of the separated flowers they obtained a yield of 1.23 per cent of concrete. From his own observations in Perth (West Australia), the author learned that the yield of concrete is about 0.7 per cent and that the concrete yields about 60 per cent of absolute. One thousand pounds of *B. megastigma* blossoms, when extracted with petroleum ether in industrial operation, yield about 66 oz. of absolute.

Physicochemical Properties.—Concretes of *B. megastigma* investigated by Penfold [5] had properties varying within these limits:

Year	*m.p.*	$d^{t}_{15°}$	n_D	*Acid No.*	*Ester No.*	*Ester No. after Acetylation*
1924	35°–36°	0.8989/15°	1.4752/38°	27.5	106.7	139.5
1926	40°	0.9091/40°	1.4826/40°	24.2	95.9	136.5
1925	40°–41°	0.9189/40°	1.4842/39°	22.8	109.3	149.0
1926	39°–40°	0.9173/40°	1.4852/38°	30.5	107.3	147.8

The concrete usually is of butter-like consistency and of green color.

The alcohol soluble, green absolute prepared from the concrete (yield 47.6 per cent) by Garner [6] had these properties: d_{22} 0.9625, α_D ca. 0°, n_D 1.501.

[2] *Ibid.*
[3] "Natural Perfume Materials," Reinhold Publishing Co., New York (1947), 169.
[4] *Perfumery Essential Oil Record* **38** (1947), 129.
[5] *J. Roy. Soc. W. Australia* **14** (1927), 1.
[6] *Austral. J. Pharm.* (1926), 932.

By steam distillation of a concrete of known purity, Naves, Sabetay and Palfray [7] obtained 20.4 per cent of a volatile oil with the following properties:

Specific Gravity at 15°/15°	0.896
Optical Rotation	−3° 20′
Refractive Index at 20°	1.4737
Acid Number	22.4
Ester Number	67.2
Ketone Content, Calculated as Ionones (Hydroxylamine Method)	40.1%

Distilling the (alcohol soluble) absolute with superheated steam at reduced pressure, Naves and Parry [8] recovered 13.2 per cent (calculated on the concrete) of a waxy, yellow distillate which contained 18.6 per cent of oximable substances (expressed as ionones). By treatment with alcohol, *n*-heptacosane m. 58°–59° and hentriacontane were separated, and the deparaffinated fraction had these properties:

Specific Gravity at 20°/4°	0.9393
Specific Optical Rotation	−1° 7′
Refractive Index at 20°	1.49497
Acid Number	3.8
Ester Number	91.0

Chemical Composition.—The alcohol insoluble fraction of the concrete (separated at 15°, and representing 15 per cent of the concrete) was studied by Penfold [9] and found to consist mainly of triacontane m. 64°. The alcohol soluble fractions included small quantities of glycerides of palmitic and stearic acid, and free formic, caprylic, and palmitic acids; also phytosterol $C_{27}H_{46}O$, m. 162°, $[\alpha]_D^{20}$ +60° 0′ (c = 0.723 in chloroform), the acetate of which melted at 120°–130°. Penfold furthermore noted the presence of phenols, ethyl alcohol, and ethyl formate.

In their deparaffinated volatile oil, described above, Naves and Parry identified eugenol (yield 0.33 per cent, calculated on the concrete) by the preparation of its dinitrophenyl ether m. 115°–115.5°.

The most important constituent occurring in boronia flower oil is β-ionone. It was first noted by Penfold [10] who prepared the semicarbazone m. 145°–146° (no depression of melting point in a mixture with the semicarbazone of synthetic β-ionone). Later Sabetay [11] confirmed the presence

[7] *Perfumery Essential Oil Record* **28** (1937), 336.
[8] *Helv. Chim. Acta* **30** (1947), 419. *Perfumery Essential Oil Record* **38** (1947), 129.
[9] *J. Roy. Soc. W. Australia* **14** (1927), 2.
[10] *Ibid.*
[11] *Compt. rend.* **189** (1929), 808.

of β-ionone in boronia flower oil by the preparation of a semicarbazone m. 149°, and of a *p*-bromophenylhydrazone m. 120°. Since β-ionone had never been observed in any other plant, doubts were expressed regarding the purity of the boronia oil investigated by Penfold, and by Sabetay. To clear up the matter, Naves and Parry [12] extracted freshly picked boronia flowers, growing near Melbourne, with benzene and, investigating the extract (see above), found that the natural flower oil of *B. megastigma* contains a mixture of β-ionone, *d*-α-ionone, and *d,l*-α-ionone. The α-ionones amounted to 5 per cent of the mixture; racemic α-ionone constituted two-fifths of the α-ionone. The presence of α-ionone could be established by careful examination of the mother liquors resulting from the recrystallization of the semicarbazone of β-ionone. Naves and Parry identified the *d*-α-ionone by the preparation of its semicarbazone m. 157°–157.5°, and the *d,l*-α-ionone through its semicarbazone m. 140°–141° (no depression in a mixed melting point determination with a synthetic product). The semicarbazone of the regenerated β-ionone melted at 149°, the 2,4-dinitrophenylhydrazone at 128.5°–129° (no depression in a mixed melting point determination).

Naves and Parry believe the β-ionone in boronia flower oil to be a result possibly of the oxidation of carotenoids, which action would give rise to this ketone. Thus, the biogenesis of β-ionone depends, perhaps, on the presence of carotenoids possessing the terminal β-iononylidene or pseudo-iononylidene group, notably that of β-carotene and of xanthophyll (lutein). In the same way that it is possible to associate β-ionone with such carotenoid pigments, α-ionone can be linked with corresponding substances possessing the α-iononylidene or pseudo-iononylidene structure. α-Carotene and xanthophyll occur in many plants, and more recently α-carotene-epoxide and xanthophyll-epoxide, as well as the dihydrofurane derivatives flavoxanthine and chrysanthemaxanthine [13] have been observed.

Use.—Absolute of *Boronia megastigma* Nees possesses an odor suggestive of cassie (*Acacia farnesiana*) and violet, and to a lesser degree of fruity notes such as raspberry, peach, and apricot. The odor is most pleasant and lasting. This absolute should enable the perfumer to impart novel tonalities to his creations.

[12] *Helv. Chim. Acta* **30** (1947), 419. *Perfumery Essential Oil Record* **38** (1947), 129.

[13] Cf. Karrer, Morf and Walker, *Helv. Chim. Acta* **16** (1933), 975. Kuhn and Grundmann, *Ber.* **67** (1934), 597. Karrer et al., *Helv. Chim. Acta* **28** (1945), 300, 1146.

OIL OF BUCHU LEAVES

Essence de Feuilles de Bucco *Aceite Esencial Buchú* *Buccublätteröl*
Oleum Buccu Foliorum

Botanical and Geographical Origin.—The genus *Barosma* comprises more than a dozen species, which grow wild in the southern part of Africa (Union of South Africa) where the natives use the leaves for medicinal purposes and to ward off insects.[1] Several hundred thousand pounds of leaves are exported yearly from Capetown, mainly to the United States and United Kingdom, where the oil is occasionally extracted by steam distillation. The collecting and marketing of the leaves in the Union of South Africa is now regulated by law, perhaps due to increasing scarcity of the wild growing plant material. Attempts to cultivate the buchu bush have been made in Kirstenbosch.[2]

According to van Wielligh,[3] the true buchu leaves of commerce are derived from three species, viz., (1) round leaves from *Barosma betulina* Bartl. or "mountain buchu," and from *B. crenulata* (L.) Hook.; (2) long leaves from *B. serratifolia* Willd. or "kloof buchu." Leaves from other *Barosma* species are called false buchu leaves. Holmes,[4] and Mansfield[5] reported on the admixture of other, spurious leaves with true buchu leaves.

Clevenger[6] classifies the leaves of *Barosma betulina* as "short buchu," and those of *B. crenulata* as "oval buchu." Other varieties of buchu referred to as "long buchu" (*B. serratifolia* and *Epleurum serratum*) are known but have not been imported into New York during recent years.

In a more recent publication Lum[7] reported that the three chief varieties of buchu grow in the southern part of the Union of South Africa, but that the variety official in the British Pharmacopoeia is indigenous to the Cape Province. This variety, *Barosma betulina,* occurs as pale green leaves, 1 to 2 cm. in length, with characteristic rhomboid—ovate shape and margins having small, sharp teeth. The other chief varieties of the herb are known as "long" buchu (*B. serratifolia*) and "crenate" buchu (*B. crenulata*), but these are not normally used medicinally, as the oil present in the glands,

[1] *Chemist Druggist* **76** (1910), 358; **77** (1910), 17, 622.
[2] *Ibid.* **92** (1920), 909.
[3] *Agr. J. Union South Africa,* July (1913). Cf. *Commerce Reports* (June 11, 1918); *Am. J. Pharm.* **90** (1918), 600.
[4] *Pharm. J.* **73** (1904), 893; **85** (1910), 69, 464.
[5] *Chemist Druggist* **81** (1912), 546.
[6] *J. Assocn. Official Agr. Chem.* **26** (1943), 396.
[7] *Mfg. Chemist* **18** (1947), 393.

which is visible on holding the leaf to the light, contains little or no diosphenol, the main active principle of the oil.

Yield of Oil.—The yields of oil recorded in Table 1.27 were obtained by distillation of dried, imported leaf material:

TABLE 1.27

Authors	*B. betulina* "Short Buchu"	*B. crenulata* "Oval Buchu"	*B. serratifolia* "Long Buchu"
Gildemeister & Hoffmann [a]	1.3 to 2.5%	1.7%	0.8 to 1.0%
Am. Pharm. Assocn. Laboratories [b]	1.9%	2.2%	...
Feldman & Youngken [c]	1.95% (average—Clevenger Method)	1.13% (average—Clevenger Method)	0.81% (average—Clevenger Method)
Clevenger [d]	1.1 to 2.9 ml. per 100 g.	1.2 to 3.5 ml. per 100 g.	...

[a] "Die Ätherischen Öle," 3d Ed., Vol. II, 940.
[b] *Bull. Natl. Form. Comm.* **8** (1940), 181.
[c] *J. Am. Pharm. Assocn.* **33** (1944), 285.
[d] *J. Assocn. Official Agr. Chem.* **26** (1943), 396.

Clevenger arrived at the conclusion that the yield of volatile oil is somewhat greater from the leaves of the oval buchu than that from the leaves of the short buchu.

Physicochemical Properties.—Oil of buchu leaves is usually of dark color and possesses a strong, sweetish, mint-like, rather unpleasant odor. The flavor is bitter and cool.

Clevenger [8] reported these properties for oil of *Barosma betulina* (short buchu):

Specific Gravity at 25°/25°	0.943 to 0.966
Optical Rotation at 25°	−20° 42′ to −34° 36′
Refractive Index at 20°	1.477 to 1.491
Acid Number	2.4 to 8.0
Ester Number	25.8 to 57

Comparative studies led Clevenger to the conclusions:

1. That the specific gravity and acid number for the volatile oils of the short buchu are somewhat higher than in the case of the oval buchu (see below).

[8] *Ibid.*

2. That the volatile oil of the short buchu gives a markedly higher laevorotation than in the case of the volatile oil of the oval buchu (see below).

Matthews [9] described two buchu leaf oils distilled from *Barosma betulina* (yield 2 per cent and 1.63 per cent):

	I	*II*
Specific Gravity at 15°	0.969	0.930
Optical Rotation	−25° 0′	−24° 18′
Refractive Index at 20°	1.4814	1.4778
Diosphenol Content	39%	30%
Solubility in 70% Alcohol	Soluble in 1 to 12 vol. with opalescence	

An oil distilled from fresh leaves of *Barosma betulina* Bartl. (yield 1.2 per cent) in Piquetberg (South African Union) by van der Riet,[10] on freezing, separated about 8 per cent of crystalline diosphenol m. 82°–83°, phenylurethane m. 113°, benzoate m. 115°–117°, diphenylurethane m. 76°–78°. (Asahina and Kuwada [11] reported a monoxime m. 123°, and a dioxime m. 154°–157°.) In most cases, however, the oil from *B. betulina* separates diosphenol in crystalline form on standing even at room temperature. Kondakov and Bachtschiev,[12] and Gildemeister and Hoffmann [13] found that liquid oils drawn off from the separated crystals had these properties:

Specific Gravity at 15°	0.937 to 0.97
Optical Rotation	−14° 0′ to −48° 0′
Refractive Index at 20°	1.474 to 1.487
Diosphenol Content (by Repeated Shaking with 5% Sodium Hydroxide Solution)	17 to 30%
Solubility	Usually soluble in 3 to 5 vol., occasionally only in 8 to 10 vol. of 70% alcohol

As far as the oil of *Barosma crenulata* (oval buchu) is concerned, Clevenger [14] found that its properties vary within these limits:

Specific Gravity at 25°/25°	0.924 to 0.956
Optical Rotation at 25°	−8° 18′ to −21° 48′
Refractive Index at 20°	1.474 to 1.488
Acid Number	1.0 to 3.4
Ester Number	20.0 to 84.4

[9] *Perfumery Essential Oil Record* **31** (1940), 60.
[10] *J. Chem. Met. Mining Soc. S. Africa* **34** (1933), 82.
[11] *J. Pharm. Chem. Soc. Japan* **491** (1923), 1.
[12] *J. prakt. Chem.* [2], **63** (1901), 50.
[13] "Die Ätherischen Öle," 3d Ed., Vol. II, 940.
[14] *J. Assocn. Official Agr. Chem.* **26** (1943), 396.

Schimmel & Co.[15] reported the following properties for an oil distilled from *Barosma crenulata* (L.) Hook.:

Specific Gravity at 15°	0.9364
Optical Rotation	−15° 22′
Refractive Index at 20°	1.48005
Solubility	Soluble in 2.5 vol. and more of 70% alcohol, with separation of paraffins

The content of diosphenol was very small, as on cooling in a freezing mixture only paraffins separated. The odor was mint-like.

Not much is known about the oil distilled from *Barosma serratifolia* Willd. (long buchu). Gildemeister and Hoffmann[16] mention a specific gravity at 15° of 0.918 to 0.961, and an optical rotation of −12° 0′ to −36° 0′. The content of diosphenol is so small that even on cooling no crystals separate.

The same authors recommend that, for the separation of diosphenol from oil of buchu leaves, the oil be shaken repeatedly with a 5 per cent solution of sodium hydroxide. Treating the oil for the first time with sodium hydroxide, 15 per cent of diosphenol was obtained; a second treatment yielded another 5 per cent of diosphenol. On acidification, the alkaline solution of the phenols will develop hydrogen sulfide, as side reaction.

Chemical Composition.—As has been pointed out, the main constituent of buchu leaf oil is diosphenol (buchu camphor) $C_{10}H_{16}O_2$, a ketophenol m. 83°–84°, b_{10} 109°–110°, a detailed description of which will be found in the monograph on "Diosphenol" in Vol. II of this work, p. 542. The compound was the subject of many investigations until Semmler and McKenzie[17] finally established its constitution.

The following compounds have been identified in oil of buchu leaves:

Diosphenol. According to Kondakov,[18] this ketophenol occurs in the oil partly free, partly esterified with an acid m. 94°.

d-Limonene. Identified as tetrabromide m. 104°.

Dipentene. Small quantities; characterized as tetrabromide m. 119°.

l-Menthone. Identified by Kondakov[19] who found that oil of *Barosma serratifolia* contains more *l*-menthone than oil of *B. betulina*. Characterized by the preparation of a hydrazone m. 80°, and of two semicarbazones m. 180° and 123°.

[15] *Ber. Schimmel & Co.*, October (1911), 20.
[16] "Die Ätherischen Öle," 3d Ed., Vol. II, 940.
[17] *Ber.* **39** (1906), 1158. *Chem. Ztg.* **30** (1906), 1208.
[18] *J. prakt. Chem.* [2], **72** (1905), 186.
[19] *Ibid.* Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 941.

Use.—In former years small quantities of buchu leaf oil were used in pharmaceutical preparations intended for the treatment of cystitis and inflammatory conditions of the urinary organs in general, the oil acting as an antiseptic. Today, oil of buchu leaves is used very little in our industries.

SUGGESTED ADDITIONAL LITERATURE

"Volatile Oil Content of Buchu and Its Fluid Extract," Report American Pharmaceutical Association Laboratories, *Bull. Natl. Form. Comm.* **8** (1940), 221.

OIL OF *CLAUSENA ANISATA*

Botany, Geographical Distribution, and General Description.—The botanical nomenclature of the tree or shrub (fam. *Rutaceae*), the leaves of which contain this oil, has not yet been definitely established. Bacon [1] speaks of *Clausena anisum-olens* (Blanco) Merr.; Busse [2] describes it as *C. anisata* Willd.; Dalziel [3] as *C. anisata* Oliv.; whereas Meijer [4] temporarily suggests *C. anisata* Hook. f.

The tree grows abundantly in some sections of the Philippine Islands, Java, Tanganyika, the Belgian Congo, and in other tropical countries.

Experiments made in Buitenzorg (Java) [5] with regard to the best way of propagating this plant indicate that production from seed meets with difficulties. The most promising way, evidently, is by grafting on stems of *Clausena excavata.* Experiments as to the most suitable altitude at which this plant will thrive have shown that it grows best in the lower regions.

The leaves of the plant possess a strong and characteristic anise-like odor for which reason alcoholic extracts of these leaves are used, in the Philippines, for the flavoring of "anisados"—favorite alcoholic beverages among the natives.

Yield of Oil.—Meijer [6] reported a yield of 4.32 per cent, calculated on moisture-free leaves. He also found that, as a rule, the young leaves have

[1] *Philippine J. Sci.* **4** (1909), 130.
[2] *Ber. deut. pharm. Ges.* **14** (1904), 215.
[3] "The Useful Plants of West Tropical Africa," p. 307. Cf. Meijer, *Rec. trav. chim.* **66** (1947), 395.
[4] *Rec. trav. chim.* **66** (1947), 395.
[5] *Ibid.*
[6] *Ibid.*

a much higher essential oil content, varying in the cases investigated from 6.4 to 8.2 per cent. In the course of a year the essential oil content undergoes but small fluctuations. The anethole content of the oil, however, seems to be less constant, although the differences are comparatively small.

Nondried leaves collected from trees cultivated from seedlings, and from trees cultivated by the grafting of *Clausena anisata* on stems of *C. excavata* Burm. f. gave oil yields of 2.1 per cent (anethole content 91.5 per cent), and 1.8 per cent (anethole content 92.3 per cent), respectively. Meijer[7] recommended using fresh leaf material for distillation, as on drying the oil content decreases considerably. In one case a loss of nearly 80 per cent was noticed.

Submitting the stems to steam distillation, Meijer observed a yield of 2.1 per cent of oil.

Physicochemical Properties.—According to the same author,[8] the Agricultural Experiment Station in Buitenzorg (Java) found these properties of an oil of *Clausena anisata* Hook. f., distilled from dried leaves:

Specific Gravity at 26°/4°	0.9611
Optical Rotation	−0° 4′
Refractive Index at 30°	1.5613
Anethole Content	82.5%

An oil distilled from the stems exhibited the following properties:

Specific Gravity at 27.5°/4°	0.9797
Optical Rotation	−0° 36′
Refractive Index at 26°	1.5532
Anethole Content	85.2%

The odor of the oil is typically anise-like, but perhaps not as fine as that of *Pimpinella anisum* or that of *Illicium verum* Hook. f. However, it seems quite possible that on rectification the odor of the oil of *Clausena anisata* could be greatly improved.

Chemical Composition.—The principal constituent of oil of *Clausena anisata* Hook. f. is *anethole* which occurs in the oil to the extent of 94.1 per cent (determined by freezing and pressing). Another, but minor, constituent of the oil is *anisaldehyde* which was isolated from the oil by shaking it with a 30 per cent solution of sodium bisulfite, and by regeneration of the aldehyde from the bisulfite layer by means of soda. The anisaldehyde was identified by the preparation of its *p*-nitrophenylhydrazone m. 160°.

[7] *Ibid.*
[8] *Ibid.*

Use.—Oil of *Clausena anisata* has not yet attained any commercial importance, although in the opinion of Meijer,[9] it seems plausible that this oil will find a ready market as it may probably be produced cheaper than either oil of *Pimpinella anisum* or even *Illicium verum.*

OIL OF JABORANDI LEAVES

According to Gildemeister and Hoffmann,[1] the term jaborandi leaves includes leaves of various *Pilocarpus* species, e.g., *P. jaborandi* Holmes, *P. racemosus* Vahl, *P. microphyllus* Stapf, *P. spicatus* St. Hil., and others.

On steam distillation the leaves of *P. jaborandi,* depending upon their condition—fresh or dried—yield 0.2 to 1.1 per cent of a volatile oil, which possesses a somewhat fruity flavor, and a strong odor reminiscent of rue.

Physicochemical Properties.—The same authors reported these properties of jaborandi leaf oil:

Specific Gravity at 15°	0.865 to 0.895
Optical Rotation	+0° 50′ to +3° 25′
Solubility	Clearly soluble in 1.5 to 2 vol. of 80% alcohol

The oil boils from 180°–290° at atmospheric pressure and congeals on cooling.

Gildemeister and Hoffmann [2] also recorded the properties of two oils examined by Schimmel & Co.:

An oil (*I*) originating in Paraguay, and probably distilled from *P. racemosus* Vahl,[3] locally called "Yvirá tai." It had a pronounced rue-like odor and contained 83 per cent of methyl nonyl ketone (semicarbazone m. 123°), as determined by the hydroxylamine method. The oil congealed at +5.2° (undercooled to +4°).

An oil (*II*) distilled from commercial jaborandi leaves consisting chiefly of *P. microphyllus* and some *P. spicatus.* The yield was 0.24 per cent. The odor of the oil was balsamic, reminiscent of birch bud oil (*Betula alba*),

[9] *Ibid.*

[1] "Die Ätherischen Öle," 3d Ed., Vol. II, 945. Cf. Holmes, *Pharm. J.* **55** (1895), 522, 539; **73** (1904), 891, 970; **84** (1910), 52.

[2] *Ibid.*

[3] Cf. Rocher, *J. pharm. chim.* [6], **10** (1899), 236. Holmes, *Pharm. J.* **71** (1903), 713.

but not of rue. The oil, which did not congeal, contained only 20.6 per cent of methyl nonyl ketone.

	I	*II*
Specific Gravity at 15°	0.8393	0.9288
Optical Rotation	−5° 59′	−9° 10′
Refractive Index at 20°	1.44018	1.48809
Acid Number	0	11.2
Ester Number	5.6	13.1
Ester Number after Acetylation	...	89.6 (= 26.4%, calculated as alcohol $C_{10}H_{18}O$)
Solubility	Soluble in 6 vol. and more of 70% alcohol with slight turbidity; soluble in 1 vol. of 80% alcohol. The dilute solution displays faint opalescence	Soluble in 7 vol. of 80% alcohol with separation of paraffins. Soluble in 0.3 vol. of 90% alcohol. Separation of paraffins on dilution

Chemical Composition.—The chemical composition of jaborandi leaf oil is not well known.

Years ago Hardy [4] isolated, by fractionation, a hydrocarbon b. 178°, d_{18} 0.852, $[\alpha]_D$ +1° 13′, which yielded a solid dihydrochloride, and which he named *pilocarpene*. Judging from the properties, this hydrocarbon was probably a terpinene or dipentene accompanied by small quantities of an optically active substance.

More recently Schimmel and Co.[5] fractionated an oil of jaborandi leaves (d_{15} 0.8694, α_D +0° 54′, n_D^{20} 1.45442, A.N. 6.72, E.N. 7.65) and, after repeated distillation over metallic sodium, obtained a *hydrocarbon* b. 162°–166°, d_{15} 0.8519, α_D +17° 4′, n_D^{20} 1.46757 which did not yield a solid dihydrochloride. Extraction of the oil with sodium bisulfite gave *methyl nonyl ketone*, the principal constituent of the oil. The fractions of the oil boiling above 260° congealed in the cold and contained compounds m. 27°–28° which probably were *olefinic hydrocarbons*.

Use.—Oil of jaborandi leaves has not attained any commercial importance.

[4] *Bull. soc. chim.* [2], **24** (1875), 497.
[5] *Ber. Schimmel & Co.* (1924), 50.

OIL OF JAPANESE PEPPER
(Oil of *Piper japonicum*—"Oil of Sansho")

Botany and Origin.—The fruit and leaves of *Xanthoxylum piperitum* D.C., also known as *Piper japonicum*, or "Sansho" (in Japanese) are used in China and Japan as a popular spice. On steam distillation the fruit yields from 2 to 4 per cent of a yellowish, usually mobile, volatile oil which possesses a poignant taste and an agreeable odor reminiscent of lemon and citronella oils.

According to Gildemeister and Hoffmann,[1] the oil has been produced and investigated on several occasions, but the yields, the physicochemical properties, and chemical composition of the oil lots obtained by various workers display such marked differences that it appears doubtful whether the oils were distilled from the same *Xanthoxylum* species.

Physicochemical Properties and Chemical Composition.—An oil distilled by Thoms[2] (yield 4.33 per cent) and investigated by Duruttis[3] had these properties:

Specific Gravity at 20°	0.890
Optical Rotation	+26° 30′
Refractive Index	1.47320

This oil contained 90 per cent of terpenes (probably a mixture of *d*-limonene and dipentene). The fractions boiling above 180° consisted of cuminaldehyde, geraniol, acetic acid—esterified, and palmitic acid—free.

An oil distilled by Uchida[4] from the dried fruit (yield 5.7 per cent) possessed an odor reminiscent of citronella oil and had the following properties:

Specific Gravity at 15.5°	0.8504
Optical Rotation at 20°	+46° 30′
Refractive Index at 20°	1.4600
Acid Number	3.3
Ester Number	19.28
Ester Number after Acetylation	23.23

This oil contained:

	Per Cent
Terpenes (Mainly Dipentene)	77
Aldehydes	15
Free Acids (Chiefly Palmitic Acid)	2

[1] "Die Ätherischen Öle," 3d Ed., Vol. II, 912.
[2] *Arb. pharm. Inst. Univ. Berlin* **11** (1914), 58.
[3] *Ibid.*, 60.
[4] *J. Soc. Chem. Ind. Japan* **15** (1912), 941, 1066.

Another oil (yield 4.20 per cent) distilled from the unripe fruit and investigated by the same author [5] had these properties:

Specific Gravity at 15°/4°	0.8736
Specific Optical Rotation (18.63% solution in chloroform)	+11° 41′
Refractive Index at 15°	1.4720
Acid Number	6.7
Ester Number after Acetylation	104.6

This oil contained:

	Per Cent
Dipentene	54
Esters (Geranyl Acetate and Citronellyl Acetate 20%, Esters of Citronellic Acid 4%)	24
Citronellal	8
Alcohols (Chiefly Geraniol and Some Citronellol, Both Free)	10
Acids (Citronellic Acid and Small Quantities of Palmitic Acid, Both Free)	1
Tricyclic Sesquiterpene b_{12} 165°–175°, d_{18}^{18} 0.9002, n_D^{18} 1.4975, Hydrochloride $C_{15}H_{24}HCl$ Liquid	3

An oil prepared by Asahina and Konno [6] had the following properties:

Specific Gravity at 19°/4°	0.8511
Specific Optical Rotation at 20°	+45° 27′
Acid Number	1.35

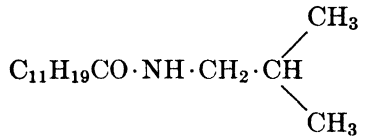
and contained:

Citronellal and *l*-β-Phellandrene	13%

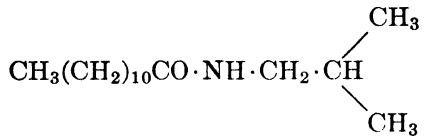
As regards the flavoring principle which imparts a characteristic biting effect to the fruit of *Xanthoxylum piperitum* D.C., Murayama and Shinozaki [7] extracted the fresh fruit of "Asakura Sansho" with ether, and removed the volatile oil by steam distillation. The distillate was shaken with 30% potassium hydroxide solution to remove alkali-soluble substances. The residual liquid was then treated with petroleum ether. Murayama and Shinozaki thus obtained 1.83 per cent of a substance possessing a sharp taste, which they named sanshoöl. The same authors also prepared hydrosanshoöl, m. 61°, b_3 192°–194°; this they assumed to be an isomer of dodecyl hydroxylamine, $C_{12}H_{25}NHOH$, or lauric acid amide, $C_{12}H_{25}NO$.

[5] *Ibid.* **31** (1928), 896. *Chem. Zentr.* II (1928), 2296.
[6] *J. Pharm. Soc. Japan* (1916), 801.
[7] *Ibid.*, **51** (1931), 379. *Chem. Abstracts* **25** (1931), 4270.

Asano and Kanematsu,[8] however, suggest a different formula from that of Murayama and Shinozaki. Using the method of the latter, they obtained hydrosanshoöl, m. 55°, b_4 187°–200°, and expressed the opinion that this hydrosanshoöl (as well as the hydrosanshoöl of Murayama and Shinozaki) was not quite pure. Since hydrolysis of the hydrosanshoöl yielded lauric acid and isobutylamine, Asano and Kanematsu suggested the following formulae:



Sanshoöl



Hydrosanshoöl

Use.—In former years from 50 to 300 lb. of oil were produced annually in the Prefecture of Shizuoka, but at present the oil has no commercial importance and is not used.

OIL OF RUE

Essence de Rue *Aceite Esencial Ruda* *Rautenöl* *Oleum Rutae*

Introduction.—There are several types of rue oil:

1. The Spanish oil, commercially the most important.
2. The North African oil, produced chiefly in Algeria.
3. The French oil, produced mostly in Southern France.
4. The Italian oil, produced in Sicily and Sardinia, commercially unimportant.

Botany.—Simmons [1] expressed the opinion that Spanish rue oil is obtained chiefly from *Ruta montana* L. (summer rue), whereas Dorronsoro [2] reports

[8] *J. Pharm. Soc. Japan* **51** (1931), 384. *Chem. Abstracts* **25** (1931), 4270.
[1] *Perfumery Essential Oil Record* **14** (1923), 236.
[2] *Mem. acad. cienc. exactas Madrid* **29** (1919). *Ber. Schimmel & Co.*, April (1921), 80.

that the Spanish producers also use *R. bracteosa* L. (winter rue) and *R. graveolens* L. (garden rue) for distillation.[3] In Spain, as a matter of fact, distillation of rue oil actually takes place in July–August, when the wild growing plant material blooms. The date of bloom indicates that Spanish rue oil is derived principally from *Ruta montana.*

According to Naves,[4] Spanish oil originates from *R. montana,* often mixed with *R. graveolens;* and North African rue oil is distilled from *R. montana, R. bracteosa,* and a species allied to the latter, viz., *R. angustifolia* Pers.

French rue oil is derived from (cultivated) *R. graveolens,* Sicilian rue oil from *R. bracteosa,* and Sardinian oil from *R. angustifolia* Pers.

Producing Regions.—The producing regions of Spanish rue oil are located in the sections forming the western part of Andalusia and Estremadura and comprising the provinces of Badajos, Cádiz, Seville, Cordoba, and Huelva.

Distillation.—In Spain distillation of rue oil is carried on from the end of July through the early part of August and lasts about twenty days. The wild growing plant material is collected during the blooming period, and the fresh plants are charged, without previous drying, into field stills 2 m. high and 1.6 or 1.8 m. wide, the former type holding 70 arrobas, and the latter 90 arrobas of fresh plant material. (1 arroba = 11.5 kg. or about 25 lb.) Distillation of one batch, including charging of the stills, lasts about 6 hr. and is completed when 200 or 240 liters of water (depending upon the size of the still) have distilled over.

It should be pointed out in this connection that the gathering and handling of flowering rue plants present quite a problem, as the pollen of the plants may cause skin blisters, particularly among workers who have had blood diseases or who have not yet become immune by previous exposure to the plant.

Yield of Oil.—When distilled freshly, 90 kg. of rue plants yield on the average 1 kg. of oil. On drying, or on exposure to air for a few days, the yield of oil diminishes considerably, and 160 kg. of plant material may be required to give 1 kg. of oil.

Total Production.—Prior to the Spanish Civil War (1936–1939) Spain produced annually several tons of rue oil. During World War II the demand for this oil increased greatly, particularly on the part of Germany, with the result that in 1942 Spain produced 8 metric tons, and in 1943 12 metric tons. During 1945 production fell to 2 metric tons, but rose to 5 metric tons in 1946. For 1948 the figure was 3 metric tons.

North Africa and France supply small quantities only.

[3] See Jadin, *Repts. Roure-Bertrand Fils,* April (1911), 11. *Ber. Schimmel & Co.,* October (1911), 73.

[4] *Perfumery Essential Oil Record* **30** (1939), 93.

Physicochemical Properties.—From a study of the physicochemical properties recorded in literature for oils of different geographical origin, it appears that the oils distilled from *Ruta montana* L. (summer rue) have a much higher congealing point (+7.5° to +10.5°) than the oils distilled from *R. bracteosa* (winter rue), the latter oils congealing below 0° and in some cases not even at −15°. Oils derived from *R. graveolens* (garden rue) congeal at +5.8° to +10.5°, and usually at about +7°. The congealing point of the rue oils depends primarily upon their content of two ketones, viz., methyl heptyl ketone, and methyl nonyl ketone, which form the main constituents (80 to 90 per cent, often even more) of these oils. Methyl heptyl ketone congeals at −15° to −17°, methyl nonyl ketone at +12.5° to +13°. The congealing point of a rue oil thus indicates the ratio at which these ketones occur in the oil under examination. Rue oils of high quality possess a high ketone content, a low specific gravity, and are soluble in 70 per cent alcohol.

Genuine Spanish rue oils imported by Fritzsche Brothers, Inc., New York, had physicochemical properties ranging within these limits:

Specific Gravity at 15°/15°	0.834 to 0.844
Optical Rotation	+0° 18′ to +1° 20′
Refractive Index	1.4301 to 1.4355
Congealing Point	+8.2° to +10.4°
Ketone Content (Calculated as Methyl Nonyl Ketone, Hydroxylamine Hydrochloride Method)	85.5% to 97.8%
Solubility	Soluble in 2 to 3.5 vol. of 70% alcohol

Gildemeister and Hoffmann [5] recorded the properties given in Table 1.28 for French, Spanish, and Algerian rue oils.

TABLE 1.28

Properties	French Oil	Spanish Oil	Algerian Oil	
			R. montana	*R. bracteosa*
d_{15}	0.8325 to 0.8437	0.8319 to 0.8470	0.8351 to 0.8383	0.8373 to 0.8455
α_D	−0° 40′ to +2° 10′	−1° 0′ to +2° 0′	+0° to +1° 35′	−1° 14′ to −5° 0′
n_D^{20}	1.430 to 1.437	1.430 to 1.434	1.430 to 1.434	Ca. 1.430
Cong. Point	+5.8° to +10.5° mostly above +7	+1° to +10.3° mostly above +8	+7.3° to +10.4°	Below 0°
Solubility in 70% Alcohol	Soluble in 1.5 to 3 vol., occasionally with separation of paraffins	Soluble in 2 to 4 vol.	Soluble in 2 to 3 vol., occasionally with separation of paraffins	Soluble in 2 to 3 vol., occasionally with separation of paraffins

[5] "Die Ätherischen Öle," 3d Ed., Vol. II, 927.

Chiris [6] suggested the following properties for Algerian rue oils:

	Ruta bracteosa	*Ruta montana*
Specific Gravity at 15°	0.836 to 0.8455	0.834 to 0.8387
Optical Rotation	0° to −6° 15′	Inactive or slightly *d*-rotatory
Refractive Index at 20°	1.429 to 1.434	1.430 to 1.436
Solidifying Point	Below 0°; to −5°	Up to +12.5°
Solubility in 70% Alcohol	Soluble in 2 to 4.5 vol., often with considerable precipitation of paraffins	

Naves [7] reported these limits for North African rue oils distilled from *R. bracteosa* and *R. montana:*

	Ruta bracteosa	*Ruta montana*
Specific Gravity at 20°	0.830 to 0.839	0.828 to 0.834
Optical Rotation	−1° 0′ to +6° 10′ [8]	+0° to +1° 45′
Refractive Index at 20°	1.427 to 1.432	1.429 to 1.4325
Solidifying Point	Below 0°	+8.5° to +10.3°
Ketones as $C_{11}H_{22}O$ (Oximation)	89 to 96.4%	93 to 97.5%
Solubility in 70% Alcohol	1 vol. of oil soluble in 2 to 3 vol. of alcohol, with separation of paraffins	

Morocco, too, offers good possibilities for the production of rue oil, large quantities of rue growing wild in the Medium Atlas and in some parts of the Riff Mountains, at altitudes ranging from 600 to 1,000 m. According to information gathered by the writer while surveying the producing regions of Morocco, the oil is distilled there from fresh plants from the middle of June to the beginning of September, when the plants go into seed. The best distillation material consists of the tops of the fresh plants, which are clipped off during the second part of August, just before the seed develops. The lower leaves, too, contain some essential oil, and may be distilled, but the stalks are eliminated as valueless. Depending upon time of harvest and maturity of the plant material, the yield of oil varies from 0.75 to 1.2 per cent.

An oil of rue distilled in the Medium Atlas under the writer's supervision from the entire plants before the seeds had matured possessed the following properties:

Specific Gravity at 15°	0.833
Optical Rotation	+0° 22′
Refractive Index at 20°	1.4301
Congealing Point	+10.4°

[6] *Parfums France* **10** (1932), 316.
[7] *Perfumery Essential Oil Record* **30** (1939), 93.
[8] Should probably read −1° 0′ to −6° 10′ (the Author).

Ketone Content (Calculated as Methyl Nonyl Ketone, Hydroxylamine Hydrochloride Method)	96.0%
Solubility at 20°	Soluble in 2 to 2.5 vol. and more of 70% alcohol

The high congealing point in conjunction with the high percentage of ketones indicates the presence of a large percentage of methyl nonyl ketone in this oil.

Several tons of rue oil could be produced annually in Morocco without too much difficulty.

Trabaud [9] determined the properties of three North African rue oils, distilled south of Fez from *Ruta montana* (*I* and *II*), and in the valley of the Chelif (Oran) from *R. angustifolia* (*III*):

	I	*II*	*III*
Specific Gravity at 15°	0.8450	0.8347	0.8350
Optical Rotation	+0° 28′	+0° 30′	+0° 32′
Refractive Index at 20°	1.4387	1.4327	1.4341
Congealing Point	+7.6°	+10°	+9.2°
Ketone Content (Calculated as Methyl Nonyl Ketone, Oximation in the Cold)	86%	91%	86.5%
Solubility in 70% Alcohol	Soluble in 3.5 vol.	Soluble in 3 vol.	Soluble in 2.4 vol.

Sorgonà Luisi [10] described an oil of rue distilled from *R. bracteosa* in Sicily:

Specific Gravity at 26°	0.8389
Specific Optical Rotation	−3° 12′
Refractive Index at 26°	1.4302
Ester Content	29.64%
Freezing Point	−15°
Solubility	Soluble in 3 vol. of 70% alcohol

Oil of rue is examined and evaluated by determining congealing point and by assaying the content of ketones with the hydroxylamine method. The higher the ketone content, the better will be the quality of the oil under examination. In doubtful cases the ketones should be removed from the oil by treatment of the latter with bisulfite solution: the residual neutral oil which has not reacted with bisulfite can then be fractionated and tested for the presence of extraneous constituents. Similarly, the ketones should

[9] *Ann. chim. anal.* **24** (1942), 184.

[10] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **6** (1931), 110.

be regenerated from the bisulfite compound, fractionated, and examined for the presence of adulterants which react with bisulfite and simulate a high ketone content.

When preparing the bisulfite compounds, it should be kept in mind that methyl nonyl ketone and methyl heptyl ketone do not readily react with sodium bisulfite solution. In order to isolate these ketones from rue oil through their bisulfite addition compounds, Sornet [11] recommended first washing the oil with a dilute solution of sodium carbonate to remove the volatile acids and pelargonic acid usually present in the oil. A (second) washing with dilute sodium hydroxide solution will eliminate any phenols contained in the oil. Then the sodium bisulfite compound is prepared, washed with ether, and decomposed by means of a 5 per cent sodium hydroxide solution. The recovered ketones should be fractionated, after discarding the first fractions of low boiling point.

Studying the ketonic constituents of Algerian rue oil, Morgan and Holmes [12] used a somewhat different approach. These workers first isolated methyl nonyl ketone, by way of its sodium bisulfite compound, from the fraction b. 225°–235° of the oil, and obtained a yield of 70 per cent. The purity of the methyl nonyl ketone, i.e., the absence of notable amounts of methyl heptyl ketone, was determined by converting methyl nonyl ketone into pale blue copper decoylacetone by means of the Claisen condensation, and by determining the melting point and the copper content. Decoylacetone was recovered by treating the copper compound with dilute sulfuric acid and with ether.

Chemical Composition.—As was explained in the chapter on physicochemical properties, rue oil contains up to 90 per cent and even more of two ketones, viz., methyl nonyl ketone and methyl heptyl ketone, the content of either ketone being expressed by the congealing point of the oil. The oils distilled from *Ruta montana* (summer rue) and *R. graveolens* (garden rue), which are produced in Spain, France, and Morocco, thus contain chiefly methyl nonyl ketone and correspondingly less methyl heptyl ketone, whereas the oils distilled from *R. bracteosa* (winter rue), e.g., some of the Algerian oils, contain chiefly methyl heptyl ketone.

The following compounds have been identified in rue oils of various origin:

Methyl Nonyl Ketone. By Giesecke,[13] and by von Gorup-Besanez and Grimm.[14]

Methyl Heptyl Ketone. By Thoms.[15]

[11] *Rev. Marques* **13** (1935), 98, 164.
[12] *Pharm. J.* **112** (1924), 640.
[13] *Z. Chem.* **13** (1870), 428.
[14] *Liebigs. Ann.* **157** (1871), 275.
[15] *Ber. deut. pharm. Ges.* **11** (1901), 3.

Constituents boiling below 190° are present only in small quantities:

l-α-Pinene. Identified as nitrolpiperidine m. 119°–120° by Power and Lees.[16] The same workers found in rue oil of probably Algerian origin the following compounds:

l-Limonene. Identified as tetrabromide m. 103°.

Cineole. Characterized as iodol compound m. 114°–115°.

Methyl-*n*-Heptyl Carbinol and Methyl-*n*-Nonyl Carbinol. These (laevorotatory) secondary alcohols occur in the oil up to 10 per cent, partly free, partly as acetic esters.

Esters of Valeric Acid. Probably as ethyl ester.

Caprylic Acid(?). B. 236°–238°.

Salicylic Acid. Present in the oil probably as methyl ester.

Methyl Ester of Methyl Anthranilic Acid. The acid recovered from this ester melted at 173°, instead of at 178°–179°, according to Schimmel & Co.[17]

A Base(?). Possessing a quinoline-like odor.

A Blue Azulene(?). In the high boiling fractions b. 250°–320°.

More recently Pfau [18] investigated an Algerian rue oil distilled from *Ruta montana* and established the presence of the following constituents, all of which occur in the oil in very small quantities (about 0.1 per cent): methyl-*n*-amyl ketone, methyl-*n*-hexyl ketone, methyl-*n*-octyl ketone, benzaldehyde, cuminaldehyde, *p*-cymene, carbolic acid, carvacrol, guaiacol, vanillin, caproic acid, caprylic acid, capric acid (and esters), lauric acid, myristic acid, palmitic acid (and esters), anisic acid, umbelliferone methyl ether, xanthotoxin, α- and β-anethole glycol, a lactone $C_{15}H_{14}O_3$ (rutolide) (m. 85.5°–86°), dioxime of *n*-heptane-3,4-dione (m. 167.5°–168°—one of the most unusual constituents observed in essential oils).

Use.—Oil of rue as such has not found any wide use. Small quantities are employed in flavor work, and in certain types of perfumes and soap scents. However, oils containing a high percentage of methyl nonyl ketone are particularly in demand as starting material for the preparation of methyl nonyl acetaldehyde.

Suggested Additional Literature

K. Täufel, H. Thaler, and O. Bauer, "Seed Fat of the Garden Rue (*Ruta graveolens*)," *Fettchem. Umschau.* **43** (1936), 55. *Chem. Abstracts* **30** (1936), 7370.

[16] *J. Chem. Soc.* **81** (1902), 1585.
[17] *Ber. Schimmel & Co.*, Oct. (1901), 47.
[18] *Helv. Chim. Acta* **15** (1932), 1267; **22** (1939), 382.

André Patoir, Gérard Patoir and H. Bédrine, "Action of Essential Oil of Rue on Animal Organism," *Compt. rend. soc. biol.* **127** (1938), 1324. *Chem. Abstracts* **32** (1938), 5918.

P. F. Fávero, H. Veiga de Carvalho, and E. Novah, "Experimental Study of Apiole, Savin and Rue," *Anais faculdade med. univ. São Paulo* **16** (1940), 499. *Chem. Abstracts* **37** (1943), 6338.

OIL OF SANDALWOOD, WEST INDIAN

Essence de Bois de Santal des Indes Occidentales
Aceite Esencial Sandalo Indias Occidentales *Westindisches Sandelholzöl*
Oleum Santali ex India Occidentali

Botany and Producing Regions.—The botanical classification of the West Indian sandalwood tree was a matter of considerable controversy until Urban and Holmes [1] identified the tree as *Amyris balsamifera* L. which belongs to the family *Rutaceae*. The West Indian sandalwood tree, therefore, has no relationship to the East Indian sandalwood (*Santalum album* L., fam. *Santalaceae*) or with the West Australian (*Santalum spicatum* A, D.C., S. *cygnorum* Mig., *Eucarya spicata* Sprag. et Summ.). It is possible that *Amyris balsamifera* L. exists in several local varieties; at least the oils distilled from it vary somewhat, according to regions of production. Prior to World War II substantial quantities of billets were exported from Venezuela for distillation of the wood (chiefly in Germany). Small lots of oil from the islands of Haiti and Jamaica were also offered. In 1942 the production of West Indian sandalwood oil in Haiti was expanded considerably, due mainly to the efforts of Senator Louis Dejoie of Port-au-Prince.

Amyris balsamifera L. flourishes in the wild state all over Haiti, particularly in the southern part near Aquin and Saltrou. The tree grows in small thickets in areas of low rainfall, on calcareous soil, and on eroded mountain slopes. The natives call the wood "candle wood" (*Bois chandelle*). Because of its oil content it burns like a candle and is used as a torch by fishermen at night to catch sea crabs along the seashore, and by the peasants traveling at night when they bring farm products from their mountain habitations to the village and city markets. The trees were once used also as firewood, but of late a substantial part of the wood is dis-

[1] See Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 951.

tilled for the essential oil which it contains. The supply of wood being plentiful, the production of oil of *Amyris balsamifera* is not limited.

In Haiti the distilleries are located in Ducis, Maniche, Miragoane, and Jacmel. They receive their wood supply by truck and cart from the neighboring dry areas, and sometimes by barge from the island of La Gonave, in the Bay of Port-au-Prince.

Distillation, Yield, and Quality of Oil.—In Haiti the trunks and large branches of the tree are chopped by hand (with machetes), and the pieces put through a hammer mill, using a ½ in. screen. If the wood is ground too finely, steam channeling will take place during distillation, and the yield of oil will be reduced. From 72 to 84 hr. are required to exhaust one charge of wood material. Distillation will be more effective if a steam pressure of 2 to 3 lb. (as measured in the retort) is used. A steam boiler of about 8 h.p. capacity is required for the distillation of 1 metric ton of reduced wood. The yield of oil varies from 2 to 4 per cent and depends upon the quality of the wood (i.e., the part of the tree from which it comes, the moisture content, and the age of the tree). In Haiti the wood of *Amyris balsamifera* is often employed for the making of fence posts which may last in the ground for more than 100 years. Dejoie [2] has distilled some of these fence posts and obtained an oil of excellent quality, but in poor yield. Oil derived from fresh wood exhibits a lower specific gravity and a harsher odor than the oil distilled from wood that has been seasoned for 5 or 6 months prior to distillation. However, after 2 to 3 months of storage in open drums, the oil changes in character; its odor improves and approaches that of oil distilled from seasoned wood.

Total Production.—In Haiti the following quantities of oil of *Amyris balsamifera* were produced from 1943–1944 to 1947–1948 inclusive:

Fiscal Year	*Quantity of Oil (kg.)*
1943–1944	2,112
1944–1945	10,216
1945–1946	8,511
1946–1947	17,613
1947–1948	10,316

As was pointed out above, production could be augmented largely, perhaps to about 50 metric tons annually, if the demand and prices should warrant. Supply of wood is ample, but distillation facilities would have to be increased.

[2] Private communication of Senator Louis Dejoie, Port-au-Prince, Haiti.

Physicochemical Properties.—The oils mentioned by Gildemeister and Hoffmann (probably from Venezuela wood), had properties varying within these limits:

Specific Gravity at 15°	0.950 to 0.970
Optical Rotation	+19° 0′ to +29° 0′, seldom lower
Refractive Index at 20°	1.508 to 1.513
Acid Number	Up to 3.0
Ester Number	Up to 6.0
Ester Number after Acetylation	66 to 125 (corresponding to 27-55% of alcohol $C_{15}H_{26}O$). For the complete saponification of the acetylized oil a large excess of alkali has to be employed and the duration should be not less than 2 hr.
Solubility	Soluble in 1 vol. or less of 90% alcohol; occasionally soluble in 2 to 10 vol. of 80% alcohol

Distilling imported billets of *Amyris balsamifera* L. (apparently from Venezuela), Schimmel & Co.[3] found that the oil from thick billets generally had a higher specific gravity, a higher optical rotation, and a higher content of sesquiterpene alcohols than oils derived from thin billets (Table 1.29).

Oil I was distilled from thick billets, oils IIa and IIb from medium sized billets; but these three oils differed from the others in their high optical rotation and in their high content of sesquiterpene alcohol. Perhaps the wood originated from a different but closely related variety.

Distilling two lots of West Indian sandalwood, originating from Jamaica, Schimmel & Co.[4] obtained a yield of 4.5 per cent. The two oils had these properties:

Specific Gravity at 15°	0.9798	0.9840
Optical Rotation	+50° 56′	+63° 30′
Refractive Index at 20°	1.50790	1.50596
Acid Number	0.4	1.9
Ester Number	0.9	2.8
Ester Number after Acetylation (2 Hr. Saponification)	169.9	166.1
Alcohol Content (Calculated as $C_{15}H_{26}O$)	77.2%	75.2%
Solubility	Soluble in 1 vol. and more of 80% alcohol; soluble in 3.5 vol. and more of 70% alcohol	

[3] *Ber. Schimmel & Co.* (1938), 99.
[4] *Ibid.* (1932), 59.

TABLE 1.29

Properties	Oil from Thick Billets	Oil from Thin Billets	Oil I	Oil IIa	Oil IIb
Specific Gravity at 15°	0.9593 to 0.9675	0.9459 to 0.9612	0.9828	0.9814	0.9612
Optical Rotation	+18° 17′ to +39° 46′	+0° 59′ to +29° 19′	+61° 31′	+57° 30′	+60° 50′
Refractive Index at 20°	1.50689 to 1.50937	1.50289 to 1.50937	1.50956	1.50882	1.50946
Acid Number	0.4 to 1.5	0.4 to 1.9	0.7	0.4	0.7
Ester Number	0.9 to 5.6	2.8 to 3.7	1.9	3.7	3.7
Ester Number after Acetylation	105.5 to 149.3	81.2 to 135.5	168.0	160.5	169.9
Solubility	Soluble in 1.2 to 18 vol. of 80% alcohol	Soluble in 1.3 to 25 vol. of 80% alcohol	Soluble in 3 vol. and more of 70% alcohol	Soluble in 1.5 vol. and more of 70% alcohol	Soluble in 1.5 vol. and more of 80% alcohol

At a temperature of −20° the oils congealed to a very viscous, glass-like mass.

Distilling West Indian sandalwood imported from Haiti, Roure-Bertrand Fils [5] obtained a yield of 3.8 per cent. The oil had the following properties:

Specific Gravity at 15°	0.9799
Optical Rotation	+47° 4′
Ester Content (Calculated as $CH_3 \cdot COOC_{15}H_{23}$)	0.4%
Total Alcohol Content (Calculated as $C_{15}H_{24}O$)	44.1%
Solubility	Soluble in 3 vol. and more of 70% alcohol

Numerous lots of West Indian sandalwood oil examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.957 to 0.971, usually about 0.960
Optical Rotation	+18° 0′ to +34° 0′
Refractive Index at 20°	1.5050 to 1.5090
Saponification Number	0 to 5
Total Alcohol Content (Calculated as $C_{15}H_{26}O$)	45 to 70%, usually 50 to 60%
Solubility at 20°	Soluble in 1 to 3 vol. of 80% alcohol; usually opalescent to turbid with more

Oils originating from Haiti are not included in these figures. Genuine oils of *Amyris balsamifera* L. distilled in Haiti analyzed as follows:

Specific Gravity at 15°	0.959 to 0.974
Optical Rotation	+30° 0′ to +42° 0′
Refractive Index at 20°	1.5050 to 1.5070
Total Alcohol Content (Calculated as $C_{15}H_{26}O$)	63 to 76.6%
Ester Content (Calculated as Acetate of Alcohol $C_{15}H_{26}O$)	About 1%
Solubility at 20°	Soluble in 1 to 3 vol. of 80% alcohol, frequently opalescent with more

From these figures it appears that, in general, the Haiti oils have a higher specific gravity, optical rotation, and alcohol content than West Indian sandalwood oils of other origin.

The oils were of somewhat viscous consistency, yellow-brown color, and possessed a peculiar, balsamic odor, not too pronounced.

[5] *Repts. Roure-Bertrand Fils,* October (1907), 15. *Ber. Schimmel & Co.,* April (1908), 94.

Chemical Composition.—The chemical composition of West Indian sandalwood oil has been investigated by several workers, but the difficulties encountered have resulted in considerable confusion. The oil seems to be composed mainly of sesquiterpene alcohols (probably a mixture of cadinols), and of 30 to 40 per cent of sesquiterpenes (of which 16 to 17 per cent is cadinene, the balance β-caryophyllene). The following compounds have been isolated by the various investigators:

β-Caryophyllene. Identified by Deussen [6] as nitro-β-caryopnyllene m. 156°–157° in the lowest boiling fractions, b_{17} 137°–139°, d_{18} 0.9125, α_D +7° 0′, of the oil.

d-Cadinene. The same author [7] reported the presence of *d*-cadinene in West Indian sandalwood oil. Cleaving hydrogen chloride from cadinene dihydrochloride m. 117°–118°, Deussen obtained *l*-cadinene. Therefore, it is not proved definitely that the oil contains cadinene in the *d*-modification, as claimed by Deussen in his first paper on the subject. Later, Deussen and Awramoff,[8] fractionating West Indian sandalwood oil repeatedly and finally over metallic potassium, obtained two *d*-cadinene-containing fractions $b_{10.5}$ 131°–133.5°, α +31° 36′, and b_{13} 138°–140°, α +38° 43′ which on dehydrogenation with sulfur yielded cadalene. Catalytic hydrogenation of cadinene with platinum black yielded tetrahydrocadinene, b_{14} 135°–137°, α −10° 4′, the properties of which agreed with those observed by Semmler and Jonas on a hydrogenation product of *l*-cadinene.

Cadinol. Years ago, von Soden [9] isolated from West Indian sandalwood oil a sesquiterpene alcohol $C_{15}H_{26}O$ which he called *Amyrol*. Shortly afterward, von Soden and Rojahn [10] found that amyrol was not a uniform compound but that, by repeated fractionation, it could be separated into several alcohols. Years later, Deussen and Awramoff,[11] investigating the sesquiterpene alcohols of West Indian sandalwood oil, reported the presence of two isomers, viz., α-amyrol b_5 137°–138°, α +56° 2′ and β-amyrol b_{10} 149.5°–150.5°, α +9° 42′, and noted the presence of a double bond, as in cadinol.

At about the same time, Ruzicka, Capato and Huyser [12] fractionated the last runs of West Indian sandalwood oil and obtained three fractions of approximately the same weight: b_7 152°–158°, b_7 158°–165°, and b_7 165°–175°. These fractions represented a mixture of mainly bicyclic (although not absolutely pure) sesquiterpene alcohols, principally of the formula $C_{15}H_{26}O$. Heating of the fraction 2, first with phthalic anhydride to 100°, then to 120°–130°, partly resulted in the cleavage of water, as is usually the case with tertiary alcohols. Further heating to 160° yielded a sesquiterpene $C_{15}H_{24}$, b_{16} 134°–138° which gave a dihydrochloride m. 117°, identical with *l*-cadinene dihydrochloride.

Ruzicka and collaborators thus arrived at the conclusion that the sesquiterpene alcohols of West Indian sandalwood oil consist mainly of a cadinol, or of a mixture of several cadinols. The designation amyrol for the sesquiterpene alcohols of West Indian sandalwood oil, in the opinion of Ruzicka et al. is, therefore, no longer tenable, at least not until new evidence in favor of amyrol has been established.

[6] *Liebigs Ann.* **388** (1912), 144.
[7] *Arch. Pharm.* **238** (1900), 149; **240** (1902), 288.
[8] *J. prakt. Chem.* [2], **120** (1928), 119.
[9] *Pharm. Ztg.* **45** (1900), 229.
[10] *Ibid.*, 878.
[11] *J. prakt. Chem.* [2], **120** (1928), 119.
[12] *Rec. trav. chim.* **47** (1928), 378.

Amyrolin(?), $C_{14}H_{12}O_3$. When saponifying West Indian sandalwood oil, von Soden and Rojahn [13] obtained an alkaline liquor which, on acidification with sulfuric acid, gave a partly crystalline oil with a strong odor of acetic acid. To remove this acid the oil was shaken with a solution of sodium bicarbonate. The remaining crystals, after recrystallization from methyl alcohol, melted at 117°. The compound thus obtained was free of nitrogen, contained no methoxy group, and had the empirical formula $C_{14}H_{12}O_3$. It dissolved in alcoholic alkali solutions with yellow-green fluorescence, and it added bromine, yielding an amorphous, white dibromide m. 157°–159°. Von Soden and Rojahn named this compound Amyrolin; it seemed to be a lactone belonging to the aromatic series.

A Compound, $(C_{21}H_{30}O)_5$(?). In the distillation residue of West Indian sandalwood oil Deussen [14] observed a compound $(C_{21}H_{30}O)_5$ which was not identified.

Methyl Alcohol, Diacetyl, and Furfural. These compounds were observed in the distillation waters of West Indian sandalwood oil by Schimmel & Co.[15]

Use.—West Indian sandalwood oil is used chiefly as a perfume fixative in soaps. In low-priced perfumes, cosmetics, and soaps the oil occasionally serves as a substitute of the more expensive East Indian sandalwood oil, but due to its much weaker odor the West Indian oil has to be applied in correspondingly larger doses. However, even when this is done, the odor effect is not the same as that produced by the East Indian oil.

Suggested Additional Literature

L. Fuchs, "Testing Sandal Oil," *Scientia pharm.* **13** (1942), 21. *Chem. Abstracts* **37** (1943), 6820.

[13] *Pharm. Ztg.* **45** (1900), 878.
[14] *Liebigs Ann.* **388** (1912), 144.
[15] *Ber. Schimmel & Co.*, April (1903), 72.

CHAPTER II

ESSENTIAL OILS OF THE PLANT FAMILY *LABIATAE*

OIL OF BALM

Essence de Mélisse *Aceite Esencial de Melisa* *Melissenöl*
Oleum Melissae

Melissa officinalis L., a native of the countries bordering on the northern Mediterranean, grows wild, and also is cultivated in gardens as a medicinal herb. It has been naturalized in the United States. The plant, which reproduces itself spontaneously, can be observed along fence rows in shaded, uncultivated places. It grows in the Alps and in the Pyrenees. The dried herb offered on the market originates usually from cultivated plants.

Melissa officinalis is a herbaceous plant with a strong, agreeable odor, reminiscent of lemon. An evergreen, 30 to 60 cm. in height, it lasts two years or longer. The blossoms are small, of white or light rose color.

Cultivation.—The *Melissa* plant being easily affected by cold, a sunny and warm location should be chosen. Although it will grow almost anywhere, deep and shaded soils of medium consistency (which can be irrigated) are preferable. The plant will thrive well in a fresh and fertile, alluvial land, but will suffer by excessive moisture. In light and dry soils the leaves turn yellow and the yield greatly diminishes.

According to Papaceit,[1] the soil should be prepared to a depth of about 30 to 35 cm., and during the second tilling manure and fertilizers should be applied.

The plant can be propagated either from seed or from cuttings. In places near Paris, the first method is usually preferred. The seed is planted in July, in a greenhouse, and the young plants are placed into their permanent position in October. In other regions, the seeds are planted directly into their permanent place in April. The planting of the cuttings takes place in the fall or in March–April, 50 to 60 cm. apart.

Cultivation consists of irrigating, repeated turning over of the soil, and weeding. Although the plant requires moisture in the soil, excessive watering is harmful. At the beginning of the winter season the land should be tilled, fertilized, and in a cold climate the soil should be mounted at the base of the plants.

The plants may last for about ten years but are maintained for only five years for the purpose of obtaining the largest yield. After that period the crop is rotated.

[1] *Afinidad* **18** (1941), 169.

Harvest.—In the first year the harvest takes place in August, when the flowers are well formed; thereafter, two cuttings can be made, one in June and one in August. It is advisable to harvest on a clear day, after the dew has evaporated, otherwise the moist leaves would turn black on drying. The plants are very susceptible to heat and sunlight and should be transported as soon as possible to the distillery, or to the artificial dryer if the leaves are to be used in the liquor industry, etc. In this case the leaves are cleaned and dried, cleaning being accomplished after the stalks of the suspended plants have dried.

In Anjou (France) about 1,800 kg. of cleaned and dried leaves are obtained per hectare; they are sold on the market at attractive prices to the liquor industry, to the pharmaceutical trade, to herborists, etc.

Yield of Oil.—The yield of volatile oil from *Melissa officinalis* L. is so small that the cost of production becomes almost prohibitive. The commercial oil, therefore, is seldom, if ever, pure, and consists largely of mixtures of lemongrass and citronella oil, or fractions thereof. In European countries it is sometimes prepared by distilling lemon oil over *Melissa officinalis* L. herb (*Oleum Melissae citratum*).

Physicochemical Properties.—Distilling fresh *Melissa officinalis* L. at the beginning of the flowering stage, Schimmel & Co.[2] obtained 0.014 per cent of the true oil, with a specific gravity (15°) 0.924 and an optical rotation +0° 30′.

The fresh herb during full bloom gave 0.010 per cent of oil, with a specific gravity (15°) 0.894; the oil was optically inactive. The odor suggested the presence of citral and citronellal; the scent of the first mentioned oil was more agreeable, typical of *melissa*.

A Spanish oil of *Melissa officinalis* L., distilled in Sevilla, had the following properties, according to Dorronsoro: [3]

Specific Gravity at 25°	0.8910
Optical Rotation at 22°	+2° 8′
Refractive Index at 22°	1.4704
Acid Number	2.2
Ester Number	27.42
Ester Number after Acetylation	236.28
Aldehyde Content (Bisulfite Method)	42.0%
Solubility	Soluble in 0.5 vol. of 90% alcohol; in 2 vol. of 80% alcohol with slight turbidity upon further addition of alcohol

[2] *Ber. Schimmel & Co.*, October (1894), 37; October (1895), 58.
[3] *Mem. acad. cienc. exactas, Madrid* **29** (1919). *Ber. Schimmel & Co.*, April (1921), 88.

Distilling dried herb of *Melissa officinalis* L., Chiris [4] obtained 0.112 per cent of an oil with these properties:

Specific Gravity at 15°	0.9578
Optical Rotation	Inactive
Acid Number	40.88
Ester Number	18.20
Ester Number after Acetylation	135.8
Congealing Point	+12°
Solubility at 18°	Soluble in 1.5 vol. of 90% alcohol; soluble in 10 vol. of 90% alcohol with slight turbidity; soluble in 0.5 vol. and more of 95% alcohol

The oil had no odor of citral. This fact and the high congealing point, in addition to the other rather abnormal properties, make it appear doubtful that this oil was distilled from true *Melissa officinalis* L.

Distilling *Melissa officinalis* L., planted in Calabria, Albricci [5] obtained 0.014 per cent of an oil which analyzed as follows:

Specific Gravity at 15°	0.9026
Optical Rotation	−7° 48′
Acid Number	1.19
Saponification Number	44.32
Saponification Number after Acetylation	182.03
Aldehyde Content, Calculated as Citral	31.82%

A Russian oil distilled by Rutovski and collaborators [6] on the Crimean peninsula had these properties:

Specific Gravity at 20°/4°	0.8967
Optical Rotation	−30° 5′
Refractive Index at 20°	1.4890
Acid Number	3.75
Ester Number	12.08
Ester Number after Acetylation	152.32
Solubility	Soluble in 0.2 vol. of 90% alcohol

Distilling (with boiling water) *Melissa officinalis* L. collected in Oregon, cohobating and extracting the distillation waters, Burlage [7] obtained 0.13% (!) oil possessing the following properties:

[4] *Parfums France* (1924), 152.
[5] *Rivista ital. essenze profumi* **7** (1925), 16. *Ber. Schimmel & Co.* (1926), 71.
[6] *Bull. Sci. Chem. Pharm. Inst. Moscow* (1925), 11, 83. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 718.
[7] *J. Am. Pharm. Assocn.* **20** (1931), 38.

Specific Gravity at 20°	0.9632
Specific Optical Rotation at 20°	−10° 6′
Refractive Index at 20°	1.4999
Acid Number	9.28
Saponification Number	34.41
Ester Number after Acetylation	43.3
Phenol Content (Determined with 5% NaOH Solution)	4.0%
Aldehyde and Ketone Content (Determined with 35% $NaHSO_3$ Solution)	17.0%
Solubility	Insoluble in 20 vol. of 80% alcohol

Chemical Composition.—About 50 years ago the Schimmel chemists [8] found that the oil contains a high percentage of citral, accompanied probably by citronellal. Dorronsoro [9] reported that an oil distilled in Sevilla (Spain) contained 42 per cent of aldehydes (bisulfite method), while Albricci [10] reported 31.82 per cent of citral in an oil from Calabria.

Burlage [11] examined an oil distilled from plants collected in Oregon and found that it contained 4 per cent of phenols and 17 per cent of aldehydes and ketones.

More recently, Salgues [12] indicated the following composition of an oil of *Melissa officinalis* distilled in Provence (France), during the flowering period of the herb:

	Per Cent
Geraniol	12.38
Linaloöl	14.21
Citronellol	8.23
Total alcohol content	34.82
Citronellal	3.90
Citral	0.96
Total aldehyde content	4.86

Use.—As Braun [13] pointed out, oil of balm is a sedative whose individual properties resemble chamomile and peppermint oils. Balm distillates can act as mild spasmolytic agents.

[8] *Ber. Schimmel & Co.*, October (1894), 37; October (1895), 58.
[9] *Mem. acad. cienc. exactas Madrid* **29** (1919). *Ber. Schimmel & Co.*, April (1921), 88.
[10] *Rivista ital. essenze profumi* **7** (1925), 16. *Ber. Schimmel & Co.* (1926), 71.
[11] *J. Am. Pharm. Assocn.* **20** (1931), 38.
[12] *Rev. gen. sci.* **52** (1942), 35. *Chem. Abstracts* **39** (1945), 5398.
[13] *Fortschr. Therap.* **18** (1942), 80. *Klin. Wochenschr.* **21** (1942), 1020. *Chem. Abstracts* **38** (1944), 2731.

In the perfume industry oil of *Melissa officinalis* L. has not attained any commercial importance because of its excessively high price. It is possible to simulate its odor by a combination of other oils—lemon, lemongrass, citronella, and fractions thereof, for example.

OIL OF BASIL

Essence de Basilic *Aceite Esencial de Albahaca* *Basilicumöl*
Oleum Basilici

Introduction.—The botanical nomenclature of the *Ocimum basilicum* L. varieties from which the different types of basil oil are distilled is extremely complicated, because botanists seem to have assigned several designations to the same varieties, and in some instances confused varieties and forms of other species. According to Hegi,[1] there are 50–60 *Ocimum* species in tropical Asia, Africa, and America. It is a well-known fact that polymorphism in the species *Basilicum* is responsible for the very great number of subspecies, varieties, and forms. Furthermore, the basil flowers, although hermaphrodite, show an abundant cross pollination, possibly by bees, with subsequent hybridization into abnormal and subnormal forms or strains of unstable character.

Because of the impossibility of ascribing the different types of basil oil to definite plant varieties, it seems appropriate to classify these oil types according to their chemical composition and geographical source. (See also "Oils of Other *Ocimum* Species.")

On this basis it becomes possible to differentiate between:

I. European Type of Sweet Basil Oil.—Distilled in Europe and America from true *Ocimum basilicum* L.

The oil contains as principal constituent methyl chavicol and linaloöl, but no camphor. The oils are laevorotatory. This type represents the highest quality, with the finest odor.

II. Réunion Type of Basil Oil.—Distilled originally on Réunion Island, but now on the Comoros, Madagascar, and the Seychelles Islands from plants of still doubtful botany.

The oil contains methyl chavicol as main constituent, also camphor, but

[1] "Illustrierte Flora von Mittel-Europa," Vol. V, 4.

no linaloöl. The oils are dextrorotatory, possess a slight camphoraceous "by-note" and, therefore, represent a somewhat lower quality.

Commercially only the European and Réunion types of oil are important. The following types have been produced occasionally and experimentally:

III. Methyl Cinnamate Type of Basil Oil.—Such oils have been distilled in Bulgaria, Sicily, Egypt, British East India, and lately in Haiti (W.I.), supposedly from *Ocimum basilicum* L.

They show laevorotation, contain methyl chavicol as main constituent, linaloöl, and a substantial amount of methyl cinnamate. This fact suggests that the plant is not true *Ocimum basilicum* L., but perhaps *Ocimum canum* Sims or an allied species.

IV. Eugenol Type of Basil Oil.—Such oils have been distilled in Java, the Seychelles and Samoa, and lately also in the U.S.S.R.

They show dextrorotation, in general, and contain eugenol as main constituent, which permits the conclusion that the plant is not true *Ocimum basilicum* L., but perhaps *Ocimum minimum* or *O. gratissimum* L., or an allied species.

I. Oil of Sweet Basil (European Type)

Sweet basil, an annual plant and a popular condiment in Europe, is grown in gardens in many countries—in France, Italy, Spain, Germany, the Balkans, North Africa, and North America; large plantations for the production of the essential oil exist only in Southern France, however.

A. French Sweet Basil Oil

Botany.—As has been said, the botanical classification of *Ocimum basilicum* L. is very complicated, because of the many existing varieties and forms.

The flowers are borne in long terminal racemose inflorescences. The greenish corolla is small and inconspicuous. The calyx, partly grown together with bracts, enlarges itself postflorally and remains with the latter dry on the plant.

According to Camus [2] the following varieties of *Ocimum basilicum* L. are grown in Southern France:

O. b. var. *purpurascens,* Benth.
O. b. var. *thyrsiflorum,* Benth.
O. b. var. *album,* Benth.
O. b. var. *crispum,* E.G. Camus.

[2] *Repts. Roure-Bertrand Fils,* October (1910), 23.

The curly leafed variety is said to give the best yield of oil and, incidentally, of the finest quality.

According to Boischot,[3] only the original type *Ocimum basilicum* L., locally called *grand basilic*, is now being grown in Southern France for distillation purposes. Seed growers offer also other local varieties—*B. grand vert* and *B. Feuille de laitue*, for example, but they are of no commercial importance.

Producing Regions.—Years ago sweet basil was grown on a relatively large scale in the regions of Pegomas, Mandelieu, and Grasse, of the Département Alpes-Maritimes in Southern France, production of the herb amounting annually to about 300,000 kg., of which Pegomas produced half. Since the world depression of 1930, however, these quantities have been reduced to only a few thousand kilograms, the growers having become discouraged by the low prices offered by the Grasse distillers. Production of this annual could easily be increased again if conditions should warrant it.

Planting, Cultivating and Harvesting (see also American Sweet Basil Oil). —The seed is first planted under glass in winter; in spring the seedlings are transplanted into nurseries, and during April–May into the fields, the rows being spaced about 1 m. apart, the plants in each row 60 to 70 cm. distant. It is necessary to eradicate weeds, to irrigate regularly, and to replant every year. The plants reach a height of 60 to 70 cm. Harvest takes place in July and August, when the flowering tops are carefully clipped off, altogether three or four times. Depending upon the prevailing weather, one woman may collect in one day 50 to 60 kg. of material. It is a cumbersome and expensive method. Flowers develop again within a period of ten or fifteen days, when they are again clipped off. The sweet basil harvest thus lasts for almost two months. In France only the flowering tops (which give an extremely fine oil) are distilled, but toward the end of the harvest the whole overground parts of the plant are cut and distilled, which results in an oil of slightly inferior odor.

Distillation and Yield of Oil.—Distillation in the Pegomas region is carried out in direct steam stills of medium capacity, a charge consisting of about 400 kg. of flowering tops. Distillation lasts approximately 1½ hr. From 900 kg. to 1,100 kg. of flowering tops yield 1 kg. of oil. The flowering whole overground parts of the plant, distilled at the end of the harvest, contain considerably less oil, 1,400 to 1,500 kg. yielding about 1 kg. of oil.

Physicochemical Properties.—Years ago Roure-Bertrand Fils[4] studied the properties of sweet basil oils from the different varieties grown then in

[3] Private communication of Mr. Boischot, Director of the Experimental Garden in Grasse (A.M.), France.

[4] *Repts. Roure-Bertrand Fils,* October (1910), 39.

the Grasse region and found that the properties of these oils varied within the following limits:

Specific Gravity at 15°	0.8959 to 0.9168
Optical Rotation	−10° 14′ to −13° 52′
Refractive Index at 20°	1.477 to 1.488
Acid Number	0.7 to 3.5
Ester Number	3.5 to 9.8
Alcohol Content, Calculated as Linaloöl	34.50 to 39.66%

The methyl chavicol content of all these oils was about 55 per cent, calculated by determining the methoxy number according to Zeisel's method.

Genuine oils distilled in France and analyzed by Fritzsche Brothers, Inc., New York, had properties falling within these limits:

Specific Gravity at 15°/15°	0.912 to 0.935
Optical Rotation	−7° 24′ to −10° 36′
Refractive Index at 20°	1.4821 to 1.4939
Ester Content, Calculated as Linalyl Acetate	0.8 to 5.2%
Total Alcohol Content, Calculated as Linaloöl	31.7 to 41.8%
Solubility	Soluble in 1 vol. of 80% alcohol, clear to opalescent with more. Occasional oils soluble in 70% alcohol

Methyl chavicol, the main constituent of sweet basil oil, is oxidized on aging and exposure of the oil to light and air; thus older oils usually show a higher specific gravity and a higher refractive index. Sweet basil oil must, therefore, be stored carefully.

Two oils experimentally distilled in Java apparently from true *Ocimum basilicum* L. and analyzed by Schimmel & Co.[5] had properties and odor qualities resembling those of the French type of oil:

	I	*II*
Specific Gravity at 15°/15°	0.9303	0.9246
Optical Rotation	−7° 0′	−8° 15′
Refractive Index at 20°	1.49497	1.49250
Acid Number	1.5	0.8
Ester Number	7.5	6.5

Adulteration of Sweet Basil Oil.—Sweet basil oil is frequently adulterated with the much lower priced Réunion basil oil. Such an addition is indicated by increased specific gravity and refractive index and by a lowered laevorotation, or slight dextrorotation, depending upon the amount of Réunion oil present. These discrepancies can be partly corrected by the

[5] *Ber. Schimmel & Co.* (1936), 8.

addition of *l*-linaloöl; therefore adulteration of sweet basil oil is not always detected by mere routine analysis. The expert will submit the oil to a careful organoleptic test, watching especially for the presence of camphor which does not occur in true sweet basil oil.

Chemical Composition.—The chemistry of European (French and German) sweet basil oil was investigated more than a century ago by Bonastre,[6] later by Dupont and Guerlain [7] who examined a French oil, and by Bertram and Walbaum,[8] who used a German oil as the basis of their work.

The presence of the following compounds has been established:

Cineole. In the lowest boiling fractions. Identified as iodol compound m. 112°.

Linaloöl. Dupont and Guerlain,[9] and Bertram and Walbaum [10] reported the occurrence of linaloöl in the fractions b. ~200°.

Methyl Chavicol (Isoanethole). Identified in the fraction b. ~215° by Bertram and Walbaum through oxidation to homoanisic acid (*p*-methoxyphenylacetic acid) m. 84°–85°.

A quantitative methoxy determination showed that the oil contained 24 per cent of methyl chavicol.

Neither the French nor the German oil contained camphor.

Use.—Although not used in large quantities, oil of sweet basil is employed quite extensively in all kinds of flavors, including those for confectionery, baked goods, and condimentary products (chili sauces, catsups, tomato pastes, pickles, fancy vinegars) and in spiced meats, sausages, etc. The oil serves also for imparting distinction to flavors in certain dental and oral products.

Sweet basil oil has its place in certain perfume compounds. For the scenting of soaps the lower priced Réunion oil is preferable.

B. American Sweet Basil Oil

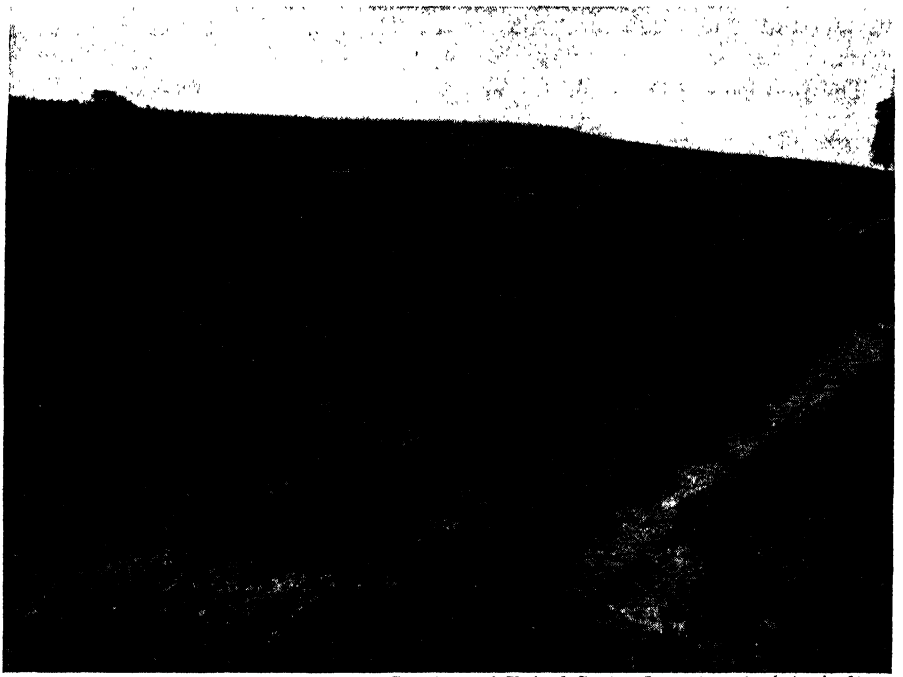
The Division of Drug and Related Plants of the U. S. Department of Agriculture experimented for several years with *Ocimum basilicum* L. at the Arlington Experimental Farm in Virginia.

The seed, imported from France, was derived from the large green variety of true *Ocimum basilicum* L. ("Grand Basilic"). For distillation the whole fresh flowering herb was used.

[6] *J. Pharm.* [2], **17** (1831), 647. *Pharm. Zentr.* (1831), 848.
[7] *Compt. rend.* **124** (1897), 300. *Bull. soc. chim.* [3] **19** (1898), 151.
[8] *Arch. Pharm.* **235** (1897), 183.
[9] *Compt. rend.* **124** (1897), 300. *Bull. soc. chim.* [3] **19** (1898), 151.
[10] *Arch. Pharm.* **235** (1897), 183.

According to Lowman [11] the growing of this annual in the United States should present no unusual difficulties, as the harvesting and distilling resemble those of peppermint.

Land of medium fertility lends itself to the growth of sweet basil. A heavy clay soil that bakes or crusts on the surface is unsuitable, because the tender seedlings are unable to penetrate a crusted surface. Such soils



Courtesy of United States Department of Agriculture.

American sweet basil at Woodbine, Maryland.

may be improved, however, by mulching with an application of pulverized stable manure. The plants grow quite rapidly, a too fertile soil producing large succulent plants, poor, however, in oil.

Preparation of Land and Sowing.—Lowman recommended preparing the land by plowing, preferably in the fall, since the alternate freezing and thawing during the winter aids in producing a finer textured soil. Before planting, the land should be harrowed as smooth as possible, because the small seed must be drilled into a uniform depth, to obtain a good stand of plants. An ordinary onion drill or small seed drill may be used for this purpose. The seed will not germinate if covered to a depth of more than

[11] *Am. Perfumer,* April (1935), 76.

a half to one-quarter of an inch. For this reason it is very important that the land be smooth and well-settled before sowing. Four to eight pounds of seed are required to sow an acre, depending on the viability of the seed and the distance between the rows. The drill should be set so as to drop about twelve seed to the foot, and proportionately more if it is of poor quality. The seed should not be sown until all danger of frost is past and the ground sufficiently warm to insure quick germination, as otherwise it may rot before germination takes place. At Arlington Farm it has been found that the proper time for planting is between the first and the last week in May. Germination begins ten days to two weeks after sowing, and flowering follows in eight to ten weeks, while the full blooming stage is reached in twelve to fourteen weeks after seeding. If weather conditions are favorable a second crop may be ready in about eight weeks after the cutting of the first crop.

On land comparatively free from weeds, very little cultivation is required. Any necessary cultivating should be done while the plants are small, so as not to disturb the rapidly developing root system. The soil should not be disturbed after the first crop is cut. Any large weeds should be removed by hand before cutting the second crop.

In most of the plantings at Arlington Farm the rows were spaced 1 m. (about 39 in.) apart, which allows ample room for complete development of the plants, but considerably more tonnage can be obtained by closer spacing of the rows. Rows 0.66 m. (about 2 ft.) apart would undoubtedly give an increased tonnage over the 1-m. spacing and with less crowding of the plants than results from 0.5-m. spacing. Rows spaced closer than 2 ft. are difficult to cultivate. In addition to the yield increase resulting from certain row spacing, yields may also be increased by the proper use of fertilizer elements that induce leafy growth, especially where the soil is deficient in such elements.

Harvesting and Distilling.—According to Lowman, the crop is ready to harvest when the plants are in full bloom and the lower leaves begin to turn yellow. Harvesting is accomplished without difficulty with an ordinary hay mower or hand scythe. The plants should be cut at least 6 in. above the ground level to insure a good second crop. If cut too near the ground the plants may either die or produce a very short second crop. After cutting, the herb may be allowed to lie in the sun and wilt for 2 or 3 hr., to facilitate packing in the distilling vats, but prolonged drying may affect the quality of the oil. The wilted herb may be raked into windrows with a hay rake, or forked into heaps and hauled immediately to the distillery, where it should be firmly packed into the distilling vats. About 1 hr. is required

to exhaust a charge completely. The distillate should run warm as it emerges from the condenser. After separation of the oil the distillation water may be run into a separate tank and redistilled for recovering the small amount of oil which it holds in suspension. However, if an efficient receiver is used for the separation of the oil, the loss from discarding the distillation water is negligible. Since the crop is easily grown and good yields are obtained, the oil could be produced in many localities of the United States, and at reasonable prices.

The yields of herb and the percentages of oil vary greatly. The amount of herb obtained depends directly upon the fertility of the soil and seasonal conditions, both of which may also greatly affect the percentage of oil in the herb. The oil is contained principally in the leaves and flowers of the plant; therefore, the more bushy type of plants with as few large stems as possible will produce a higher yield of oil. Cloudy or rainy weather immediately preceding the harvest decreases the yield of oil from the plants, while bright sunny weather has the opposite effect.

The highest yield of oil per acre was obtained in 1931, when two crops were cut from a plot representing 0.24 acre. The total calculated per acre yield from the two crops was 43.2 lb. of oil. The highest yield from a single cutting was in 1915, based on the herb from one row, a yield equivalent to 31.5 lb. of oil per acre being obtained.

About fertilization and cultivation of American basil, see also Bulletin No. 4, The Herb Society of America, Boston, Mass., March, 1944.

Physicochemical Properties.—Table 2.1 gives the properties [12] that Lowman reported for sweet basil oils produced at Arlington, Virginia, in 1931 and 1932:

TABLE 2.1

Season	Harvests	Distance Between Rows (m.)	Acid Number	Refr. Index at 15°	Spec. Grav. at 15°	Optical Rotation
1931	First	1	1.37	1.4920	.9217	−8° 0′
	Second	½	1.85	1.4932	.9278	−6° 21′
		1	1.51	1.4943	.9267	−7° 45′
		½	1.10	1.4936	.9215	−8° 15′
1932	First	1	.68	1.4883	.9132	−9° 42′
		½	.69	1.4888	.9150	−9° 24′

[12] Properties taken in January, 1935.

The oils were not completely soluble in 70 per cent alcohol, but formed a clear solution in 1 volume or more of 80 per cent alcohol.

There existed a correlation between the acid numbers, specific gravities, and optical rotations of the oils.

The oils obtained by Lowman possessed an agreeable odor and flavor, resembling that of good French oils.

Lowman recommended growing of basil in the United States because this annual permits seasonal adjustments in acreage according to the fluctuations and demand for the oil.

Chemical Composition.—Nelson and Lowman [13] investigated the chemical composition of sweet basil oil produced in Virginia. The oil had been distilled from the whole fresh flowering herb of *Ocimum basilicum* L., large green variety, grown from imported French seed. Nelson and Lowman found that the chemical composition of the Virginia oil closely resembles that of the European sweet basil oil. These authors established the presence of the following constituents:

A Terpene(?). The fraction b. 175°–179°, α_D +3° 36′, contains small quantities of a dextrorotatory terpene such as *d*-limonene.

Cineole. Identified by the preparation of the crystalline cineole-resorcinol compound.

l-Linaloöl. Identified in the fraction b_{10} 84°–85°, α_D −13° 18′, by means of the phenylurethane m. 65°–66°.

Methyl Chavicol. Characterized by conversion into anethole m. 21°.

Eugenol. The total phenol recovered from 500 cc. of the oil amounted to 8.7 cc. Eugenol was identified by the preparation of its benzoate m. 69°–70°, and of its phenylurethane m. 95°.

A Sesquiterpene(?). Two fractions b. 255°–259° and b. 265°–270° were found to contain a sesquiterpene which was not cadinene. The fractions investigated gave no nitrosite, nor a crystalline hydrochloride.

The work of Nelson and Lowman proved that more than half of the oil is *l*-linaloöl. Considerable methyl chavicol (about 30 per cent) and smaller amounts of cineole, eugenol, and sesquiterpenes are present. The oil may also contain a very small amount of dextrorotatory terpene.

II. Réunion Type of Basil Oil

Introduction.—The so-called Réunion basil oil has been known for quite some years. Originally it was produced on Réunion Island, but now it is distilled almost exclusively on the island of Mayotte in the Comoros group, and on some of the Seychelles Islands. Because of the presence of camphor

[13] *Am. Perfumer* **31,** December (1935), 69.

this oil, in regard to odor, is inferior to the European, especially French sweet basil oils which are derived from true *Ocimum basilicum* L. As has been pointed out, the botanical classification of the plant from which the Réunion oil originates is doubtful. On account of its lower price, the Réunion oil has lately replaced the much more expensive French oil in many formulas.

Planting, Cultivating, and Harvesting.—The plantings are started in December, at the beginning of the rainy season. The plants grow 50 to 60 cm. high and are cut immediately after the flowering period, when the first seeds appear. There are two harvests a year, viz., April to May and August to September. A planting lasts only one year.

The stills hold about 2,000 liters; distillation (with direct steam) of one charge requires several hours. One hectare yields about 30 kg. of oil.

Total oil production on the island of Mayotte fluctuates; on the average it amounts to several hundred kilograms annually.

Physicochemical Properties.—The Réunion type of basil oil differs from true sweet basil oil by a higher specific gravity, a higher refractive index, and dextro- instead of laevorotation.

According to Gildemeister and Hoffmann[14] the properties of Réunion basil oils are as follows:

Specific Gravity at 15°/15°	0.945 to 0.987
Optical Rotation	+0° 22′ to +12° 0′
Refractive Index at 20°	1.512 to 1.518
Acid Number	Up to 3
Ester Number	9 to 22
Solubility	Soluble in 3 to 7 vol. of 80% alcohol, occasionally with separation of paraffins

Genuine Réunion basil oils imported from the Comoro Islands, and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within these limits:

Specific Gravity at 15°/15°	0.965 to 0.974
Optical Rotation	+0° 16′ to +0° 30′
Refractive Index at 20°	1.5162 to 1.5182
Saponification Number	4.3 to 9.3
Solubility	Clear to turbid in 4.5 to 5.5 vol. and more of 80% alcohol

An oil distilled under the author's supervision on the island of Mayotte, in 1937, had the following properties:

Specific Gravity at 15°/15°	0.962
Optical Rotation	+0° 40′

[14] "Die Ätherischen Öle," 3d Ed., Vol. III, 913.

Refractive Index at 20°	1.5153
Saponification Number	5.6
Ester Number after Acetylation	28.9
Total Alcohol Content, Calculated as Linaloöl	8.1%
Solubility	Hazy in 6 vol. and more of 80% alcohol

The Experimental Station in Buitenzorg on Java has occasionally distilled basil oils (yield 0.2 per cent) from *Ocimum basilicum* L. var. *selasih hidjau* which resembled the Réunion type in regard to physicochemical properties. They contained a high percentage of methyl chavicol. Three oils of that origin, analyzed by Schimmel & Co.,[15] had the following properties:

	I	*II*	*III*
Specific Gravity at 15°/15°	0.9636	0.9603	0.9650
Optical Rotation	+0° 23′	+0° 38′	+0° 6′
Refractive Index at 20°	1.51691	1.51520	1.51673
Ester Number	5.6	11.2	14.9
Solubility in 80% Alcohol	Slightly turbid in 6.5 vol. and more	Slightly turbid in 7 vol. and more	Slightly turbid in 7 vol. and more

Van Romburgh[16] found that the oil distilled from the variety *Selasih hidjau* growing in Java contained cineole, methyl chavicol, and low boiling hydrocarbons, among them pinene and olefinic terpene.

The Java basil oils have not attained any commercial importance.

Two oils of *Ocimum basilicum* L. ("Toc Maria") distilled in the Seychelles Islands and analyzed in the Imperial Institute of London[17] had these properties:

	I	*II*
Specific Gravity at 15.5°	0.9616	0.9746
Optical Rotation	−0.64° at 24°	−0.4° at 19°
Refractive Index at 20°	1.5160	1.5180
Acid Number	0.2	
Ester Number	6.3	
Solubility in 80% Alcohol at 15.5°	Soluble in 6.7 vol.	Soluble in 4.6 vol. with slight opalescence

The high specific gravity and refractive index points toward the Réunion type, whereas the slight laevorotation classifies these oils as standing be-

[15] *Ber. Schimmel & Co.* (1936), 9.

[16] *Verslag Plantentuin Buitenzorg* (1898), 28; (1901), 58. *Verslag Akad. Wetenschappen Amsterdam* (1900), 446; (1904), 700; (1909), 15. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 915.

[17] *Bull. Imp. Inst.* **32** (1934), 530.

tween the Réunion type and that distilled in France from true *Ocimum basilicum* L.

Chemical Composition.—The chemistry of Réunion basil oil was investigated by Bertram and Walbaum [18] who established the presence of the following compounds:

d-α-Pinene. Identified as nitrolbenzylamine m. 123°.

Cineole. Identified as iodol compound m. 112°.

d-Camphor. Identified as oxime m. 118°. Réunion and Madagascar basil oil is characterized by the presence of camphor which does not occur in the European oil.

Linaloöl, on the other hand, is present in the latter oil, but not in the Réunion or Madagascar type.

Methyl Chavicol. Conversion to the isomeric anethole; oxidation to homoanisic acid. A quantitative methoxy determination showed the presence of 67.8 per cent of methyl chavicol in Réunion basil oil.

Use of Réunion Basil Oil.—Réunion basil oil is employed in all cases where the high price of the true sweet basil oil makes the use of the latter prohibitive.

III. Methyl Cinnamate Type of Basil Oil

From time to time there appear on the market so-called basil oils distilled in foreign countries—Bulgaria, Egypt, Haiti, etc.—supposedly from *Ocimum basilicum* L. Like true sweet basil oil they are laevorotatory and contain methyl chavicol and linaloöl. In addition, the oils of this type contain substantial amounts of methyl cinnamate, which feature points toward *Ocimum canum* Sims. Hence it is doubtful whether the original plants from which such oils are distilled have been identified correctly, from the botanical point of view.

Physicochemical Properties.—An oil procured by the author in Egypt during 1934 had the following properties:

Specific Gravity at 15°/15°	0.940
Optical Rotation	−7° 6′
Acid Number	2.8
Ester Number	40.1, representing an apparent linalyl acetate content of 14.0%, or 10.0% of methyl cinnamate
Ester Number after Acetylation	136.5, representing an apparent total linaloöl content of 40.6%
Solubility at 20°	Soluble in 1 vol. and more of 80% alcohol

[18] *Arch. Pharm.* **235** (1897), 176.

A similar oil distilled in Bulgaria and described by Schimmel & Co.[19] had these properties:

Specific Gravity at 15°/15°	0.9546
Optical Rotation	−6° 44′
Refractive Index	1.50466
Acid Number	0.8
Ester Number	126.9, representing 36.7% of methyl cinnamate
Congealing Point	−3.9°
Solubility	Soluble in 0.9 vol. and more of 80% alcohol

Bonaccorsi [20] reported about oils distilled from two subspecies of *Ocimum basilicum* L. grown experimentally in Calabria.

The oils obtained from the fresh herb, var. small leaves (yield 0.011 to 0.073 per cent), had the following properties:

Specific Gravity at 15°	0.9340 to 0.9473
Optical Rotation at 15°	−5° 6′ to −7° 0′
Refractive Index at 20°	1.5050 to 1.5060
Acid Number	0.93 to 1.95
Ester Number	45.15 to 60.10
Saponification Number	46.10 to 61.83, representing 13.07 to 17.62% methyl cinnamate
Free Alcohol Content, Calculated as Linaloöl	39.0 to 42.5%
Methyl Chavicol Content	29.8 to 35.9%
Solubility	Soluble in 1.4 to 2 vol. of 75% alcohol

The chemical composition of these oils was approximately as follows:

	Per Cent
Cineole	2.5
l-Linaloöl	40.0
Methyl Cinnamate	15.0
Eugenol	0.3
Methyl Chavicol	33.0
Small Quantities of Sesquiterpenes	

The properties of the oils obtained from the fresh herb, var. large leaves (yield 0.024 to 0.067 per cent), varied between these limits:

Specific Gravity at 15°	0.9309 to 0.9357
Optical Rotation at 15°	−7° 12′ to −8° 30′
Refractive Index at 20°	1.4980 to 1.5020
Acid Number	0.4 to 1.32

[19] *Ber. Schimmel & Co.* (1932), 6.
[20] *Rivista ital.* **18** (1936), No. 8, XXI.

Ester Number	46.0 to 79.05
Saponification Number	57.32 to 79.73, representing 16.2 to 22.9% of methyl cinnamate
Free Alcohol Content, Calculated as Linaloöl	46.17 to 52.7%
Methyl Chavicol Content	18.42 to 26.58%
Solubility	Soluble in 1.5 to 2.5 vol. of 75% alcohol

The chemical composition of these oils was approximately as follows:

	Per Cent
Cineole	2.5
l-Linaloöl	48.0
Methyl Cinnamate	21.0
Eugenol	2.0
Methyl Chavicol	21.0
Small Quantities of Sesquiterpenes	

Rakshit [21] distilled the leaves, stalks, and flowering tops of *Ocimum basilicum* L.(?) in Ghazipur (India) and obtained an oil (yield 0.4 per cent) with these properties:

Specific Gravity at 20°/20°	0.9666
Optical Rotation at 20°	−4° 54′
Refractive Index at 20°	1.5122
Acid Number	2.0
Ester Number	178.7
Ester Number after Acetylation	259.2

The oil consisted of about 45 per cent of *l*-linaloöl and about 52 per cent of methyl cinnamate.

Nigam and Dutt [22] distilled an oil of basil from the leaves of *Ocimum basilicum* (*album*) and obtained 0.5 per cent of an oil which after rectification *in vacuo* contained 20.85 per cent of terpinene, 4.36 per cent of *l*-linaloöl, and 56.67 per cent of methyl cinnamate.

Haiti Basil Oil

The shortage of French sweet basil oil during the years of World War II induced a grower on the island of Haiti in the West Indies to extend his plantings of what he believed to be true *Ocimum basilicum*, European (French) type, and to distill substantial quantities of oil, which he later offered on the American market.

[21] *Perfumery Essential Oil Record* **29** (1938), 89.
[22] *Indian Soap J.* **11** (1946), 210. *Chem. Abstracts* **42** (1948), 4717.

However, a thorough examination of a Haiti basil oil in the laboratories of Fritzsche Brothers, Inc., proved definitely that it contained a considerable percentage of cinnamates (isolated cinnamic acid m. 131°–132.5°). The odor of the evaporation residue clearly indicated that the esters consisted mainly of methyl cinnamate. The Haiti oil must, therefore, be considered as belonging to the methyl cinnamate group of basil oils and not to the group of sweet or European (French) basil oils.

The repeated analyses of Fritzsche Brothers confirmed the following physicochemical properties of a sample of Haiti basil oil:

Specific Gravity at 15°/15°	0.966
Optical Rotation	−2° 5′
Refractive Index at 20°	1.5113
Saponification Number	93.0
Ester Content, Calculated as Methyl Cinnamate	27.0%
Free Alcohol Content (Fiore Method), Calculated as Linaloöl	35.2%
Solubility	Soluble in 1 vol. of 80% alcohol, opalescent in 10 vol.

These figures differ considerably from those described by Dejoie.[23] The odor of this type of oil is pleasant, sweet, and, because of the content of cinnamates, very lasting. The oil, therefore, lends itself to perfume work but not to employment in flavors.

According to recent information,[24] the plantings of this type of basil oil have now been discontinued and efforts are being made to cultivate the French type of basil in Haiti.

IV. Eugenol Type of Basil Oil

Van Romburgh [25] distilled in the Experimental Station of Buitenzorg, Java, *Ocimum basilicum* L. var. *selasih mekah* and *selasih besar* and obtained oils (yield 0.18 to 0.32 per cent) which had these properties:

Specific Gravity at 26°	0.890 to 0.940
Optical Rotation	−11° 15′ to −18° 0′

The oil contained ocimene, but no myrcene; also 30 to 46 per cent of eugenol.

[23] *Drug Cosmetic Ind.*, November (1943), 580.
[24] Private communication by Mr. Louis Dejoie, Port-au-Prince, Haiti.
[25] *Verslag. Plantentuin Buitenzorg* (1898), 28; (1901), 58. *Verslag Akad. Wetenschappen Amsterdam* (1900), 446; (1904), 700; (1909), 15. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 915.

An oil probably of similar botanical origin was distilled in the Comoros and analyzed by Schimmel & Co.: [26]

Specific Gravity at 15°/15°	0.9607
Optical Rotation	−14° 54′
Acid Number	4.7
Ester Number	3.7
Ester Number after Acetylation	140.1
Eugenol Content	38.0%
Solubility	Soluble in 7 vol. and more of 90% alcohol, with slight turbidity

An oil distilled on Samoa [27] supposedly from *Ocimum basilicum* (?) had the following properties:

Specific Gravity at 15°/15°	1.0027
Optical Rotation	+1° 52′
Refractive Index at 20°	1.52324
Eugenol Content	61.0%
Solubility	Clearly soluble in 0.7 vol. of 80% alcohol; turbid in 1.2 vol. and more

Hosking [28] examined an oil which had also been distilled in Samoa, supposedly from the fresh leaves of *Ocimum basilicum* L.(?) (yield 0.2 per cent), and reported these properties:

Specific Gravity at 20°/20°	1.000
Optical Rotation	+1° 1′
Refractive Index at 19°	1.5240
Acid Number	10.2
Ester Number	0
Phenol Content	61.0%

The oils falling into this group have never reached any commercial importance.

It is possible that these oils were not distilled from true *Ocimum basilicum* L., but from varieties or other species, *O. minimum* L. or *O. gratissimum* L., for example.

Markov,[29] distilled *Ocimum basilicum* in the U.S.S.R. and found that sun drying and ordinary drying of basil did not affect either the yield of volatile oil or the content of phenols. The yield of crude eugenol was 78.0 per cent and that of the pure rectified product 50.0 per cent, as based on the

[26] *Ber. Schimmel & Co.*, April (1908), 123.
[27] *Ibid.* (1932), 6.
[28] *Perfumery Essential Oil Record* **24** (1933), 2.
[29] *Trudy Vsesoyuz. Inst. Efirno-Maslichnoi Prom.* (1940), No. 8, 97. *Chem. Abstracts* **37** (1943), 3557.

analytical content of eugenol in the volatile oil. The yield of camphor was 25.1 to 25.6 per cent. Treatment of the residual oil with sulfuric acid yielded 18.3 to 19.9 per cent of technical camphor.

Suggested Additional Literature

Anon., "Essential Oils from the Belgian Congo," *Bull. Imp. Inst.* **41** (1943), 167.

Wm. H. Finney and Carlos E. Warriner, "California Sweet Basil Oil," *Proc. Conf. on Cultivation Drug and Assocd. Econ. Plants Calif.* (1947), 214. *Chem. Abstracts* **43** (1948), 9085.

C. Griebel, "Basil (*Ocimum basilicum*)," *Z. Lebensm.-Untersuch. u.-Forsch.* **88** (1948), 28. *Chem. Abstracts* **42** (1948), 4308.

ESSENTIAL OILS OF OTHER *OCIMUM* SPECIES

The botany of *Ocimum* species and varieties being very complicated and in many cases utterly confused, it is practically impossible to classify the types of oil reported in literature according to the botanical nomenclature of the plants from which they are derived. It appears, further, that in several instances morphologically identical plant species yield oils of different physicochemical properties and chemical composition; in other words, they may be typical cases of purely physiological forms. Also, there exist many hybrids of the various *Ocimum* species, the volatile oils of which approach those of the parent plants. It is, therefore, logical to classify the different types of oil rather by their chemical composition than by their botanical origin.

Oil of Ocimum Canum Sims

Ocimum canum Sims is an Old World plant, native to the Paleotropics; it occurs wild in tropical West Africa (Guinea, Ivory Coast, Congo), East Africa (Tanganyika, Mozambique, the Comoro Islands, and Madagascar), in East India, and Ceylon; and naturalized in tropical South America. In several places *Ocimum canum* has also been cultivated, but mostly on a small scale. Two principal types of oil are distilled from the plant, one containing methyl cinnamate as principal constituent, the other *d*-camphor. The latter type was recommended as a source of natural camphor during World War II, when the Japanese, Chinese, and Formosan products

(from camphor oil), which dominated the world's market for many years, became temporarily unavailable. A third type of *Ocimum canum* oil contains citral as main constituent.

It is uncertain whether the existence of three or perhaps more types of oil must be attributed to local soil and climatic conditions or to different plant varieties, perhaps purely physiological forms.

A. Methyl Cinnamate Type

This type of oil has occasionally been produced on the Ivory Coast, in French Congo (Ubangi-Schari), in the Comoros (Anjouan), and on Madagascar.

Roure-Bertrand Fils [1] examined an oil distilled in Grasse from dried *Ocimum canum* Sims imported from Dabakala (Ivory Coast). The yield was 0.65 per cent; the properties as follows:

Specific Gravity at 32°	1.0330
Optical Rotation at 30°	−2° 30′
Acid Number	0
Saponification Number	301.4, representing 87.0% methyl cinnamate
Solubility	Soluble in 2.25 vol. and more of 75% alcohol; soluble in 80% alcohol

When standing at room temperature the oil deposited crystals in the form of long needles m. 35°–37°.

Schimmel & Co.[2] examined a similar oil from Central Africa:

Specific Gravity at 30°	1.0431
Optical Rotation	−2° 25′
Refractive Index at 30°	1.55611
Acid Number	0.6
Ester Number	289.8, representing 83.8% methyl cinnamate
Solubility	Not clearly soluble in 10 vol. of 70% alcohol; soluble in 1 vol. and more of 80% alcohol

The crystals separated from the oil proved to be methyl cinnamate m. 36°.

Two oils of *Ocimum canum* Sims distilled in Patsy, Anjouan (Comoro Islands), were described by Glichitch: [3]

[1] *Repts. Roure-Bertrand Fils,* October (1913), 19. *Ber. Schimmel & Co.,* April (1914), 73.
[2] *Ber. Schimmel & Co.,* April (1914), 72.
[3] *Parfums France* (1924), 314.

	I	*II*
Specific Gravity at 15°	0.9870	0.9942
Optical Rotation at 23°	−5° 4′	−3° 50′
Refractive Index at 20°	1.52492	1.52494
Acid Number	0.42	0.70
Ester Number	186.2, representing 54.19%[4] methyl cinnamate	194.6, representing 56.30% methyl cinnamate
Ester Number, after Cold Formylation	280.0	273.67
Free Alcohol Content, Calculated as $C_{10}H_{18}O$	29.99%	25.18%
Congealing Point	+6.2°	+6.3°
Solubility in 75% Alcohol	Soluble in 1 to 1.5 vol. at 18°	

Chiris [5] reported on two oils of *Ocimum canum* Sims from Bambari (French Congo):

	I	*II*
Specific Gravity at 20°	1.0412	0.9484
Optical Rotation	+1° 30′	+3° 36′
Refractive Index at 20°	1.54842	1.49490
Acid Number	0.68	0.22
Ester Number	269.5, representing 78.44%[6] methyl cinnamate	101.15, representing 29.26% methyl cinnamate
Congealing Point	+17.2°	...
Solubility	Soluble in 2.5 vol. of 70% alcohol; soluble in 0.6 vol. of 85% alcohol	

These two oils contained no linaloöl and were dextrorotatory, whereas the previously described oils showed laevorotation.

According to Glichitch and Naves [7] oils of *Ocimum canum* Sims produced on the Comoros and in Madagascar contained 54.0 to 85.0 per cent of methyl cinnamate, those from Ubangi-Schari (French Congo) 9.6 to 78.0 per cent.

In more recent years Joly [8] reported that the natives of French Ubangi use the dried, powdered leaves of *Ocimum canum* Sims for head colds. An oil distilled from the herb had the following properties:

Specific Gravity at 15°	1.045
Optical Rotation at 23°	+1° 30′
Refractive Index at 20°	1.5484

[4] Should read 53.9% (correction by the author).
[5] *Parfums France* **3** (1925), 139.
[6] Should read 78.0% (correction by the author).
[7] *Chimie & industrie* **29** (1933), Numéro Spécial, 1029.
[8] *Parfumerie moderne* **31** (1937), 203.

Acid Number	0.68
Saponification Number	269.5, representing 78.44% [9] methyl cinnamate
Congealing Point	+17.2°
Solubility	Soluble in 1 to 10 vol. of 85% alcohol

Joly also observed that some oils distilled from *Ocimum canum* Sims contained a high percentage of methyl cinnamate, others very little.

Chemical Composition.—Glichitch [10] established the presence of the following compounds in two oils of *Ocimum canum,* methyl cinnamate type, distilled in Anjouan (Comoro Islands):

1% Cineole. Identified as hydrobromide m. 56°.

25% *l*-Linaloöl. Phenylurethane m. 63°–64°.

2% Methyl Chavicol. Homoanisic acid m. 85°–86°.

0.5% Geraniol. Silver salt of the acid phthalic ester, m. 132°–133°.

1% Other Alcohols (Terpineol?). These alcohols consist possibly of terpineol.

55% *allo*-Cinnamic Acid Methyl Ester. Free acids m. 70°–75°, and 133°, respectively.

Methyl Cinnamate. According to Glichitch and Naves,[11] *Ocimum canum* oils distilled in Madagascar and on the Comoros contain from 54 to 85 per cent of methyl cinnamate, while those produced in Ubangi-Schari (French Congo) contain 9.6 to 78.0 per cent of this ester.

0.5% Esters of Fatty Acids, C_6 to C_8. Analysis of the silver salt.

10% of a Bicyclic *l*-Sesquiterpene(?).

4% of an Apparently Tricyclic *d*-Sesquiterpene(?).

The oils examined by Glichitch differ considerably from a camphor-containing type of oil which had also been produced in Anjouan (Comoro Islands).

Rakshit [12] described an oil distilled (yield 0.38 per cent) from the stalks, leaves, and flowers of *Ocimum canum* growing wild in the northern parts of India. The chemical composition of this oil was quite different from that described above; it contained the following constituents:

	Per Cent
Citral	About 50
Citronellal (15.7%)	About 10–16
Linaloöl	About 15
Methyl cinnamate	About 5

[9] Should read 78.0% (correction by the author).
[10] *Parfums France* (1924), 314.
[11] *Chimie & industrie* **29** (1933), Numéro Spécial, 1029.
[12] *Perfumery Essential Oil Record* **29** (1938), 402.

	Per Cent
Eugenol	Small quantities only
Acetic acid	
Citronellic acid	
Phenols(?)	
Terpenes(?)	

Use.—If produced at sufficiently low prices, oils with a high content of methyl cinnamate could be used for the isolation of this ester. The oil may be employed in perfumes, cosmetics, and especially for the scenting of soaps. So far, however, oil of *Ocimum canum* Sims, methyl cinnamate type, has not attained any commercial importance.

B. Camphor Type

Charabot [18] called the attention of the essential oil industry to the fact that the oil distilled from *Ocimum canum* Sims contains a high percentage of *d*-camphor, and suggested cultivating this plant as a new source of natural camphor. Similar oils from Mayotte (Comoro Islands) were reported by Schimmel & Co.[14] Later Charabot [15] isolated by simple freezing about 35 per cent of *d*-camphor from an oil produced in Kenya Colony, the residual oil still containing substantial quantities of camphor in solution.

According to an official French report [16] experimental plantings of *Ocimum canum* Sims were undertaken in the Comoro Islands. One hectare gave 12 to 13 metric tons of fresh herb which, upon distillation, yielded 61 kg. (0.47 per cent) of oil. Twenty kilograms of camphor could be isolated from these 61 kg. of oil.

Experiments with *Ocimum canum* Sims proved, according to Nesterenko,[17] that this plant can be grown successfully in the southern and central sections of the Ukraine, in Tschernosem (the very fertile part of Central Russia), and in the Northern Caucasus. One hectare produced 8 to 10 metric tons of herb, which yielded 50 kg. of oil containing 30 to 35 kg. of *d*-camphor. The plants can be harvested once in the northern regions, but twice in the south. Depending upon the age of the plants, the oil yield varies from 0.46 to 0.56 per cent, calculated upon the fresh herb. The

[18] *Bull. Jardin Colonial* (1903). *Repts. Roure-Bertrand Fils,* April (1903), 33. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 918.

[14] *Ber. Schimmel & Co.,* April (1908), 123.

[15] *"L'Ocimum canum,* source naturelle de camphre droit," *Acad. d'Agriculture de France* (Extrait du Procès Verbal de la Séance du 21. Décembre 1927). *Ber. Schimmel & Co.* (1929), 70.

[16] *L'Agronomie Coloniale* **18** (1929), 85. *Ber. Schimmel & Co.* (1930), 60.

[17] *"Ocimum canum* Sims," Report Government Botanical Garden, Nikitski Yalka (1934); through *Ber. Schimmel & Co.* (1935), 53.

camphor content of the oil increases in fall; an oil obtained during the August harvest contained 47 per cent of camphor, an oil distilled in October, 74 per cent. Nesterenko came to the conclusion that large quantities of camphor could be produced in the U.S.S.R. from *Ocimum canum* Sims.

Rotermel [18] reported that 1,000 kg. of fresh herb *Ocimum canum* var. *camphoratum* gave 7.67 kg. of an essential oil with these properties:

Specific Gravity	0.934
Specific Optical Rotation	+10° 3′
Refractive Index at 65°	1.4940
Acid Number	0.2
Ester Number	188.2

At freezing temperature 54.0 per cent of camphor separated from the oil.

Steam distilling the flowers and floral stalks of *Ocimum canum* Sims, collected during January and February in India, Sanjiva Rao, Mathen, Kelkar, and Jagjit Singh [19] obtained 0.22 to 0.30 per cent of oil from the dry herb, and 0.13 to 0.21 per cent from the fresh herb. The oils possessed a mild camphoraceous odor and had properties varying within the following limits:

Specific Gravity at 30°/30°	0.9205 to 0.9249
Specific Optical Rotation at 30°	+23° 48′ to +31° 42′
Refractive Index at 30°	1.4830 to 1.4865
Acid Number	0.6 to 1.5
Ester Number	4.5 to 5.5
Saponification Number after Acetylation	39.3 to 44.8
Solubility	Soluble in 0.5 vol. of 90% alcohol

Gaponenkov and Bering [20] distilled 200 kg. of air dried and pulverized *Ocimum canum* Sims and obtained by fractional distillation 1.20 kg. of crystalline, and 2.50 kg. of liquid, fractions. The latter were cooled to yield an additional crystalline fraction. The total yield of oil was 1.85 per cent, calculated upon the air-dried herb. The oil contained about 66.00 per cent of crystalline constituents, which in turn consisted of 99.16 per cent of camphor and 0.84 per cent of borneol. Borneol was separated from camphor as tribornyl borate.

Beckley [21] distilled *Ocimum canum* Sims growing in East Africa and obtained 0.6 per cent of an oil which, upon cooling, separated 16.0 to 25.0 per cent of camphor.

[18] *Sovietskaya Pharmacia* **5** (1934), No. 5. *Ber. Schimmel & Co.* (1935), 53.
[19] *Perfumery Essential Oil Record* **28** (1937), 412.
[20] *Farmats. i Farmakol.* (1937), No. 4, 17. *Chem. Abstracts* **33** (1939), 5594. *Chem. Zentr.* I (1938), 935.
[21] *East African Agr. J.* **1** (1936), 469.

Radilevski [22] reported that *Ocimum canum* Sims cultivated in the U.S.S.R. yielded as much as 100 kg. of camphor per hectare. The essential oil of the plant contains from 50.0 to 60.0 per cent of camphor.

African *Ocimum Canum* Oil (Kenya Colony).—According to Thomssen,[23] *Ocimum canum* Sims, formerly called *Ocimum americanum* L., is a hardy perennial which so far has not suffered from any known disease. Herbivorous animals refuse to eat it. The stalk is killed by frost, but moderate cold does not destroy the entire plant. The seed is very small, about 1 mm. long, black, and plum-shaped. A row of plants 1 ft. long usually produces enough seed for planting a row 20 ft. long.

Thomssen reported that *Ocimum canum* Sims, called "Kisi" in Kenya, produces seed every three months, under ideal East African climatic conditions, from small mauve flowers resembling those of sweet basil.

The planting is done by drilling seed rapidly in the same type of mechanical seeder used for grain. In proper climates, the plant can be permanently seeded in rows about 3 ft. apart so as to permit cultivation from time to time. When the seed germinates ample watering is necessary. It takes about six months for the shrub to grow from the time of the first planting until the blossoming stage. After the harvest, the regrowth is more rapid, and under proper climatic conditions occurs every three months.

In order to obtain a maximum of oil, the plant should not be cut before complete maturity.

Under normal conditions the first harvest, six months or less after planting of the seeds, produces 7 tons of cuttings per acre. After the first cutting, the root system develops more fully and the foliage becomes denser with each harvest. The second cutting increases 40 per cent, and the third cutting 100 per cent, over the first harvest. Thus, it has been estimated that from 40 to 50 tons of branches and leaves may be produced per acre under proper conditions.

Volcanic soils seem to favor the development of camphor in the plant. The refuse matters from the stills can be employed for fertilizing.

The total yield of oil, as calculated upon the green overground parts, varies from 0.5 to 0.8 per cent during and after maturity of the seed.

Distillation is carried out in the usual way, 20 to 25 liters of condensed water being required to carry over 3 kg. of oil.

The oil is a semisolid mass containing about 65 per cent of camphor and 35 per cent of liquid. The camphor can be separated by cooling and centrifuging, whereby about 65 per cent of pure crystallized camphor may be isolated. The oil separated from the camphor resembles oil of eucalyptus.

[22] *Farm. zhur.* **11**, No. 1 (1938), 27. *Chem. Abstracts* **33** (1939), 316.
[23] *Drug & Cosmetic Ind.* November (1938), 546.

The crystalline white camphor isolated from *Ocimum canum* oil has the same physicochemical properties (m. 178°, optical rotation +40° 8′ in benzene) as the camphor obtained from Japanese camphor oil.

An anonymous writer [24] described an oil of *Ocimum americanum* L. (now called *O. canum* Sims) which was distilled from plants grown in Nyasaland (East Africa). This oil (d. 0.9219, α_D^{20} +45° 5′, n_{20}^{D} 1.4715, acid number 0.6, ester number 0, ester number after acetylation 15.5) had an odor indicating the presence of camphor, but separated no camphor on cooling to −5°. Therefore, the oil must have contained only small quantities of camphor.

American *Ocimum Canum* Oil.—In 1936 the J. R. Watkins Co. of Winona, Minnesota, started to experiment in the United States with the growing of *Ocimum canum* Sims. According to Thomssen [25] the plantings were transferred from Winona to Daytona Beach, Florida. Upon distillation 3,600 lb. of leaves and stalks yielded 18 lb. of oil and camphor mixture, 13¼ lb. obtained by direct distillation and 4¾ lb. by extracting the water. Camphor was separated from both the directly distilled oil and camphor mixture, and the product extracted from the water.

From the steam distilled mixture Thomssen obtained 6½ lb. of crude camphor and from the extracted product 2 lb. of crude camphor. This left 5¾ lb. of camphor-free oil from the steam distilled oil and 3¾ lb. of oil from the extracted product. The total yield of camphor from the total amount of oil, therefore, was 47.2 per cent, and the yield of oil in the greens produced was 0.5 per cent from the first cutting. Thomssen considers it unfortunate that perennials do not thrive very well in Florida and, as a result, the second growth of the shrub is not very satisfactory.

The work was later continued in Michigan to discover whether the seed could be produced also in a cooler climate.

According to Thomssen,[26] there could be produced about 400 lb. of camphor-oil mixture per acre by three cuttings, provided the yield of herb can be approximated to that produced in Africa (see above). This would yield approximately 200 lb. of camphor and 200 lb. of oil as a first year crop and more in the second year.

Chemical Composition.—As its name implies, oil of *Ocimum canum*, camphor type contains considerable amounts of camphor. Charabot [27] reported an oil distilled in Kenya Colony which, upon standing, separated 35

[24] *Bull. Imp. Inst.* **32** (1934), 195.
[25] *Drug & Cosmetic Ind.*, November (1938), 548.
[26] *Ibid.*
[27] *Bull. Jardin Colonial* (1903). Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 918. See also Charabot, "*L'Ocimum canum*, source naturelle de camphre droit," *Acad. d'Agriculture de France* (Extrait du Procès Verbal de la Séance du 21. Décembre 1927). *Ber. Schimmel & Co.* (1929), 70.

per cent of camphor, a further portion remaining liquid in the oil. Charabot suggested this type of *Ocimum canum* oil as a source of natural camphor.

According to trade news reports,[28] an oil distilled in Khartum (Sudan) from the dried leaves (yield about 5 per cent) of supposed *Ocimum kilimandscharicum* contained at least 77 per cent of camphor aside from terpenes (see also oil of *Ocimum kilimandscharicum*).

Feltman and Vasilev [29] examined the essential oil of camphor basil (*Ocimum canum*) and found that it contains camphor, camphene, dipentene, cadinene, an unsaturated alcohol $C_{10}H_{17}\cdot OH$, and an ester $C_{10}H_{17}\cdot COOCH_3$.

A few years earlier, Konavalov [30] had reported that the oil derived from camphor basil contains these constituents: dipentene, terpinolene, crithmene, limonene, *d*-α-pinene, sabinene, camphene, camphor, alcohols, aldehydes, caryophyllene, traces of phenols and acetic acid.

According to an anonymous writer,[31] the leaves of *Ocimum kilimandscharicum* growing in the Sudan, upon steam distillation, yielded 5.0 per cent of a volatile oil which contained about 77.0 per cent of total camphor. The camphor expressed from the oil was considered to be of normal quality, and the residual oil resembled light camphor or spike lavender oil.

Because of its high camphor content it seems doubtful whether this oil was actually distilled from *Ocimum kilimandscharicum* rather than from *Ocimum canum*, camphor type.

C. Citral Type

According to Tayal and Dutt,[32] the shrub *Ocimum canum* Sims contains on an average 0.7 per cent of essential oil which can be easily isolated by steam distillation. The oil obtained by these authors had an intense and characteristic odor of lemon with an appreciable note of lavender; it contained over 68 per cent of aldehydes, calculated as citral (sodium bisulfite method). From the aldehydic portion a small quantity of methyl heptenone and citronellal, together with a large proportion of citral was isolated; whereas from the nonaldehydic portion, linaloöl, geraniol, citronellol, and esters of these alcohols were isolated. The oil, which in India is called Maniri oil, appears to be a good source of citral.

[28] *Oil, Paint Drug Reporter* **134** (December 19, 1938), 5.
[29] *Farmatsiya* **4** (1941), No. 6–7, 31. *Chem. Abstracts* **38** (1944), 2453.
[30] *Farmatsiya* (1938), No. 5, 13. *Chem. Abstracts* **33** (1939), 8914.
[31] *Bull. Imp. Inst.* **39** (1941), 217. *Chem. Abstracts* **36** (1942), 615.
[32] *Proc. Natl. Acad. Sci. India* **8** (1938), 120. *Chem. Abstracts* **33** (1939), 5992. Cf. Dutt, *Indian Soap J.* **6** (1940), 248. *Chem. Abstracts* **34** (1940), 6015.

Oil of Ocimum Canum Hybrid

Knishevetskaya [33] investigated the volatile oil of the hybrids F_1 *Ocimum* sp. No. 49 × *Ocimum canum* for the purpose of studying the genetics of chemical characteristics and the direction of possible new chemical formation from remote hybridization of various plant types. Whole plants cut during the period of full blossoming were used for distillation.

The oil of the hybrids contained borneol (not present in any of the parent plants) but no linaloöl (which was present in one of the hybrids). The oil contained also

17.7% methyl chavicol (against 65.0 per cent in *Ocimum* sp. No. 49)
and
18.2% camphor (against 65.0 to 70.0 per cent in *Ocimum canum*)

The results of the experiments indicate that considerable changes might take place in the synthetic activity of the plants under the influence of remote hybridization.

Oil of Ocimum Canum × Ocimum Gratissimum

According to Snegirev,[34] the oils distilled from the hybrids of *Ocimum canum* L. and *Ocimum gratissimum* (?) contain the constituents present in the oils of the two parent plants. Thus, the camphor content of one hybrid ranged from 5.0 to 27.0 per cent, the eugenol content from 5.0 to 29.0 per cent. A higher content of camphor was usually associated with a correspondingly higher content of eugenol. The oils of another hybrid contained more than twice as much eugenol as the oil from *Ocimum gratissimum*, but the camphor content was never higher than that of the oil from *Ocimum canum*. Snegirev came to the conclusion that hybridization experiments with aromatic plants would be of great benefit in the industrial production of volatile oils.

Oil of Ocimum Gratissimum L.

The oils distilled from *Ocimum gratissimum* L. are characterized by their high phenol content, the phenols consisting mainly of thymol or eugenol.

[33] *Trudy Gosudarst. Nikitskogo Botan. Sada* **21**, No. 2 (1939), **29**. *Khim. Referat. Zhur.* (1940), No. 6, 128. *Chem. Abstracts* **36** (1942), 5207.

[34] *Lenin. Acad. Agr. Sci. Inst.* III (1936), 245; through *Ber. Schimmel & Co.* (1938), 172. Cf. *Chem. Abstracts* **31** (1937), 5513.

Ocimum gratissimum L. occurs in tropical West Africa, in the Seychelles and Comoro Islands, and also in Madagascar. A number of samples have been described in literature, but the oil has not attained any commercial importance.

A. Thymol Type.—An oil distilled on the Ivory Coast and examined by Roure-Bertrand Fils [35] had the following properties:

Specific Gravity at 15°	0.9105
Optical Rotation	+0° 58′
Phenol Content (Mainly Thymol)	44.0%
Solubility	Soluble in 1.2 vol. of 80% alcohol

Rolland [36] reported that *Ocimum gratissimum* L. was cultivated in Dabakala (Ivory Coast), the fresh herb yielding on an average 0.6 per cent of oil containing 56.0 per cent of total phenols and 39.0 per cent of thymol.

Schimmel & Co.[37] examined a similar oil from Central Africa which had these properties:

Specific Gravity at 15°/15°	0.9055
Optical Rotation	+0° 50′
Refractive Index at 20°	1.49373
Acid Number	0.4
Ester Number	3.5
Phenol Content (Mainly Thymol)	35.0%
Solubility	Not clearly soluble in 10 vol. of 70% alcohol; soluble in 9 vol. and more of 80% alcohol with slight opalescence; soluble in 0.5 vol. and more of 90% alcohol

Glichitch and Naves [38] described oils of *Ocimum gratissimum* L. distilled on the Ivory Coast, in the French Congo, on the Comoros, and in Grasse, which contained from 23.0 to 44.0 per cent of phenols, mainly thymol with traces of carvacrol.

B. Eugenol Type.—An entirely different type of *Ocimum gratissimum* oil is that which contains as main constituent not thymol but eugenol. It remains doubtful whether the plant from which this type of oil is distilled is actually *Ocimum gratissimum* L.; perhaps it is an allied species or variety. The possibility cannot be excluded that we have here a typical case of physiological forms. Such an oil distilled in Mahé (Seychelles Islands) was described by the Imperial Institute [39] after the plant was

[35] *Repts. Roure-Bertrand Fils,* October (1913), 21.
[36] *Perfumery Essential Oil Record* **14** (1923), 154.
[37] *Ber. Schimmel & Co.,* April (1914), 73.
[38] *Chimie & industrie* **29** (1933), Numéro Spécial, 1029.
[39] *Bull. Imp. Inst.* **16** (1918), 32; **22** (1924), 265.

identified in Kew as *Ocimum gratissimum* L. The yield of oil was 0.1 per cent. It had the following properties:

Specific Gravity at 15°	0.995
Optical Rotation	−14° 6′
Refractive Index at 21°	1.526
Phenol Content	62%
Solubility at 15°	Soluble in 0.7 vol. of 80% alcohol

A similar oil was examined by Roberts;[40] it contained:

	Per Cent
Terpenes, Mainly Ocimene	16.0
Phenols, Mainly Eugenol	55.0
Phenolethers, Calculated as Methyl Chavicol	5.6
Alcohols, Probably Linaloöl	13.0
Esters	0.6
Residue and Losses	9.8

This type resembles oil of *Ocimum basilicum* L. var. *selasih mekah* distilled by Van Romburgh[41] in Java.

Chiris[42] described oils of *Ocimum gratissimum* L. distilled in Madagascar and the Comoro Islands which contained:

	Per Cent
Ocimene	12.0
Polyterpene Compounds and Cadinene	3.0
Eugenol	89.0
Phenols with an Odor of Creosol and Guaiacol	Traces
	104.0[43]

Later Glichitch and Naves[44] investigated other oils of *Ocimum gratissimum* L. distilled on Madagascar and the Comoros, and reported these properties:

Specific Gravity at 15°	0.9980 to 1.0000
Optical Rotation	−16° 32′ to −26° 16′
Refractive Index at 20°	1.5223 to 1.5289

[40] *J. Soc. Chem. Ind.* **40** (1921), 164 T.

[41] *Verslag Plantentuin Buitenzorg* (1898), 28; (1901), 58. *Verslag Akad. Wetenschappen Amsterdam* (1900), 446; (1904), 700; (1909), 15. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 915.

[42] *Parfums France* **7** (1929), 186.

[43] The percentages indicated total above 100 (the Author).

[44] *Chimie & industrie* **29** (1933), Numéro Spécial, 1029.

Saponification Number	4.2 to 11.2
Solubility	Soluble in 1 vol. and more of 75% alcohol

The oils contained:

	Per Cent
d-α-Pinene	...
Ocimene	12.0
Amyl Alcohol	Traces
l-Linaloöl and α-Terpineol	3.5–3.8
Eugenol	62.5
Other Phenols	Traces
Methyl Chavicol	Small quantities
Sesquiterpenes, Mainly Strongly Laevorotatory Cadinene	15.0
Polyterpenes	3.0

Glichitch and Naves claimed that the oils were distilled from pure *Ocimum gratissimum* L. and concluded that morphologically identical plants in some cases yield oils of entirely different composition.

According to Knishevetskaya,[45] a variety of *Ocimum gratissimum* yielding 0.3 per cent of volatile oil was cultivated in the Nikitin Botanical Garden. Three distillations were made during various periods of growth in order to study the dynamics of the accumulation of oil and the content of eugenol. It was found that the time of mass blossoming coincides with the optimum for harvesting and treating the plant material. The volatile oil is contained principally in the leaves and blossoms. After one to two days, the harvested plant loses much of its eugenol, after eleven days the content of eugenol decreases to 10 per cent.

The essential oil had a specific gravity of 1.0118 and a refractive index at 18° of 1.5220.

It contained 7–8% myrcene; 20–30% monocyclic terpenes; and 70%– eugenol.

C. Citral Type.—According to an anonymous author,[46] *Ocimum gratissimum* Roxb., fam. *Labiatae,* is a native of Persia, Sind, Punjab, East Bengal, Nepal, and Deccan Peninsula, which on steam distillation yields 0.1 per cent of a greenish-yellowish oil. An oil of this type possessed these properties:

Specific Gravity at 26°	0.8890
Optical Rotation	±0°
Refractive Index at 26°	1.4965

[45] *Doklady Vsesoyuz. Akad. Sel'skokhoz. Nauk im. Lenina* (1940), No. 6, 15. *Khim. Referat. Zhur.* (1940), No. 9, 107. *Chem. Abstracts* **37** (1943), 722.

[46] *Soap, Perfumery, Cosmetics* **19** (1946), 285. *Chem. Abstracts* **40** (1946), 7520. Cf. Nigam and Dutt, *Indian Soap J.* **10** (1944), 19. *Chem. Abstracts* **42** (1948), 3911.

Acid Number	12.2
Saponification Number	37.5
Saponification Number after Acetylation	175.3

On closer examination the oil was found to consist of:

	Per Cent
Citral	66.6
Geraniol	25.7
Citronellal	2.8
Geranyl Acetate	1.5
Sesquiterpenes	2.4
Unidentified Residues	6.6

In the case of this type of oil, also, there is some doubt as to the botany of the parent plant.

Oil of Ocimum Viride Willd.

Ocimum viride Willd., the so-called mosquito plant, is said to possess mosquito repellent properties.

It occurs in tropical West and East Africa, on the Seychelles Islands, in Madagascar, and in New Caledonia. Steam distillation yields from 0.35 to 2.59 per cent of a volatile oil.

A number of samples have been described in literature, but the oil has not attained any commercial importance.

Physicochemical Properties.—Gildemeister and Hoffmann [47] suggested these rather wide limits:

Specific Gravity at 15°	0.910 to 0.933
Optical Rotation	±0° 0′ to +1° 30′
Refractive Index at 20°	1.494 to 1.504
Phenol Content (Thymol)	18.0 to 65.0%

According to a report of the Imperial Institute,[48] experimental plantings of *Ocimum viride* proved successful on the Seychelles Islands. It was estimated that the herb could be harvested five to six times a year. The yield of oil, calculated upon the fresh herb, ranged around 0.5 per cent. The oils obtained by steam distillation had the following properties:

	Four Month Old Plants	*Eight Month Old Plants*
Specific Gravity at 15°/15°	0.942	0.924
Optical Rotation	+1° 5′	+0° 36′
Phenol Content	62.0%	52.0%

[47] "Die Ätherischen Öle," 3d Ed., Vol. III, 921.
[48] *Bull. Imp. Inst.* **15** (1917), 322.

Glichitch [49] described an oil distilled from *Ocimum viride* Willd. planted in Grasse (A.M., France) from Madagascar seed. The yield was 2.6 per cent. It possessed a characteristic odor of thymol and had these properties:

Specific Gravity at 15°	0.9104
Specific Optical Rotation	+0° 53′
Refractive Index at 22°	1.4962
Ester Content, Calculated as Linalyl Acetate	1.96%
Combined Alcohol Content	1.54%
Free Alcohol Content	30.99%
Phenol Content	38.00%
Solubility at 15°	Soluble in 1.5 vol. of 80% alcohol

The same author also reported about an oil of *Ocimum viride* Willd. from New Caledonia which analyzed as follows:

Specific Gravity at 24.5°	0.9235
Optical Rotation at 22°	+1° 30′
Refractive Index at 22°	1.4945
Ester Content, Calculated as Linalyl Acetate	0.73%
Combined Alcohol Content	0.58%
Free Alcohol Content	25.76%
Thymol Content	18.00%

Chemical Composition.—Thymol, the main constituent of *Ocimum viride* oil, was identified by Goulding and Pelly.[50] Later Glichitch [51] reported the occurrence of other compounds in an oil distilled in New Caledonia.

The presence of the following constituents has been established:

d-Limonene.

α- and γ-Terpinene. Identified as nitrosite m. 153°–155°.

Dipentene(?). Presence possible.

Terpineol(?). Presence probable.

Thymol. M. 50°–51°; phenylurethane m. 107°–107.3°.

The oil contains from 18 to 65 per cent of phenols, mainly thymol. According to Glichitch, carvacrol is not present.

Oil of Ocimum Kilimandscharicum

The oil distilled from *Ocimum kilimandscharicum* is somewhat similar to the eugenol type oil of *Ocimum gratissimum*, and during the last few years

[49] *Bull. soc. chim.* [4], **33** (1923), 1536.
[50] *Proc. Chem. Soc.* **24** (1908), 63. *Bull. Imp. Inst.* **6** (1908), 209.
[51] *Bull. soc. chim.* [4], **33** (1923), 1536.

has been produced in British East Africa, and especially in the Belgian Congo. The phenol content of this oil varies around 30 per cent.

Two samples of oil of *Ocimum kilimandscharicum* distilled in the Belgian Congo and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	I	*II*
Specific Gravity at 15°/15°....	0.964	0.965
Optical Rotation.....	−1° 48′	−1° 54′
Refractive Index at 20°.....	1.4959	1.4963
Acid Number.....	3.7	3.7
Saponification Number.....	3.7	6.5
Phenol Content (Eugenol).....	30.0%	31.0%
Solubility at 20°.....	Soluble in 3 vol. of 70% alcohol, opalescent in 10 vol.	Soluble in 0.5 vol. and more of 80% alcohol

Recently Youngken and Hassan [52] studied the morphology of *Ocimum kilimandscharicum*, and described the histology of the stem, leaf, floral parts and bracts. Distilling the plant, they obtained an oil with the following properties:

Specific Gravity at 25°..... 0.9225
Refractive Index at 20°..... 1.4752

The average oil content (free of camphor) of the dried leaves and flowering tops was 2.50%; the camphor content averaged 2.54%. The camphor melted at 174°–176°. It was identified by preparation of the oxime m. 116°, and of the semicarbazone m. 234°.

Oil of Ocimum Suave

The so-called tree basil is a shrub with many branches growing to a height of about 8 ft. and native to India and Africa.

The essential oil contains moderate quantities of eugenol. Two samples distilled in the Belgian Congo and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	I	*II*
Specific Gravity at 15°/15°....	0.953	0.954
Optical Rotation.....	−20° 0′	−19° 35′
Refractive Index at 20°.....	1.5210	1.5210
Acid Number.....	3.7	2.8
Saponification Number.....	7.5	2.8
Phenol Content (Eugenol).....	13.5%	14.0%

[52] *J. Am. Pharm. Assocn.* **37** (1948), **360.**

	I	II
Solubility at 20°	Soluble in 0.5 to 1 vol. and more of 90% alcohol	Soluble in 0.5 vol. and more of 90% alcohol

The eugenol content of these oils is similar to that of *Ocimum nakurense* Gürke, as reported by Beckley.[53]

According to an anonymous writer,[54] an oil of *Ocimum suave* produced in Tanganyika had these properties:

Specific Gravity at 15.5°/15.5°	0.9696
Optical Rotation at 21°	−22° 15′
Refractive Index at 20°	1.5188
Phenol Content (Eugenol)	53.0%

This oil was very similar to oil of *Ocimum gratissimum,* eugenol type, from the Seychelles Islands.

Oil of Ocimum Minimum

Years ago Schimmel & Co.[55] received from Southern France two samples of essential oils supposedly distilled from *Ocimum minimum* L., which in France is called "Petit Basilic." The physicochemical properties of these two oils coincided with those of the regular French or German oils of *Ocimum basilicum* L. (called in France "Grand Basilic"). However, the two samples were distinguished by a peculiar spicy odor and had a chemical composition quite different from the regular commercial *Ocimum basilicum* oils. They contained about 14 per cent of eugenol, which was identified by the preparation of the benzoyl compound m. 69°. Furthermore, the oils apparently contained linaloöl. Due to the small quantities of the two samples, it was not possible to determine whether they also contained methyl chavicol.

The two samples had the following properties:

	I	*II*
Specific Gravity at 15°	0.9102	0.8901
Optical Rotation	−11° 58′	−13° 36′
Acid Number	5.3	...
Ester Number	12.5	...
Phenol Content	14%	...
Solubility	Soluble in 2 vol. of 70% alcohol, opalescent in 10 vol.	Soluble in 2.5 vol. of 70% alcohol, turbid in 4.5 vol. and more

[53] *East African Agr. J.* **1** (1936), 469.
[54] *Bull. Imp. Inst.* **39** (1941), 217. *Chem. Abstracts* **36** (1942), 615.
[55] *Ber. Schimmel & Co.,* April (1909), 19.

Oil of Ocimum Sanctum

The leaves of *Ocimum sanctum* L., which in the Philippine Islands is cultivated as a garden plant, yield on steam distillation 0.6 per cent of an oil with a sweet anise-like odor. Bacon [56] obtained an oil (d_{30}^{30} 0.952, $\alpha_D^{30} \pm 0°$, n_D^{30} 1.5070, sap. number 2.8) which contained substantial quantities of methyl chavicol in the fraction b_9 85°–95°.

Shortly afterward, Brooks [57] identified cineole and linaloöl in the oil.

Of entirely different character and composition is the oil of *Ocimum sanctum* L. described by Dutt.[58] According to Dutt, the sacred Tulsi plant is not only of religious significance but its leaves have medicinal properties, acting as an expectorant and antiseptic, in addition to having use as an insect repellent. On steam distillation the leaves yield 0.7 per cent of an essential oil which has a strong odor of cloves. Dutt [59] identified in the oil 3 per cent of carvacrol, 71 per cent of eugenol, and 20 per cent of eugenol methyl ether.

Oil of Ocimum Menthaefolium

Rovesti [60] investigated an oil distilled from the flowering herb of *Ocimum menthaefolium* Hochst., a labiate occurring in Eritrea and locally called "ciòmar" and "sessèk sebi." The yield of oil was 0.327 per cent; the odor recalled that of basil. The oil had these properties:

d_{15}^{25}	0.9496
α_D^{22}	+1° 24′
n_D^{24}	1.5165
Acid Number	0.31
Ester Number	7.2
Ester Number after Acetylation	29.3
Solubility	Soluble in 3.1 vol. of 80% alcohol, at 25°

The oil consisted mainly of methyl chavicol and anethole. It also contained alcohols—free and esterified—hydrocarbons, and sesquiterpenes.

Oil of Ocimum Micranthum

Peckolt [61] obtained from the fragrant leaves of *Ocimum micranthum* Willd., which in Brazil is called large marjoram, 0.14 per cent of an essential oil, d_{23} 0.982.

[56] *Philippine J. Sci.* **5** (1910), A261.
[57] *Ibid.* **6** (1911), A345.
[58] *Proc. Indian Acad. Sci.* **9A** (1939), 72. *Chem. Abstracts* **33** (1939), 3963.
[59] *Ibid.*
[60] *Ann. chim. applicata* **17** (1927), 564.
[61] *Ber. deut. pharm. Ges.* **14** (1904), 374.

The same author [62] also distilled the leaves of the closely related *Ocimum carnosum* Lk. et Otto, and obtained 0.25 per cent of essential oil.

Oil of Ocimum Pilosum

Bhaduri [63] distilled from the *fresh* seeds and leaves of *Ocimum pilosum* Roxb. an oil ($d_{25.5}$ 0.8872, α_D − 3° 42′, $n_D^{24.5}$ 1.4843) which contained 41 per cent of citral, 34 per cent of citronellal, some cineole, limonene, and thymol.

Oils originating from Java and analyzed by Schimmel & Co.[64] had similar properties (d_{15} 0.8942, α_D − 7° 6′, n_D^{20} 1.48335, aldehyde content 65 per cent).

Suggested Additional Literature

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J. B. H. Lejeune, "Effect of the Preparation of the Product Prior to Distillation and of the Age of the Plants on the Yields of Essential Oils," *Agron. Coloniale* **22** (1933), 161. *Parfums France* **12** (1934), 46. *Chem. Abstracts* **28** (1934), 3180.

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V. S. Konavalov, "Extraction and Purification of Camphor from the Essential Oil of *Ocimum canum*," *Farmatsiya i Farmakol.* (1938), No. 6, 8. *Chem. Zentr.* I (1939), 1268. *Chem. Abstracts* **34** (1940), 6764.

J. Nath Rakshit, "Development of Essential Oil Industry," *Science and Culture* **5** (1939), 108.

H. W. Youngken and W. E. Hassan, Jr., "Studies on the Camphor Basil, *Ocimum kilimandscharicum* Gürke," *J. Am. Pharm. Assocn.* **37** (1948), 360.

M. I. Kalinkevich, "Effect of Potassium on Accumulation of Essential Oils in the Leaves of *Ocimum canum*," *Doklady Akad. Nauk U.S.S.R.* **60** (1948), 1363. *Chem. Abstracts* **42** (1948), 7375.

[62] *Ibid.*

[63] *J. Am. Chem. Soc.* **36** (1914), 1772.

[64] *Ber. Schimmel & Co.* (1936), 9.

OIL OF CATNIP

Essence de Cataire *Aceite Esencial de Calamento* *Katzenminzöl*
Oleum Catariae

A. Oil of Nepeta Cataria L.

The common catnip plant, *Nepeta Cataria* L., indigenous to Asia Minor and to Southeast Europe, but now naturalized and widely distributed throughout the United States, contains about 0.3 per cent of a volatile oil. This oil carries the characteristic odor of the plant, and generally is obtained from the whole fresh plant by distillation with steam.

Physicochemical Properties.—Genuine American catnip oils examined in the laboratories of Fritzsche Brothers, Inc.—some of them of their own distillation—had physicochemical properties which varied within the following limits:

Specific Gravity at 15°/15°	0.986 to 1.083
Refractive Index at 20°	1.4872 to 1.4913
Optical Rotation	+1° 20′ to +13° 20′. In some cases too dark for exact determination
Acid Number	292.1 to 311.7
Solubility	Usually soluble in 0.5 to 1 vol. and more of 80% alcohol, often with slight opalescence and even turbidity. In some cases separation of paraffins takes place

Chemical Composition.—A Sicilian oil, according to Liotta,[1] contained considerable quantities of carvacrol, in addition to an alcohol which he named "nepetol," and traces of pulegone and thymol. Liotta, however, did not give any evidence as to how he identified these compounds.

Hixon[2] reported a saponification number of 319 in a catnip oil, and expressed the opinion that this high saponification number might be caused by the presence of lactones.

Kremers[3] first found about 85 per cent of the oil to be soluble in an aqueous sodium hydroxide solution; acidification of the resulting alkaline solution precipitated a practically odorless acid as a viscous oil, that slowly

[1] *Rivista ital. essenze profumi* **5** (1923), 140; **7** (1925), 129.
[2] *J. Am. Pharm. Assocn.* **11** (1922), 96.
[3] Unpublished work of the late Dr. Edward Kremers, Professor Emeritus of Pharmaceutical Chemistry at the University of Wisconsin.

crystallized on standing. The characteristic catnip odor remained in the relatively small neutral portion of the oil (about 15 per cent).

An investigation of the chemical nature of the acidic fraction of catnip oil was made by Meyer [4] who studied the crystalline acid m. 71°–72°, obtained from the acidic fraction. Determining the molecular weight, analyzing the acid and a number of its salts and solid esters, Meyer assigned to it the formula $C_{10}H_{16}O_3$.

The most complete investigation of the chemical composition of American catnip oil was undertaken by McElvain, Bright and Johnson,[5] and by McElvain, Walters and Bright,[6] who reported the presence of the following compounds:

Nepetalic Acid.[7] When extracting catnip oil with a dilute (10 per cent) aqueous sodium hydroxide solution, 85 to 90 per cent of the oil goes into solution. Acidification yields an acid m. 75°–76°, to which the name nepetalic acid was assigned.

An investigation of the alkali insoluble portion (10 per cent) of the volatile oil of catnip showed that it consists of:

β-Caryophyllene. (About 14 per cent) b_{10} 112°–113°, d_4^{25} 0.9027, $[\alpha]_D^{25}$ −11° 25′ (in chloroform solution), n_D^{25} 1.4962.

Nepetalactone.[8] (About 42 per cent); conversion into nepetalic acid.

Nepetalic "Anhydride."[9] (About 36 per cent) isolated from the fraction $b_{0.1}$ 200°–210°, in the form of white crystals m. 139°–140° (petroleum ether as solvent). Confirmation by combustion analysis.

Two Substances(?). In addition to these compounds, two other substances comprising not more than 0.5 per cent of the oil were isolated but not identified.

The investigation of the above cited authors combined with experiments on animals proved that nepetalactone is the component of the oil, the odor of which makes the catnip plant so attractive to certain species of the cat family.

Use.—Oil of catnip is employed successfully as an efficient lure for the trapping of bobcats, lynx, cougars, pumas, mountain lions and all predatory felines. The oil has been successfully used in every section of North America where wild cats are hunted.

For the purpose of trapping animals, oil of catnip should be diluted in the proportion of 35 drops of pure oil to 2 oz. of petrolatum, which is used to give body to the oil, and to prevent loss of the scent by evaporation or

[4] *Pharm. Arch.* **7** (1936), 17.
[5] *J. Am. Chem. Soc.* **63** (1941), 1558.
[6] *Ibid.* **64** (1942), 1828.
[7] Regarding the chemistry of these substances, see the corresponding monographs in Vol. II of this work, p. 607.
[8] *Ibid.*, p. 690.
[9] *Ibid.*, p. 613.

exposure to rain. Further details may be found in Leaflet No. 78, "Hints on Bobcat Trapping," by Stanley P. Young, Bureau of Biological Survey, Washington, D. C., June, 1931.

B. Oil of Nepeta Cataria var. Citriodora

Investigating an oil distilled in the U.S.S.R., Rutovski and Vinogradova [10] identified the following constituents:

An Acid, Probably Tiglic Acid(?). M. 60°–62°.

Citral a- and b-. Identified as semicarbazone m. 168°–171° and 118°–120°, respectively; α-citrylidene β-naphthocinchoninic acid m. 197°.

Limonene and Dipentene. Identified as tetrabromide m. 120°–122°.

Geraniol. Diphenylurethane m. 80°–82°.

Citronellol. Citronellal semicarbazone m. 83°–84°.

Nerol. Tetrabromide m. 117°–118°.

A Sesquiterpene(?). Not further identified.

Acetic, Butyric, and Valeric Acid. Present as esters.

As far as known, this type of oil has not attained any commercial importance.

OIL OF HYSSOP

Essence d'Hysope *Aceite Esencial de Hisopo* *Ysopöl*
Oleum Hyssopi

Botany.—*Hyssopus officinalis* L. is a perennial shrub, native to Southern Europe and the temperate zones of Asia. It has been naturalized in the United States, where it grows in gardens and along roadsides.

The flowering tops and leaves contain a volatile oil of agreeable, aromatic, somewhat camphoraceous odor, and warm, slightly bitter taste; it can be isolated by steam distillation. The dried plant is known as a gentle stimulant aromatic used in medicines, tonics, bitters, and alcoholic liqueurs. Lately the volatile oil has increasingly replaced the tinctures made from the dried plants.

[10] *Riechstoff Ind.* **4** (1929), 43, 64.

Occurrence, Habitat and Range.—Hyssop grows wild in the countries bordering the Mediterranean; it is also cultivated in patch plantings, especially in Southern France, the principal producing regions being near Aix-en-Provence and Malmorte, also around the Mont Ventoux (Drôme), and in the Ardèche. Small hyssop fields are located in the vicinity of Grasse (A.M.). Like lavender, the plant grows in calcareous soil.

Planting and Cultivating.—Planting of hyssop resembles that of lavender. Slips are grown in nurseries during the fall, and in the following spring are transplanted to the field, 1 m. distant, in rows 1 m. apart. The first harvest takes place in July, two years after planting. One hectare with approximately 10,000 plants yields on the average 3,000 kg. of plant material. A field of hyssop has a life span of six to seven years.

Distillation.—Most hyssop originates from plantings, the wild growing kind being so scattered that collection becomes too costly. Wild plants are, therefore, used only if the cultivated material does not meet the demand.

Distillation of hyssop is carried out by farmer-producers in the type of stills usually employed for lavender. Some of these are of the old-fashioned direct fire stills, provided with a grid above which the plants are charged. Distillation of one charge lasts several hours.

Yield of Oil.—The oil yield varies greatly with the condition of the plant material, depending chiefly upon its dryness. It averages from 0.15 to 0.3 per cent for fresh to clover-dry, and from 0.3 to 0.8 per cent for clover-dry to completely dried material.

Chiris [1] found that the maximum yield of oil is obtained right after the blooming period, that the properties of the oil vary only little during the period of flowering and withering, and that the oil in all overground parts of the plant is of uniform quality.

Physicochemical Properties.—Genuine oils distilled under the author's supervision in Southern France had these properties:

Specific Gravity at 15°/15°..	0.952	0.956	0.946	0.940	0.947
Optical Rotation.....	−16° 40′	−16° 18′	−16° 24′	−18° 20′	−18° 10′
Saponification Number.....	11.2	12.1	6.5	4.7	12.1
Refractive Index at 20°.....	1.4811	1.4819	1.4800	1.4810	1.4829

The oils were soluble in one volume of 80 per cent alcohol, but opalescent to turbid with more alcohol.

The ketone (*l*-pinocamphone) content of these oils ranged around 54 per cent, which proves their high quality.

Oils produced in Southern France and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

[1] *Parfums France* **7** (1929), 201.

Specific Gravity at 15°/15°	0.935 to 0.952
Optical Rotation	−15° 45′ to −18° 20′
Refractive Index at 20°	1.4783 to 1.4829
Saponification Number	2.8 to 12.1
Solubility	Soluble in 1 vol. of 80% alcohol, clear to cloudy with more; in exceptional cases incompletely soluble in 80% alcohol

According to Chiris,[2] the specific gravity (at 15°) of hyssop oil frequently exceeds 0.945 and might be as high as 0.969. The ester number is usually low, from 1.4 to 13.0, exceptionally as high as 33.0. The refractive index varies from 1.476 to 1.482, and in a few cases may reach 1.490. The content of free alcohols, calculated as $C_{10}H_{18}O$ and determined by cold formylation, ranges from 10.4 to 15.1 per cent. Complete solubility of hyssop oil in 70 per cent alcohol is rare.

A hyssop oil produced near Yalta on the Crimean Peninsula (U.S.S.R.) (yield 0.23 per cent as calculated upon the fresh plant material) was investigated by Rutovski and Vinogradova [3] who found these properties:

Specific Gravity at 20°/4°	0.9573
Optical Rotation	−19° 17′
Refractive Index	1.4805
Acid Number	4.03
Ester Number	35.86
Ester Number after Acetylation	98.02
Solubility	Soluble in 1.4 vol. of 70% alcohol; soluble in 0.9 vol. of 80% alcohol

Distilling the flowering tops of hyssop cultivated in Reggio Calabria, La Face [4] obtained 0.2 per cent of a yellow oil with the following properties:

Specific Gravity at 15°	0.9237
Optical Rotation at 20°	−6° 54′
Refractive Index at 20°	1.4820
Acid Number	1.4
Ester Number	17.06
Ester Number after Acetylation	73.0

The bulk of the oil distilled between 165° and 222° at atmospheric pressure; it contained about 34 per cent of pinocamphone.

Sorgonà Luisi [5] reported about an oil of hyssop distilled during 1939 in Calabria which had these properties:

[2] *Ibid.* **13** (1935), 239.
[3] *Bull. Sci. Chem. Pharm. Inst. Moscow* (1924), No. 10, 34. *Ber. Schimmel & Co.* (1925), 96.
[4] *Rivista ital. essenze profumi* **6** (1924), 111.
[5] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi Reggio Calabria* **15** (1940), 38. *Chem. Abstracts* **37** (1943), 3561.

Specific Gravity at 20°	0.9200
Optical Rotation at 20°	−25° 0′
Refractive Index	1.4405
Acid Number	0.65
Ester Number	9.20
Ester Content, Calculated as Linalyl Acetate	3.23%
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	26.72%
Solubility	Soluble in 1.4 vol. of 85% alcohol

Chemical Composition.—The earliest investigations on the chemistry of hyssop oil, which date back a century or more, attained no results. The same is true of the later work of Genvresse and Verrier [6] who reported the presence of cineole. Since later investigations did not confirm this claim, some doubt may be entertained as to the purity of the oil examined by Genvresse and Verrier. In order to be sure about the authenticity of the starting material, Gildemeister and Köhler [7] investigated a (German) hyssop oil of their own distillation.

The presence of the following compounds has been established:

β-Pinene. Identified by Gildemeister and Köhler by oxidation to nopinic acid m. 126°–127°, in the lowest boiling fractions (about 14%).

α-Pinene. Identified as nitrosochloride m. 101.5°; oxidation to pinonic acid, semicarbazone m. 200°–202°.

Camphene. Conversion to borneol and isoborneol m. 192°. *α*-Pinene and camphene were identified by Rutovski and Vinogradova,[8] and by Gusseva.[9]

l-Pinocamphone. Gildemeister and Köhler [10] found that almost 50 per cent of hyssop oil consists of this compound which, until then, had been obtained only synthetically, and only in its optically inactive modification, by reduction of nitrosopinene, according to Wallach et al.[11]

Identified as semicarbazone m. 228°–229°.

l-Pinocamphone, as present in hyssop oil, possesses the following properties:

b_{752}	212°–213°
d_{15}	0.9662
α_D	−13° 42′
n_D^{20}	1.47421
Mol. Refr.	44.40

[6] *Bull. soc. chim.* [3] **27** (1902), 829. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 733.

[7] "Festschrift Otto Wallach," Göttingen (1909), 414.

[8] *Bull. Sci. Chem. Pharm. Inst. Moscow* (1924), No. 10, **34**, 733. *Ber. Schimmel & Co.* (1925), 96.

[9] *Bull. Sci. Chem. Pharm. Inst. Moscow* (1927), No. 17, **166**. *Ber. Schimmel & Co.* (1928), 106.

[10] "Festschrift Otto Wallach," Göttingen (1909), 414.

[11] *Liebigs Ann.* **300** (1898), 287; **346** (1906), 235; **360** (1908), 92.

Recently Delépine and Badoche [*Ann. chim.* [12], **3** (1948), 591] expressed the opinion that the principal pinocamphone in hyssop oil is *l*-iso- or *cis*-pinocamphone, the semicarbazone of which melts at 281°.

l-Pinocampheol. Gildemeister and Köhler also found that the oil contained small quantities of an alcohol b. 221°–222° which is probably identical with *l*-pinocampheol, as reported later by Rutovski and Vinogradova, and by Gusseva.[12]

An Aldehyde(?). The same authors also established the presence of an aldehyde which gave a semicarbazone m. 202°–203°.

Sesquiterpenes(?) and Sesquiterpene Alcohols(?). Ruzicka, Pontalti and Balas [13] found that German hyssop oil contains in the highest boiling fractions one or several bicyclic sesquiterpenes of the cadinene type, and bicyclic, mainly tertiary sesquiterpene alcohols b_{12} 150°–152°, also of the cadinene type. The quantity of the sesquiterpenes amounts to 2–3 per cent, and that of the sesquiterpene alcohols to about 2 per cent of the total oil.

Aside from the tertiary sesquiterpene alcohols, the same authors observed in hyssop oil small quantities of primary and secondary alcohols.

Adulteration.—Because of its relatively high price, hyssop oil is occasionally adulterated with spike, lavandin, lavender, or rosemary oils.

Most dangerous are additions of camphor oil fractions, because they are not easily detected in routine analysis. In fact, the presence of camphor may denote a high content of pinocamphone, the latter in pure oils being indicative of a good quality. Obviously, the addition of *d*-camphor would affect the laevorotation of pure hyssop oil.

Use.—Hyssop oil is employed mostly in flavor work, giving excellent results in bitters, tonics, and especially in liqueurs of the French type—in imitations of Chartreuse and Benedictine, for example.

OIL OF LAVENDER

Essence de Lavande *Aceite Esencial de Lavanda* *Lavendelöl*
Oleum Lavandulae

Introduction.—Oil of lavender, one of the most popular essential oils, has for many years been produced almost exclusively in Southern France. The French oil excels all other types in quality, possessing a characteristic

[12] *Bull. Sci. Chem. Pharm. Inst. Moscow* (1927), No. 17, 166. *Ber. Schimmel & Co.* (1928), 106.
[13] *Helv. Chim. Acta.* **6** (1923), 855, 858.

sweetness of odor; certain sections of Southern France produce lavender oils with a high ester content unequaled elsewhere.

Other producing regions, much less important, are to be found in Italy, Southern Russia, Hungary, England, Australia (Tasmania), and the United States (Puget Sound). In a few other countries experimental work is being done. Today France is still supplying most of the world's lavender oil demand.

Botany, Habitat and Range.—*Lavandula officinalis* Chaix, according to Green [1] the correct designation for this plant, is a small shrub, with linear leaves and terminal inflorescences of small, bilabiate, lavender colored, highly fragrant flowers, containing a volatile oil which is isolated mainly by steam distillation and occasionally by extraction with solvents.

The pretty plant, a native of Mediterranean regions, grows wild and spontaneously on the dry, barren, sunny mountain slopes of Southern France and adjacent Italy. Lavender prefers loose, silico-calcareous soil, and has invaded many farmlands of insufficient fertility abandoned years ago when the increasing industrialization of France drew its rural population to the cities. A relatively hardy plant, able to withstand the cold winter storms which rage over the high snow-covered mountains, it grows abundantly after heavy rainfalls in spring and ample sunshine in summer.

Lavender thrives most luxuriantly between rocks, along the roadsides, and on inaccessible precipices. During the blooming period, in late July and early August, distant mountain slopes in the setting sun often glow in bluish shades of indescribable delicacy.

There exist several subspecies or varieties of *Lavandula officinalis* Chaix (*Lavandula vera* D.C.), exhibiting extreme forms of variation according to position and soil, each having its natural habitat at a particular altitude, and in a particular soil, and each yielding an oil of characteristic quality. The question of whether a distinction between varieties can be made on strictly morphological grounds, or whether these varieties should be considered merely as local ones, depending upon soil, climate, and altitude, is still open to dispute.

I. L. officinalis Chaix var. *delphinensis* Jord.—The small form (*petite* or *fine lavande*) grows wild on poor calcareous soil, at the highest altitudes (up to about 1,300 m. or 4,300 ft.), and the more northern sections of the Départements Basses-Alpes, Drôme, Vaucluse, and Hautes-Alpes. It is relatively hardy and resistant to climatic inclemencies, such as extreme cold, fog, rain, and exposure to strong sunlight in summer. Var. *delphinensis* produces oil of highest quality.

[1] *Bull. Kew* (1932), 295. *Ber. Schimmel & Co.* (1933), 104.

II. L. officinalis Chaix var. *fragrans* Jord.—The slightly larger form (*moyenne lavande*) also grows wild, but at somewhat lower altitudes (from approximately 500 m. or 1,650 ft. upward), and the more southern sections of the same Départements. It prefers the dry slopes of hillsides; produces an oil of slightly lower quality.

Var. *fragrans* has also been extensively cultivated, as we shall describe later.

III. L. officinalis Chaix × *L. latifolia* Vill. (*Lavandula hybrida* Reverchon).—Lavandin (*grosse lavande*) is a hybrid between true lavender (*L. officinalis* Chaix) and spike lavender (*L. latifolia* Vill.) growing wild at medium altitudes [2] and yielding the lower priced oil of lavandin; it occupies a position between true lavender and spike. (The designation "oil of spike" or "oil of spike lavender" is derived from the French term *aspic* and has no connection whatsoever with the word "spike," a botanical term for a kind of inflorescence with an unbranched axis and stalkless flowers attached to it.

As a hybrid, lavandin is a very hardy plant, giving a better yield of oil than lavender. Because the plant is long-lived and yields a high percentage of oil, many lavandin plantations were started before and during World War II, with a resulting increase in the production and consumption of lavandin oil.

IV. L. latifolia Vill.—Spike or spike lavender (*grande lavande*) grows wild at low altitudes. It is not planted, since it occurs naturally and abundantly in Spain, the present main producing regions of spike oil. The latter is of still lower quality than lavandin; it possesses a somewhat harsh, camphoraceous odor, lacking the sweetness of true lavender.

From this classification it appears that the highest altitudes produce plants yielding the best oil, while plants from low elevations yield oils of lowest quality, with a whole range of intermediary grades between the two extremes. Incidentally, the quality of lavender oil is now evaluated mainly by its ester content (linalyl acetate): provided it is properly distilled, lavender var. *delphinensis*, which occurs in the highest altitudes, yields oils containing 50 to 55 per cent of esters, while *L. latifolia* from the low elevations gives oils containing only 2 to 3 per cent of esters.

This, however, applies only to wild growing plants. It has been proved that true lavender (*L. officinalis* Chaix) with an oil of high ester content can be planted successfully also at low altitudes, even at sea level, if due consideration is given to factors of climate, soil, cultivation, and the dangers of hybridization.

[2] According to Hegi "Illustrierte Flora von Mitteleuropa," Vol. V/4, lavandin as a wild flower occurs only in the Alpes-Maritimes.

The amount of lavender harvested every year in Southern France depends largely upon weather conditions. Frosts (especially in the springtime), and continued heat without rain in summer, are the principal causes of a poor crop; an absence of frost, abundant rain during May and June, with a few good showers in July, favor a plentiful harvest.

French Lavender Oil

Wild Growing Lavender.—On the sunny hillsides and mountain slopes of the Départements Basses-Alpes, Drôme, Vaucluse and Hautes-Alpes, the wild herb grows freely. The most beautiful plants seem to be located among heaps of stones or rocks. The wild plant has also invaded many of the farms abandoned before World War I; in fact, it has multiplied to such an extent that the overcrowded plants often remain small and sickly, the cutting then becoming burdensome. Many steep mountainous slopes, where the plants grow abundantly, are too dangerous of access to permit harvesting of the flowers.

Such, at least, was the picture until, in the early 1930's, there occurred a strange, still largely unexplained, decline in the growth of natural lavender. From certain sections, where once wild lavender had flourished abundantly, it began to disappear; other sections were less affected. In previous years, when the plants still abounded, a visitor on his way to the lavender regions could stop along the road between Castellane and Barrême to pick a bunch of the lovely, fragrant lavender growing so richly near the roadside. In 1936, one had to climb between the rocks and make a search to find even a few lonely plants.

To emphasize the results of the peculiar blight, we quote the following figures, given to the author by old-time distillers:

	Tons in 1930	*Tons in 1936*
Plant harvest around Ballons	55	2
Plant harvest around Lachoux	80	6
Plant harvest around Aygalaye	20	2

In certain parts of the community of Sahune (Drôme) there were harvested in 1928, 35 and 42 tons of plants; in 1936, 5.5 and 7.5 tons.

What caused the gradual disappearance of wild lavender? A number of theories were advanced by experts, none fully explanatory, some contradictory. Perhaps a combination of factors was responsible. Some claimed that the soil was slowly getting tired of lavender, that in the course of time it had become exhausted, so far as lavender was concerned.

Others attributed the gradual disappearance of wild lavender in certain sections to the increase of weeds like *genêt* (broom), which crowds out and suffocates the more delicate lavender. In former years, large flocks of sheep and goats used to graze on the mountain slopes and munch the weeds in preference to the fragrant lavender. However, during the years of world depression (1929–1933) the sheep raising in Southern France suffered a serious setback and some of the mountain sections became almost deserted. The observation that lavender is easily crowded out by weeds confirms the opinion that wild lavender, especially on the more accessible



Courtesy of Fritzsche Brothers, Inc., New York.

Cutting wild lavender in southern France.

slopes, should be plowed under from time to time, permitting the remaining lavender plants to acquire more room to grow freely.

Other lavender experts believed that the wild lavender in past years was often cut too early and, incidentally, too low, which practice damaged the plants. (If, on the other hand, harvested rather late in the season, the plants should not be cut too high.) So far as insect pests and diseases are concerned, some lavender producers claimed that they did considerable harm in certain sections.

Another explanation might be the following: More than fifty years ago consumption and production of lavender oil was small, and most of the wild plants remained untouched. They were used to growing without any cutting. During the following years, ever increasing quantities of wild flower material were harvested, and the plants gradually became accustomed to being cut during the full flowering period when, physiologically speaking, the plant has to exercise the greatest efforts. The cutting at that moment spared the plant much work and made it metabolically laggard. However, during the years 1929–1934 (when lavender oil prices were very

low), much of the wild lavender was not cut at all. Thus the wild plants were allowed to develop longer stalks and larger leaves. With this coincided two years of excessive drought, which caused the larger stalks and leaves of the plants to evaporate a great deal of moisture. In other words, the plants exhausted themselves.

Whatever the causes, the result was that wild growing lavender disappeared in certain sections. The plant material therefore had to be collected in more and more remote sections, where the wild plants were not yet afflicted. Cutting in those regions, however, is more costly and can be undertaken only if sufficiently high prices are paid for the oil to allow for greater harvesting expense. There is no reason to fear that wild lavender will disappear, but the fact remains that large quantities of lavender oil can be produced only if high oil (and flower) prices encourage the cutters and distillers. Whenever lavender oil prices suffer a serious decline, production of the oil falls to a low figure.

Thirty or forty years ago, lavender oil was distilled exclusively from the wild growing plants, planting and cultivating not having come into vogue then. Even today a good percentage of the total production of lavender oil is distilled from the wild plants. One man can collect daily about 60 kg. of wild plants. Because of the scattered growth, the yield of wild lavender per acre cannot be estimated.

Since the mountain slopes are, in general, the property of various communities, the villages, each spring, auction off the right of harvesting the wild flowers within their territory. These adjudications present an event of considerable interest to the oil producers. The buying of such rights assures the distiller a guarantee for the supply of a given quantity of plant material and enables him to lower the price of other lots of lavender flowers, originating from other sources. The regions where gatherers of lavender can cut freely on community territories or on private property are becoming fewer and fewer. The most important is that at the Mont Ventoux which covers more than 2,300 hectares.

It has recently become increasingly difficult to find labor to harvest the wild growing plants. Up to 1927, Italian labor was imported for the purpose, but then the Italian Fascist Government prohibited emigration of seasonal labor. This condition, however, has changed again with the conclusion of World War II and the establishment of a new labor policy by the Italian and French authorities.

Plowed Wild Lavender.—For all these reasons the collection of wild lavender has decreased in past years, and methods of cultivation have had to be introduced. The simplest way is to plow through a field of wild lavender, the plow being pulled by a tractor or horses. The ground is turned over once and back again. Many plants are destroyed, but those surviving gain

space and access to air, and develop more fully. Rain penetrates into the loosened soil, and a more abundant harvest results. This work can obviously be carried out only on slightly inclined slopes, and not on the steeper hills or mountains. Plowing results in a small harvest during the first year, a more abundant harvest in the second and third years, a notable decrease during the fourth year, and a still further decline in the fifth year. However, under favorable climatic conditions one may still harvest where it was not worthwhile to cut before plowing.

For plowing, a natural lavender field is divided into four or five sections, one section being plowed annually. Since only one-fourth of the field is plowed every year, the cost of labor remains low. It is difficult to approximate the average yield, which ranges from 400 to 600 kg. of plant material per hectare for the second harvest after plowing.

Planted Lavender.—As far back as 1910, experimental lavender plantations were started by a number of distillers. Aside from an independent and regular flower supply, plantations promised lower cost of cutting. Cultivated lavender grows much taller than the wild, and permits quicker cutting, one man being able to harvest daily several times the quantity of wild plants.

During, and especially right after, World War I, the planting of lavender was advocated in agricultural journals throughout the producing regions of Southern France, and much was expected from this new development. Unfortunately, the high hopes were not entirely fulfilled. After several years of rather disappointing experience, the disadvantages were judged to outweigh the advantages. One of the gravest handicaps is the rather high cost of initial investment which has to be written off and increases the overhead expenses of the enterprise. Even more disastrous was the unexpectedly short life of the plantations. Whereas some lavender plantings lasted up to eight, ten, and even more years, many perished after three to four years, causing heavy losses to the owners. Soon it became evident that a lavender plantation was a paying proposition only if it formed part of another agricultural enterprise. In other words, a small farmer growing cereals and olives could devote his and his family's spare time to the cultivating of lavender. But the plantations started by large-scale distillers for their own independent flower supply proved to be a rather expensive venture raising the cost of the distillation material (and hence the cost of the oil) far above the level of those oils produced by small grower-distillers.

It is interesting to note, in this connection, that through this development the lavender oil industry of Southern France experienced an almost complete cycle, proceeding from the early days of distilling wild growing plants in portable stills to large-scale plantations and regular factory distillation, then reverting to small-scale operation in field stills operated by farmer-

producers, who today employ as raw material either wild growing lavender or lavender from their patch plantings. A large enterprise specializing in the growing and distilling of lavender is burdened with heavy overhead expenses, such as labor—mechanics, foremen, managers, and office force—and taxes; this in addition to the fact that the factory operates only for a few weeks during the whole year. In other words, all overhead expenses must be borne by one product, viz., lavender oil. The small farmer, on the other hand, does not count his and his family's labor; he has no overhead expenses to speak of and does not and cannot calculate the cost of his oil; he simply sells it at the prevailing market price. It is, therefore, not surprising that a large distillery can hardly compete with a small producer.

Planting and Cultivation of Lavender.—Silico-calcareous, loose, easily drained soil is best suited for the growing of lavender. The ground, as in vineyards, is plowed, hoed, and leveled.

Lavender may be planted by any one of the following methods.

1. By Seed.—Since lavender seed possesses a very hard pericarp, it must be kept at room temperature, in humid sand or sawdust, for some time, in order to bring about germination. As soon as the young shoots emerge they are transplanted into nurseries and watered frequently. After several months, the plants can be transplanted into the open fields.

2. With Cuttings—"Bouturage."—This method does not always succeed very well; it demands considerable cultivation and frequent irrigation, which often lead to abandonment of the method. The cuttings should be raised for some time in nurseries before final transplantation to the fields.

3. With Young Wild Plants.—Some lavender growers give preference to young plants taken from elevated altitudes, where only the best lavender is found. These plants, less expensive than those from seedlings, are hardier because they originate from very poor ground and from a severe climate. However, these wild plants must be carefully selected and collected when very young. This is usually done during May; they are then raised in a nursery for a half year, frequently watered and, during the fall, transplanted to the open fields.

4. By slips or layered shoots taken from older plantations. (Cf. "American Lavender Oil," below.)

Methods of Planting.—At one time lavender was planted at a distance of 1.25 to 1.50 m. between the rows, and 0.60 to 0.75 m. between the plants; later it was found that 1.70 to 2 m. between the rows and 0.50 to 0.60 m. between the plants give better results. This means approximately 10,000 plants per hectare. It was believed that the plants, if set out close in the rows, have a better opportunity to combat weeds and drought. On the

other hand, a larger distance between the rows is preferable for cultivating.

During the first two years, one annual plowing in fall or winter should be undertaken, followed by one or two superficial tillings with a cultivator, and finally by at least one hoeing. After the second year the hoeing may be omitted.

Harvesting of Planted Lavender.—Although the yield is insignificant in the first, and small in the second, year, the young plants must be cut, care being taken not to injure them. The third year produces the first sizable crop; this increases during the fourth and fifth year.

Despite many attempts, French lavender growers never succeeded in constructing machines for the harvesting of planted lavender, primarily because the stalks bend from the base of the stocks toward the periphery and, in fully matured stocks, almost touch the ground with the flowering tops. Hence, lavender, wild or cultivated, is always cut by hand with sickles. In a well-developed plantation a skilled cutter can daily collect several hundred kilograms of plant material (flowering tops and stalks).

Yield of Plants per Hectare.—Theoretically, one lavender stock, when cut, should yield from 500 to 600 g. of stalks and flowers. Ten thousand plants on one hectare should, therefore, give from 5,000 to 6,000 kg. of plant material. In reality, however, from the third year on, a yield of 2,000 kg. per hectare is considered normal and a yield of 3,000 kg. quite satisfactory. (Cf. "Oil of Lavandin," Planting.)

Fertilizing.—Autran and Fondard [3] reported that the most prolific growth is obtained by fertilization with nitrogen in the form of sodium nitrate or ammonium sulfate, whereas potassium salts are harmful. For a high yield of oil per acre, these authors recommended fertilizing with nitrogen and phosphates.

Oil Development in the Plants.—Charabot [4] showed that the content of free linaloöl and acetic acid decreases as the plant develops annually; whereas the content of linalyl acetate increases and reaches its maximum during full bloom. At that time the plants should be cut and distilled.

Longevity of Lavender Plantings.—As has been said, many newly started plantations have in the past perished prematurely. This has been attributed variously to faulty cultivation, to soil conditions, and to the location (exposure) of the field. Undoubtedly a severe drought can be disastrous to a plantation located at low altitude and with a particularly hot exposure. Yet, the same early decay has been observed at altitudes of 700 m. and more; failure of a plantation, therefore, may be attributed largely to soil conditions, perhaps chiefly to insufficient porosity. Unfortunately, the

[3] *Office Regionale Agricole du Midi* (1923), No. 7, 1.
[4] *Compt. rend* **130** (1900), 257.



Courtesy of Fritzsche Brothers, Inc., New York.

Lavender harvest in southern France.

chemical composition of the soil required for successful lavender growing has never been studied systematically.

An investigation made in 1934 by Bordas, Joessel and Aurès of the Agricultural Station in Avignon, in cooperation with Professor Dumont of Myons (Drôme),[5] indicates that the mortality of the lavender plantings is not due to any parasitic plant disease but rather to the careless, and in fact ignorant, way in which most new plantations were planted after World War I. The high lavender oil prices paid in the years following that war induced many peasants to start plantations of true lavender under conditions and in locations where lavender should never have been grown. Planting and cultivating of lavender requires infinitely more care and experience than is usually presumed. According to Bordas, Joessel and Aurès, certain fundamental rules must be observed:

1. Selection of a suitable location and altitude; exposure to the north, affording protection against excessive sun and drought; well chosen local climate and soil composition, which must be silico-calcareous, easily permeable, and neither too hot nor too humid.
2. Proper way of planting and cultivating; cautious selection of young but strong plants; very careful weeding and cutting.

Exposure to the north, proper composition of the soil, and careful planting seem to be of prime importance. There is no doubt that pools of stagnant water remaining around the plants after a downpour are deadly to the plant.

During the summer of 1936, the author visited the lavender producing regions, and consulted many growers and distillers with long experience in the cultivation of lavender. There was a surprising divergence of opinion as to the best method (indeed, advice was sometimes directly contradictory), but most growers agreed that in general the views expressed by Bordas, Joessel and Aurès hold true. Some growers claimed, however, that there must also exist an unknown root disease, at least in certain localities, because lavender roots pulled out appeared white and almost powdery. Others attributed the premature dying of lavender plantations to the dropping of the upper stalks and seeds, which they believed to be caused by recent damage by caterpillars. This view was later confirmed by Pussard,[6] who reported that the caterpillars of a tiny butterfly, *Sophronia humerella* Schiff., attack the inflorescence and often completely destroy the plant. Pussard recommended spraying the plants in spring with a nicotine soap solution.

[5] *Parfumerie moderne* **28** (1934), 223.
[6] *Parfums France* **15** (1937), 128. In this connection, Salgues [*Compt. rend. Soc. biol.* **120** (1935), 703] speaks of the parasite *Septoria lavandulae* Desm.

The consensus indicated that a multitude of factors were responsible for the rather alarming mortality among lavender plantations. An old grower and distiller in Ballons (Drôme) expressed the opinion that the decline of lavender is probably caused by some kind of disease which, however, was aggravated by the excessive drought of the two years previous to 1936. A plantation started by him gave only one harvest, in the third year. Immediately afterward, it died.

Most interesting was an interview with a well versed agricultural expert in the Basses-Alpes, who attributed the premature mortality of lavender plantations to the following causes:

1. The plants are often planted too close together. The roots of lavender are easily damaged by plowing; instead of deep plowing, therefore, only hoeing should be employed.
2. In most cases the plantations were fertilized too late in the season. Fertilizing is often done in April, during plant growth, instead of in November, during the periods of abundant rains. Osmotic pressure thus forces the plants to give off their water content into the surrounding dry soil charged with fertilizing salts. The plants therefore dry out and perish.
3. It is still open to dispute whether new lavender plantations should be started from selected young plants or from selected old plants growing wild on mountain slopes. The older plants have already withstood all kinds of attacks and, therefore, give more assurance of continued life, if planted in a proper environment and cultivated with proper care.
4. It is by no means sure yet that lavender really is ready for cultivating. Lavender so far has grown wild for ages on mountain slopes, and it might take many more plant generations before the plants accustom themselves to the richer and easier life in plantations, and withstand it for a prolonged period.

Several years ago the author had occasion to survey lavender production in Hungary, and he learned a few facts about cultivating and harvesting which the French growers seem to have overlooked. They may well offer a clue to the French lavender producers. (See also "Hungarian Lavender Oil.")

Whatever the cause, the fact remains that practically all of the rather carelessly, and even some of the most carefully, started lavender plantations were at one time rapidly dying out. They did not give the expected returns; and this completely discouraged the peasants of the French lavender regions from replacing the disappearing lavender plantations with new ones. It must be remembered that the planting of lavender is a rather costly enterprise, requiring the investment of considerable capital. Returns cannot be expected for the first three years and, in order to write off the

investment and show profits, a plantation should survive for eight to ten years (always depending upon the market prices of the oil). However, many plantations died after five to six years, and some even earlier; for this reason, practically no new lavender plantations were started for some years prior to World War II. The growers will be induced to replant only if lavender oil and, therefore, flower prices are high enough to warrant the risk, even if the life of the plantations should be short. Practically, it does not matter if a plantation dies after four or five years, so long as the returns during those few years leave sufficient profit. In other words, French lavender oil, distilled from planted lavender, demands, and is dependent upon, a good market price.

The cost of planted lavender, however, is not the only factor upon which the price of the French lavender oil depends. In fact, this has become a less important factor, since a good part of French lavender oil is now distilled, as formerly, from plants growing wild on mountain slopes. Even during the years of numerous and plentiful lavender plantations, preceding the general decline, two-thirds of lavender oil was produced from wild growing, and only one-third from planted material. Collection of wild lavender, however, is much more difficult, tedious and, therefore, expensive—as we have pointed out previously. The quantity of planted lavender available used to be sufficiently large to prevent a too high rise in the prices of wild plants, and vice versa. There exists, indeed, a ratio between the harvest of wild and planted lavender, which acts as a sort of mutual brake, but this equilibrium can easily be upset by either a further decline in the production on the plantations or of the quantity of wild plants available.

Since the end of World War II renewed efforts have been made toward the establishment of regular plantations in which lavender is cultivated. These attempts, however, have been local rather than general, and limited to certain Départements only, in the area of Barrême, Moriez, Thorame, on the plain of Valensole, near Die, Sault and Garde Saint-Christophe, for example. From these efforts it appears that the curve of lavender production in France, which had fallen off considerably prior to the outbreak of World War II, is gradually rising again.

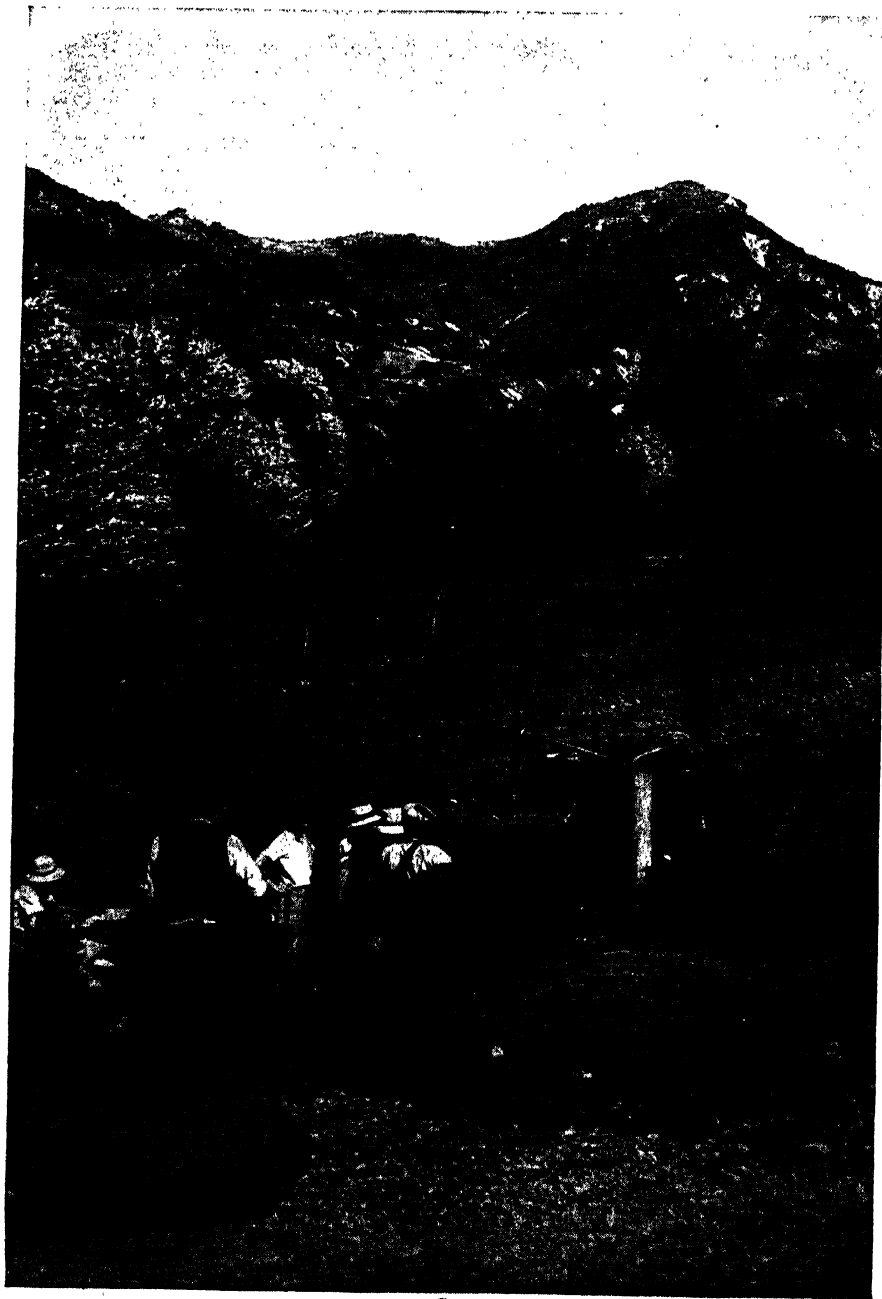
Some of these new plantations were started in regions where lavender grows naturally; others were laid out in places where plenty of space is available and where all necessary precautions can be observed in cultivation. It is probable that these new plantations will not suffer from the high rate of mortality with which the old ones were afflicted, fifteen years ago. These recent developments will be facilitated also by the fact that numerous distilleries are already established in this area processing wild growing lavender and cultivated lavandin, those treating lavandin being particularly numerous and of large capacity.

Distillation of Lavender Oil.—Until about forty years ago, in Southern France all lavender oil was distilled in portable direct fire stills. These small stills, with their characteristic still heads (*tête des Maures*), held about 50 kg. of plants and 50 kg. of water. The plant material was completely immersed in water, and the latter brought to a boil by fire beneath the still. Wood from the nearby forests served as fuel. The stills were practical, as they could easily be installed in any locality favored by ample lavender growth; a brook or fountain supplied the water for the condensers. So long as the operator took care not to "burn" the flower material through contact of the open fire with the still walls, the oil was of good quality and represented the only type of oil known at that time. The oils were evaluated by their perfume, which depended upon the region, the altitude, and the quality of the plant material employed.

A new chapter in the story of lavender oil opened when, in 1892, Bertram and Walbaum (see "Chemical Composition") investigated the chemistry of lavender oil and proved linalyl acetate and linaloöl to be the main constituents. Theoretical considerations led to the conclusion that the action of boiling water upon the immersed plant material during distillation would bring about partial hydrolysis of the esters. In order to increase the ester content of lavender oil the plant material must not be in contact with boiling water; it should instead be distilled rapidly with direct steam. In 1905, Schimmel & Co. erected a modern distillation plant in Barrême (B.A.), then the center of the French lavender region. The work accomplished therein had a far-reaching and most beneficial influence upon the lavender oil industry in general. Through a series of systematic experiments the Schimmel chemists [7] proved that steam distillation, as compared with water distillation (plant material immersed in boiling water), had the advantage of giving a higher yield of oil and, moreover, oils with a considerably higher ester content (up to 10 per cent more) than those obtained by the old-fashioned water distillation. The results of a typical distillation test follow:

		Oil Yield (%)	d_{15}	α_D	*Ester Content* (%)	*Solubility in 70% Alcohol*
1.	Steam distillation...	0.81	0.8894	−8° 4′	50.9	Soluble in 6 to 7 vol. and more with slight opalescence
	Water distillation...	0.71	0.8871	−6° 47′	44.0	Soluble in 3 vol. and more
2.	Steam distillation...	0.82	0.8905	−8° 0′	53.7	Soluble in 7 vol. and more with slight turbidity
	Water distillation...	0.75	0.8880	−6° 21′	43.6	Soluble in 3.3 vol. and more

[7] *Ber. Schimmel & Co.*, April (1907), 71.



Courtesy of Fritzsche Brothers, Inc., New York.

Field distillation of lavender in southern France.

It was also found that *rapid* distillation, with steam from a separate steam boiler, increased the ester content of the oil from the same plant material by about 4 per cent.

In the course of their work Schimmel & Co. further proved that the plants during drying lose considerable weight (from ⅓ to almost ½ of the weight of the freshly cut plants) by evaporation of water. This is accompanied by a slight loss in oil, particularly of the more volatile terpenes. Oils distilled from dried plant material possess, therefore, usually a somewhat higher specific gravity. The evaporation of ester during the drying of the plants is slight, but may amount to 10, and even 25, per cent of the total loss in oil. Table 2.2 [8] gives a good indication of the quality of oils obtained from fresh and dried lavender (flavoring stalks).

TABLE 2.2

Material Used	Loss of Weight upon Drying (%)	Yield of Oil Computed with Reference to Fresh Flowers (%)	$d_{15°}$	α_D	Ester Content (%)	Solubility in 70% Alcohol
1a. Fresh	...	0.84	0.8891	−7° 20′	50.3	Soluble in 6 vol. and more with slight turbidity.
1b. The same after drying 1½ days	35	0.79	0.8905	−7° 33′	51.8	Opalescence rem. after addition of 10 vol.
2a. Fresh		0.87	0.8859	−9° 4′	46.9	Soluble in 4.5 vol. and more, with opalescence.
2b. The same after drying 4 days	47	0.79	0.8884	−9° 33′	49.2	
3a. Fresh		0.80	0.8875	−8° 10′	47.1	Sol. in 3 vol. and more.
3b. The same after drying 5 days	47	0.72	0.8899	−8° 44′	51.1	Sol. in 4.2 vol. and more.

In this connection, it is interesting to compare the more recent findings of Jud [9] who studied the effect of various conditions of plant drying (lavender, mint, balm, rosemary, sage, and thyme) upon the yield of oil. Jud found the loss of essential oil to be as high as 24 per cent on drying in direct sunlight, and between 2 and 10 per cent on drying in the shade.

The work undertaken by Schimmel & Co. in Barrême proved conclusively that *rapid* distillation of *fresh* plant material with *direct steam* (generated in a separate steam boiler) gives a better yield of oil, and oils of considerably higher ester content, than distillation of lavender immersed in boiling water.

[8] *Ibid.*

[9] *Ber. schweiz. botan. Ges.* **50** (1940), 19. *Chem. Abstracts* **35** (1941), 6736.

In efficient steam stills of average size, dried or semi-dried lavender can be distilled within 40 or 45 min.; wet or fresh plant material requires more time. The bulk of the oil usually distills over after about 20 min., provided the plants have been properly charged into the still. The steam connecting pipe (gooseneck) and the condenser tubes must be of sufficiently large diameter to permit rapid distillation. For the same reason, the stills should not be of too large capacity, unless a large volume of steam can be generated in the steam boiler. The distillate must run cold, since otherwise some oil remains dissolved or suspended in the warm distillation (condensed) water and is lost.

The distillation waters are sometimes redistilled, but this oil of cohobation is of inferior quality—low in esters, and high in free alcohols. It must not be added to the direct oil as it would impair its quality. Accumulated quantities of cohobation oil are occasionally "reconstituted" by acetylation in order to increase the ester content. Such oils form a good natural base for synthetic lavender oils.

Toward the end of the last century the Schimmel laboratories developed new methods of analysis, basing the evaluation of lavender oil primarily upon its ester content (chiefly linalyl acetate). This gave the buyers a reliable method of testing the quality of this oil which, so far, had been judged merely by olfactory tests.

It could be shown that plant material growing in the highest altitudes, when distilled rapidly with direct steam, yielded oils containing as much as 52 and, in a few exceptional cases, even 60 per cent of esters. The old method of distillation with boiling water would yield, with the same plant material, only about 40 per cent of ester. The work of Schimmel & Co., although in the beginning much disputed [10] and fought by old-time distillers, affected the structure of the entire French lavender industry. More and more the direct fire stills were discarded and replaced by field stills, where the steam was generated in a separate steam boiler. The result was a general increase in the ester content of commercial lavender oils. The old direct fire stills, too, were improved by inserting grids above which the flowers were packed without coming in contact with the boiling water beneath. This feature alone increased the ester content of lavender oil by about 5 per cent, as compared with the old-fashioned distillation method. Aside from this improvement, many new types of portable stills were constructed—e.g., small stills mounted on carriages with separate steam boilers, which could easily be transported into the mountains where the flower supply was ample and of easy access.

At the same time a decided trend toward large-scale factory distillation

[10] The main objection to the steam distilled oils was their slightly inferior solubility.

set in. The idea first developed by Schimmel & Co. was soon followed by other operators. Slowly production of lavender oil became organized along the lines of modern agriculture and industry. In Barrême, headquarters for the highest quality of lavender, other distillation plants sprung up, until this village in the Basses-Alpes boasted more than a half dozen good sized distilleries. This trend remained by no means confined to Barrême. Distillation plants, capable of handling large quantities of plant material daily, were constructed in other sections of the lavender region, particularly in the Départements of Drôme and Vaucluse.

Concomitant with this development the problem of flower supply became ever more acute in certain centers of the lavender regions. Large-scale production required a regular supply of plant material, which still had to be brought over long distances from the slopes of the surrounding mountains. It became necessary for each distiller to set up a regular purchasing organization, with flower brokers and weighing posts distributed throughout various villages in the growing regions. The cutters would then cart their daily harvest from the mountains down to the next village, where the brokers, working mostly on a commission basis, weighed the plants, paid or credited the cutter, and stored the material until a sufficiently large lot warranted transportation to the factory. Competition for flowers among the agents buying for various distillers frequently tends to drive the prices to unwarranted levels, and the cutters and small growers take advantage of the situation.

During storage, and particularly during the transport to the distilleries, the plants lose considerable weight by evaporation and by the shattering of the dried flowering tops; the distiller, therefore, is unable to check the actual weight and the prices paid by his agents to the plant cutter. In other words, the distiller is completely at the mercy of his field brokers as to weights and prices of his raw material, and consequently in regard to yield of oil, and finally, success or failure of his whole distillation campaign. This practice has often been criticized and severely condemned as the main disadvantage at which the large distiller is placed nowadays, in comparison with the small operator, who processes only his own lavender supply from his nearby patch fields. It is actually one of the main reasons why the entire industry has reverted to small-scale operation. Today, the bulk of lavender oil is again produced by a great number of small lavender growers and distillers, who process their own plant material in small, but modernized, stills. The large lavender distilleries which were constructed years ago now produce only a small percentage of the total output. A few years ago a very efficient, small and movable type of still was designed in Grasse; it is now widely used by the farmer-distillers in the lavender regions. The actual still body (retort) is surrounded by a closed steam bath,

which prevents any condensation of steam *within* the still. The principle of operation is that of water *and* steam distillation, i.e., at low steam pressure, but very rapidly carried out, without any excess moistening of the plant charge within the still. Exhausted and sun dried plant material can be used as fuel, which means considerable economy in the final cost calculation.

Yield of Oil.—The yield of lavender oil depends upon many factors, particularly climatic and weather conditions, altitude, method of cutting, the condition of the plant material (fresh or dry), and the method of distillation.

1. The weather considerably affects the yield of oil, plant material cut during dry and sunny days yielding more oil than that cut on cloudy or rainy days.
2. At the beginning and toward the end of the harvest, the yield is lower than during the period of full bloom.
3. The altitude also seems to influence the yield. At an elevation of about 1,000 m. the average yield of oil from wild growing lavender is about 500 g. per 100 kg. of plant material; lavender from altitudes of about 1,400 m., however, yields only from 300 to 400 g. of oil. Exceptional yields of 600 to 700 g. have been reported for wild growing plants.

It is said that lavender from plantations gives a better yield of oil than that growing wild, 700 to 900 g. being normal, 800 to 850 g. the average. Exceptional yields of 1 kg. and even more have been encountered. (Lavandin gives a considerably higher yield than true lavender.)

So far as the yield of oil per acreage is concerned, Chiris [11] reported:

Age of Plantation (years)	*Kg. of Oil per Hectare*
2	8 to 10
3	18 to 23
4	18 to 30.4
5	14 to 30.5
6	18 to 32

Purchasing of Oil of Lavender in France.—Since the bulk of French lavender oil is produced by small operators, the exporters must purchase their requirements through a network of field brokers, who are intimately acquainted with, indeed often related to, the peasant producers. As it is almost impossible to analyze every small lot of lavender, which varies sometimes from 10 to 20 kg., the field broker must be assured of the hon-

[11] *Parfums France* **8** (1930), 227.

esty of various producers and buy only those lots which he trusts and evaluates as pure. For these "field" experts a simple odor test is a surer guide than a lengthy chemical analysis.

There are also lavender markets held regularly in the main centers of the producing regions—in Digne (B.A.), e.g., where the farmer-producers offer their output of oil to the exporters, to the houses in Grasse (A.M.), or to their representatives. The actual buying, however, is usually done during the following days, when the commotion of the market has abated and the farmers no longer expect higher prices. As a rule, the small producers prefer to hold on to their oil until the market, in their opinion, has reached its highest level. Unless pressed by financial obligations, they are usually in no hurry to sell. For a foreign buyer, the most opportune time of purchasing lavender oil is right after the harvest; at that moment heavy stocks of oil have accumulated, and the small producers are disposed to realize some cash for the continuance of their other agricultural activities.

Total Production of Lavender Oil in Southern France.—About twenty-five years ago the production of lavender oil in Southern France amounted to 140–150 metric tons. However, for the reasons explained above, production fell off considerably in the years prior to World War II, and in certain years was less than 50 tons. Thus, in 1937 Abrial and Gattefossé [12] reported the following figures for lavender oil production in the various départements of Southern France:

	Kg.	*Kg.*
Bouches-du-Rhône		100
Alpes-Maritimes:		
Arrondissement Grasse	2,200	
Arrondissement Puget-Theniers	170	
Arrondissement Nice	2,800	
Sub-Total		5,170
Basses-Alpes:		
Arrondissement Barcelonnette and Arrondissement Castellane	3,100	
Arrondissement Digne	2,750	
Arrondissement Forcalquier	5,700	
Arrondissement Sisteron	1,300	
Sub-Total		12,850
Hautes-Alpes		7,000
Vaucluse		9,500
Drôme		30,000
Grand Total		64,620

[12] *Parfumerie moderne* **31** (1937), 87.

During the years 1942–1944 the production varied from 50–60 metric tons, but in 1946 the figures mounted to 80 tons, because a number of new plantations came into being. In 1947 the production in the various départements was as follows: [13]

	Kg.	
Basses-Alpes	22,000	
Drôme	17,000	
Vaucluse	10,000	
Alpes-Maritimes	2,000	
Bouches-du-Rhône	2,000	
Lozère	2,000	
Var	3,000	
Hautes-Alpes	3,000	
Various other regions	4,000	(approx.)
	65,000	

It should be pointed out that it is very difficult to obtain exact production figures as they are all based on estimates by various producers but not on actual counts; e.g., another expert [14] in the lavender region estimated the 1946 production of lavender oil in Southern France as 65,000 kg. only, and that of 1947 at 55,000 kg. For 1948, figures somewhat below 45,000 kg. were given by several sources.

In general it can be said that for the past twenty-five years the production of lavender oil in Southern France has fallen off substantially, reaching its lowest point in 1940–1941, but since then production has been rising again.

Physicochemical Properties of French Lavender Oils.—Genuine lavender oils, imported from Southern France and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within these limits:

Oil of Lavender, Type 50% Ester Content

Specific Gravity at 25°/25°	0.882 to 0.887
Optical Rotation at 25°	−6° 37′ to −8° 50′
Refractive Index at 20°	1.4588 to 1.4600
Ester Content, Calculated as Linalyl Acetate	49.2 to 53.7%
Solubility at 25°	Soluble in 2.5 to 3.5 vol. of 70% alcohol; clear to opalescent with more

Oil of Lavender, Type 38 to 42% Ester Content

Specific Gravity at 25°/25°	0.880 to 0.888
Optical Rotation at 25°	−5° 28′ to −8° 40′

[13] The author is greatly obliged to Mr. Pierre Chauvet, Seillans (Var) France, for this information.

[14] Courtesy of Messrs. H. Reynaud et Fils, Montbrun-les-Bains (Drôme), France.

Refractive Index at 20°	1.4598 to 1.4638
Ester Content, Calculated as Linalyl Acetate	37.3 to 43.7%
Solubility at 25°	Soluble in 2 to 3 vol. of 70% alcohol; clear to opalescent with more

Intermediate Type

Specific Gravity at 25°/25°	0.880 to 0.886
Optical Rotation at 25°	−7° 58′ to −8° 45′
Refractive Index at 20°	1.4585 to 1.4607
Ester Content, Calculated as Linalyl Acetate	44.8 to 48.8%
Solubility at 25°	Soluble in 2 to 3 vol. of 70% alcohol; clear to opalescent with more

Gildemeister and Hoffmann [15] reported the following limits for French lavender oil:

Specific Gravity at 15°/15°	0.880 to 0.896
Optical Rotation	−3° 0′ to −11° 0′
Refractive Index at 20°	1.4580 to 1.4640
Ester Content, Calculated as Linalyl Acetate	30.0 to 40.0%; in high grade oils above 50.0%, up to 61.7% as highest observed limit
Solubility at 20°	Usually soluble in 2–3 vol. and more of 70% alcohol. Some oils, especially those distilled with live steam require 10 vol. of 70% alcohol, the solutions occasionally remaining opalescent

Adulteration.—Oil of lavender is frequently adulterated. This regrettable condition, provoked, if not forced, by unreasonable price demands on the part of the buyers, is aggravated by the fact that skillful sophistication cannot be detected by mere routine chemical analysis because the adulterants used most commonly for this purpose—e.g., linaloöl and linalyl acetate, which can be obtained from much cheaper sources, occur in lavender oil as principal natural constituents.

Cutting lavender oil with the lower priced lavandin oil cannot actually be considered an adulteration,[16] since it lowers the ester content and, therefore, the quality, but without affecting the naturalness of the oil. However, an addition of linalyl acetate or other esters to reconstitute the original ester content of the lavender oil definitely represents a form of sophistication.

[15] "Die Ätherischen Öle," 3d. Ed., Vol. III, 654.

[16] Note, however, that the U.S.P. XIII, p. 285, defines as genuine lavender oils only those distilled from *Lavandula officinalis* Chaix ex Villars (*Lavandula vera* De Candolle). Oil of lavandin is distilled from a hybrid of *Lavandula officinalis* and *L. latifolia* Vill.

Another more dangerous and frequently employed adulterant is ho oil (Japanese shiu oil), and particularly partly acetylized ho oil. Ho oil contains a high percentage of linaloöl, which can be fully or partly acetylized. In addition, the oil is laevorotatory, and hence does not materially alter the optical rotation of the lavender oil.

Years ago, before ho oil was available, a great variety of synthetics was employed for adulterating lavender oil—e.g., linaloöl, linalyl acetate, geraniol, geranyl acetate, terpenyl acetate, and many other esters, which lent a high ester content to the adulterated oil.

In view of these facts, it is important to submit lavender oil not only to a chemical analysis and to compare the ratio between the physical properties, but also to study the oil most carefully from the organoleptic point of view. A real expert, familiar with the scent of true lavender, will usually have no difficulty in distinguishing a genuine oil from an adulterated one.

Many efforts have been made toward the development of simple and reliable methods which would permit the detection of added spike or lavandin oil in oil of lavender. (See in this connection the papers of Ripert,[17] Atkins,[18] Crabalona,[19] Naves and Angla,[20] Naves,[21] Igolen,[22] and Gilly and Igolen.[23]) The measurement of the dispersion of the optical rotation requires costly instruments and great skill and experience on the part of the worker; the method is therefore not practical. For this reason Naves and Angla [24] developed a much simpler method, which is based upon the fact that the specific optical rotation of an essential oil depends upon the solvent, being somewhat different in alcohol from what it is in cyclohexane. Lavender oils, for example, are optically more active in a cyclohexane solution than they are in an alcoholic solution. In the case of lavender this difference $\Delta[\alpha]$ in specific optical rotation (20 to 25 per cent solutions of the oil in the solvent) is generally from 0.4° to 1°; whereas in the case of most lavandin oils it is from 1° to 1.5°. The method of Naves and Angla undoubtedly appears promising, but will require considerably more data on all kinds and types of genuine lavender, lavandin, and

[17] *Ann. fals.* **30** (1937), 217, 276.
[18] *Perfumery Essential Oil Record* **29** (1938), 85.
[19] *Recherches* **2** (1938), 155; **3** (1939), 63. *Chem. Abstracts* **33** (1939), 4374, 7483.
[20] *Ann. chim. anal.* **23** (1941), 201, 229. *Ber. Schimmel & Co.* (1942/43), 23.
[21] *Helv. Chim. Acta* **27** (1944), 942; **28** (1945), 279, 1222. *Soap* **22** (1946), 40.
[22] Doctorate Thesis, Marseille (1944), 49.
[23] *Ann. chim. anal.* **25** (1943), 130. *Chem. Abstracts* **40** (1946), 1281.
[24] *Ann. chim. anal.* **23** (1941), 201, 209. *Ber. Schimmel & Co.* (1942/43), 23. *Compt. rend.* **213** (1941), 570. *Chem. Abstracts* **37** (1943), 3877. Naves, *Helv. Chim. Acta* **28** (1945), 1222.

spike oil before it can be generally adapted as a reliable analytical routine method for detection of admixtures in true lavender oils.

So far as the older, well established analytical methods are concerned (determination of ester number, content of linaloöl, etc.), they have been described in Vol. I of this work, pp. 265, 276, etc.).

One of the most frequent adulterants of lavender oil, used much more in former years than at present, is terpinyl acetate. It can be detected by the fractional saponification procedure outlined in Vol. I of this work, p. 336. Pure lavender oils, on fractional saponification, exhibit a difference in the ester numbers of not more than 4 (Gildemeister and Hoffmann).[25] Occasionally certain high boiling esters are employed as adulterants of lavender oils, i.e., acetins, succinates, tartrates, citrates, oxalates, phthalates, esters of high boiling fatty acids such as laurates, etc. They simulate a high ester content in the usual routine analysis and, being odorless, do not affect the odor of the oil, if only moderate quantities have been added. Tests for these esters will be found in Vol. I of this work, pp. 338, 340, 341, and 342. In a pure oil of lavender the difference between saponification number and acid number II is generally not higher than 5 (Gildemeister and Hoffmann).[26] Somewhat greater differences may be due to resinification of the oil. In cases of doubt the oil should then be rectified with steam and the tests repeated on the rectified oil.

Chemical Composition.—The earliest investigations on the chemistry of lavender oil date back more than a century but require no discussion as the findings were inconclusive. We owe our present extensive knowledge about the chemical composition of lavender oil mainly to the classical work of Bertram and Walbaum,[27] to Schimmel & Co., and to the more recent investigations of Swiss and French chemists who identified many constituents, linalyl acetate being the principal one. According to Naves,[28] the chemical composition of lavender oil differs from that of lavandin oil notably by the absence of dextrorotatory camphor, borneol, and camphene in true lavender oil.

The presence of the following compounds has been established:

Furfural. In the first fractions; positive reaction with aniline hydrochloride.[29]

Valeric Aldehyde(?). According to Schimmel & Co.,[30] the oil contains an aldehyde, seemingly valeric aldehyde.

Amyl Alcohol. Probably as mixture of several isomers, b. 129°–133°; identified as phenylurethane m. 39°–41°.[31]

[25] "Die Ätherischen Öle," 3d Ed., Vol. III, 667.
[26] *Ibid.*
[27] *J. prakt. Chem.* [2], **45** (1892), 590.
[28] *Helv. Chim. Acta* **28** (1945), 1222.
[29] *Ber. Schimmel & Co.,* October (1903), 44.
[30] *Ibid.,* April (1903), 41.
[31] *Ibid.,* October (1903), 42.

β-Ocimene. According to Crabalona,[32] the first fractions of oil of lavender are particularly susceptible to oxidation because of the presence of ocimene not previously recorded in lavender oil.

Examining the head fractions of true French lavender oil, Crabalona [33] found that they are composed of β-ocimene (50–60 per cent), ethyl amyl ketone (7.0–7.5 per cent), cineole (about 2 per cent), *l*-α-pinene (about 2 per cent), linaloöl, linalyl acetate, etc.

These proportions vary according to country of origin, altitude of location, state of the inflorescence, method of distillation, etc. For oils preserved without special precautions, the proportions vary also with age, ocimene being easily oxidized and polymerized to a viscous substance of high refractive index.

Ethyl-*n*-Amyl Ketone (3-Octanone). Very small quantities only; identified as semicarbazone m. 117°–117.5°; oxidation gave caproic acid.[34]

Because of its refreshing, characteristic odor, this compound plays an important role in the odor of the oil.

Distilling dried lavender, Ripert [35] found that the first 33 per cent of the oil contained 6 to 7 per cent of ketones; whereas the corresponding fraction of lavandin oil contained only 0.8 to 1.2 per cent. The total content of ketones, calculated as ethyl-*n*-amyl ketone, in true lavender oil varies from 1.3 to 3.0 per cent.

Isolating the ketones from 800 g. of genuine lavender oil with trimethyl acetylhydrazide ammonium chloride, according to the method of Girard and Sandulesco,[36] Sandulesco and Sabetay [37] obtained 30 g. of ketones which, upon fractionation, showed the characteristic odor of methyl heptenone.

Methyl Heptenone(?). B. 160°–175°, n_D 1.4327; semicarbazone m. 111°.

Carvone(?). B_3 80°–100°, n_D 1.488.

Another Ketone(?). Of very agreeable odor, in the residual ketone fraction.

α-Pinene. Characterized as nitrosochloride m. 102°, and as nitrol benzylamine m. 122°–123°.[38] Only very little α-pinene is present in pure oils; [39] larger quantities indicate adulteration with oil of turpentine.

Cineole. Only traces have been found in genuine lavender oils.[40] Formation of hydrobromide takes place and iodol reaction is positive only after destruction of the linaloöl present in the same fraction, by heating with formic acid.[41]

Larger quantities of cineole in an oil of lavender indicate adulteration with oil of spike or oil of lavandin.

[32] *Recherches* **2** (1938), 155. *Chem. Abstracts* **33** (1939), 4374.
[33] *Recherches* **3** (1939), 63. *Chem. Abstracts* **33** (1939), 7483.
[34] *Ber. Schimmel & Co.*, April (1903), 41; October (1903), 44.
[35] *Ann. fals.* **342** (1937), 276. *Brit. Chem. Abstracts* B (1937), 1268.
[36] *Helv. Chim. Acta* **19** (1936), 1095. See also Ripert, *Parfumerie moderne* **32** (1938), 181.
[37] *Riechstoff Ind.* **8** (1937), 161. *Parfums France* **16** (1938), 35.
[38] *Ber. Schimmel & Co.*, October (1893), 25.
[39] Cf. above, re β-ocimene.
[40] *Ibid.*
[41] *Ber. Schimmel & Co.*, October (1893), 25.

d-Borneol and *d*-Bornyl Acetate. Present in free form and as acetate.[42] Identified by oxidation to camphor, oxime m. 118°–119°.

l-Linaloöl and *l*-Linalyl Acetate. The acetate, according to Bertram and Walbaum,[43] forms the main constituent, ranging from 30 to 60 per cent of the oil. Analysis of the silver salts showed that aside from the acetic ester, the oil contains small quantities of butyric, valeric, and caproic esters of linaloöl.[44]

The contention of Dalton [45] that the linaloöl esters present in lavender oil consisted not of acetates but mostly of butyrates and some propionate was disproved by several investigators.[46] Langlais, Goby and Reclaire [47] showed finally that 94 per cent of the acids liberated from the potassium salts of the saponified esters consisted of acetic acid.

Applying the Glichitch method of cold formylation,[48] Chiris [49] found that pure lavender oils contain 28 to 46 per cent free alcohols, 28 to 46 per cent combined, and 73 to 81 per cent total alcohol. The total amount of oxygenated compounds in pure oils, according to the same author, varies between 81 and 91 per cent.

Geraniol. Linaloöl is accompanied by another terpene alcohol, viz., geraniol which occurs in the fractions b_{13} 110°–120°. Isolated as calcium chloride compound and identified as diphenylurethane m. 82°.[50] Geraniol is present as free alcohol, also as ester of acetic, butyric, valeric and caproic acid.[51]

Lavandulol $C_{10}H_{18}O$. More recently, Schinz and Seidel [52] discovered in an oil distilled from true French lavender, *Lavandula officinalis* Chaix, a new primary terpene alcohol, with two double bonds occurring (less than 1 per cent of the total oil) in the free as well as the ester form, which they named lavandulol.

Purified over the allophanate m. 117°–118°, lavandulol had these properties: b_{13} 94°–95°, d_4^{17} 0.8785, α_D^{16} −10° 12′, n_D^{17} 1.4683.

The constitution of lavandulol, an isomer of geraniol, was investigated by Schinz and Bourquin.[53] (Cf. Vol. II of this work, p. 177.)

Nerol. Identified by Elze [54] as tetrabromide m. 118°–118.5°, and as diphenylurethane m. 50°.

Thymol(?). According to the same author;[55] m. 50°–51°; phenylurethane m. 107°–107.5°; nitroso compound m. 160°–160.5°. The presence of thymol in *genuine* lavender oil, however, is doubtful.[56] (Cf. the work of Bénezet, below.)

Caryophyllene. Isolated from the sesquiterpene fraction and converted into caryophyllene alcohol m. 93°–94.5°; phenylurethane m. 136°–137°, after hydration according to the Bertram-Walbaum method.[57]

[42] *Ibid.*, April (1903), 43.
[43] *J. prakt. Chem.* [2], **45** (1892), 590.
[44] *Ber. Schimmel & Co.*, April (1903), 44; April (1904), 60.
[45] *Perfumery Essential Oil Record* **17** (1926), 433.
[46] Chiris, *Parfums France* **4** (1926), 358. Langlais and Goby, *Perfumery Essential Oil Record* **17** (1926), 520. Dupont and Labaune, *Rev. des Marques* **4** (1926), 609.
[47] *Perfumery Essential Oil Record* **18** (1927), 47.
[48] *Parfums France* (1923), 30. *Bull. soc. chim.* [4], **33** (1923), 1284.
[49] *Parfums France* (1924), 262.
[50] *Ber. Schimmel & Co.*, April (1898), 32.
[51] *Ibid.*, April (1903), 44.
[52] *Helv. Chim. Acta* **25** (1942), 1572.
[53] *Ibid.*, 1591.
[54] *Chem. Ztg.* **34** (1910), 1029.
[55] *Ibid.*
[56] *Ber. Schimmel & Co.*, October (1915), 27.
[57] *Ibid.*, April (1913), 66.

Coumarin. The presence of coumarin, first reported in 1900,[58] was confirmed by Ellmer [59] who isolated about 0.8 per cent from distilled lavender oil and 3.4 per cent from an extracted lavender oil.

Investigating an oil of lavender distilled the middle of August from *Lavandula delphinensis* plants (yield = 1.2 per cent) grown near Moustiers-Ste.-Marie, at an altitude of 800 m., Bénezet [60] found these physicochemical properties:

Specific Gravity at 15°/15°	0.8837
Optical Rotation at 20°	−7° 46′
Refractive Index at 20°	1.4640
Acid Number	0.56
Ester Number	150.10
Ester Number after Cold Formylation	218.84
Carbonyl Number	11.74
Ester Content	52.47%
Free Alcohol Content	21.35%
Total Alcohol Content	62.49%
Alcohol Content by Phthalization in Pyridine	4.6% (mol. weight 154)

Bénezet studied the chemical composition of this oil on a 40 kg. sample and reported the presence of the compounds listed below.

Extraction of the oil with sodium bisulfite solution yielded a portion (80 g. = 0.2%) which, calculated on the basis of the original oil, contained

Furfural	Trace
Diacetyl	Present
Butyraldehyde	0.01%
Isovaleraldehyde	0.02%
2-Hexenal	0.016%
Caprylaldehyde	0.03%
Citronellal	0.016%
Capraldehyde	0.028%
Citral	0.016%
Cuminaldehyde	0.028%
Unidentified Aldehyde	0.028%

After treatment with sodium bisulfite solution, the residual oil was extracted with cold (20°) 3 per cent sodium hydroxide solution to remove phenols, lactones, and free acids. The fraction soluble in sodium hydroxide had the following approximate composition, calculated on the basis of the original oil:

[58] *Ibid.*, October (1900), 40; April (1903), 44.
[59] *Riechstoff Ind.* (1927), 206.
[60] *Parfumerie* **1** (1943), 153. Through *Chem. Abstracts* **40** (1946), 6757.

Acetic Acid	0.003%
Butyric Acid	0.002%
Isovaleric Acid	0.0007%
Caproic Acid	0.0037%
Capric Acid	0.0025%
Unidentified Acid	0.01%
Unidentified Lactone	0.01%
Coumarin	0.04%
Unidentified Phenol	0.01%
Thymol	0.005%
Eugenol	0.005%

The residual oil remaining after extraction with sodium hydroxide solution was borated by refluxing with butyl borate at 150° under 4 mm., the borates were saponified, and the mixture was steam distilled yielding about 20–21 per cent of free alcohols, which contained the following constituents, the quantities being based on the original oil:

l-Linaloöl 13%.

Ethylamylcarbinol 0.02% (3-Octanol). Identified as allophanate m. 167°, as *l*-naphthylurethane m. 81°, and as acid phthalate m. 65°–66°.

Low Boiling Alcohols (Including an Unidentified Alcohol with Amyl-like Odor) 0.1%.

About one year after the above described work of Bénezet appeared in print, Crabalona [61] reported the occurrence in lavender oil, of

Amylvinylcarbinol Acetate. b_{746} 190°, $b_{5.5}$ 65°–66°; d_4^{20} 0.873; α_D^{20} +3° 30′; n_D^{20} 1.4223. Hydrolysis gave amylvinylcarbinol b_{742} 173.5°, b_5 55°–55.5°; d_4^{13} 0.8395, α_D^{13} −17° 0′; n_D^{12} 1.4391. Acid phthalate m. 57°.

An equally recent work on the chemical composition of French lavender oil is that of Seidel, Schinz and Müller [62] who investigated the fraction b_{11} above 100° in two procedures. The processing of 4.5 kg. of oil was undertaken to detect the monoterpene esters and the acids formed on hydrolysis. The working up of 2.7 kg. of distillate b_{11} above 100°, from 19.25 kg. of oil was carried out to isolate the free monoterpene alcohols.

The fraction (298.8 g.) $b_{0.2}$ 75°–125° from fractional distillation of 4.5 kg. of oil was freed from aldehydes, ketones and free alcohols, yielding

Fraction I (33 g.) b_{10} 100°–105°,
Fraction II (114 g.) b_{10} 105°–120°, and
Fraction III (43.9 g.) $b_{0.1}$ 75°–110°.

A Saturated and an Unsaturated Caproic Acid. Fraction I was saponified and the free alcohols were removed with ethyl borate. Conversion of the free acids into

[61] *Bull. soc. chim.* **11** (1944), 67. *Chem. Abstracts* **39** (1945), 388.
[62] *Helv. Chim. Acta* **27** (1944), 663, 738.

the S-benzylthiuronium derivative m. 158°–159° indicated the presence of a mixture of acids $C_6H_{12}O_2$ and $C_6H_{10}O_2$.

Corresponding treatment of fraction II yielded a benzylthiuronium salt m. 148°–149°. Combustion analysis suggested a saturated caproic acid.

Investigation of fraction III revealed the presence of the following four acids:

Acetic Acid. The thiuronium salt melted at 146°–147°.

d-Methylethylacetic Acid. This optically active valeric acid b_{10} 75°–77°, $[\alpha]_D$ +11° 0′ yielded a thiuronium salt m. 147°–148°.

A Heptoic Acid. Thiuronium salt m. 153°.

Benzoic Acid. M. 121°.

The alcohols separated by the borate method from the fractions b_{10} 100° to $b_{0.1}$ 110° were collected (60.7 g.) and fractionated, yielding:

n-Hexanol. Identified as allophanate m. 160°–161°.

l-Linaloöl. (7.4 g.), b_{11} 84°–85°, d_4^{20} 0.8702, $[\alpha]_D$ −16° 48′; identified as phenylurethane m. 61°–62°.

Geraniol. Identified as allophanate m. 115°–116°.

Lavandulol. Identified as allophanate.

Nerol. Identified as diphenylurethane m. 55°–62°.

d-Citronellol. Identified as allophanate m. 105°–106°.

The 2.7 kg. of distillate, b_{11} above 100°, was freed from 49.8 g. of crude ketones, 105 g. of primary alcohols and 27 g. of secondary alcohols by successive treatment with Girard T reagent and with phthalic anhydride at 100° and at 120°–130°. Distillation of the remainder at 10 mm. yielded 687.5 g. of oil, b_{10} above 112°, which was freed from sesquiterpene alcohols by treatment with ethyl borate. The nonreactive material was then saponified and separated into acid and neutral fractions. The neutral fraction was separated into primary, secondary, and tertiary alcohols and a residual mixture of hydrocarbons and oxides. The primary and secondary alcohols were combined and separated by a series of fractionations after contaminating *l*-linaloöl had been removed.

The fractionation produced:

d-Borneol. Several grams. M. 203°–204°.

Geraniol. 22.1 g.

Nerol. A small quantity; identified as diphenylurethane m. 55°–62°.

Cuminyl Alcohol (Cuminalcohol). About 1 g.; purified through the allophanate m. 184°–185° (after repeated recrystallization from benzene-cyclohexane), and identified as 3,5-dinitrobenzoate m. 95°–96° (recrystallized).

The acidic fraction consisted mainly of:

Acetic Acid.

Benzoic Acid. Small amounts.

Tiglic Acid. M. 63°–64° (recrystallized).

Coumarin. M. 69°–70°.

Valeric Acid. Identified as thiuronium salt m. 147°–148°. The acid was optically active α_D +12° 54′.

n-Caproic Acid. Identified as thiuronium salt m. 154°–155°, and as anilide m. 95°–96°.

An Unsaturated Acid $C_8H_{14}O_2$. Characterized as thiuronium salt m. 150°–151°.

Pelargonic Acid. This acid, too, gave a thiuronium salt m. 150°–151°.

Herniarin (7-Methoxycoumarin, Umbelliferone Methyl Ether). M. 117°–118°.

A Monocyclic Unsaturated Acid $C_9H_{14}O_2$. $B_{0.1}$ 75°–90°; catalytic reduction yielded an acid b_{10} 130°–135° which was characterized by the preparation of its thiuronium salt m. 154°–155°.

A Phenylbutyric Acid(?) $C_{10}H_{12}O_2$. $B_{0.1}$ 90°–120°; thiuronium salt m. 184°–185°.

The same authors [63] also investigated the sesquiterpene compounds occurring in lavender oil which until then had been little known. The following compounds could be isolated:

A Sesquiterpene Alcohol $C_{15}H_{24}O$. This primary (or perhaps secondary), probably tricyclic alcohol $b_{0.07}$ 96°, d_4^{20} 0.9890, n_D^{20} 1.5067, occurs in the oil free, and yields a poorly crystallizing allophanate m. 183°–187°.

A Sesquiterpene Alcohol $C_{15}H_{26}O$. This primary, monocyclic alcohol $b_{0.07}$ 107°, d_4^{19} 0.9708, α_D −25° 36′, n_D^{19} 1.5096, too, occurs in the oil in free form. It yields a tetrahydro compound and can be oxidized to an aldehyde.

A Sesquiterpene Alcohol $C_{15}H_{24}O$. This primary, bicyclic alcohol $b_{0.04}$ 100°–104°, d_4^{13} 0.9806, α_D −66° 58′, n_D^{13} 1.5140, occurs in the oil as ester and could be characterized by the preparation of its allophanate m. 188°–189°. Hydrogenation added 2 mols of hydrogen; oxidation yielded an aldehyde.

A Diol $C_{15}H_{26}O$. This tricyclic sesquiterpene diol m. 150°–151° occurs in the oil as ester. Found in the last runs of the bicyclic alcohol $C_{15}H_{24}O$ which were also obtained by ester saponification.

Cadinol, Free. Identified as cadinene dihydrochloride.

Bisabolol, Free. Admixed to cadinol in a quantity of 5 per cent; identified as bisabolene trihydrochloride.

Caryophyllene. Identified as dihydrochloride and as caryophyllene alcohol.

[63] *Ibid.*, 738.

Cadinene. Identified as dihydrochloride.

Bisabolene. Identified as trihydrochloride.

An Oxide $C_{15}H_{24}O$. This bicyclic (without counting the oxide ring) and crystalline oxide m. 62°–63° was separated from the hydrocarbons by absorption on silica gel; it yielded a dihydro compound. In a recent publication on caryophyllene oxide, Treibs [64] claimed that the sesquiterpene oxide observed by Seidel, Müller and Schinz in lavender oil is undoubtedly *caryophyllene oxide.*

Seidel, Schinz and Müller [65] could not find any cedrene in the lavender oil which they investigated although it had been reported as occurring in lavender oil by earlier workers. According to Seidel, Schinz and Müller, such oils were either adulterated or the too low melting glycol consisted of another compound.

Extracted Lavender Oil (Concrete and Absolute).—About 1925, some essential oil houses in Grasse (A.M.), France, started to offer on the market lavender concretes and absolutes extracted from the flowering dried herb with volatile solvents. The concretes are dark green solid masses, only partly soluble in 95 per cent alcohol, and in volatile oils; the absolutes, from which the alcohol-insoluble waxes have been removed in the usual way, are liquid, soluble in 95 per cent alcohol and in volatile oils.

The solvent usually employed is benzol (benzene); it gives a somewhat higher yield of concrete but a product of slightly darker color than that obtained with petrol ether. The yield of concrete varies from 1.5 to 2.2 per cent, according to the number of extractions. The concretes, in turn, yield from 50 to 60 per cent, and in some cases much more, absolute, the yield depending upon the number of extractions made of the plant material and, therefore, upon the quantity of waxes present in the concrete. The first extraction of the plants gives a concrete of high oil content and of low wax content, the latter increasing (relatively) with each successive extraction until the plant is completely exhausted after the fourth extraction.

Concretes and absolutes of lavender contain a high percentage of high boiling compounds (coumarin, coumarin derivatives, etc.) which, by steam distillation of the plant material, are not carried over into the distillate and, therefore, are lost. Over the distilled oil the concretes and absolutes possess the advantage of much greater fixation value, and a more suave, slightly hay-like, true to nature odor, but they do have the disadvantage of dark color [66] and of insolubility in dilute alcohol. Concretes and absolutes are, therefore, not suitable for toilet waters and eaux de cologne. However, they give excellent results in face and toilet powders, in bath

[64] *Chem. Ber.* **80**, No. 1 (1947), 56.

[65] *Ibid.*

[66] Lately decolorized, or partly decolorized concretes and absolutes of lavender have been introduced on the market.

salts, and similar preparations. The concretes are highly recommended for the scenting of soaps and shaving creams, where they serve as an odoriferant and as a fixative par excellence.

Because of the complicated apparatus required, the concretes and absolutes of lavender are not produced in the regular lavender distilleries located in the lavender growing regions, but by the manufacturers of natural flower oils in Grasse, Bar, and Seillans. A small extraction plant exists in Barrême and another, much larger one is being constructed in Valensole. There, in the heart of the lavender regions, the freshly harvested flowers can be processed immediately, without undergoing the long transport to Grasse, on which occasion much of the flower material is lost by shattering. When extracted directly in the growing regions, the concretes and absolutes possess a much more delicate and more true-to-nature perfume.

Chemical Composition.—The chemical composition of extracted lavender oil is similar to that of the distilled oil except that the former contains more of the high boiling constituents which are not carried over in steam distillation.

The presence of the following compounds has been established in extracted lavender oil.

Esters of Linaloöl, mainly Linalyl Acetate. According to Kleber.[67]

Coumarin. M. 69°. Identified by Kleber,[68] and by Ellmer [69] who isolated 3.4 per cent of coumarin from an extracted oil. Ellmer found that 1,000 kg. of lavender plants contain 227 g. of coumarin. The content of coumarin in extracted oils is about four times higher than in distilled oils. Ellmer explained this by the theory that the ferments in the plants are immediately destroyed by distillation and that only so much coumarin distills over as is present in free form in the plant cells. During cold extraction with volatile solvents, on the other hand, the ferments are not destroyed: they continue splitting the coumarin glycosides and additional amounts of coumarin are formed even during the process of extraction.

Umbelliferone Methyl Ether (7-Methoxy-Coumarin). Identified in the extracted oil by Kaufmann and Kjelsberg,[70] and by Pfau [71] who reported that 2.5 per cent of this compound separated as crystals m. 117°–118° from a concrete of lavender. Ellmer [72] found about 5 per cent in a concrete made by extracting lavender with benzene. According to Ellmer, at least 60 g. of umbelliferone methyl ether are contained in 1,000 kg. of lavender plants.

Ellmer also suggested a method of isolating coumarin and umbelliferone methyl ether from essential oils:

The oil is dissolved in the same quantity of methyl alcohol and, for the separation of free acids, is very quickly titrated to red with normal alkali solution and

[67] *Am. Perfumer* **21** (1927), 680; **22** (1927), 275.
[68] *Ibid.*
[69] *Riechstoff Ind.* (1927), 206.
[70] *Parfumerie moderne* **20** (1927), 198.
[71] *Perfumery Essential Oil Record* **18** (1927), 205.
[72] *Riechstoff Ind.* (1927), 206.

phenolphthalein. The solution is immediately shaken with ether and ice water and the separated ether layer extracted three times, for 1 hr, with concentrated barium hydroxide solution. The lactones are then separated from the united barium hydroxide solutions by means of dilute hydrochloric acid, extracted with ether, and recovered.

Cedrene(?). This compound is present in lavender extracts, according to Volmar and Thurkauf.[73] However, their contention remains doubtful, as the cedreneglycol $C_{15}H_{26}O_2$ (oxidation of cedrene with potassium permanganate) actually melts at 160°, according to Chiris,[74] even at 167.5°–168°, and not at 150° as reported by Volmar and Thurkauf.

Coumaric Acid. Identified by the same author; m. 207°.

Chlorophyll.

In a more recent investigation of lavender concrete and absolute, Angla [75] found that in the concrete product the esters of the volatile acids are acetates, and that the concrete contains also considerable quantities (about 35 per cent) of esters of nonvolatile acids. So far as the absolute of lavender is concerned, it contains not only acetates of volatile acids but apparently also propionates, buyrates, and isobutyrates. The percentage of the esters of nonvolatile acids in the absolute is even higher (about 45 per cent). This is one of the principal reasons for the considerable difference between absolute of lavender and distilled lavender oil. The latter product contains very little, if any, esters of nonvolatile acids, and the esters of the volatile acids consist exclusively of acetates.

Italian Lavender Oil

For many years limited quantities of lavender oil have been distilled in the Italian part (Piemonte) of the Sea-Alps (Alpes-Maritimes), adjacent to the French lavender regions. The principal producing sections in Italy are located in the province of Cuneo (around Demonte and Ormea) and Imperia (around Carpasio, Cosio di Arroscia, and Vallecrosia). The oil is distilled from wild growing, and lately also from planted, lavender. The total annual production of oil varies from 8,000 to 12,000 kg., most of which is employed in Italy; some is shipped to Grasse (A.M.), France, where it is probably bulked with French oil and exported as such. Direct shipments of Italian lavender oil have seldom reached oversea countries.

[73] *J. pharm. chim.* [8], **10** (1929), 199. *Ber. Schimmel & Co.* (1930), 52.
[74] *Parfums France* **3** (1925), 168.
[75] *Ibid.* **14** (1936), 242.

Until some years ago, the Italian oils were produced mainly in old-fashioned direct-fire stills such as the French distillers employed until about 1910. Because the plant material was completely immersed in boiling water during distillation, the oils usually had a low ester content, ranging around 30 per cent or a little higher. In other words, they resembled the type of French oils produced many years ago.

Lately, however, the experience of the French producers has spread to the Italian lavender regions: the direct-fire stills are now equipped with grids above the boiling water, and a few steam distilleries have been erected. The result is a marked improvement in the ester content of the oils. Thus, Italian lavender oils containing up to 45 per cent of esters have been offered in Grasse; their average ester content, however, still remains below that of the French oils.

According to Rovesti,[76] twenty-one Italian lavender oils distilled from plants growing between 600 and 1,400 m. altitude had properties which varied within the following limits.

	Steam Distilled Oils	*Water Distilled Oils*
Specific Gravity at 15°	0.889 to 0.893	0.8798 to 0.8910
Optical Rotation at 20°	−6° 6′ to −8° 12′	−4° 12′ to −8° 18′
Refractive Index at 20°	1.4610 to 1.4628	1.4619 to 1.4639
Ester Content, Calculated as Linalyl Acetate	38.54 to 43.12%	5.22 to 37.89%
Solubility	Soluble in 2.8 to 3.1 vol. of 78% alcohol	Soluble in 0.3 to 2.9 vol. of 78% alcohol

Most of the oils distilled from wild growing lavender contained 25 to 33 per cent of linalyl acetate, a few 35 to 38 per cent, while the oils from planted lavender contained up to 43 per cent of linalyl acetate.

Massera [77] reported about lavender oils produced experimentally in other parts of Italy. *Lavandula officinalis* planted in the province of Salerno gave, upon steam distillation, 0.55 per cent of oil, and *Lavandula delphinensis* planted in the province of Perugia 0.7 per cent of oil. The properties were:

	Salerno Oil	*Perugia Oil*
Specific Gravity at 15°	0.900	0.888
Optical Rotation at 20°	−4° 6′	−9° 18′
Refractive Index at 20°	1.4630	1.4648
Ester Content, Calculated as Linalyl Acetate	32.8%	48.0%

[76] *Profumi Italici* **3** (1925), 208. *Ber. Schimmel & Co.* (1926), 66.
[77] *Boll. chim. farm.* **76** (1937), 531. *Ber. Schimmel & Co.* (1939), 47.

Russian Lavender Oil

Nesterenko [78] reported that since 1930 lavender has been planted extensively near Yalta and Aluschta on the Crimean Peninsula (U.S.S.R.). In 1932, plantations in the plains of the southern districts (Baktschissarai and Simferopol) reached considerable importance.

It was found that the oil yield varied according to the variety of the plants, a good variety yielding more oil, even under unfavorable conditions, than a mediocre one. About 900 botanical forms of lavender were encountered in the botanical garden of Nikita, and oil was distilled experimentally from each form. The mediocre forms with a low oil content predominated, those with a good oil yield being much rarer. Oils with a high ester percentage were especially rare.

The content of oil in various types of lavender was established by microdistillation, which required only 40 to 50 g. of blossoms per plant.

Another, simpler and more rapid method consists in counting the oil-containing sacs ("oil glands" or oil secretion "cells") on the surface between six calyx ribs. Nesterenko observed that the number of oil sacs is in direct relation to the quantity of oil present in the blossoms and that various lavender varieties may be identified by the number of their oil sacs. Thus, varieties with 30 to 45 sacs yielded 2.5 to 3.0 per cent of oil, with 50 to 60 sacs 3.4 to 4.0 per cent, with 90 to 100 sacs 7.5 to 8.0 per cent, and those with 120 sacs 10.0 to 10.5 per cent of volatile oil, the yield being calculated upon the weight of the dried blossoms. The examination of only three blossoms and the counting of the oil sacs on only five sepals sufficed to obtain an approximate idea of the oil content of the variety in question. It was thus possible to select varieties and forms with a high oil content, which were then propagated through cuttings.

Aside from these original experiments, American or Western European literature reports little [79] about the further development of the lavender oil industry in the U.S.S.R., which has remained somewhat shrouded in mystery. As a matter of fact, however, it seems to have progressed considerably, although interrupted probably by World War II. As in other agricultural products, the southern part of the U.S.S.R., with its temperate climate, undoubtedly offers great possibilities for the production of lavender oil, the importance of which cannot be gauged yet. It was reported that as far back as 1932 Soviet Russia shipped 5 tons of lavender oil to America.

[78] *Parfumerie moderne* **30** (1936), 387. Cf. "The Number of Glandular Hairs as a Measure of the Oil Content of Lavender Blossoms," Schratz and Spaning, *Deut. Heilpflanze* **10** (1944), 1. *Chem. Zentr.* II (1944), 341. *Chem. Abstracts* **40** (1946), 6756.

[79] See also *Ber. Schimmel & Co.* (1933), 83.

Even during World War II, that country offered on the American market substantial stocks of lavender oil, the quality of which resembled that of fair French oils.

Two lots, analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	I	*II*
Specific Gravity at 25°/25°	0.881	0.881
Optical Rotation	−6° 53′	−6° 51′
Refractive Index at 20°	1.4643	1.4630
Ester Content, Calculated as Linalyl Acetate	37.2%	39.9%
Solubility	Turbid in 10 vol. of 70% alcohol	Soluble in 3 to 3.5 vol. of 70% alcohol; opalescent in 5 vol. and more

These properties were closely akin to those of good quality French oils. The odor, however, was slightly harsher, somewhat lacking in the characteristic sweetness of the French oils.

Chemical Composition.—Williams and Smirnov [80] investigated a lavender oil (*Lavandula vera* D.C.) distilled on the Crimean peninsula and reported the presence of the following constituents:

8%	α-Pinene and Phellandrene(?)
10%	Ethyl-*n*-amyl Ketone Citral(?) Isoamyl Alcohol
	and
1.6%	Linaloöl
55.25%	Esters of These Alcohols, and of *geraniol* and of *isobutyl alcohol* with *acetic* *propionic* *isovaleric* and *butyric acid*

Williams and Smirnov did not establish the presence, in the Crimean oil, of other compounds which occur in French lavender oil.

Judging from his experience with Russian lavender oil, the author considers the chemical composition of the oil investigated by Williams and Smirnov rather abnormal. As has been pointed out, genuine U.S.S.R. lavender oils examined in New York possessed physicochemical properties and an odor similar to those of good French oils.

[80] *J. Gen. Chem. Russ.* **6** (1936), 190. *Brit. Chem. Abstracts* **B** (1936), 715.

Hungarian Lavender Oil

Lavender grows wild, often along vineyards and roads, on the hills near Budapest and Szentendre, a small town about ten miles north of Budapest. Some of these plants are quite old, having been planted many years ago. Patch plantings may be found also in numerous orchards and gardens, the plants being sold as cut flowers in Budapest.

It is said that lavender was originally introduced by the Turks during the sixteenth and seventeenth centuries, when they occupied a large part of Hungary. The lavender found in the above-mentioned localities resembles that grown in Southern France, but the ester content of the volatile oils is lower than that of the French oils. Experimental growing of lavender in Hungary on a commercial scale was first undertaken about 1922.

Climatic and Soil Conditions.—It was by no means certain that the climate of Hungary would be conducive to the growth of a plant generally considered Mediterranean. Hungary has more severe winters than Southern France. However, the fact that some of the lavender growing wild on the hills near Budapest was thirty to forty years old lent encouragement to large-scale planting. Another difficulty consisted in the selection of a proper site for plantings. The peninsula of Tihany on Lake Balaton was finally chosen because of its protection by the Bakony Mountains against north winds and because the large expanse of Lake Balaton promised a somewhat regulated temperature and humidity. This fact seemed especially desirable in view of the continental climate of Hungary. The chosen site opened toward the south.

The soil, too, seemed favorable for lavender, as the upper layers consisted of loam and sand mixed with disintegrated tuffaceous basalt and silicated lime. The clearing and cultivating of former sheep and goat pastures presented a difficult task because machines could not be employed. Bushes, trees, roots, stones, boulders, and grass had to be removed from the slopes by hand labor. This was done during summer and fall so that in the following winter the loosened grass sods dried out, froze, and perished.

Planting.—Finally the lavender was planted 60 cm. apart, in rows 1 m. distant. The original idea of planting the wild growing lavender of Hungary had to be abandoned, because of the too low ester content of these oils. French seed was, therefore, imported, but further difficulties arose when the imported seed germinated poorly and, besides, contained spike and other lower grades. By careful plant selection and after years of experimenting, a sufficient number of true lavender plants were raised to permit further expansion of the plantings.

Twelve acres were planted from 1924 to 1927 near Tihany, which acreage has since been considerably enlarged. The plants proved to be vivacious and beautiful, most of them having a diameter of 80 to 100 cm. After more than fifteen years the oldest planting showed no sign of decline.

The plantations were attacked by pests only once, when a swarm of caterpillars (*Agrotis segetum* L.) invaded the plantings and gave much trouble. No known spray destroyed these pests and, therefore, the caterpillars had to be picked off the plants by groups of children, or caught in trenches or ditches. They finally disappeared during the following winter, which happened to be very humid. Meanwhile, more than one-third of the plantation had perished.

In the last few years the lavender plantations near Tihany have suffered greatly from winter frost. This has happened not only where the winters are very cold (−15° to −25° C.) and snow-free, but even in mild winters, in the lower areas of cultivation. The damage by frost is very irregular, affecting only parts of a plant, or, on occasion, killing whole plants while neighboring plants are not affected at all. This seems to indicate that the frost damage is caused by very low temperatures at night followed by strong sunlight during the day. It is now planned to strengthen the plantation by selection and propagation of the frost-resistant plants.

Harvesting.—According to Dr. Jules de Bittera,[81] Budapest, the founder of these plantings, great care must be taken not to cut the plants too low, as cutting of the lower stalk parts, which contain the small leaves, may cause the plants to dry out and perish during a hot, dry August. Improper cutting and damage to the woody parts of the stem during hoeing cause the greatest losses. Furthermore, it is important that during their growth the plants assume a proper shape. Many are inclined to flourish loosely; the principal stalks grow too long, and the whole bush more or less "falls apart." Such plants perish after a few years. Whenever such growth is noticed, the bushes should be trimmed and forced to grow spherically. Much work must be done if the planting is to remain in a healthy condition; in fact, every single lavender plant, like every fruit tree, requires individual care, although this is practically impossible in a large planting.

The harvest takes place according to the prevailing weather, between June 25 and July 20. Cutting is often done as piece work by girls who can cut 150 to 550 kg. of plant material daily. However, the workers have to be supervised carefully to prevent their cutting the plants too low. About 20,000 kg. of lavender plants were harvested during 1935 from the

[81] Information gathered by the author during a visit to Lake Balaton. See also "Hungarian Essential Oils," *Am. Perfumer* **35** (October–December 1937); **36** (January–June 1938); **39** (July 1938).

Tihany plantation, which figure was increased during the years preceding World War II. In 1947 the lavender plantation near Tihany covered about 30 hectares. Since no more land remains available in that section for an extension of the lavender acreage, it is planned to start new plantings of 50 to 75 hectares on the southern slopes of the hills north of Lake Velence. The extended sheep pastures existing there could readily be converted into lavender plantations. The soil of these hill slopes is of volcanic origin, but granitic and not basaltic as in Tihany.

Distillation.—The plant material is distilled in movable stills of 1,000 liter capacity by steam generated in a separate boiler of 5 atm. pr. A charge of plant material weighs 160 to 200 kg. and can be completely distilled in 1 hr. Thirteen to fifteen charges can be completed daily, which means the processing of 2,500 to 3,000 kg. of lavender.

The yield of oil ranges from 0.7 to 0.9 per cent.

Other Lavender Varieties.—The above described Hungarian-grown lavender is of the French type. Some years ago another variety was introduced, allegedly from England, and planted in Pécel, near Budapest. This type, distinguished by its very green leaflets, has been widely advertised in Hungary because it is easy to grow and gives a high yield of blossoms and oil. For this reason many small peasant growers planted the so-called Pécel type of lavender in various sections of Hungary. In the fourth year after planting of the cuttings, 36 kg. of oil were obtained per hectare and yields up to 50 kg. are expected in the sixth year of a planting. From 1,000 kg. to 2,000 kg. of this type of oil were produced in 1946.

Physicochemical Properties.—The properties of Hungarian lavender oils vary between the following limits:

	Oil from Plants Growing Wild near Szentendre	*Oil from Plants Cultivated in Tihany*
Specific Gravity at 15°	0.8846 to 0.8875	0.8866 to 0.8973
Optical Rotation	−10° 22′ to −11° 17′	−6° 26′ to −8° 30′
Linalyl Acetate Content	33.3 to 37.2%	41.2 to 61.7%
Solubility	Not entirely soluble in 10 vol. of 70% alcohol	Soluble in 2 to 7 vol. of 70% alcohol

Some of the oils originating from the Tihany plantations possess a remarkably high ester content, which proves that the soil and climate of that region are well adapted for the production of a good grade of lavender oil. Oils containing 60 per cent of ester are rarely found in Southern France—and then only in a few localities, in particularly favorable years.

Two Hungarian lavender oils analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	Oil from the French Type of Plants Grown in Tihany (1936 Harvest)	*Oil from the Mitcham Type of Plants Experimentally Grown in Hungary*
Specific Gravity at 25°/25°	0.882	0.894
Specific Gravity at 15°	0.888	0.901
Optical Rotation	−7° 35′	−2° 52′
Refractive Index at 20°	1.4621	1.4674
Acid Number	0.5	0.6
Ester Number	123.1	47.2
Ester Number after Acetylation (Boulez Method, 6 Hr., Xylene Diluent)	226.1	233.8
Ester Content, Calculated as Linalyl Acetate	43.1%	16.5%
Free Alcohol Content, Calculated as Linaloöl	30.7%	59.6%
Total Alcohol Content, Calculated as Linaloöl	64.5%	72.5%
Solubility	Soluble in 2 vol. of 70% alcohol; opalescent with more	Soluble in 1.5 vol. of 70% alcohol; opalescent with more

An oil distilled from the above-described plant variety developed in Pécel, had the following properties:

Specific Gravity at 25°	0.885
Optical Rotation	−3° 23′
Refractive Index at 20°	1.4656
Linalyl Acetate Content	8.8%
Solubility at 25°	Soluble in 2 vol. of 70% alcohol, opalescent in 3.5 vol. and more

The odor of this oil was not lavender like, but had a character typical of lavandin and spike lavender.

A sample of French type lavender oil distilled in Tihany after World War II (1947) was analyzed by Fritzsche Brothers, Inc., New York:

Specific Gravity at 25°/25°	0.891
Optical Rotation	−7° 35′
Refractive Index at 20°	1.4624
Ester Content, Calculated as Linalyl Acetate	43.4%
Solubility in 70% Alcohol at 25°	Slightly opalescent in 1.5–2.5 vol.; clearly soluble in 2.5–6.5 vol.; opalescent in 6.5 vol. and more

The odor of this oil resembled that of French oils, but had a "by-note" of lavandin. Note the somewhat high specific gravity of the oil which confirms a slight lavandin character.

The odor of the French type of lavender oil produced in Tihany compares very well with the best grades of French oils of corresponding ester content. Because of the lower labor cost prevailing in Hungary and the fact that Hungarian lavender plantations have not yet suffered from diseases or high mortality, the future production of lavender oil in Hungary seems assured. So far no commercial lots of Hungarian lavender oil have been exported overseas, the output being entirely consumed by the perfume and soap industries of Hungary and other Central European countries.

English Lavender Oil

The scent of lavender has always been popular in England, and lavender has been freely planted in English gardens. It is said that lavender was introduced to England in the sixteenth century by French Huguenots, who probably came from Southern France at a time when the religious wars were particularly violent. According to Hardy,[82] in England lavender was first grown at Hitchin as far back as 1568.

English oil of lavender is distilled from particular strains of the hybrid *Lavandula intermedia* Loisel.[83] According to Seager,[84] two strains are at present under cultivation, viz., a selected stock called Dwarf Munstead, and a very prolific type called Giant Blue. The English type of lavender oil differs considerably from that produced in Southern France, the former containing a much lower percentage of esters (chiefly linalyl acetate) and somewhat resembling lavandin oil. Nevertheless, some English experts value their native oil above the French, owing to the peculiar heavy and slightly camphoraceous note of the English oil. This, however, is a matter of purely individual taste and opinion.

The former center of lavender-growing in England was Mitcham (in Surrey), but the steady expansion of London has forced the removal of the center to other areas, viz., the counties of Suffolk (Long Melford), Hertfordshire (Hitchin), Norfolk (Fring, Sandringham, etc.), Hampshire, and Dorset where a considerable acreage of lavender is now under cultivation. The development of a lavender industry in Norfolk was sponsored princi-

[82] *Perfumery Essential Oil Record* **35** (1944), 251.
[83] Private communication, courtesy Messrs. Stafford Allen & Sons, Ltd., London.
[84] Private communication, courtesy Mr. J. H. Seager, Technical Director, Yardley & Co., Ltd., London.

pally by Messrs. Yardley & Co., Ltd., London, who installed a modern distillery in Fring.

Prior to planting the ground must be well cleaned of weeds. A calcareous, well-drained soil with a southern exposure is most suitable. High grounds will not be affected by late frosts. Cuttings of young shoots 6 to 9 in. long are taken in the autumn, and planted in light soil, in cold frames or beds. They root readily. They may be set out the following spring or autumn, being placed carefully on the square 18 in. to 2 ft. apart each way. They should be planted deep and very firmly. After they have occupied the ground for a year, each alternate row and each alternate plant in the remaining rows is removed, thus leaving the plants 3 or 4 ft. apart each way. The plants taken out can be transplanted to fresh ground. While there is space, cultivation is carried out thoroughly between the bushes.

Harvesting takes place at the end of July or the beginning of August during the period of full bloom; the flower heads are cut by hand using knives; distillers prefer as little stalk as possible to be cut (inflorescence with 9–10 in. of stem for Giant Blue, and 5–6 in. of stem for Dwarf Munstead), but the cultivators prefer to leave the bushes neatly trimmed.

During the first year the young plants yield only 7 to 8 lb. of oil per acre, a little more during the second year. The highest yield of oil is obtained in the third, fourth, and fifth years, when the Giant Blues give from 15 to 25 lb. of oil per acre on the basis of a 4 ft. by 4 ft. planting, and only about half this quantity from the Dwarf Munstead on the basis of a 3 ft. by 3 ft. planting. From other sources [85] yields of 10 to 40 lb. of oil per acre have been reported. Sunny weather favors a good yield, while rain or cloudy weather may produce a fair crop of flowers but a poor yield of oil. After the fifth year the productivity of the field starts to decline and the planting should be discontinued.

The cut plant material is packed in sacks and transported to the distillery as quickly as possible.

Distillation is carried out in modern steam stills constructed of copper, with pure tin condensers. Direct steam of about 60 lb. pressure is blown through the plant material. Some stills operate on the principle of water *and* steam distillation (cf. section "English Oil of Peppermint"). The yield of oil ranges from one-half to one per cent from the Giant Blue, but only half as much from the Munstead.

Physicochemical Properties.—According to Poucher,[86] the oils examined in the Yardley laboratories from 1933 to 1940, had the following properties:

[85] Private communication, courtesy Messrs. Stafford Allen & Sons, Ltd., London.
[86] "Perfumes, Cosmetics and Soaps," 5th Ed., Vol. I (1942), 239, N. Y., D. Van Nostrand.

	Giant Blue
Ester Content, Calculated as Linalyl Acetate	8.4 to 16.2%; mostly 11.0 to 13.0%
Free Alcohol Content, Calculated as Linaloöl (Glichitch Method)	48.0 to 59.0%

In 1937, however, the free alcohols ranged from 74.0 to 78.0 per cent, 5.0 to 8.0 per cent of which were primary or secondary alcohols.

	Dwarf Munstead
Ester Content, Calculated as Linalyl Acetate	17.0 to 25.0%
Free Alcohol Content, Calculated as Linaloöl (Glichitch Method)	52.0 to 59.0%, of which 6.0 to 7.0% were primary or secondary alcohols

Seager[87] distilled lavender grown near Sandringham (Norfolk), including an "Old English" variety, and reported the following properties:

	Var. "Old English"	*Var. "Giant Blue"*
Specific Gravity	0.8841 to 0.8962	0.8809 to 0.8963
Optical Rotation	−3° 42′ to −5° 18′	−9° 24′ to −12° 0′
Refractive Index	1.4671 to 1.4682	1.4666 to 1.4680
Acid Number	0.45 to 0.66	0.50 to 0.60
Ester Content, Calculated as Linalyl Acetate	10.4 to 15.8%	10.1 to 13.0%
Free Alcohol Content, Calculated as Linaloöl	50.5 to 56.7%	50.7 to 57.8%
Cineole Content	Absent	About 2.0% (estimated)

Two samples of English lavender oil obtained by the author during a visit to Sandringham (Norfolk) in 1936 and analyzed in New York had these properties:

	Var. "Old English"	*Var. "Giant Blue"*
Specific Gravity at 15°	0.890	0.882
Specific Gravity at 25°	0.883	0.875
Optical Rotation	−6° 3′	−11° 45′
Refractive Index at 20°	1.4685	1.4677
Ester Content, Calculated as Linalyl Acetate	17.3%	13.5%
Solubility in 70% Alcohol	Soluble in 2 vol.; strongly opalescent in 3.5 vol. and more	Soluble in 2 vol.; opalescent with more

[87] *Am. Perfumer* **35** (August 1937), 33.

According to Allen,[88] the physicochemical properties of English lavender oils vary within the following limits:

Specific Gravity at 15.5°	0.882 to 0.907
Optical Rotation at 20°	−5° 0′ to −11° 0′
Refractive Index at 20°	1.4630 to 1.4730
Acid Number	0 to 3.0
Ester Content, Calculated as Linalyl Acetate	8.0 to 18.0%
Solubility in 70% Alcohol at 15.5°	Frequently not completely soluble in 10 vol., or only soluble with opalescence

As has been pointed out, the odor of English lavender oil differs from that of high-grade French oils, lacking their sweetness and being more cineole-like and camphoraceous. The English product represents that typical lavender scent to which England has been accustomed for generations.

American Lavender Oil

True lavender, from imported French seed and a few French plants, has been grown in the Puget Sound district of the State of Washington by L. J. Wyckoff, Olympia, who spent more than twenty years of pioneer work on this task.[89] Earlier experiments with local material, supposed to be true lavender, but which turned out to be a hybrid, had produced an oil of the lavandin type. The project, comprising three major plantings of 3 to 14 acres, with a few test plantings at other locations, definitely established the fact that a good grade of lavender oil, similar to the French type, can be produced in that area, with some slight variations due to location, soil, and climatic factors.

The upland soils of the Puget Sound area are of glacial formation with a sand or gravel subsoil and top soil varying from a very fine sandy loam to heavy gravel. Drainage is excessive almost everywhere, but the deep rooting habits of the plant permit its growth even in the worst grounds, provided reasonable cultivation is practiced to preserve as much moisture as possible. However, lavender will not grow in soils of high clay content, or where local drainage has produced hard spots. A light, well-drained, sandy loam gives the best results, with a substantial increase in green material, as well as in quantity and quality of oil. This is particularly true of a new, fairly strong soil, as compared with continuously cropped, worn out soil. Although lavender is supposed to prefer soil with a good lime content, it apparently does as well, near Puget Sound, on lime

[88] Private communication of Mr. R. K. Allen of Stafford Allen & Sons, Ltd., London.
[89] See also Wyckoff and Sievers, *Am. Perfumer* **31** (September 1935), 67.

deficient soils. Experiments with liming and fertilizing showed that they are of little, if any, benefit.

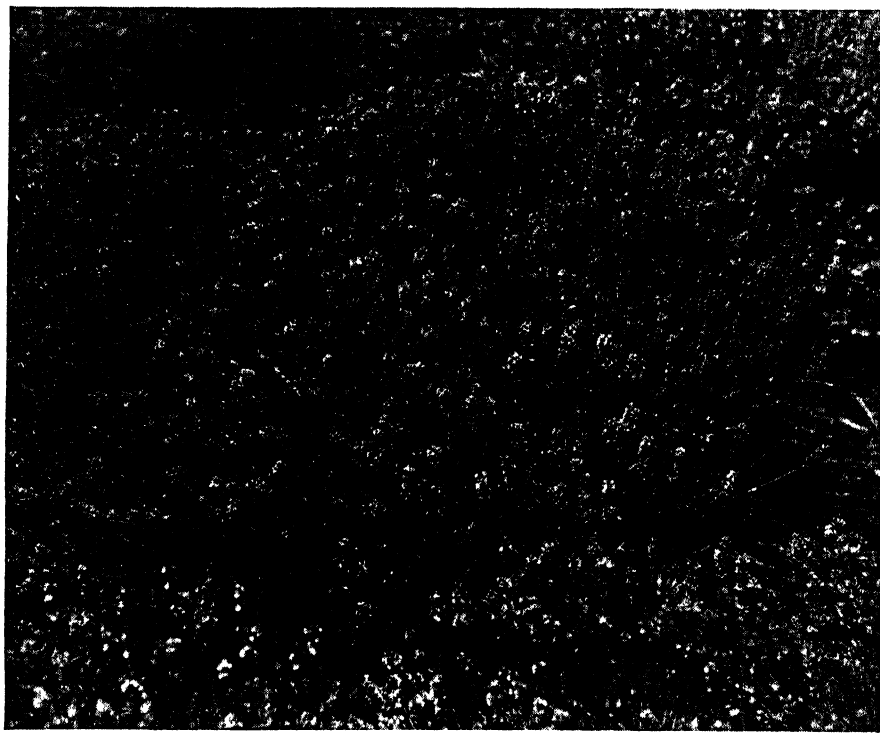
Climatic conditions around Puget Sound are very favorable, with ample rain during winter and short freezing spells which provide the needed dormant period. Summers are dry and warm without being excessively hot, and the actual harvesting period in late July is generally free from rain. Locations close to the Sound afford much more frost protection and would be preferable; at some points a few miles back, late spring frost might injure the current crop of blossoms or a very severe winter freeze may kill the plants back to the ground. In this case a year's crop would be lost, as the new growth from the crown produces only a few blossoms the first year after the freeze. Such frost damage is rare even in the less favorable locations and does not occur close to the Sound.

Starting the crop from seed is slow, and germination is uncertain. However, seed sown in the fall, on top of a firm seed bed, lightly mulched, will usually give a good stand of plants, which should remain in place during the first year and then be transplanted. With propagating stock available, either slips or layered shoots will come into production much sooner, and can be set out any time duing the dormant season. Slips can be started at any time, but during the summer months they should be set in a bed where they can be well watered. For large-scale operation, direct setting during winter and early spring produces best results. Plants up to 10 or 12 in. spread can be easily transplanted if most of the top is cut off and if the roots are cut back to a few inches. However, as the plants grow larger, it becomes more difficult to move them; in fact, a plant with a top spread of 2 to 3 ft. should not be transplanted without first being divided into several sections. As a rule, the larger the section, the less will be its chance of doing well. Moving of a large plant as a rule results in a very poor growth, and in the development of only few, short, and poor blossoms. Smaller layered shoots can be handled with impunity at any time during the dormant period, but will not do well if moved after growth starts in the spring, unless set where they may be watered and given special care.

A two-row transplanter can be used where similar two-row cultivation is planned, but should be operated with a special slow-speed gear in the tractor, as the slips or layers cannot be separated and handled as rapidly as most plants set in this manner. Even at best it is necessary to fill in many misses by hand.

The amount of cultivation required varies widely with location and condition of the ground, but the mild equable climate keeps many weeds growing the year round, and there are a number of wild grasses which, once established, may require two or three years to eliminate. Bracken is also troublesome in most locations, but can be fairly well killed off within

two years if cut off as it comes up. Even on a well-kept tract the plant will require two cultivations during the spring and early summer and another in the late fall, about the time of the first frost. This, in conjunction with a hoeing after each spring cultivation, will keep the average planting in good shape. Weedy ground that has not been previously fal-



Courtesy of Mr. L. J. Wyckoff, Olympia, Washington.

Lavender plants (Puget Sound).

lowed will call for much extra weeding and hoeing the first year, the amount depending entirely on individual local conditions.

Hand cutting of the crop is expensive and unsatisfactory, even when a sufficient crew of cutters is available, as they leave the planting in bad shape and the cutting cost would run from 20 to 40 per cent of the gross crop value. Several experimental harvesters have been tried. A small header mounted in front of a tractor has been used, the material being carried by a draper to large boxes mounted on a frame on the side of the tractor. Together with reserve boxes on a rear frame, they serve the present operations, but modifications are being made from year to year in an attempt to secure the best possible results.

The plants are set in rows 3 by 3 ft. apart, which is about the minimum for adequate feeding area and permits hoeing without hurting the roots. A distance of 3 by 3 ft. gives a flat topped, low hedge, which the harvester cuts with reasonable efficiency.

Distilling is done as soon as possible after cutting, each cut being processed the same day. A locomotive type boiler generates live steam, the steam pressure being reduced before entering the stills to an average of about 7 lb. Nevertheless, considerably higher boiler pressures are maintained to avoid fluctuations. The steam enters the stills through a hydraulic joint (which permits swinging of the stills for dumping) and thence to a perforated grill in the bottom of the stills. The latter are of shallow type, i.e., larger in diameter than in height, which permits rapid distillation. Distillation lasts only about 30 min. but the bulk of the oil comes over in the first 15 to 20 min.; runs longer than 30 min. produce very little, if any, oil. This, according to Mr. Wyckoff, is probably due in part to the type of equipment employed; even when using a taller still, the time is short enough to show that the condition of the plant material is of prime influence upon the length of distillation. After being condensed in a long tubular condenser, the oil is collected in a special three-chambered receiver which answers the purpose of several receivers, arranged in series. The yield of oil from different locations averages about 0.50 to 1.00 per cent, but the actual location and general condition of the planting play an important role in this respect.

The total quantity of green material produced varies considerably with location and age of the plants. On reasonably good ground, the quantity will amount to about one ton per acre by the third year, increasing up to about 3 tons per acre by the fifth to sixth year. Even on poor, exhausted ground, one to two tons per acre can be secured by the fifth year, but as yet there has been no real large-scale planting which would give a fair average.

The present plantings are on very poor ground, which was utilized as a matter of expediency; they can only be considered as a large-scale experiment, a pilot operation for other possible developments. The work has been hampered by insufficient financing and other factors, but at least it indicates that lavender can be produced successfully in the Puget Sound area.

Preliminary experiments with some lavender plantings have established strains of equal blooming date and have proceeded far enough to prove that the blooming time of any given plant is a fixed characteristic. Thus, it becomes possible to propagate from early bearing strains; such a planting will mature two to three weeks before the average. This also indicates conversely—although as yet no planting has actually been made—that late

blooming plantings could be established. It would permit harvesting at a time when the majority of the plants are in full bloom, instead of harvesting many that are immature or over-ripe—the practice followed at present. This promises not only a better oil percentage but also a longer harvesting season. Another problem being experimented with is the establishment of strains that would give a higher percentage of oil. A substantial area of the planting is set with groups of plants derived from a common ancestor; distillation tests indicate that the ester content of the oil of one group is as low as 24 per cent, in other groups as high as 55 per cent. Experiments of plant selection (employing a count of the oil glands in the blossoms) [90] are being undertaken to combine both quantity and quality of oil in newly developed strains.

In general it can be said that lavender seems to take kindly to the peculiar climatic conditions prevailing around Puget Sound, as is indicated by the ease of propagation and the fact that it seeds itself freely, i.e., volunteer seedlings are always present throughout a planting. Furthermore, the life span of the plants is much longer than in other countries. Plants set for three years in one location, and then moved to another, where they remained for ten years before being used for propagating, continued to increase in size and productivity. Thus, the life of a planting would seem to be at least twenty-five years, numerous hybrid plants of that age having been observed. It is also possible to renew the plants when they get tall and "leggy" by cutting them down to the ground; a new head will be formed in a single year.

Physicochemical Properties.—American lavender oils distilled on the Puget Sound and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within the following limits:

Specific Gravity at 25°	0.876 to 0.884
Optical Rotation	−5° 56′ to −8° 17′
Refractive Index at 20°	1.4615 to 1.4656
Ester Content, Calculated as Linalyl Acetate	32.7 to 42.1% [91]
Solubility at 25°	Soluble in 2 to 4.5 vol. and more of 70% alcohol. Several lots were incompletely soluble in 10 vol. of 70% alcohol

The odor of these American oils was, in general, very good, although perhaps not quite as fine and "sweet" as that of selected genuine French oils. However, it was characteristic of true lavender, French type, with no indi-

[90] Cf. Section on "Russian Lavender Oil."

[91] Small experimental samples distilled from new strains had ester contents ranging as high as 60%. The odor of these oils was excellent, equalling the best French oils.

cation of lavandin or spike lavender. The same is true of the physico-chemical properties.

Another type of American lavender oil distilled from *Lavandula vera compacta* grown in Sherwood Valley, California, at an altitude of 2,600 ft. was analyzed by the author and found to possess the following properties:

Specific Gravity at 25°	0.876
Optical Rotation	−7° 59′
Refractive Index at 20°	1.4632
Ester Content, Calculated as Linalyl Acetate	38.1%
Solubility at 25°	Not soluble in 4 vol. of 70% alcohol; faintly hazy in 10 vol. of 70% alcohol. Clearly soluble in 1 vol. and more of 80% alcohol

Except for solubility, the oil met all the U.S.P. requirements. Its odor was not quite as fine as that of French lavender oils containing 38 per cent of esters; it lacked the very sweet "top note" of the latter. Otherwise the odor was very good and strong, somewhat reminiscent of the English type lavender oil. The odor of the evaporation residue was especially characteristic of high-grade lavender oils.

Australian Lavender Oil

According to Kenny,[92] small quantities of lavender oil have been produced near Launceston in Northern Tasmania. The southern latitude of this section is approximately the same as that of Southern France in the Northern Hemisphere. The land around Launceston consists of hills originally covered with eucalyptus and mimosa and is well adapted for lavender. The plantings were started in 1922 from imported French seed. In 1937 they covered about 200 acres yielding approximately 6,000 lb. of plant material per day during the harvesting season. The oil is said to be of very good quality with a high ester content. It has been exported mainly to England.

A sample examined by the author in Australia, at the end of 1938, closely resembled the French type of oil.

South African Lavender Oil

Lavender has been grown experimentally in Kirstenbosch, South Africa, from seed obtained through the Botanical Garden in Kew, England.

[92] *Perfumery Essential Oil Record* **27** (1936), 194. *Soap, Perfumery & Cosmetics* **10** (1937), 676.

The oil (yield 0.7 per cent as calculated upon the fresh flowers; 22.5 lb. of oil per acre) had the following properties: [93]

Specific Gravity at 15°	0.8901
Optical Rotation	−7° 15′
Refractive Index at 20°	1.463
Acid Number	0.7
Ester Content, Calculated as Linalyl Acetate	49.0%
Solubility at 20°	Insoluble in 10 vol. of 70% alcohol; soluble in 0.9 vol. of 80% alcohol

The odor resembled that of French lavender oil but was somewhat weaker.

East African Lavender Oil

During a survey of Kenya Colony in 1937, the author visited the estate of Mr. Cecil T. Soames in Marindas, Molo, and found lavender plantings covering about 50 acres. The greatest part was planted with lavender imported from Seal Herb Farm in Kent, England. Despite an altitude of 12,300 ft., this type of lavender seemed to grow well in Marindas. The oil obtained had a low ester content and resembled the English type in physico-chemical properties as well as in odor.

A sample examined in New York by the author had the following properties:

Specific Gravity at 25°	0.877
Optical Rotation	−12° 25′
Refractive Index at 20°	1.4699
Ester Content, Calculated as Linalyl Acetate	8.8%
Solubility	Soluble in 1 vol. of 80% alcohol, opalescent with more

Efforts to raise the French type of lavender, from imported French plants, failed completely, perhaps for climatic reasons. In Southern France, lavender undergoes a dormant period during the winter, which was evidently not the case in East Africa.

It is interesting to mention that Mr. Soames also experimented with spike lavender which seemed to grow very well in the high altitudes of Kenya.

[93] *Bull. Imp. Inst.* **28** (1930), 8.

Argentine Lavender Oil

Although the total production of lavender oil in Argentina is small, it is increasing as a result of its development during World War II, when the imported French oil was no longer available. The first plantations were started about 1940, in the highlands of Mendoza, at altitudes ranging from 600 to 900 m. Due to the paucity of rain (about 6 in. per year), the land around Mendoza must be irrigated; but irrigated land here has always been expensive and in great demand. Most lavender plantings in the Mendoza section, therefore, are small, and quite widely scattered.

Nothing is known about the origin of the planting material. Some plants are said to have been imported from England; others were raised from French imported seed; still others were taken from local gardens. Today, there appear to be at least seven varieties of lavender under cultivation, which were gradually developed by plant selection. They range from a type of spike lavender to true lavender. Unfortunately, no reliable data on the physicochemical properties of the various types of oil seem to have been published in literature.

When a lavender field is started, the plants are spaced 1.5 m. apart in rows 1.5 m. distant; but even at such intervals the plants in the third year of growth close in on top. As a rule, the stalks of Argentine lavender grow up straight from the stock and do not bend outward (as they usually do in France); this facilitates the cutting of the plants in Argentina. The cutting is done by hand, with sickles, as in France; but mechanical harvesters are being experimented with. The plants are cut about 2 ft. below the flowering top. A newly planted field yields a small harvest in the second year of growth, and a full harvest in the third year. The cutting is done in January and February (Argentina's summer), with a second, but small, yearly cutting following at the end of March. The yield of oil per hectare, including the two yearly harvests, amounts to 40–60 kg., after a planting has reached full production in the third year of its growth.

The cut plant material is distilled while clover dry. The stills are of modern construction, direct steam being employed. The yield of oil ranges from 0.8 to 1 per cent, calculated upon the clover dried plant material.

A sample of Argentine oil of lavender analyzed in the laboratories of Fritzsche Brothers, Inc., New York, in 1947, had the following physicochemical properties:

Specific Gravity at 25°	0.885
Optical Rotation	−3° 12′
Refractive Index at 20°	1.4687

Ester Content, Calculated as Linalyl Acetate	10.1%
Solubility	Soluble in 2 to 2.5 vol. of 70% alcohol; opalescent in 10 vol.

The total production of oil of lavender in Argentina was about 1,000 kg. in 1947; an increase in production is anticipated. So far all the oil has been sold locally.

Use of Lavender Oil

Oil of lavender has a delightfully clean and refreshing, yet sweet odor, which blends with many other essential oils. The use of lavender oil in perfumes and toilet waters goes back for centuries; it has always been one of the most popular scents, especially in English speaking countries.

The trade today distinguishes between three grades of lavender oil, viz., those containing 30 to 35 per cent of esters, 38 to 42 per cent of esters, and those of about 50 per cent esters. These oils, however, are not always produced as such and are frequently the result of bulkings. In other words, an exporter receiving numerous small lots with a certain ester range from the producing regions will bulk them into the standard types demanded by his customers.

For high-grade perfumes, the finest quality of lavender oil, with an ester content of about 50 per cent, is recommended. For lower priced preparations, especially for lavender waters, eaux de Cologne, and toilet waters in general, the qualities containing 40 per cent of esters are better suited. For all around use this type of oil is probably the most economical.

The bulk of lavender oil, particularly the grades containing 30 per cent of esters, has always been employed in soap work. Lately, however, many soap manufacturers have shifted to oil of lavandin, replacing thereby lavender oil and this, as pointed out, has been one of the main reasons for the decreased production of lavender oil in recent years.

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OIL OF LAVANDIN

Essence de Lavandin *Aceite Esencial de Lavandin* *Lavandinöl*

Botany.—Lavandin (*Lavandula hybrida* Reverchon) is a hybrid between true lavender (*L. officinalis* Chaix) and spike lavender (*L. latifolia* Vill.); as such it combines the characteristics of the two parent plants. The color of the inflorescence ranges from the deeper blue of lavender to the grayer shades of spike. The flowering period falls between that of lavender in early August and that of spike in September. From spike, lavandin has inherited a hardiness superior to that of the more delicate lavender. The chemical composition of lavandin oil corroborates the hybrid nature of this plant: oil of lavandin has a much lower ester content than oil of lavender but contains some cineole, and hence possesses a somewhat harsher and more pungent odor than does lavender oil.

In Southern France wild growing lavandin has been known for a long time, but the farmer-distillers considered the plant simply a lower type of lavender, *"lavande grosse."* It was only about twenty-five years ago that the designation lavandin was adopted to specify a hybrid between lavender and spike.

Habitat and Range.—Lavandin grows in medium altitudes, between the lower regions of spike and the higher elevations of true lavender. For many years small quantities of wild growing lavandin have been distilled in the usual field stills. The oil, however, was not exported as such but was employed by producers and exporters for the cutting of high-grade lavender oils—a practice still in vogue. True lavender oil has an ester content ranging from about 35 to 55 per cent of linalyl acetate and, therefore, the lower priced oil of lavandin, with its ester content of only 18 to 25 per cent, serves ideally for making up lots of low-priced lavender oils (of low ester content).

Years ago well-known lavender experts frequently expressed their resentment against large-scale production of lavandin oil, as its employment might severely impair consumption of the more expensive lavender oil. Despite these warnings the interest in lavandin mounted, and about twenty years ago the first plantings were undertaken. In the years prior to World War II production of the oil increased to such an extent that the former ratio was reversed, and total yearly production of lavandin oil substantially exceeded that of lavender. The reasons are obvious: the planting of lavandin is less hazardous, the plants being hardier and more resistant, and less affected by premature dying out; the prolific lavandin gives a better yield per acre; the cutting is easier and less expensive; and the yield of oil higher than that of lavender.

Hybridization of the wild plants takes place spontaneously in regions where true lavender and spike lavender overlap. Natural cross-pollination is probably caused by bees, which are greatly attracted to these plants. Wild lavender grows in Southern France at altitudes of from 500 m. upward; spike lavender does not flourish higher than at 700 m. The natural habitat of wild lavandin may thus be said to lie in altitudes of from 500 to 700 m., approximately. The first centers of lavandin distillation using wild plant material were:

Dépt. Basses-Alpes	Allemagne, Riez, Reillannes
Dépt. Var	Châteaudouble, Rians, Aups
Dépt. Vaucluse	Gordes, Malaucène
Dépt. Drôme	Buis-les-Baronnies, Saillans
Dépt. Lozère	Meyrueis

Planting and Cultivating.—The first lavandin plantings were made according to the methods then employed for the cultivation of lavender.

Young lavandin plants collected from the mountains were planted in plowed fields and cultivated like lavender. This procedure is still employed, although planting today is done largely with slips. For this purpose healthy and strong plants are selected from an existing lavandin plantation, pulled out, divided, and slips of one-year old wood prepared. During winter they are planted in a nursery, spaced from 2 to 3 cm. in rows 30 cm. apart. In the following spring and summer, the ground is frequently irrigated and hoed. By fall, the young plants have taken root, and can be transplanted into clean soil, which had been well plowed in the previous summer.

The present method of planting varies according to growers and regions. The plants may be set out in straight rows, or staggered, spaced from 1 to 2 m. apart. If the rows are 1.5 m. apart and the plants 1.0 m. apart, one hectare will theoretically grow 6,666 plants. If the rows are 2.0 m. spaced and the plants 1.0 m., a hectare will contain 5,000 plants; if 1.25 m. by 1.25 m., 6,400 plants; and if 1.5 by 1.5 m., 4,444 plants. Thus from about 4,400 to 6,700 stocks can be planted per hectare. (One acre = 0.404 hectares). Rows offer the advantage of a greater number of plants per hectare, whereas staggered planting facilitates cultivating. The principal care of the young plants consists in frequent and light hoeings. The first year each stock bears only 10 to 20 g. of stalks and flowers, the second year about 200 g., the third year about 600 g. and the following years 1 kg. In some very exceptional cases up to 4 kg. per stock were obtained. A fully developed plantation yields on the average from 4,000 to 5,000 kg. of plant material per hectare.[1]

Regions of Production in France.[2]—Prior to World War II, lavandin plantations were located in the Départements which are listed below in the order of their importance. According to latest information, production within these Départements has increased.

1. Basses-Alpes.—This Département is the heaviest producer of lavandin; here the largest and most beautiful plantations may be found, especially in the high plateau district of the Basses-Alpes. This district is known as the "plains of Valensole" and is bounded by the rivers Asse, Verdon, and Durance.

Other plantations, of lesser importance, are located on the right banks of the Asse and the Durance.

In the Basses-Alpes the principal production centers are: Riez, Saint-

[1] For comparison we note that true lavender is sometimes planted in spaces of 1 x 1 m., i.e., closer together, thus giving 10,000 plants per hectare. From 250 to 350 g. of plant material per stock, therefore, yield 2,500 to 3,500 kg. per hectare.

[2] The author is greatly obliged to his friend, Mr. Pierre Chauvet, Seillans (Var), for much of the information contained in this section.

Jurs, Valensole, Allemagne, Quinson, Montagnac, and the ancient and picturesque village of Moustiers, towns located near the famous canyon of the Verdon river. On the right bank of the Asse lie Puimichel and Châteauredon; on the right bank of the Durance lie Reillanne and Banon.

2. Vaucluse.—Far behind the Basses-Alpes in regard to production. Malaucène, Apt, Entrechaux are the chief centers here.

3. Drôme.—About equal, as a producer, to Vaucluse. Its principal centers are Buis-les-Baronnies, Valréas, Saillans, and Ballons.

4. Var.—Of much less importance as a producer, this region is separated from the Basses-Alpes by the river Verdon. The present plantations are located near the villages of Rians, Ginasservis, Montmeyan, and Fayence.

5. Other Départements.—Other plantations are scattered throughout the Départements which border the above. For example, several small plantings exist near Grasse (Alpes-Maritimes), and in the Départements Lozère, Gard, and Bouches-du-Rhône.

Harvest.—Harvesting is begun several days after full florescence, which occurs, as a rule, after true lavender has reached full bloom, and before spike lavender reaches it. Generally, harvesting takes place during August, but frequently it may last into the month of September. Cutting of the flowering stalks requires much labor, since no adequate machine for the purpose has been developed. The sickle is still the only implement employed. Certain workers, however, have attained great skill, and can cut up to 1,000 kg. flowering stalks in 12 hr. The average cut, however, is 400 to 500 kg. per man in a 12-hr. period.

The size of the harvest is influenced by seasonal conditions. Although lavandin prefers a sunny location, any prolonged period of drought prior to harvesting will result in a lowered yield. Hail storms may also do a great deal of damage to the plants and diminish the yield of oil.

Immediately after the harvesting, the flowers are transported to the distilleries by cart. On more modern and better equipped plantations, use is made of tractors, which drag heavy loads.

Distillation.—Years ago movable stills were employed, of the same type as then used for the distillation of lavender. Gradually, however, rural distilleries have been erected, and the owners of large plantings now operate their own distilleries which, although occasionally somewhat crude, are quite adequate.

Such distilleries can be classified into four groups:

1. Small movable stills, of 200 to 500 liters capacity. These are equipped with a grid, above which the plants are charged. The water at the bottom of the still (and beneath the grid) is fired directly.

2. Special stills, with a capacity of 600 to 800 liters. The retort is imbedded in the boiler, which is itself heated with direct fire and by burning exhausted plant material.

3. Stills of 500 to 1,000 (occasionally of 1,500) liters capacity. This type is characteristic of the older medium sized stills used for the distillation of lavender oil. The steam for distillation is generated in a separate boiler, heated either by burning coal, wood, or exhausted plant material.

4. One of the most important producers of lavandin oil has equipped his distilleries with very large stills (10,000-liter capacity). Steam is obtained from boilers heated by burning exhausted plant material. Yield and quality of the oil have been equal to that obtained in smaller stills. This system has the advantage that the plant material can be distilled as soon as it is harvested and arrives at the distillery.

In general it may be said that the distillation of lavandin resembles that of lavender; it should be carried out either right where the plant grows, or in the immediate neighborhood.

Yield of Oil.—One hundred kilograms of lavandin plants (stalks with attached flowers) yield from 1 to 1.8 kg. of oil—the average being 1.5 kg. (The yield of lavender oil ranges from 0.5 to 1 per cent.) Distillation is rapid, but depends upon the capacity of the still employed. If distillation lasts 40 min. (as is the case with small stills), 65 per cent of the oil passes over within 10 min. During the next 10 min. 20 per cent distills over; the remaining 15 per cent distills over in the last 20 min. When distillation is continued, about 50 g. more of oil will be obtained, but the difference in yield does not compensate the increased cost of distillation.

Extraction.—Lavandin oil is obtained by steam distillation, but a part of the plant harvest is processed by the same method of extraction with volatile solvents (usually benzene, in rarer cases petroleum ether) as applied to expensive flowers such as jasmine, rose, etc. The product obtained by this process, concrete of lavandin, is a mixture of volatile oil, and odoriferous and nonodoriferous compounds which do not distill with steam. Concrete of lavandin reproduces the odor of the natural flower more faithfully than does the steam distilled oil and lasts longer when employed in soaps. It is the nondistillable constituents which impart this remarkable fixative quality to the concrete of lavandin. Experiments of Chauvet [3] indicate that the entire volatile oil content of the lavandin plant is contained in the blossoms, whereas those constituents which do not distill with steam are contained both in the flowers and in the stalks.

[3] Private communication of Mr. Pierre Chauvet, Seillans (Var), France.

Concrete of lavandin, like all floral concretes, can be converted into an alcohol soluble absolute.

Physicochemical Properties.—The properties of lavandin oil fall between those of true lavender and spike lavender oils. Shipments of genuine lavandin oils analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within the following limits:

Specific Gravity at 15°/15°	0.886 to 0.896
Optical Rotation at 25°	−2° 53′ to −5° 26′
Refractive Index at 20°	1.4616 to 1.4640
Ester Content, Calculated as Linalyl Acetate	19.6 to 26.1%
Solubility at 20°	Soluble in 2 to 2.5 vol. of 70% alcohol, clear to opalescent with more

Genuine samples distilled under the author's supervision during a visit to the lavandin regions of Southern France in August, 1936, and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties given in Table 2.3.

TABLE 2.3

Place of Production [a]	Specific Gravity 15°	Optical Rotation	Refractive Index	Linalyl Acetate Content	Free Linaloöl Content [b]	Solubility
Vaucluse	0.892	−4° 22′	1.4621	24.3%	45.6%	Soluble in 2 vol. and more of 70% alcohol
Carpentras	0.896	−4° 2′	1.4625	26.4%	47.5%	Soluble in 1.5 to 2 vol. of 70% alcohol
Valréas	0.893	−4° 44′	1.4631	24.6%	47.2%	Soluble in 2 vol. and more of 70% alcohol
Sahune	0.894	−4° 27′	1.4631	24.7%	48.4%	Soluble in 2 vol. and more of 70% alcohol
St. Jurs	0.893	−5° 15′	1.4629	24.8%	46.9%	Soluble in 2 vol. and more of 70% alcohol
St. Jurs	0.893	−4° 11′	1.4622	22.8%	51.0%	Soluble in 2 vol. and more of 70% alcohol
Châteauredon	0.894	−4° 28′	1.4627	24.6%	45.2%	Soluble in 2 vol. and more of 70% alcohol
Quinson	0.893	−4° 40′	1.4617	26.0%	48.6%	Soluble in 2 vol. and more of 70% alcohol

[a] The good weather prevailing that summer was responsible for the relatively high ester content of these oils.
[b] Boulez Method, six hours' acetylation, using xylene as a diluent.

Lavandin oil, produced in various sections, may be classified into four types, although sharp lines cannot be drawn. One is tempted to base any classification upon physicochemical properties—specific gravity and ester content in particular. However, it must be remembered that these properties are influenced by annual weather conditions, and by the method of distillation—direct steam distillation giving oils of higher ester content and higher specific gravity. The properties of pure lavandin oils in general do not vary greatly, and the limits are rather narrow. Any classification

should, therefore, be undertaken rather on the basis of odor, which differs according to certain districts.

1. Type of oil distilled in the Département of Vaucluse, around Apt and Carpentras. The ester content in normal years ranges from 18 to 22 per cent. The odor of this type is quite harsh and camphoraceous. In 1946 about 20,000 kg. of oil were produced in that section.
2. Type of oil distilled in the Département of Vaucluse and Drôme, especially around Valréas, and in Basses-Alpes and other Départements. The ester content in normal years varies around 20 per cent. The odor is less harsh and camphoraceous. About 35,000 kg. were produced during 1946 in Vaucluse and Drôme, and 40,000 kg. in Basses-Alpes and other Départements.
3. Type of oil distilled in the lower altitudes of the Département of Basses-Alpes. The ester content in normal years amounts to about 20 per cent, occasionally a little higher. The odor is sweeter, less camphoraceous than that of the above oils. About 70,000 kg. were produced in 1946. The bulk of French lavandin oil represents this type.
4. Type of oil produced in the higher elevations of the Département of Basses-Alpes. The ester content varies around 25 per cent; in exceptional cases it is even higher, if the plantations are located in high altitudes and if they are started from carefully selected plant material. The perfume of these oils does not exhibit the usual camphoraceous note; it is quite sweet and tends toward true lavender. About 15,000 kg. were produced in 1946.

Undoubtedly lavandin oils of a relatively high ester content and sweet odor promise a good future, if their price does not exceed that of regular lavandin oil. Such oils will be welcomed especially by soap manufacturers. Lately substantial quantities of this type have become available, because the newly started plantations on the high plateaux in the Basses-Alpes attained full production. Although the peasant growers in most lavandin regions have done little to improve the quality of their oils and have given prime consideration to a large yield of oil, a few of the growers in the high regions of the Basses-Alpes have succeeded in creating a form of lavandin which approaches true lavender. This is especially true of the new lavandin plantations started near Châteauredon, not far from the famous lavender center in Barrême, of the plantations near Saint-Jurs, in the extreme north of the Basses-Alpes lavender regions, and, finally, of the lavandin plantings at high elevations near Ballons (Drôme).

The growing of this type was done, not by scientific plant breeding, but merely by selecting certain plants according to their odor. In other words,

for a new plantation plants were selected whose perfume most closely resembled true lavender. Furthermore, the plantations were laid out at the highest altitude at which lavandin will grow (800–900 m.). It is an often expressed belief that the color of lavandin flowers offers a good indication of the predominance of one of the two parent plants, spike being grayish and true lavender of blue color. Color, however, is not always a guide so far as the desired odor is concerned. Therefore, a new lavandin plantation in which the quality of oil, and not its yield, is of prime importance should be started by selecting planting material according to odor.

Abrial [4] reported on a particularly valuable type of lavandin, *L. hybrida* Abrial, which was discovered after a careful study of the plants near Crest (Département Drôme) where this variety grows in arid localities. The hardy plants gave a good yield (3 per cent) of oil containing from 30 to 32 per cent of esters. Abrial recommended the commercial planting of this new variety in preference to the older types. However, where this hybrid has been actually propagated, oils have been obtained the ester content of which did not exceed 22–24 per cent. Furthermore, the plant did not develop as fully as the common variety and hence the yield of plant material per hectare was found not so large as with the usual type.

Total Production.—In 1939, production of lavandin oil in France reached 100,000 kg., but from 1940 to 1943 the figures were lower because of mobilization of man power, a shortage of fertilizers, and the efforts of the French peasants to increase food crops. However, since some new plantations had been opened in the high plateau districts of the Basses-Alpes in late 1941, production rose to 120 metric tons in 1944, increased to 150 tons in 1945, and reached 180 tons in 1946. The 1947 harvest of oil of lavandin may be classified as follows: [5]

	Kg.
Basses-Alpes	125,000
Drôme	30,000
Vaucluse	25,000
Var	5,000
Other Départements	10,000
	195,000

According to another estimate,[6] France produced 170,000 kg. of oil of lavandin in 1947. None of these quantities include the relatively small amounts of concrete extracted in the factories of Grasse and Seillans. For 1948 the production was estimated as about 200,000 kg.

[4] *Parfumerie moderne* **29** (1935), 503.
[5] Courtesy of Mr. Pierre Chauvet, Seillans (Var), France.
[6] Courtesy of Messrs. H. Reynaud et Fils, Montbrun-les-Bains (Drôme), France.

The above figures indicate the importance of lavandin oil, especially to the soap trade. The use of this oil can be safely encouraged, since an ample supply seems assured. Besides, large-scale production will no doubt tend to stabilize prices.

Chemical Composition.—The chemical composition of oil of lavandin was investigated only a few years ago. Since this oil is derived from a plant hybrid between true lavender (*Lavandula officinalis*, Chaix) and spike lavender (*L. latifolia*, Vill.), and since the chemistry of these two oils had been fairly well established, it was formerly simply assumed that oil of lavandin contains the natural constituents of both oil of lavender and oil of spike. Real progress in our knowledge of the chemistry of lavandin oil was made during World War II, while France was entirely cut off from supplies of tropical essential oils—e.g., oil of bois de rose, shiu, linaloe, citronella and lemongrass—which serve as starting material for the extraction of important aromatic isolates. The French industry of aromatic synthetics, therefore, resorted then to oil of lavandin as a new and temporary, although not very economical, source for the preparation of synthetics—such as citral, citronellal, geraniol, civronellol, esters therefrom, hydroxycitronellal and even ionones—derived from linaloöl, which is a principal constituent of lavandin oil. Large quantities of this oil were thus processed and, as a result of research along these lines, the French essential oil chemists became well acquainted with the chemical composition of lavandin oil. Numerous investigations to this effect were carried out in France between 1942 and 1945.

As early as 1937, Ripert [7] noted the presence of camphor in lavandin oil; a few years later Angla and Naves [8] identified *d*-borneol, *d*-camphene, and *d*-camphor in this oil. The most thorough investigation of lavandin oil was undertaken by Sfiras and Vanderstreek,[9] and by Naves,[10] the results of which are given below. Naves [11] established the presence of the following compounds in oil of lavandin:

d- and *l*-α-Pinene. Oxidation with potassium permanganate yielded a mixture of acids, the main fraction b_3 165°–170° of which contained optically inactive *cis*-pinonic acid m. 103°–104° (mixed melting point determination, preparation of the semicarbazone m. 206°–207°), and *d-cis*-pinonic acid m. 68°–69°.

d- and *l*-Camphene. M. 46°–47°, $[\alpha]_D$ +60° 14′ (in chloroform, c = 10).

When treated with benzoyl chloride, according to the method of Lipp, Küppers and Holl,[12] camphene yielded the benzoyl compound of borneol, which could be

[7] *Ann. fals.* **342** (1937), 284.
[8] *Ann. chim. anal.* Ser. 3, **23** (1941), 203. Cf. Naves, *Fette u. Seifen* **49** (1942), 187.
[9] *Parfumerie* **1** (1943), 235. Through *Chem. Abstracts* **40** (1946), 4480.
[10] *Helv. Chim. Acta* **28** (1945), 1220, 1231. [12] *Ber.* **60** (1927), 1578.
[11] *Ibid.*

identified by the preparation of its semicarbazone m. 210°–212° (mixed melting point determination).

l-Limonene and Dipentene. B_{728} 174°–175.5°; preparation of dipentene dihydrochloride m. 50°–51°, and dihydroiodide m. 78°–79°.

Ocimene and *Allo*-Ocimene. Also occur in lavandin oil.

According to Naves, the terpene fraction of lavandin oil consists of about 60% pinene, 20% camphene, 10% limonene and dipentene, and 10% ocimene and *allo*-ocimene (the latter originating probably during distillation *in vacuo*).

d-Camphor. M. 178°; isolated by means of its semicarbazone and identified as dinitro-2,4-phenylhydrazone m. 178° (mixed melting point determination).

d-Borneol. M. 205°–206°; identified as *p*-nitrobenzoate m. 135.5°–136°. According to Naves, the oil contains 2.3 per cent of borneol in free form, but none in esterified form.

l-α-Terpineol. $B_{3.8}$ 80°–84°; identified as nitrosochloride m. 108°, and as nitrolpiperidine m. 151°–152° (mixed melting point determination). According to Naves, the oil contains less than 1 per cent of terpineol.

l-Lavandulol. $B_{2.8}$ 64°–65°; identified as allophanate m. 120°–121°. According to Naves, the oil contains less than 0.1 per cent of lavandulol.

Nerol. Identified in the fraction $b_{2.8}$ 82°–86° by the preparation of the tetrabromide m. 117°–118° (mixed melting point determination).

l-Perillyl Alcohol. $B_{2.8}$ 88°–89°; characterized by oxidation to perillaldehyde (preparation of its semicarbazone m. 200°–201°—mixed melting point determination), and to perillic acid m. 133°–133.5°.

Linaloöl and Linalyl Acetate. Naves [13] isolated and purified linaloöl by its *p*-nitrobenzoate and observed $[\alpha]_D^{20}$ −20° 21′.

Linaloöl Oxide (Epoxylinaloöl) or Its Acetate. According to the same author,[14] lavandin oil contains free or esterified epoxylinaloöl. The acetate was separated quantitatively from the acetates of accompanying alcohols by the preparation of its complex with ferrocyanic acid. Two lavandin oils investigated by Naves contained 3.3 and 2.8 per cent of free epoxylinaloöl, and 4.2 and ca. 0.5 per cent of epoxylinalyl acetate, respectively.

In a publication preceding that of Naves, two other workers, viz., Sfiras and Vanderstreek,[15] had suggested the following quantitative composition of lavandin oil:

8% Terpenes.

Ocimene (3.4%).

d-Pinene.

Other unidentified terpenes.

[13] *Helv. Chim. Acta* **28** (1945), 1220.

[14] *Ibid.*, 1231.

[15] *Parfumerie* **1** (1943), 235. Through *Chem. Abstracts* **40** (1946), 4480. Cf. Sfiras, *Ind. parfum.* **3** (1948), 352.

8% Primary and Secondary Alcohols.
1-Octen-3-ol (ca. 0.7%).
One or two primary or secondary alcohols (0.1%).
Geraniol and its paragen (ca. 0.2%).
d-Borneol (7%).

44–45% Free Tertiary Alcohols.
Linaloöl (43–44%).
Terpineol or 4-terpinenol.
Sesquiterpene alcohols (1%).

24–25% Esters.
A volatile ester with amyl-like odor (trace).
1-Octen-3-yl acetate (0.1%).
Acetate of one or possibly two primary or secondary alcohols (0.1%).
Terpenyl(?) acetate (0.1%).
Linalyl formate (ca. 0.2%).
1-Octen-3-yl butyrate.
Linalyl butyrate.
Possibly geranyl acetate.
Another unidentified ester of geraniol and its paragen.
Linalyl acetate (ca. 22%).

12% Aldehydes and Ketones.
A volatile aldehyde (trace).
Amyl ethyl ketone (ca. 0.4%).
Aldehydes or ketones of which probably one is terpenic and one sesquiterpenic (0.1%).
Camphor (11–11.5%).

3–3.5% Oxides.
Cineole (re linaloöl oxide, see the above-cited investigation by Naves).

1–2% Sesquiterpenes.
A sesquiterpene of the caryophyllene group.

In 1944, Igolen[16] published the results of still another research on the chemical composition of lavandin oil:

4.5% Terpenes.
d-Pinene (4.5%).

4.4–6.8% Free Primary and Secondary Alcohols.
n-Hexanol (0.5%).
d-*n*-Octanol (0.6–1%).
Geraniol (0.3%).
Borneol (3–5%).
Sesquiterpene alcohols (1%).

43–44% Free Tertiary Alcohols.
Linaloöl (43–44%).

[16] George Igolen, Thèse doctorate, Marseille (1944), 65. Cf. Spiras, *Ind. parfum.* **3** (1948), 352.

23.5% Esters.
- Hexyl acetate (0.8–0.9%).
- *d*-*n*-Octyl acetate (0.27%).
- Butyric esters (traces).
- Caproic esters (traces).
- Linalyl acetate (20%).

8.1% Aldehydes and Ketones.
- Amyl ethyl ketone (1.6%).
- *d*-Camphor (6.5%).
- Diacetyl (traces).
- *n*-Hexanol (traces).
- *n*-Octanol (traces).
- Cuminaldehyde (traces).
- Furfural (traces).

4.8% Oxides.
- Cineole (4.8%).

0.5% Sesquiterpenes.
- Bisabolene (0.5%).

Traces of Phenols.
- Eugenol (traces).

Traces of Lactones.
- Coumarin (traces).

Traces of Free Acids.
- Acetic acid (traces).
- Butyric acid (traces).
- Caproic acid (traces).
- Unsaturated acids (traces).

Use.—Before 1930—which is to say, at a time when only small quantities of oil of lavandin were produced—the oil was used almost exclusively to cut lavender oils. Some buyers of oil of lavender always insist on lower prices on part of their suppliers than are current in production sections; it is principally for this reason that the reduction of lavender oil with lavandin oil has been practiced quite frequently.

Gradually, however, from 1930 to 1940, leading soapmakers became acquainted with the merits of oil of lavandin, and the oil was more widely used. In a number of cases, soapmakers substituted oil of lavandin for the more expensive oil of lavender in their formulas.

The strong and slightly camphoraceous odor of lavandin oil has even in some instances added to its desirability. Addition of linalyl acetate (synthetic), or of small quantities of benzyl acetate imparts a fresher and sweeter note to oil of lavandin.

In the years to come, it will be largely in the field of soapmaking that oil and concrete of lavandin will find their greatest outlet. As was said

previously, the increased production of the oil will serve all needs, and will stabilize the prices. Some application in the perfume field may be found for the decolorized concrete of lavandin, which not only has an excellent odor, but also high fixative qualities.

SUGGESTED ADDITIONAL LITERATURE

R. M. Gattefossé, "Industrial Cultivation of Lavandin," *La Nature* No. 2989 (1936), 461.

OIL OF SPIKE LAVENDER

(Oil of Spike)

Essence d'Aspic *Aceite Esencial de Espliego* *Spiköl* *Oleum Spicae*

Botany.—Spike or spike lavender, *Lavandula latifolia* Vill. (*L. spica* D.C.), resembles true lavender, but grows somewhat taller (80 to 90 cm.). The color of the flowers is grayish rather than bluish. The volatile oil contained in the flowers possesses an odor reminiscent of lavender, but harsher, more camphoraceous.

Habitat and Range.—Because of its 30 to 40 cm. deep root, spike lavender prefers alluvial soil; but as a relatively hardy plant it thrives well even in dry lime soil, on arid sun-exposed hills and slopes up to 700 m. altitude. Spike lavender flourishes wild and abundantly in certain sections of some of the temperate countries bordering the western Mediterranean, and particularly in Spain, Southern France, and, to a much smaller extent, in Italy and Dalmatia. Owing to the ample supply of wild growing plant material and the low price of the oil in normal times the plant is not cultivated in those countries. Today Spain supplies the bulk of spike oil; in fact, for about forty years that country has held practically a world's monopoly on the production of this oil. Spain's main producing regions are located in Cuenca, Guadalajara, Soria, Granada, Teruel, North Jaén, Albacete, Jaén, Murcia, Castellón, Southern Cuenca, and Northern Almeria, these regions being listed according to their importance as producing areas and according to the quality of oils originating from them. Details will be found under "Physicochemical Properties" of this oil. It remains problematic whether the difference in the quality of the oil is caused by botanical variations of the plants or by local conditions of soil, climate, and altitude. No detailed

botanical study of the *Lavandula latifolia* growing in Spain has of late been undertaken. Even if distinct varieties or forms should actually exist, the native collectors would never be able to differentiate between them sufficiently to gather only a particular variety. This, by the way, holds true of most Spanish aromatic plants.

Collection of the Plant Material.—As spike lavender flourishes in a wild state over wide areas of Spain's arid interior, remote from the cities and large villages, the collection of the plants presents considerable difficulties. The cutting of spike, like that of other aromatic plants, is a tedious, "back-breaking" task. Sturdy men and women must stoop for endless hours in Spain's burning summer sun (August and September) cutting the scattered herb with a sickle; they then must carry the heavy bundles until they can be transferred to donkeyback and carried for miles over steep paths to the nearest distillation post—all this at low wages. It has been possible only because of the general poverty, the lack of other work, and the low standard of living prevailing among Spain's rural population up to the Civil War, and to a large extent even today.

Distillation.—Since in Spain's interior good roads are nonexistent, the plant material cannot be carted or trucked to centrally located distilleries; in other words the distilling apparatus must be installed near the places where the plants grow, movable field stills of simple construction being employed for this purpose. Oil of spike, like most essential oils in Spain, is produced by large operators and exporters located in Sevilla, Barcelona, Malaga, and a few other cities. The organizing of a distillation campaign prior to the harvest imposes a problem which almost follows the pattern of strategy: careful selection of proper sites with an assured and abundant supply of plant material and access to water for distillation—not always readily available in Spain's arid interior; hiring of good, reliable labor, which cannot be regularly controlled and supervised; entrusting experienced, honest foremen with each post; and transporting of hundreds of stills, condensers, drums, etc., to the interior. All this requires most careful planning, lest the whole campaign be doomed to failure. The problem is aggravated by the fact that in many regions several distilling organizations compete for the flower supply, one outbidding the other when contracting with the harvesters in the small villages. And last, but not least, during normal times prices of Spanish essential oils have always been low and highly competitive.

Once a distillation post is established the foreman takes charge of it; he must be provided with sufficient funds to pay cash for the arriving plant material, after it has been weighed. Upon his honesty and experience the exporter has to depend; the foreman controls the yield of oil and can easily



Courtesy of Fritzsche Brothers, Inc., New York.

Field distillation of spike lavender oil in Spain.

deceive his employer, who visits the distillation post only once or twice, when making his rounds during the campaign.

The crew camps for weeks or months near the stills, sleeping under a shed without any conveniences or distractions. The work goes on day and night, without interruption, as huge quantities of plants must be processed during the height of the season. Four men handle the work of one post.



Courtesy of Fritzsche Brothers, Inc., New York.

Field distillation of essential oils in Spain.

One distillation post consists usually of two stills; while one is in operation, the other one is being emptied of exhausted plants and recharged with fresh material. The stills are of simple construction, made of sheet iron, 2 m. high and 1.2 m. wide in the case of spike lavender, rosemary, sage and thyme, each holding from 30 to 40 arrobas (1 arroba = 11.5 kg. or about 25 lb.) of plant material. In the case of eucalyptus, origanum, pennyroyal, and rue, the stills are 2 m. high and 1.6 or 1.8 m. wide, holding 70 to 90 arrobas of plant material. They are half imbedded in the ground, usually on a slope, with a "firebox" dug into the ground beneath the still. Spent and sun-dried plant material serves as fuel. A perforated grate inserted 15 cm. above the still bottom prevents "burning" of the plants due to direct contact with the lower still walls surrounded by open flames. The condenser, usually a long pipe, is sunk into a brook or waterhole. After being dried for some time in the sun, the plant bundles are charged into the

still, tramped down, and sufficient water (200 liters or more) is poured into the still to fill the space between still bottom and grid.

The time of charge lasts 30 minutes, and another 30 minutes are required to get the steam up and start actual distillation, which ends after 2 hr. Thus complete distillation of one charge requires 3 to 4 hr. in the case of spike lavender, rosemary, and sage, when 100 to 120 liters of water have distilled over; 5 to 6 hr. with thyme when 140 to 180 liters of water have come over; 6 hr. with eucalyptus, rue, and pennyroyal, when 200 to 240 liters of water have distilled over; and 9 hr. in the case of origanum, with 240 to 300 liters of distillation water. The length of distillation depends upon the intensity of the fire, the efficiency of the condenser, and the condition of the plant material (fresh or dried). Distillation completed, the still is emptied and recharged. Two to six charges, according to the plant material, can thus be completed within 24 hr. The oil is collected in a simple separator, decanted from the distillation water and collected in drums which, when filled, are transported to the nearest village and from there to the warehouses or the exporters in town. The task of the latter is to filter and analyze the oils and make up bulkings for the export trade.

Yield of Oil.—Ten arrobas or 115 kg. of spike plants yield on the average 1 kg. of oil (about 0.88 per cent), the yield varying considerably with seasonal and weather conditions.

It is quite possible that this yield could be increased in more efficient stills—in direct steam stills, for instance. Studying the effects of direct steam distillation and water distillation on French spike plants Schimmel & Co.[1] obtained a yield of 1.1 per cent in the first and only 0.98 per cent in the second case.

The explanation is probably that, in the present-day Spanish stills, the lower part of the plant charge often becomes soaked with water, especially when the stills are not provided with grids and not insulated (as is frequently the case in Spain). The plant charge agglutinates, especially toward the bottom, forming a heavy mass through which the steam can no longer penetrate uniformly, and therefore forms channels. It is then very difficult, if not impossible, to exhaust the material with low pressure steam. The relatively long time (3 hr.) required for one charge in the Spanish stills seems to lend support to this theory, lavender plants being exhausted in France with direct steam in less than 1 hr. The method employed in Spain is actually a "water *and* steam distillation" which gives good results only if the plant material is separated completely by a grid from the boiling water beneath.[2] If not properly carried out, the method suffers from

[1] Cf. Gildemeister & Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 670.
[2] Cf. Vol. I of this work, pp. 120, 147.

the drawback of frequently incomplete exhaustion and low yield. The advantage of water *and* steam distillation, on the other hand, lies in the better solubility of the oils, and in fact Spanish spike oils show good solubility.

Physicochemical Properties.—As has been pointed out, Spanish spike oils may be classified into three groups, distinguished by their properties:

1. Best quality, distilled in Cuenca, Guadalajara and Soria, i.e., chiefly at high elevation in the interior provinces.
2. Medium quality, distilled in Granada, Teruel, North Jaén, and Albacete.
3. Inferior quality, distilled in Jaén, Murcia, Castellón, Southern Cuenca, Northern Almeria, i.e., mostly at lower elevation in the provinces along the eastern coast of Spain.

Genuine oils distilled under the author's [3] supervision in various parts of Spain had the properties given in Table 2.4.

TABLE 2.4

No.	Place of Distillation and Province	Specific Gravity at 15°/15°	Optical Rotation	Solubility in 65% Alcohol at 20°	Total Alcohol Content (%)	Ester Content (%)
1	Guadalajara	0.901	−2° 56′	In 3 vol.	40.6	2.6
	Palomera, Best Quality of Cuenca	0.900	−4° 35′	In 3.5 vol.	37.5	2.0
	Ditto	0.901	−4° 54′	In 3.5 vol.	37.8	2.4
	Campillo, Regular Quality of Cuenca	0.908	−1° 53′	In 4 vol.; turbid with more	32.6	2.3
2	Huetor Santillon, Best Quality of Granada	0.905	−2° 18′	In 3 vol.	35.6	1.8
	Granada, Regular Quality	0.904	−2° 20′	In 3 vol.	36.7	2.1
3	Moral (Canada de la Cruz), Murcia	0.908	+0° 34′	In 3 vol.	35.7	2.7
	Regular Quality of Murcia	0.908	−1° 6′	Clearly soluble in 4 vol. 65% alc. at 25°; not perfectly clear in 4.5 vol. at 20°; cloudy with more	32.6	2.4

Spanish spike oils of best quality possess the following properties:

Specific Gravity at 15°/15° ..... 0.900 to 0.905
Optical Rotation ..... Inactive or laevorotatory, up to −7° 30′

[3] "Spanish Essential Oils," *Am. Perfumer* **24** (1929), 161.

Total Alcohol Content, Calculated as Linaloöl	35 to 40%
Solubility	Soluble in 3 vols. of 65% alcohol, and more

Oils of lower quality vary within these limits:

Specific Gravity at 15°/15°	0.910 to 0.920
Optical Rotation	Slightly dextrorotatory, up to +8°
Total Alcohol Content Calculated as Linaloöl	About 30%, in some cases as low as 25%
Solubility	Soluble in 2 vol. of 70% alcohol

Better solubility, a lower specific gravity, and a higher laevorotation indicate a better quality of oil.

Shipments of genuine Spanish spike lavender oils received during the past years and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 15°/15°	0.899 to 0.911
Optical Rotation	−7° 25′ to +1° 9′ (in most cases −3° 0′ to ±0°; seldom dextrorotatory)
Refractive Index at 20°	1.4624 to 1.4679
Total Alcohol Content, Calculated as Linaloöl	34.0 to 38.5%
Ester Content, Calculated as Linalyl Acetate	1.8 to 3.3%
Solubility (Best Grade of Oils)	Soluble in 3 to 4.5 vol. of 65% alcohol; clear to opalescent with more

Adulteration.—Adulteration of Spanish spike oils is a frequent practice, the result chiefly of unreasonable price demands on the part of buyers. A great variety of adulterants—e.g., steam distilled pine oil, fractions from the manufacture of terpineol, fractions of Spanish sage oil, eucalyptus, and camphor oil—permit the sophistication of spike oil in such a way that it still meets routine analytical tests.

Total Production of Spanish Spike Oil.—From 1928 to 1936 the total production of Spanish spike oil fluctuated between 80 and 125 metric tons yearly; the outbreak of the Civil War in Spain, however, reduced this quantity to about 20,000 kg. in 1937 and 12,000 kg. in 1938. In 1946 Spain produced 175 tons of spike oil, and 95 tons in 1947. In 1948 the total was 50 metric tons. Due to the decreased production in Spain during the Civil War, France again started to distill spike oil, supplying from 18,000 to 20,000 kg. in 1938. Under normal conditions, however, the French oil cannot compete successfully with the Spanish product.

Chemical Composition.—The first investigation on the chemistry of spike oil, which dates back more than a century, revealed the occurrence of camphor. More complete studies were made by Bouchardat,[4] and Voiry and Bouchardat.[5] The presence of the following constituents has been established: *

d-Camphene. Passing gaseous hydrogen chloride through a small (0.20–0.25 per cent) fraction, b. ~160°, these authors obtained a hydrochloride m. 129°. The latter could be reconverted into *d*-camphene which congealed at low temperature.

d-α-Pinene(?). Bouchardat expressed the opinion that the solid hydrochloride consisted partly of pinene hydrochloride.

Cineole. The fraction b. ~175° amounted to about 10 per cent of the oil and consisted of cineole. This was confirmed by the preparation of the dibromide.

According to Tedesko,[6] Spanish spike oils contain from 28.5–35.4 per cent of cineole (method of Kleber and von Rechenberg).

l-Linaloöl. The fraction b. ~200° consists of a mixture of *l*-linaloöl, *d*-camphor, and *d*-borneol. Linaloöl b. 198°–199°, α_D −16° 44′, was converted into geranyl acetate by boiling with acetic acid anhydride.

d-Camphor. The presence of camphor in spike oil was first reported by Kane,[7] later confirmed by Lallemand,[8] Bruylants,[9] and by Bouchardat.[10] The oxime prepared from the camphor of spike oil possessed all the characteristics of regular camphor oxime.

It is interesting to note, in this connection, that camphor is a normal constituent of spike oil but does not seem to occur in true lavender oil. Any commercial lavender oil showing the presence of camphor may, therefore, be suspected as adulterated with spike oil.

d-Borneol. This compound was identified in spike oil first by Bruylants [11] and later by Bouchardat. Separated from camphor by the action of benzoic acid anhydride.

Terpineol(?). When passing gaseous hydrogen chloride through the fraction possessing a boiling point similar to that of terpineol, Bouchardat [12] obtained dipentene

[4] *Compt. rend.* **117** (1893), 53, 1094.

[5] *Ibid.* **106** (1888), 551.

* In a report published after this volume had gone to press, Girard [*Ind. Parf.* **4** (1949), 249] announced the occurrence in oil of spike of *1-hexanol* (at least 0.03 to 0.04 per cent), *coumarin* (at least 0.05 per cent), and *formic acid* (at least 0.01 to 0.02 per cent). All three substances are present in the free state. Girard promises to continue the investigation of this oil.

[6] *Rivista ital. essenze profumi* **9** (1927), 197.

[7] *J. prakt. Chem.* **15** (1838), 163.

[8] *Liebigs Ann.* **114** (1860), 198.

[9] *J. pharm. chim.* [4], **29** (1879), 508; **30** (1879), 33, 138. *Chem. Zentr.* (1879), 616.

[10] *Compt. rend.* **117** (1893), 53, 1094.

[11] *J. pharm. chim.* [4], **29** (1879), 508; **30** (1879), 33, 138. *Chem. Zentr.* (1879), 616.

[12] *Compt. rend.* **117** (1893), 53, 1094.

dihydrochloride. Yet, the parent product which gave rise to the formation of dipentene dihydrochloride need not necessarily be terpineol, as this dihydrochloride may have been formed also from linaloöl or geraniol. The presence of geraniol, however, has not been definitely established in spike oil.

A Sesquiterpene(?). Analysis of the highest boiling fraction b. 250° pointed toward the presence of a sesquiterpene of the empirical molecular formula $C_{15}H_{24}$.

Rutovski and Makarova-Semilyanskaya [13] investigated two samples of spike oil (*Lavandula spica* D.C.) distilled in Suchum (Caucasus) and found that they contained 12.4 per cent and 25.5 per cent of camphor, and 56.2 per cent and 36 per cent of cineole (by resorcinol method). In the second sample the same authors identified furthermore α-pinene, linaloöl, and borneol.

Use.—Oil of spike lavender is widely used for the scenting of soaps. Since the odor of this oil is more camphoraceous, harsher, and stronger than that of lavender oil, it gives especially good results in lower priced types of soaps.

Spike oil finds use also in many cosmetic and technical preparations—bath salts, room sprays, disinfectants, etc. In general it represents a low priced substitute for lavender oil.

Suggested Additional Literature

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Y. R. Naves and B. Angla, "Identification of Essential Oils by the Effect of Solvents on Their Rotatory Powers," *Compt. rend.* **213** (1941), 570. Chem. Abstracts **37** (1943), 3877.

"Oil of Spike Lavender (Aspic)," *U. S. Dept. Commerce, Bur. Foreign and Domestic Commerce, Ind. Reference Series*, Pt. 2, Vol. 4, No. 28 (February 1946).

[13] *Riechstoff Ind.* **3**, No. 4 (1928), 28. *Trans. Sci. Chem.-Pharm. Inst. U.S.S.R.* No. 19 (1928), 174.

OIL OF *LAVANDULA BURMANNI* BENTH.

Botany and Origin.—The plant grows wild in India. Not exploited commercially.

Properties.—Leaf oil: d_{15}^{15} 0.9131, α_D −0° 40′, A.N. 9.9, E.N. 36.3, soluble in 1.5 and more vol. of 70% alcohol. Odor, citral-like (oil distilled in Bangalore, India, analyzed by Schimmel & Co.).

Blossom oil: d_{15}^{15} 0.9309, α_D + 1° 40′, A.N. 1.9, E.N. 115.7, soluble in 1.5 vol. and more of 80% alcohol. Odor, fenchone-like (oil distilled in Bangalore, India, analyzed by Schimmel & Co.).

Composition.—The blossom oil contains *fenchone.*

LITERATURE

Ber. Schimmel & Co., October (1913), 110. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 683.

OIL OF *LAVANDULA DENTATA* L.

Botany and Origin.—The plant grows wild in coastal regions of the Mediterranean basin (Spain, Morocco, Algeria, perhaps Italy, not in France). The oil is not produced commercially.

Physicochemical Properties.—d_{15}^{15} 0.9317 and 0.9340, α_D −39° 40′ and −40° 0′, n_D^{20} 1.47099 and 1.47058, Acid Number 2.8 and 3.3, Ester Number 101.7 and 108.8 (= 35.6% and 38%, calculated as linalyl acetate), soluble in 3.5 and more volumes of 70% alcohol (two oils distilled in Spain and analyzed by Schimmel & Co.).—Note the high ester content and the high laevorotation of these two oils!

d_{15}^{15} 0.9434, α_D + 1° 14′, n_D^{20} 1.46717, Acid Number 1.1, Ester Number 7.5; soluble in 0.5 and more volumes of 80% alcohol, opalescent on further dilution (oil of English origin, analyzed by Schimmel & Co.).

The odor of oil of *Lavandula dentata* recalls that of *Lavandula stoechas,* of hyssop, and cineole.

Chemical Composition.—*Cineole, a ketone* (semicarbazone m. 224°) of minty, camphoraceous odor which is perhaps pinocamphone, and *a strongly laevorotatory alcohol* α_D −115° 50′.

LITERATURE

Ber. Schimmel & Co. (1938), 55. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 683. *Sci. Ind. Bull. Roure-Bertrand Fils* [4], **4** (October 1921), 3.

OIL OF *LAVANDULA PEDUNCULATA* CAV.

According to Costa,[1] *Lavandula pedunculata* Cav. grows wild in Portugal and resembles *L. stoechas* L. in regard to the composition of its essential oil. Distilling the flowering heads of the fresh plants Costa obtained 0.21 per cent of an oil which had these properties:

Specific Gravity at 15°/4°	0.9354
Specific Optical Rotation at 19°	+19° 57′
Refractive Index at 20°	1.46913

The oil contained:

11.63% free alcohol, calculated as borneol
3.28% esters, calculated as bornyl acetate
59.50% ketones,
and

pinene	camphor
camphene	cineole

Thujone and linaloöl were absent

Studying the aromatic flora of Morocco, Gattefossé and Igolen [2] reported that the fresh flowers of *Lavandula pedunculata* Cav. var. *Atlantica* Braun-Blanquet gave 0.135 to 0.250 per cent of an oil which had the following properties:

Specific Gravity at 15°	0.9489
Optical Rotation at 20°	−16° 0′

[1] *Noticias Farm. Portugal* **5** (1939), 438. *Chem. Abstracts* **34** (1940), 4226.
[2] *Compt. rend.* **214** (1942), 885. *Chem. Abstracts* **38** (1944), 3777.

Refractive Index at 20°	1.4784
Acid Number	4.2
Ester Number	13.30
Ester Number after Acetylation	63.13

The oil contained:

carvacrol
β-pinene
cineole
l-borneol (free and in ester form)
l-camphor (large amount)
l-cadinene
a solid compound m. 109°

In the opinion of these authors, the content of *l*-camphor, quite rare in essential oils, is remarkably high.

An oil of *Lavandula pedunculata* distilled in Portugal years ago, and analyzed by Schimmel & Co.[3] had these properties:

Specific Gravity at 15°	0.939
Optical Rotation	−44° 54′
Saponification Number	111.7
Ester Content, Calculated as Linalyl Acetate	39%
Solubility	Soluble in equal vol. of 80% alcohol

The odor of this oil was reminiscent of cineole and thujone, not very pleasant.

Oil of *Lavandula pedunculata* Cav. has not attained any commercial importance.

OIL OF *LAVANDULA STOECHAS* L.

Botany and Origin.—According to Camus[1] *Lavandula stoechas* L. is a xerophilous plant which grows wild in arid coastal sections bordering the Mediterranean, particularly in Spain and Southern France (Esterelle Mountains). In Spain the plant is called "Romero santo" or "Cantueso." *L. stoechas* also occurs in Southern Australia, near Burnside.[2] Depending upon the condition of the plant material, yields of 0.32 to 0.75 per cent of volatile oil have been obtained (from whole overground plants and from dried flowering tops).

[3] *Ber. Schimmel & Co.*, October (1898), 33.
[1] *Sci. Ind. Bull. Roure-Bertrand Fils* [4], **4** (Oct. 1921), 3.
[2] *Perfumery Essential Oil Record* **23** (1932), 411.

Physicochemical Properties.—*L. stoechas* L. possesses a strong camphoraceous, rather harsh odor reminiscent of spike lavender and rosemary. It differs considerably from that of true lavender (*Lavandula vera*).

An oil of *L. stoechas* distilled by Schimmel & Co.[3] from dried Spanish flowers (yield 0.755 per cent) had these properties:

Specific Gravity at 15°	0.9620
Optical Rotation	+35° 30′
Refractive Index at 20°	1.47909
Acid Number	5.16
Ester Number	13.1
Ester Number after Acetylation	67.9
Solubility	Soluble in 2 vol. of 70% alcohol; opalescence and separation of paraffins on dilution

The same authors reported the following properties for oils distilled in Spain and Southern France:

Specific Gravity at 15°	0.9420 to 0.9531
Optical Rotation	+32° 6′ to +44° 46′
Refractive Index at 20°	1.46842 (one determination)
Acid Number	1.4 to 1.8
Ester Number	12.7 to 24.1
Solubility	Soluble in ca. 2 vol. of 70% alcohol; slight opalescence on dilution

Roure-Bertrand Fils[4] advanced these properties as representing French oils of good quality:

Specific Gravity at 15°	0.945 to 0.962
Optical Rotation	+35° 30′ to +47° 0′
Acid Number	0.93 to 5.16
Ester Number	13.1 to 17.74
Ester Number after Acetylation	47.14
Solubility	Soluble in 5 vol. and more of 60% alcohol

The oils should contain about 80 per cent of ketones (*d*-camphor and *d*-fenchone). Oils also contain fenchyl alcohol, probably terpineol, and a phenolic compound of unknown constitution.

[3] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 681. *Ber. Schimmel & Co.*, October (1905), 40.

[4] *Roure-Bertrand Fils. Sci. Ind. Bull.* [4], 4 (October 1921).

Dorronsoro [5] examined two oils distilled in Spain:

	Granada	*Malaga*
Specific Gravity	d_{16} 0.9485	d_{15} 0.9470
Optical Rotation	+36° 10′	+45° 44′
Refractive Index	1.4678	1.4682
Ester Number	20.95	13.43
Ester Content, Calculated as Bornyl Acetate	7.33%	4.72%
Ester Number after Acetylation	32.4	...
Total Alcohol Content, Calculated as Borneol	9.13%	...
Free Alcohol Content, Calculated as Borneol	3.18%	...
Solubility	Soluble in 2.6 vol of 70% alcohol; soluble in 1.5 vol. of 80% alcohol; soluble in 90% alcohol	Soluble in 1.5 vol. of 70% alcohol; soluble in 1 vol. of 80% alcohol; soluble in 90% alcohol

Rovesti [6] investigated two Italian oils:

	Argentina Valley	*San Lazzaro Reale*
Specific Gravity at 15°	0.9541	0.9427
Optical Rotation	+21° 41′	+18° 54′
Refractive Index at 20°	1.4794	1.4810
Acid Number	1.4	0.88
Ester Number	28.2	10.3
Ester Content, Calculated as Linalyl Acetate	9.85%	7.1%(?)
Free Alcohol Content	6.53%	6.57%
Total Alcohol Content	14.28%	12.1%(?)
Solubility	Soluble in 2.2 vol. of 70% alcohol	Soluble in 2.1 vol. of 70% alcohol

The oils investigated by Rovesti [7] contained fenchone and camphor.

Distilling the herb of *Lavandula stoechas* in Sardinia, Puxeddu [8] obtained two oils (yield 0.4 per cent and 0.32 per cent) which exhibited these properties:

Specific Gravity at 20°	0.9497	0.9450
Optical Rotation at 20°	+12° 46′	+19° 9′
Refractive Index at 20°	1.4676	1.4687
Acid Number	0.8	
Saponification Number	20.9	

[5] *Mem. acad. cienc. Madrid* **29** (1919). Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 681.

[6] *Profumi italici* **3** (1925), 218.

[7] *Ibid.*

[8] *Ann. chim. applicata* **15** (1925), 161, 166.

Ester Content, Calculated as Bornyl Acetate	7.07%
Saponification Number after Acetylation	69
Free Alcohol Content	13.45%
Total Alcohol Content	19%
Solubility in 80% Alcohol	Soluble in 1 vol.

Chemical Composition.—The above named authors established the presence of the following compounds in the oil of *Lavandula stoechas* L.:

d-Camphor. M. 175°-175.5°; identified by means of its oxime m. 117°–118°, and of its semicarbazone m. 231°. (Schimmel & Co.)

d-Fenchone. Identified by preparation of its oxime m. 165°. (Schimmel & Co.) The same components were observed by Rovesti, and by Roure-Bertrand Fils. The chemists of the last named firm expressed the opinion that the oil contains also

Fenchyl Alcohol(?).

Terpineol(?) and a Phenol(?).

Cineole. The presence of cineole was proved by Dorronsoro.

Use.—Oil of *Lavandula stoechas* L. has not attained any commercial importance.

OIL OF *LAVANDULA VIRIDIS*

Distilling the fresh flowering tops of *Lavandula viridis,* which grows wild in Portugal, Costa and do Vale [1] obtained 0.5 to 0.8 per cent of essential oil which had these properties:

Specific Gravity at 14°	0.9239
Specific Optical Rotation at 14°	+2° 56′
Refractive Index at 13°	1.4745

On closer examination the oil was shown to consist of:

	Per Cent
Terpenes (α-Pinene, Camphene, etc.)	20
Cineole	30
Alcohols (Borneol and Geraniol)	26

[1] *Bol. escola farm. univ. Coimbra Portugal* **5** (1945), 1. *Chem. Abstracts* **42** (1948), 3908.

	Per Cent
Esters	5
Aldehydes	...
Ketones (Camphor)	5
Unidentified Compounds	14

The oil has not attained any commercial importance.

OIL OF MARJORAM

Essence de Marjolaine *Aceite Esencial de Mejorana* *Majoranöl*
Oleum Majoranae

Introduction.—There exists some confusion in regard to the so-called marjoram oils and the botany of the plants from which these oils are derived. The vernacular term "marjoram" comprises several aromatic plants belonging to different species. The best known is undoubtedly *Origanum majorana* L. (fam. *Labiatae*) which grows wild as a perennial herbaceous shrub on sunny hillsides of Southern Europe and North Africa; it is cultivated extensively as sweet marjoram (*Majorana hortensis* Mnch.), an annual herb, in Central Germany, Hungary, Southern France, Tunisia, and lately also in the United States. The French term *marjolaine* includes also *Origanum vulgare* L., which grows wild in Mediterranean countries, but is not actually used for oil distillation.

The United States has for some years been importing from Spain an essential oil labeled "Oil of Marjoram" or "Wild Marjoram Oil." This oil is distilled from *Thymus mastichina* L. (fam. *Labiatae*), the Spanish *mejorana silvestre* or *tomillo blanco,* which grows wild in Southern Spain, particularly around Granada and Malaga. The chemical composition of this oil is entirely different from that of sweet or garden marjoram, its odor being harsher, and cineole-eucalyptus-like.

For clarity's sake, we shall in the following pages refer to the two oils as sweet marjoram and Spanish wild marjoram.

Oil of Sweet Marjoram

Description.—Sweet marjoram (*Majorana hortensis* Mnch.) grows in bunches or tufts 8 to 16 in. high. The flowers are small, greenish white:

the seeds oblong, very fine and dark brown in color; the leaves small, oval, whitish, and soft. Because of their strong, highly aromatic, spicy and pleasing odor and flavor, the dried leaves are widely used as a condiment for seasoning soups, dressings, stews, and especially certain types of sausage. Steam distillation of the leaves yields the volatile oil.



Courtesy of Bureau of Plant Industry, Soils & Agricultural Engineering, United States Department of Agriculture.

Marjoram plant.

Habitat and Range.—Marjoram is primarily a warm climate plant and, as such, rather sensitive to cold. Yet it is hardy enough to grow in cooler regions, provided the plants are well mulched with straw or leaves for protection against winter killing or, still better, grown as an annual crop and planted anew each season.

Sweet marjoram thrives well in fertile garden soils sufficiently loose for the very small seed to germinate and the tender little plants to penetrate the crust of earth formed by rain. Great care must be taken to select loose soil, or much of the planted seed will be lost. The ground should be well drained, exposed to ample sunlight, fertilized, and irrigated. Although the plant resists drought, prolonged periods of dryness are harmful.

The climate seems to exercise considerable influence upon the shape of the plants, those cultivated in Tunis growing sometimes more than 3 ft. high.

The leaf material of finest quality originates from Central Germany (Aschersleben, Province of Saxony) simply because the German growers do not permit the plants to go to seed. It should be noted that the seed is aromatic, containing volatile oil, for which reason it is employed in confectionaries and French confitures. When the plant is cut before the formation of seed, all its volatile oil is contained

in the leaves, for which reason the German marjoram leaves are much more fragrant and free of seed aroma. Prior to World War II the German growers used to purchase their seed material from French seed houses, which consider the dried leaves more or less a by-product, their chief aim being the production of seed for the many small farmers and gardeners who raise marjoram as a culinary garden crop.

Planting and Cultivating in Germany.—Before World War II, the region around Aschersleben, Germany, produced yearly 800 to 1,000 metric tons of dried marjoram herb. These figures represent the weight of the dried leaves after removal of the stalks, and correspond to about ½ the weight of the freshly cut plants.

In April the seed is sown with drills directly in the fields. The plants grow very densely in the rows which are spaced 8 to 9 in. apart. The depth of the drills is less than that employed for dill (*Anethum graveolens*). The plants must be resown every spring. Cutting takes place in August and September. The cut plant material is carefully dried, stalks, dust and sand are removed, and the dried leaves marketed for culinary purposes. The so-called "distillers' quality" consists of material which is not as carefully purified, containing also chaff and some stalks.

Planting and Cultivating in Hungary.—Sweet marjoram is grown by the peasants of Hungary in many localities, and usually on small lots. The center of this industry lies near Kalocsa, a town about 120 km. south of Budapest. In 1935 more than 20,000 kg. of dried marjoram leaves were exported from Hungary.

The seed is sown in hotbeds. Toward the end of April the young plants are transplanted, 25 cm. apart, in rows 30 cm. distant. Six to eight young plants are usually planted together. About a week after transplanting the field is hoed for the first time, a practice repeated every three or four weeks.

The first harvest takes place at the end of June, when the plants are cut 1 to 2 cm. above the ground. The second harvest is at the beginning of August; if possible, a third one takes place toward the end of September.

The cut plant material is spread out in well-ventilated barns and dried, so that the leaves come off easily. The leaves are then separated from the stalks by rubbing them on hand sieves of 1 to 2 cm. mesh. Subsequently, the leaves are fanned and shaken in wide meshed sacks, to remove all adhering sand, earth, seed, and dust.

Planting and Cultivating in France.—France has always preferred to cultivate sweet marjoram in the south, since plants grown too far north do not ripen to the point of seed production in which France is mainly interested. Producing regions are located around St. Rémy-en-Provence (Département Bouches-du-Rhône), and also in the Département Vaucluse.

Seeds are selected from the best plants and sown in nurseries; when the young plants are sufficiently strong, they can be transplanted. Frequent weeding, hoeing, and watering is necessary. The harvest takes place in August–September.

Planting and Cultivating in Tunis.—In recent years, Tunis has become an important producer of sweet marjoram. In fact, most of the dried leaf material used in France as condiment, or for distilling, originates from Tunis. Around Bizerte the plants grow in almost a wild state, but the most important plantings are located near the large olive orchards of Sfax. Marjoram leaves grown for the purpose of distillation should be cut when in full bloom. Therefore, in Tunis the plants are gathered during the early part of May, when the flowers begin to open; a second cutting is made in July.

Planting and Cultivating in the United States.—According to Crooks and Sievers,[1] sweet marjoram, a warm climate plant, makes good growth also in cooler regions, but is easily affected by frost. Therefore, it is preferably grown as an annual, for which purpose the very small seed is best started in the greenhouse, the seedlings to be transplanted to the fields after all danger of frost has passed. Propagation by cuttings is also entirely practical. Marjoram can be grown in many sections of the United States—as an annual in the Northern States and as a perennial or annual in the Southern States and on the West Coast. The fact must not be overlooked, however, that marjoram is a comparatively small crop and, according to Crooks and Sievers, less than 100 acres would probably be sufficient to meet annual domestic requirements. For years the United States has been receiving shipments of Spanish marjoram oil distilled from plants growing wild in Andalusia. Should these shipments be stopped for some reason, the United States food industry would probably resort to sweet marjoram oil produced domestically, in which case the acreage might be considerably increased. (About planting and harvesting, see also Bulletin No. 4, The Herb Society of America, Boston, Mass., March 1944.)

Drying and Preparation for Market.—The proper drying of sweet marjoram leaves is quite a delicate task, especially if a carefully selected and well-cleaned quality, of good color, is to be delivered. Best results are obtained in drying sheds; direct exposure to the sun tends to break the stalks and make the leaves brittle. Care must be taken also to exclude rain or dew while the leaves are being dried. Only under these conditions is it possible to preserve the original green tint of the leaves. If exposed to direct sunlight, the plants dry in two to four days; in well-ventilated drying sheds, the process lasts about one week.

To detach or strip the dried leaves from the stalks, stone rollers are often used in France, or the entire plants are beaten. The leaves and seeds are

[1] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941).

then shaken in a sieve in order to remove the seeds. Foreign matter is picked out by hand.

Crooks and Sievers [2] mention that under certain conditions some herb can be cut from the plants several times during the summer. However, there appears to be no practical way of harvesting marjoram other than by cutting the entire plant at the ground and drying the herb. If only moderate amounts are handled, the plants can be hung from poles or rails in a convenient building where they can dry thoroughly. For large acreages a more practical way would have to be found. The plants could be packed close together on trays stacked to permit good circulation of air. When the herb is dried, the small stems with the leaves are removed from the more woody parts by any practical means that can be devised. Crooks and Sievers believe that most of the desired parts of the plants can be obtained by flailing or threshing.

Yield of Leaves per Acre.—According to information obtained by the author in Hungary, 1.422 acres yield 300 to 400 kg., and in rare cases 500 kg., of cleaned and dried marjoram leaves. Crooks and Sievers indicate for the United States a possible yield of about 2,000 lb. of herb material per acre.

Distillation.—Live steam generated in a separate steam boiler is blown through the dried leaf material packed into a still and the volatile oil collected. Experimenting in Southern France, the author observed 0.4 per cent of oil from fresh French sweet marjoram herb, 0.8 per cent from dried French and German herb, and 2.25 per cent from dried Tunisian plant material. The Hungarian distillers obtain 0.53 to 1.93 per cent; an average yield is about 1 per cent of oil from the dried herb. Gildemeister and Hoffmann [3] indicate a yield of 0.3 to 0.4 per cent for fresh, flowering herbs and a yield of 0.7 to 3.5 per cent for dried herb material.

Physicochemical Properties.—Genuine oils of sweet marjoram distilled in France from dried herb material and analyzed by Fritzsche Brothers, Inc., New York, had properties which varied within the following limits:

Specific Gravity at 15°/15°	0.892 to 0.901
Optical Rotation	+14° 2′ to +19° 40′
Refractive Index at 20°	1.4707 to 1.4738
Acid Number	1.4 to 2.8
Saponification Number	32.7 to 40.1
Ester Number after Acetylation	81.2 to 86.8
Solubility	Soluble in 1 to 2 vol. and more of 80% alcohol

When treated with potassium hydroxide test solution, less than 1 per cent of the oil was found to be soluble. The alkali soluble material was tested

[2] *Ibid.*
[3] "Die Ätherischen Öle," 3d Ed., Vol. III, 737.

for phenols, both by odor and by the ferric chloride test, and was found to contain no phenols.

According to Gildemeister and Hoffmann,[4] the properties of sweet marjoram oil vary within these limits:

Specific Gravity at 15°/15°	0.894 to 0.910
Optical Rotation	+15° 0′ to +25° 0′
Refractive Index at 20°	1.470 to 1.476
Acid Number	Up to 1.5
Ester Number	10.0 to 38.0
Ester Number after Acetylation	41.0 to 78.0
Solubility	Soluble in 1 to 2 vol. and more of 80% alcohol

Janicsek [5] reported for Hungarian sweet marjoram oil the following properties:

Specific Gravity at 15°	0.9099 to 0.9164
Optical Rotation	+13° 25′ to +32° 24′
Refractive Index at 20°	1.4653 to 1.4821
Ester Number	30.94 to 60.07
Solubility	Soluble in 10 to 40 vol. of 70% alcohol

Chemical Composition.—The investigation of Beilstein and Wiegand [6] did not give a sufficiently clear picture of the chemistry of marjoram oil. Biltz,[7] and later Wallach and Boedecker [8] identified the following compounds:

Terpinene. According to Biltz,[9] oil of marjoram contains about 40 per cent of terpenes, mainly terpinene. Identified as nitrosite m. 155°–156°.

d-α-Terpineol. In the fraction b. 215°–218°. Oxidation with potassium permanganate gave trihydroxyhexahydrocymene m. 129°–130°.

Terpinen-4-ol. According to Wallach,[10] the terpineol contained in marjoram oil consists mainly of an isomer, viz., the dextrorotatory terpinen-4-ol. Oxidation with dilute potassium permanganate solution yields a glycol m. 128°–129°, viz., *p*-menthane-1,2,4-triol.

The alcohols occur in marjoram oil mainly in the free state and only to a small extent as esters.

[4] *Ibid.*

[5] *Beiträge zur Beurteilung der Majoran-Gewürzwaren, a Magyar Gyogyszerésztud. Tarsaság Ertesitöje* (1931), No. 5. Private communication from Dr. Jules de Bittera, Budapest.

[6] *Ber.* **15** (1882), 2854.

[7] Inaugural Dissertation, Greifswald (1898). *Ber.* **32** (1899), 995.

[8] *Liebigs Ann. Chem.* **350** (1906), 169; **356** (1907), 206. *Ber.* **40** (1907), 596.

[9] Inaugural Dissertation, Greifswald (1898). *Ber.* **32** (1899), 995.

[10] *Liebigs Ann. Chem.* **350** (1906), 169; **356** (1907), 206. Ber. **40** (1907), 596.

Oil of Origanum Majorana

According to Sorgonà Luisi,[11] the physicochemical properties of marjoram oil (*Origanum majorana* L.) distilled from the whole plant, during 1939 in Calabria, had these properties:

Specific Gravity	0.8840 to 0.8960
Optical Rotation	+12° 0′ to +15° 24′
Refractive Index	1.4730 to 1.4805
Saponification Number	8.50 to 19.96
Ester Content, Calculated as Linalyl Acetate	2.77 to 6.24%
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	32.40 to 41.31%
Solubility	Mostly insoluble in 80% alcohol, soluble in 0.8 to 1.2 vol. of 85% alcohol, opalescent in 8 vol. of 85% alcohol

The physicochemical properties are only slightly affected by the time of harvest. However, the resin content varies considerably.

Oil of Spanish Wild Marjoram

Thymus mastichina L., the Spanish "forest marjoram," *Mejorana silvestre* Lázaro (or "Tomillo blanco"), or as it is called vernacularly "Almoraduz," grows wild in the low sections (40–50 m. altitude) of the Provinces Sevilla, Huelva, Granada, and Almeria. The plant flowers from end of April to June when it is distilled in field stills as described under "Oil of Spanish Spike Lavender." One hundred and ten kilograms of flowering plant material yield 1.2 kg. of oil. Some years ago the plant was cultivated in Medina Sidonia (Province of Cadiz), that picturesque and historical village renowned for its Moorish character. However, the cultivated plant soon degenerated and adopted the characteristics of the wild plant, especially its camphoraceous odor.

Another plant, viz., *Thymus cephalotus* L. which grows wild at an altitude of about 400 m. in the Province of Jaén yields an oil with the same properties as that from *Thymus mastichina*. However, the main source of Spanish wild marjoram oil remains *Thymus mastichina* L.

Under normal conditions, Spain produces annually 12–13 metric tons of this oil; in 1947 only 6 tons were produced.

[11] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi* **15** (1940), 6. *Chem. Abstracts* **36** (1942), 4970.

Physicochemical Properties.—Shipments of genuine Spanish wild marjoram oils received and analyzed by Fritzsche Brothers, Inc., during the past years varied within the following limits:

Specific Gravity at 15°/15°	0.914 to 0.922
Optical Rotation	+0° 42′ to +10° 41′
Refractive Index at 20°	1.4631 to 1.4661
Saponification Number	5.1 to 13.1
Ester Number after Acetylation	46.7 to 81.2
Phenol Content	2 to 4%
Cineole Content	63.2 to 65%
Solubility	Soluble in 2.5 to 3 vol. of 70% alcohol; occasionally insoluble in 70% alcohol. All oils soluble in 1 vol. and more of 80% alcohol

In regard to physicochemical properties, see also the investigations of Dorronsoro,[12] details of which are reported in Schimmel's Berichte,[13] and by Gildemeister and Hoffmann.[14]

Chemical Composition.—The chemical composition of the Spanish wild marjoram oil is entirely different from that of sweet or garden marjoram. It contains a large amount of cineole (eucalyptol) which is the main odor principle. Dorronsoro[15] identified the following compounds:

Cineole. The main constituent, the oil containing from 64 to 72 per cent of cineole. Identified as addition compound with phosphoric acid, and with resorcinol m. 80°.

d-α-Pinene. The oil contains 7 to 8 per cent. B. 168°. Identified as nitrosochloride m. 103°, and as nitrolpiperidine m. 118°–119°.

A Phenol(?). Less than 0.1 per cent. This substance does not crystallize, neither does it give a positive color reaction with ferric chloride.

l-Linaloöl. In the fraction b. 185°–195°. Characterized by oxidation to citral and formation of the β-naphthocinchoninic acid compound m. 197°.

Acetic Acid and Isovaleric Acid. Present in free and ester form.

Use.—Oil of Spanish wild marjoram is used in spice bouquets for the seasoning of table sauces, meats, sausages, soups and food products in general. Although it possesses a marked cineole character and is less characteristic of marjoram than the oil of sweet marjoram (*Majorana hortensis*), the Spanish oil has nevertheless obtained considerable popularity as it offers the advantage of a much lower price.

Oil of sweet marjoram is employed in high-grade flavor preparations where quality is of prime importance.

[12] "Contribución al estudio de las esencias españolas. Esencia de *Mejorana silvestre*." Madrid (1910). *Ber. Schimmel & Co.*, April (1911), 118.
[13] *Ber. Schimmel & Co.*, April (1911), 118; (1921), 87.
[14] "Die Ätherischen Öle," 3d Ed., Vol. III, 770.
[15] *Ber. Schimmel & Co.*, April (1911), 118; (1921), 87.

THE MONARDA OILS

Oil of Wild Bergamot
(*Monarda fistulosa* L.)

Monarda fistulosa L., commonly called wild bergamot, is a native of North America and grows wild in many parts of the United States. According to Kremers,[1] and Melzner and Kremers [2] the oil resembles that of *Monarda punctata* L.

Distilling the flowering fresh herb Rabak [3] obtained 0.3 to 1.0 per cent of oil; the dried flowers and leaves yielded 2.71 per cent, according to Beck and Brandel; [4] and 3.1 per cent of oil, according to Rang.[5]

Physicochemical Properties.—These authors also reported the following properties:

Specific Gravity	0.916 to 0.941, for oils distilled from the whole overground parts of the flowering plants, June to September
Optical Rotation	Slightly laevorotatory
Phenol Content (Mostly Carvacrol)	52.0 to 72.0%

Distilling the fresh herb of *Monarda fistulosa* in Florida, Christensen and Justice [6] obtained 0.831 per cent of a volatile oil with these properties:

Specific Gravity at 20°	0.9382
Refractive Index at 25°	1.5000
Phenol Content (Carvacrol)	55.4%

An oil distilled by the Engineering Experiment Station, Agricultural and Mechanical College of Texas, and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 15°/15°	0.929
Optical Rotation	Too dark
Refractive Index at 20°	1.5018
Phenol Content	40.0%
Solubility	Turbid in 10 vol. of 70% alcohol

Two other oils of *Monarda fistulosa* L. were examined in the laboratories of Fritzsche Brothers, Inc.:

[1] *Pharm. Rundschau* **13** (1895), 207.
[2] *Pharm. Rev.* **14** (1896), 198.
[3] *Am. Perfumer* **5** (1910), 221.
[4] *Pharm. Rev.* **21** (1903), 109.
[5] *J. Am. Pharm. Assocn.* **17** (1928), 526.
[6] *Ibid.* **26** (1937), 11.

I. Herb collected in the summer of 1929 near Fort Collins, Colorado, at an altitude of about 5,300 feet, during late flowering period, and distilled two days later after having been left in a tightly packed pile. Yield of oil: 0.35 per cent.

II. Herb collected in the summer of 1929 near Wheatland, Wyoming, at an altitude of about 5,600 feet, during late flowering period, and distilled following day. Yield of oil: 0.51 per cent.

These two oils had the following properties:

	I	*II*
Specific Gravity at 15°/15°	0.939	0.924
Optical Rotation	Too dark	Inactive
Phenol Content	64.5%	65.0%
Solubility in 70% Alcohol	Soluble in 2.5 vol., opalescent with more	Soluble in 2.5 vol. and more

The odor of these oils was phenolic, carvacrol-like.

Chemical Composition.—The chemistry of "wild bergamot" oil (*Monarda fistulosa*) was investigated first by Kremers and collaborators, and later by Miller [7] who established the presence of the following compounds:

Limonene. Identified by Hendricks and Kremers [8] as nitrolbenzylamine derivative m. 93°.

p-Cymene. Aside from very small amounts of limonene, the oil contains, according to the same authors, *p*-cymene. Oxidation yielded hydroxyisopropylbenzoic acid m. 156°.

Carvacrol. This is the main constituent (about 67 per cent). Identified by dicarvacrol m. 147°–148°, carvacrol sulfonic acid m. 58°–59°, nitrosocarvacrol m. 153°–154°, and dinitrocarvacrol m. 117°–119°.

Thymohydroquinone. M. 140°, according to Brandel and Kremers.[9]

Thymoquinone. According to Beck and Brandel.[10]

Dihydroxythymoquinone. According to Wakeman.[11]

Later, Miller [12] identified the following compounds:

[7] *Circ. Univ. Wisconsin,* No. 4, October (1918). *Midland Drug. & Pharm. Rev.* **54** (1920), 146. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 716.

[8] *Pharm. Arch.* **2** (1899), 76.

[9] *Pharm. Rev.* **19** (1901), 200.

[10] *Ibid.* **21** (1903), 109.

[11] "The Monardas," *Bull. Univ. Wisconsin,* Madison (1911), No. 448, 23 (Science Ser. Vol. 4, No. 1). Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 716.

[12] *Circ. Univ. Wisconsin,* No. 4, October (1918). *Midland Drug. & Pharm. Rev.* **54** (1920), 146.

d- and *l*-α-Pinene. As nitrolbenzylamine derivative m. 103°, and as nitrolpiperidine m. 117°–118°.

Two Other Terpenes(?). Not further identified.

Butyric Aldehyde. *p*-Nitrophenylhydrazone m. 90°–92°.

Isovaleric Aldehyde. *p*-Nitrophenylhydrazone m. 111°.

Piperonal(?).

Dihydrocuminyl Alcohol.

Another Alcohol. Not further identified.

Acetic, Butyric, Valeric, and Caproic Acid. Analysis of the silver salts.

Basic Compounds.

Geraniol and Linaloöl(?). The presence of geraniol and probably linaloöl was reported by Christensen and Justice.[13]

The distillation waters, according to Wakeman, contained:

Acetone	Formic Acid
Formaldehyde	Acetic Acid
Methyl Alcohol	

Use.—The oil has not attained any commercial importance.

Suggested Additional Literature

S. Badzynski, "Preliminary Studies on the Oil of *Monarda fistulosa*," *Wiadomosci Farm.* **60** (1933), 689. *Chem. Abstracts* **28** (1934), 1815.

Oil of Horsemint
(*Monarda punctata* L.)

Monarda punctata L., the so-called horsemint, grows wild on light sandy soil in many parts of the United States, especially in the Southeast, also in the Middle West from Wisconsin and Kansas south to Texas and Florida. Rabak,[14] and Hood[15] recommended planting of *Monarda punctata* as a source of thymol. According to Russell,[16] such plantings were actually undertaken, but discontinued when thymol could be produced synthetically at lower prices.

[13] *J. Am. Pharm. Assocn.* **26** (1937), 11.
[14] *Am. Perfumer* **5** (1910), 220.
[15] *U. S. Dept. Agr., Bull* No. 372. *Am. J. Pharm.* **88** (1916), 287.
[16] *Am. Perfumer* **15** (1920), 365.

Distillation of fresh plants yields up to 1.0 per cent of oil, of dried plants about 3.0 per cent of oil. Hewitt [17] reported a yield of 3.45 per cent from dried flowers.

Physicochemical Properties.—Wakeman [18] reported the following properties:

Specific Gravity at 15°	0.930 to 0.940
Optical Rotation	Mostly inactive, or slightly dextro- or laevo-rotatory
Total Phenol Content	60 to 70%
Thymol Content	44 to 61%; upon standing, thymol separates occasionally from the oil in the form of a crystalline deposit

The oil has a pronounced thyme and mint-like odor.

An oil of *Monarda punctata* L. distilled in 1930 on the Gulf Coast of Florida and analyzed in the laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 15°/15°	0.949
Optical Rotation	−0° 16′
Refractive Index at 20°	1.5088
Thymol Content	71.5%; the phenols were crystallizable
Solubility	Soluble in 3 vol. and more of 90% alcohol

Another sample of oil of *Monarda punctata* L. was distilled by the Texas Engineering Experiment Station, College Station, Texas, during 1944. The analysis carried out in the laboratories of Fritzsche Brothers, Inc., New York, revealed these properties:

Specific Gravity at 15°/15°	0.941
Optical Rotation	+0° 25′
Refractive Index at 20°	1.5055
Phenol Content (Thymol)	61.0%
Solubility at 20°	Soluble in 2.5 vol. and more of 70% alcohol

The odor and flavor of this oil were quite similar to those of oil of thyme.

Studying the Texas *Monarda* oils, Albers [19] found that the various subspecies of *Monarda punctata,* on steam distillation, yielded oils possessing the properties given in Table 2.5.

[17] *J. Am. Pharm. Assocn.* **17** (1928), 457.

[18] "The Monardas," *Bull. Univ. Wisconsin,* Madison (1911), No. 448 (Science Ser. Vol. 4, No. 4). Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 711.

[19] *Pharm. Arch.* **8** (1937), 33.

TABLE 2.5

Subspecies	Yield of Oil (%)	d_{25}	$[\alpha]_D^{25}$	n_D^{20}	Phenol Content (%)
stanfieldii Epl.	1.17	0.9612	+13° 25′	1.5125	78
typica Epl.					
from green plants	0.28	0.9182	+0° 1′	1.5008	54
from dried plants	1.21	0.9304	+0° 56′	1.5054	62
immaculata Pennel	2.5	0.9653	Inactive	1.5150	57.5

Chemical Composition.—Thymol, the main constituent of oil of *Monarda punctata* was identified by Arppe [20] over a century ago. Many years later, Kremers and collaborators undertook a more detailed investigation of horsemint oil, which they had distilled from true *Monarda punctata*.

The presence of the following constituents has been established:

d-Limonene. Only traces occur in the oil, according to Hendricks and Kremers; [21] identified as nitrolbenzylamine derivative m. 94°.

p-Cymene. The principal constituent of the nonphenolic compounds present in the oil. Oxidation gave hydroxyisopropylbenzoic acid m. 155°–156°.

Thymol. The main constituent of the oil, identified first by Arppe,[22] and later by Schumann and Kremers,[23] who found 61 per cent of thymol in their oil.

Carvacrol. Aside from thymol the oil, according to Hendricks and Kremers,[24] contains another phenol, viz., carvacrol; identified as phenylurethane m. 140°.

Thymohydroquinone. M. 141°, according to Sherk.[25]

Linaloöl(?). Schumann and Kremers [26] reported that the fraction b. 186°–202° contained oxygenated compounds, among them seemingly linaloöl.

Formaldehyde and Acetaldehyde. These two aldehydes were identified in the distillation waters by Harwood.[27]

In his investigation of Texas *Monarda* oils, Albers [28] found that the phenols contained in the oil distilled from *M. punctata*, subsp. *stanfieldii* consisted chiefly of carvacrol, those in the oils of *M. punctata* subsp. *typica* and subsp. *immaculata* predominantly of thymol. The boiling points of the

[20] *Liebigs Ann.* **58** (1846), 41.
[21] *Pharm. Arch.* **2** (1899), 73.
[22] *Liebigs Ann.* **58** (1846), 41.
[23] *Pharm. Rev.* **14** (1896), 223.
[24] *Pharm. Arch.* **2** (1899), 73. *Science* **51** (1920), 397.
[25] *J. Am. Pharm. Assocn.* **10** (1921), 417.
[26] *Pharm. Rev.* **14** (1896), 223.
[27] *J. Am. Pharm. Assocn.* **20** (1931), 631.
[28] *Pharm. Arch.* **8** (1937), 33.

fractions used for the preparation of the urethanes, and the melting points of the latter were

b. 235°–243°	m. 136°–137°
b. 230°–232°	m. 105°–106°
b. 237°–240°	m. 104°–105°

respectively.

Use.—Oil of *Monarda punctata* L. has not yet attained any commercial importance; but, as has been pointed out, the oil could be used in the place of thyme oil, provided it can compete with the price of the latter.

Oil of Monarda Punctata var. Leucantha

Monarda punctata L. var. *leucantha* grows wild around Gainesville, Florida.

Distilling the various parts of the herb, Christensen and Justice [29] obtained 3.45 per cent of oil from the blossoms, 1.95 per cent from the leaves, and 0.55 per cent from the stalks.

Physicochemical Properties.—Oils distilled from the whole herb in different years had the following properties:

	A	*B*	*C*
Specific Gravity at 20°	0.9695	0.9276	0.9460
Refractive Index at 25°	1.5100	1.5000	1.5029
Phenol Content	65.4%	44.2%	65.6%

Chemical Composition.—The oil contains thymol, carvacrol, hydrothymoquinone, and terpenes.

Use.—The oil has not attained any commercial importance.

Oil of Lemon Mint
(*Monarda citriodora* Cerv.)

According to Wakeman [30] *Monarda citriodora* Cerv., the so-called lemon mint, grows wild in the United States, particularly in the section roughly bordered by Illinois, Nebraska, and Texas.

Distilling flowering dried herb, Brandel [31] obtained a yield of about 1 per cent of oil.

Physicochemical Properties.—Brandel, and Lefèbvre and Wakeman [32] found these properties:

[29] *J. Am. Pharm. Assocn.* **26** (1937), 15.
[30] "The Monardas," *Bull. Univ. Wisconsin,* Madison (1911), No. 448.
[31] *Pharm. Rev.* **22** (1904), 153.
[32] *Midland Drug. & Pharm. Rev.* **44** (1910), 526. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 712.

Specific Gravity at 20°	0.9437 to 0.9603
Phenol Content	65.0 to 80.0%
Aldehyde Content	1.2 to 4.0%

The oil has a carvacrol and lemon-like odor.

Chemical Composition.—Brandel [33] reported the presence of the following constituents:

Carvacrol. The main constituent; identified as benzoyl compound of the nitroso derivative, m. 110°.

Thymol(?). Small quantities are probably present.

Thymohydroquinone. M. 140°; occurs in the highest boiling fractions of the phenolic constituents.

Citral. According to odor, the aldehydes occurring in the oil seem to consist mainly of citral.

p-Cymene(?). Presence possible; the *p*-hydroxyisopropylbenzoic acid obtained by oxidation of the *p*-cymene fraction melted at 124°, instead of 156°.

Investigating an oil of *Monarda citriodora* Cerv. distilled from plant material (yield of oil: 0.7 per cent) collected near San Antonio, Texas, Albers [34] found that it had these properties:

Specific Gravity at 25°	0.9491
Specific Optical Rotation at 25°	+0° 19′
Refractive Index at 20°	1.5095
Phenol Content	67%

Using the fraction b. 232°–238°, Albers prepared a urethane m. 105°–106° indicating that the phenols contained in oil of *Monarda citriodora* consist predominantly of thymol, and not of carvacrol as had been reported formerly (see above).

Use.—The oil has not attained any commercial importance.

Oil of Monarda Menthaefolia R. Grah.

The herb *Monarda menthaefolia* R. Grah. grows wild in Colorado and Wyoming. The volatile oil was investigated by Justice,[35] and by Christensen and Justice.[36] The flower heads yielded 0.31 per cent, the leaves 0.32 per cent, the stems 0.05 per cent, and the roots only traces of oil.

Physicochemical Properties.—Extracting the leaves and stems with alcohol, steam distilling the extract, and cohobating the distillate, Christensen and Justice obtained two volatile oils with the following properties:

[33] *Pharm. Rev.* **22** (1904), 153.
[34] *Pharm. Arch.* **8** (1937), 33.
[35] *J. Am. Pharm. Assocn.* **25** (1936), 850.
[36] *Ibid.* **26** (1937), 12.

	Original Oil	*Cohobated Oil*
Specific Gravity at 20°	0.966	0.952
Specific Rotation at 20°	+1° 33′	+1° 34′
Refractive Index at 25°	1.5110	1.5143
Phenol Content	82.0%	93.2%

An oil of *Monarda menthaefolia* distilled in Wyoming during the summer of 1928, and examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 15°/15°	0.932
Optical Rotation	Too dark [37]
Phenol Content	65.0%
Solubility	Clearly soluble in 1 vol. of 80% alcohol, opalescent with more

The oil had an odor similar to that of *Monarda punctata* L. ("Horsemint Oil").

Chemical Composition.—According to Justice,[38] and Christensen and Justice [39] the oil contains the following constituents:

p-Cymene. In the fraction b. below 182°.

Carvacrol. The main constituent; identified as phenylurethane m. 134°.

Hydrothymoquinone.

Geraniol. In the fraction b. above 205°.

Linaloöl(?). In the fraction b. 182°–205°. However, no derivatives of linaloöl could be prepared.

Acetic Acid.

Use.—The oil has not attained any commercial importance.

Oil of Monarda Pectinata Nutt.

Distilling the fresh flowering herb of *Monarda pectinata* Nutt., collected in 1932 near Signal Hill, Scottsbluff County, Nebraska, Burt [40] obtained 0.486 per cent of a volatile oil which had these properties:

Specific Gravity at 25°	0.9496
Optical Rotation	Too dark
Refractive Index at 25°	1.5070
Phenol Content	77%

[37] Too dark for reading in a 2.5 cm. tube.
[38] *J. Am. Pharm. Assocn.* **25** (1936), 850.
[39] *Ibid.* **26** (1937), 12.
[40] *Ibid.* **25** (1936), 682.

The phenols contained in the oil consisted chiefly of carvacrol which was identified by the preparation of its nitroso compound m. 153°.

SUGGESTED ADDITIONAL LITERATURE

E. Kremers, "A Quarter Century of Chemical Investigations of *Monarda*," *J. Am. Pharm. Assocn.* **9** (1920), 1175.

OIL OF ORIGANUM

Essence d'Origan *Aceite Esencial Oregano* *Origanumöl*
Oleum Origani

Introduction.—Although in commerce frequently confused with, or mislabeled as thyme oil (see "Oil of Thyme"), origanum oil is in reality an entirely different type, distilled from a different plant species and in different regions. It has a different chemical composition, containing 63 to 74 per cent (usually 65 to 70 per cent) of phenols, which consist mainly of carvacrol (noncrystallizable phenol).

Oil of origanum is produced principally in Spain, also in Palestine, Syria, on the island of Cyprus, and of late in Morocco. Oils of similar physical properties and chemical composition have come from Asia Minor, and were known in years past as Cretan, Trieste, Cyprus, Smyrna, and Syrian origanum oils.

Botany.—It seems that several plant species and varieties yield essential oils which contain a high content of carvacrol and which are commercially known as origanum oils.

The Spanish oil, most important of all commercial origanum oils, is distilled from the flowering herb *Thymus capitatus* Hoffmg. et Link which is now considered a separate genus, viz., *Coridothymus capitatus* Rchb.

So far as the Moroccan oil of origanum is concerned, Muller[1] reports that it is derived from several species, viz.:

Origanum elongatum Emb. et Maire
Origanum grossi Pau et F. Q.
Origanum fort-queri Pau

[1] *Parfumerie moderne* **31** (1937), 377.

Origanum virens Hoffmg. et Link
Origanum compactum Benth.

Regarding the plants which serve for the distillation of the so-called Cretan, Trieste, Cyprus, Smyrna and Syrian origanum oils, there exists considerable confusion in literature.

Spanish Origanum Oil
(Carvacrol Type)

Range and Habitat.—The plant, in Spain colloquially called "tomillo andaluz" or "tomillo carrasqueño," grows wild and abundantly in Andalusia,



Courtesy of Fritzsche Brothers, Inc., New York.

Field distillation of origanum oil in southern Spain.

the southern part of Spain, particularly in the provinces of Malaga, Cadiz, Huelva, Sevilla, and on the border of Cordova. It seems to prefer lower elevations and a more humid soil than thyme.

Collection of the Plants and Distillation.—The plants are gathered from May to August.

Distillation is carried out in field stills similar to those used for spike lavender, except for the fact that the origanum stills are larger, being 2 m. high and 1.60 to 1.80 m. wide. They hold about 800 to 1,040 kg. of plant material.

Distillation of one charge requires about 9 hr., including 30 min. for packing the still and 30 min. for getting steam up. During the 8 hr. of actual distillation 240 to 300 liters of water distill over.

Yield of Oil.—Depending upon climatic and seasonal conditions, 10 arrobas (1 arroba = 11.5 kg., or about 25 lb.) of plant material yield on the average 1 kg. of oil; in other words the yield of oil is about 0.87 per cent.

Physicochemical Properties.—Origanum plants growing in the lowlands yield oils of higher phenol content than those growing at higher altitudes, a few miles distance often causing a considerable difference in this respect.

Spanish origanum oils distilled under the author's supervision had the properties given in Table 2.6.

TABLE 2.6

Locality	Spec. Grav. at 15°/15°	Phenol Content (%)	Solubility at 20°
Chiclana de la Frontera (near Cadiz)	0.950	71.0	Soluble in 2.5 vol. of 70% alcohol and more
Portal (near Jerez de la Frontera)...	0.952	71.5	Soluble in 2.5 vol. of 70% alcohol and more
Huelva.....	0.951	69.0	Soluble in 2.5 vol. of 70% alcohol
Huelva.....	0.949	67.0	Soluble in 2.5 vol. of 70% alcohol

The oils were too dark to permit determination of the optical rotation.

Genuine lots of own importation, when analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within these limits:

Specific Gravity at 15°/15°.....	0.937 to 0.955
Optical Rotation.....	Inactive to +1° 0′
Refractive Index at 20°.....	1.5024 to 1.5080
Phenol Content.....	62.0 to 71.0%
Solubility.....	Soluble in 2.5 to 3 vol. and more of 70% alcohol, sometimes with slight turbidity
Color.....	Yellow-reddish

Pure Spanish origanum oils should contain a minimum of 63 per cent phenols, although the method of distillation employed may result in some variation in this figure. The phenol content of origanum oil is determined by the method described in the chapter "Examination and Analysis of Essen-

tial Oils, Synthetics and Isolates," Vol. I, p. 291 of this work. The isolated phenols do *not* crystallize on standing at room temperature.

Adulteration.—Adulterated origanum oils have frequently been encountered in the trade. In fact, this practice has done such harm to origanum oil that in late years the demand for it has diminished considerably.

It is easy to adulterate origanum oil by adding low-priced synthetic carvacrol and *p*-cymene. The author examined samples of so-called origanum oils consisting entirely of synthetic carvacrol and *p*-cymene. Routine chemical analysis is almost useless for detecting such sophistication, but the expert can recognize the presence of synthetic carvacrol by a slight "bynote" of creosote, which becomes more noticeable as the oil evaporates on test paper.

Total Production of Spanish Origanum Oil.—In normal years, Spain's total production of origanum oil used to fluctuate between 10 and 20 tons. After the outbreak of civil war in 1936, however, it fell to a very low figure. Since 1939 production has again increased, due primarily to a heavy demand on the part of Germany during World War II. Production in 1946 amounted to about 9 tons of oil, most of which was exported to the United States and to the United Kingdom. In 1947 only 3 tons of origanum oil were produced in Spain. In 1948 5 tons were produced. (These figures represent metric tons.)

Oil of Origanum "White."—Rectifying the natural oil of origanum (which is usually of reddish color) gives an oil of light yellow color. The loss of oil connected with rectification causes a slight increase in the phenol content of the light oil. When stored in metal containers for some time, the white oil tends to darken again.

Chemical Composition.—The literature on the chemical composition of origanum oil (*Coridothymus capitatus* Rchb. f.—*Thymus capitatus* Hoffmg. et Link) is somewhat vague and limited for the reason, probably, that, in the past, this oil has often been confused with thyme oil (*Thymus vulgaris*).

The presence of the following compounds has been reported by the Schimmel chemists,[2] by Palazzo and Lutri,[3] Pellini and Morani,[4] Puxeddu,[5] Blaque,[6] and by Adida and Demigneux: [7]

Amyl Alcohol.

d-α-Pinene. 3.2 per cent.

Dipentene.

[2] *Ber. Schimmel & Co.,* October (1889), 56.
[3] *Ann. chim. applicata* **14** (1924), 109.
[4] *Ibid.* **13** (1923), 111.
[5] *Ibid.* **15** (1925), 162, 170.
[6] *Perfumery Essential Oil Record* **14** (1923), 239.
[7] *Bull. sci. pharmacol.* **33** (1926), 65. *Chem. Abstracts* **20** (1926), 1690.

p-Cymene.

Bornyl Acetate.

Thymol. About 6 per cent.

Carvacrol. The main constituent; the oil contains from 63 to 74 per cent of phenols, mainly carvacrol. Unlike thymol, which crystallizes, carvacrol remains liquid at room temperature.

Thymoquinone. Presence probable.

A Sesquiterpene(?).

In view of the importance which origanum oil has assumed in the essential oil trade, it seems desirable that a more detailed study be undertaken on an oil of botanically well-defined origin.

According to Adida and Demigneux,[8] the fraction of the terpenes distilling between 160° and 185° is called "thymene."

Use.—Origanum oil, red and white, is a powerful disinfectant. Therefore, it finds application in all kinds of pharmaceutical and semipharmaceutical, and especially oral, preparations.

Origanum oil is used widely in the scenting of soaps and to a limited extent in the flavoring of food products such as meats, sausages, sauces, canned goods, etc.

Moroccan Origanum Oil
(Carvacrol Type)

In the years prior to World War II, production of origanum oil was begun in Morocco, this development being favored by the civil war then raging in Spain.

Habitat and Range.—The plants from which the Moroccan origanum oil is distilled grow wild and abundantly throughout Morocco's Riff Mountains, especially around Quezzane, 150 km. north of Meknès, and around Terroual and Zoumi. Another producing region lies northwest of the Medium Atlas Mountains, especially around Khemiset, 60 km. north of Meknès.

Collection of Plants.—Depending upon altitude, the plants are gathered from early June to mid-September. Collecting is done in the manner described in the discussion of Moroccan Thyme Oil.

Distillation.—The same type of field stills employed for Moroccan thyme are used for distilling origanum. The similarity extends also to the plant charge, the length of distillation, and yield of oil.

Physicochemical Properties of Moroccan Origanum Oil.—Oils distilled under the author's supervision in Morocco had the properties given in Table 2.7.

[8] *Ibid.*

TABLE 2.7

Distillation	Specific Gravity at 15°/15°	Optical Rotation	Refractive Index at 20°	Phenol Content (%)	Solubility at 20°
In the western part of the Medium Atlas, August, 1937, from flowers and dry leaves. Distillation 4 hr.	0.917	+0° 40′	1.4990	45.0	Hazy in 1.5 vol. of 80% alcohol; cloudy with more
In the northwestern part of the Medium Atlas, Khemiset, August 1937, under same conditions as above.	0.936	Too dark	1.5050	57.0	Soluble in 1.5 vol. of 80% alcohol; turbid in 2.5 vol. and more
In the Medium Atlas, July 1937, from flowers and fresh leaves. Distillation 3 hr.	0.940	+0° 40′	1.5055	62.0	Soluble in 3 vol. and more of 70% alcohol

A shipment of genuine Moroccan origanum oil analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 15°/15°	0.937
Optical Rotation	+0° 48′
Refractive Index	1.5041
Phenol Content	61.5%
Solubility	Hazy in 2.5 vol. and more of 70% alcohol

Muller[9] reported these properties of Moroccan origanum oils:

	I	*II*	*III*	*IV*
Specific Gravity at 15°	0.925	0.927	0.918	0.914
Optical Rotation	...	+0° 45′	...	...
Refractive Index	1.498	1.498	1.498	1.495
Phenol Content	65%	62%	50%	52%

In order to obtain a phenol content of at least 50 per cent, Muller recommended distilling the dried plant material.

The Moroccan producers have not yet succeeded in producing origanum oils with a phenol content as high as that of the Spanish oils. Since the high boiling phenols come over very slowly, the Spanish producers distill up to 8 hr., obtaining oils of from 63 to more than 70 per cent of phenols. In other words, the longer distillation is carried out, the higher will be the phenol content of the oils. Such oils, however, are not necessarily finer in odor; in fact, oils of lower phenol content possess a more natural odor, closer to that of the blooming plant, whereas oils of high phenol content have an

[9] *Parfumerie moderne* **31** (1937), 377.

unpleasant, phenolic, almost "burnt off-note." However, since in trade practice origanum oil is evaluated by its phenol content, the Moroccan producers would do well to attain the standards established by their Spanish competitors.

So far, Moroccan origanum plants have been distilled for 3 to 4 hr. Oils obtained from green plants (around the middle of April) contain up to 50 per cent of phenol; whereas distillation of fully developed dried flowers (July to August) for 5 hr. gives oils containing up to 65 per cent of phenol. Oils from more mature plants are higher in phenols than those from younger ones. The average phenol content is approximately 60 per cent but, as pointed out, it could probably be increased by prolonged distillation. Locality, plant variety, and particularly the altitude exercise a certain influence in this respect. However, these data are still in the experimental stage and need further study.

Total Production of Moroccan Origanum Oil.—The total production of origanum oil in Morocco amounted to about 10 tons in 1937; it could have been increased considerably but for the outbreak of World War II.

Palestine and Syrian Origanum Oil

According to a trade report [10] *Coridothymus capitatus* grows quite profusely also in Palestine, particularly in the vicinity of Jerusalem on Mt. Carmel, on the hills of Rishonle-Zion, and around Tel-Aviv and Petach Tikvah. Palestine origanum oil, often confused in import statistics with thyme oil, is one of the most important essential oils Palestine produces. The export figures varied from about 13,000 to 36,000 kg. annually during the years preceding World War II. In 1939, 7,317 lb. were received from Palestine and 10,052 lb. from Syria; and two years later, 14,703 lb. were imported from Syria.

The physicochemical properties of Palestine origanum oil are very similar to those of the Spanish or Moroccan oils.

A shipment of an oil from Palestine labeled "Origanum Maru" examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°	0.942
Optical Rotation	+0° 52′
Refractive Index at 20°	1.5067
Phenol Content	65%
Solubility	Soluble in 2.5 vol. and more of 70% alcohol

[10] *Mfg. Chemist* **4** (1933), 232. See also *Drug Vitamin and Allied Industries* **31** (1945), 21.

The interesting feature in connection with this lot was that the isolated phenols crystallized on standing at room temperature, which indicates the presence of thymol, rather than of carvacrol, in this oil. It was not possible to establish the botanical identity of the plants from which this oil of "Origanum Maru" had been distilled. At any rate, this proves that the commercial term "origanum oil" is used rather indiscriminately and sometimes seems to be applied also to oils containing thymol as main constituent.

Most of the origanum oils originating in Syria contain carvacrol as chief component.

Oil of Origanum Vulgare L.

Origanum vulgare L., commonly called wild marjoram, a native of Central and Southern Europe, is also cultivated in old gardens in the eastern part of the United States. The herb contains a volatile oil of aromatic, spicy, somewhat basil-like odor. According to Schimmel & Co.,[11] Jahns,[12] and Pater,[13] the fresh herb yields 0.07 to 0.20 per cent, the dried herb 0.15 to 0.40 per cent of oil.

Physicochemical Properties.—The properties of the oil vary within the following limits:

Specific Gravity at 15°	0.868 to 0.910
Optical Rotation	−20° 0′ to −70° 0′
Ester Content, Calculated as Geranyl Acetate	2.0 to 3.0%
Phenol Content (Mainly Thymol)	Up to 7.0%

Chemical Composition.—According to Jahns,[14] and Angelescu,[15] the oil contains thymol, carvacrol, free alcohols (about 13 per cent), esters, and 12.5 per cent of a bicylic sesquiterpene b. 245°–250°, $d_4^{11.5}$ 0.9112, n_D^{18} 1.49833.

Oil of *Origanum vulgare* L. has not attained any commercial importance.

Before closing this section, it should be pointed out that the term *Origanum vulgare* occasionally seems to be used rather indiscriminately and to be applied perhaps to plants which colloquially are called so, but which, from the strictly morphological point of view, belong to some other species. For example, an "Oil of *Origanum vulgare*" produced in Guatemala during World War II and analyzed by Fritzsche Brothers, Inc., New York, had these properties:

[11] *Ber. Schimmel & Co.*, April (1891), 49.
[12] *Arch. Pharm.* **216** (1880), 277.
[13] *Heil-Gewürz-Pflanzen* **7** (1924), 138. *Ber. Schimmel & Co.* (1926), 79.
[14] *Arch. Pharm.* **216** (1880), 277.
[15] *Gazz. chim. ital.* **52** (1922), I, 157.

Specific Gravity at 15°	0.952
Optical Rotation	+0° 25′
Refractive Index at 20°	1.5084
Phenol Content	68.4%
Acid Number	3.7
Saponification Number	7.5
Solubility	Soluble in 2.5 to 3 vol. and more of 70% alcohol

The isolated phenols did not crystallize on standing at room temperature, which points toward the presence of carvacrol, rather than of thymol, as main constituent of the oil. Perhaps the oil was distilled from a plant closely allied to *Coridothymus capitatus* Rchb. (see Spanish Oil of Origanum), and not from *Origanum vulgare* L.

Oil of Origanum Vulgare L. var. Viride

Origanum vulgare L. var. *viride* grows wild in Southern Europe and also in the southern part of the U.S.S.R. including the Crimean Peninsula. It contains a volatile oil which differs from that of the *Origanum vulgare* species by a considerably higher content of thymol. It is possible that the oil is identical with that distilled from *Origanum virens* Hoffmg. et Link var. *siculum* Benth. (See below.)

Physicochemical Properties.—Distilling dried flowering herb in Sicily, Angelescu [16] obtained 1.106 per cent of an oil with these properties:

Density at 13.5°/4°	0.9244
Specific Optical Rotation at 22°	−0° 2′
Refractive Index at 22°	1.50029
Acid Number	0.74
Ester Number	2.43
Ester Content, Calculated as Geranyl Acetate	0.85%
Saponification Number	3.17
Thymol Content (according to the Method of Kremers and Schreiner)	50.3%

The oil contained about 17.5 per cent of *p*-cymene, 10.5 per cent of dipentene, and thymol as main constituent.

La Face [17] reported that the fresh flowering overground parts of *Origanum vulgare* L. var. *viride* growing near Reggio Calabria at 1,000 m. altitude, upon distillation gave 0.35 per cent of an oil with the following properties:

Specific Gravity	0.918
Optical Rotation	−1° 40′

[16] *Ibid.*

[17] *Rivista ital. essenze profumi* **4** (1922), 64. *Ber. Schimmel & Co.* (1923), 57.

Refractive Index	1.4991
Phenol Content	45.0%
Solubility	Soluble in 2 vol. of 80% alcohol

Distilling fresh herb growing wild near Tschimkent (Southern U.S.S.R.), Rutovski, Gusseva and Koroleva [18] obtained 0.4 per cent of an oil which had these properties:

Specific Gravity at 20°/20°	0.9381
Optical Rotation	Inactive
Refractive Index at 20°	1.5059
Phenol Content	60.0%

Chemical Composition.—The oils examined by Angelescu,[19] and by Rutovski and collaborators [20] contained the following compounds:

p-Cymene. About 17.5 per cent. Identified by oxidation to hydroxyisopropylbenzoic acid m. 156°–157°.

Dipentene. About 10.5 per cent. Identified as nitrosochloride m. 100°–101°; nitrolbenzylamine derivative m. 107°–108°.

A Terpene(?). Rutovski and collaborators reported the presence of a terpene which gave a nitrosochloride m. 75°; and a nitrolpiperidine m. 184°.

Thymol. The main constituent, about 50 per cent.

A Sesquiterpene(?). Similar to caryophyllene and to the sesquiterpene found by Angelescu in oil of *Origanum vulgare* L., var. *viride*, b_6 110°–115°, d_{20}^{20} 0.904, α_D −27° 4′, n_D^{20} 1.4980.

Oil of *Origanum vulgare* L. var. *viride* has not attained any commercial importance.

Oil of Origanum Virens Hoffmg. et Link

Origanum virens Hoffmg. et Link var. *siculum* Bentham, grows wild in Sicily and Calabria. Pellini and Morani [21] reported that the oil distilled from *Origanum virens* var. *siculum* is very similar to that from *Origanum vulgare* L. var. *viride*, and that both types were probably distilled from the same plant.

The fresh herb of *Origanum virens* Hoffmg. et Link var. *siculum* Bentham, according to Pellini and Morani, yielded 1.22 per cent, the dried herb 1.6 and 2.41 per cent of oil with the following properties:

[18] *Riechstoff Ind.* **8** (1933), 140.
[19] *Gazz. chim. ital.* **52** (1922), I, 161.
[20] *Riechstoff Ind.* **8** (1933), 140.
[21] *Ann. chim. applicata* **13** (1923), 113.

	I	*II*
Specific Gravity at 15°/15°	0.9245	0.9324
Optical Rotation	−1° 32′	−1° 40′
Refractive Index	1.4950	1.5002
Ester Content	...	Traces
Thymol Content	50.0%	50.0%
Solubility in 70% Alcohol	Soluble in 25 vol.	Soluble in 14 vol.

Distilling herb from the vicinity of Messina, Romeo and Giuffré [22] obtained an oil with these properties:

Specific Gravity at 15°	0.9226
Optical Rotation at 20°	−2° 10′
Refractive Index at 25°	1.4934
Acid Number	0.6
Saponification Number	2.1
Ester Number after Acetylation	170.7
Phenol Content (Mainly Thymol)	44.65%
Solubility	Soluble in 3 vol. of 75% alcohol

Aside from thymol, the oil also contained carvacrol.

Later Romeo [23] described an oil distilled from *Origanum virens* Hoffmg. et Link, growing in Sicily:

Specific Gravity at 15°	0.9285
Optical Rotation at 20°	−1° 24′
Refractive Index at 25°	1.4967
Phenol Content	48.5%; 25.0 to 26.0% of the oil consisted of thymol
Solubility	Soluble in 2.4 vol. of 75% alcohol

Oil of *Origanum virens* Hoffmg. et Link has not attained any commercial importance.

THE ORTHODON OILS

In the opinion of Fujita,[1] aromatic plants that contain essential oils should not be classified according to purely morphological distinctions, but

[22] *Ibid.* **15** (1925), 370.

[23] *Rivista ital. essenze profumi* **17** (1935), 189. *Ber. Schimmel & Co.* (1936), 53.

[1] The author is greatly obliged to Dr. Teikichi Hiraizumi, Tokyo, a personal friend of Dr. Yasuji Fujita, Osaka, for much of the data contained in this section.

rather according to the chemical composition of the essential oils contained in the plants. Fujita arrived at this conclusion after a long and detailed biogenetic study of the oils derived from thirteen species of the genus *Orthodon* (fam. *Labiatae*) growing in Eastern Asia, particularly in Japan and China. He found that his system not only agrees with the usual morphological classification, but also that morphological ambiguities can be eliminated, if chemical classification is employed. Fujita's [2] first paper on this topic appeared in 1933, his 31st communication [3] in 1944, and the series is not yet completed. The following contains a summary of Fujita's reports from the first through the 31st communication.

Except for the oil of *Orthodon perforatum* Ohwi (see the monograph on "Oil of Perilla") and a few others (see below), the *Orthodon* oils have no commercial importance. However, they have considerable scientific interest, for which reason they will be described briefly here.

Oil of *Orthodon chinense* Kudo and oil of *Orthodon hadai* Kudo (see below) contain 65 to 74 per cent of carvacrol and thus might be considered a natural source for the isolation of carvacrol when the synthetic product is expensive or unavailable. Such was the case during World War II, when a large acreage in Formosa was planted with *Orthodon chinense* Kudo, with a view to the isolation of carvacrol needed by the Japanese army as a disinfectant. However, the war ended before the fields attained the stage of production.

Another *Orthodon* oil, viz., *Orthodon linaloöliferum* Fujita, which grows wild in Formosa, offers great commercial possibilities, since it contains 82 per cent of *d*-linaloöl. According to Fujita,[4] 1 hectare yields 60 kg. of oil. The *d*-linaloöl fractionated from this oil exhibits high dextrorotation, $[\alpha]_D^{29}$ +20° 77′. Compared with that of linaloöl from ho (shiu) oil, the quality of the linaloöl from oil of *Orthodon linaloöliferum* Fujita is greatly superior, because it contains no camphor. In time the oil may well become the "Bois de Rose Oil of Formosa."

In his "Classification and Systematics of the Genus *Orthodon* by the Constituents of the Essential Oils" Fujita divided thirteen species of the genus *Orthodon* into two sections, grouped according to the constituents of the respective essential oils.

Section I, containing aromatic compounds.
Section II, lacking in aromatic, but containing terpenic (nonbenzenoid) compounds.

These will now be briefly described in order. For details the reader is referred to the original literature.

[2] *J. Chem. Soc. Japan* **54** (1933), 1181.
[3] *Ibid.* **65** (1944), 681.
[4] *Ibid.* **62** (1941), 424; **64** (1943), 12.

Section I

1. Oil of *Orthodon chinense* Kudo (*Mosla chinensis* Maxim., *M. angustifolia* Makino), Japanese name "Hosoba-Yama-Shiso."

Yield (percentage of oil to the whole fresh grass)	0.7%
Components of the essential oil	Carvacrol (65%)
	Carvacryl Acetate (6%)
	p-Cymene
	α-Thujene
	d-Linaloöl
	l-Borneol
	α-Caryophyllene
	A Monocyclic Sesquiterpene

2. Oil of *Orthodon hadai* Kudo (*Mosla hadai* Nakai), "Oh-Yama-Shiso."

Yield	0.6%
Components	Carvacrol (74%)
	Carvacryl Acetate
	Thymol
	p-Cymene

3. Oil of *Orthodon leucanthum* Kudo (*Mosla leucantha* Nakai, *M. thymolifera* Makino), "Shirobana-Yama-Shiso."

Yield	0.4%
Components	Thymol (66%)
	p-Cymene

4. Oil of *Orthodon perforatum* Ohwi (*Orthodon japonicum* Benth., *Mosla japonica* Maxim.), "Yama-Shiso."

Yield	0.3%
Components	Thymol (56%)
	p-Cymene
	γ-Terpinene
	α-Caryophyllene
	Cadinene

5. Oil of *Orthodon hirtum* Hara (*Orthodon tenuicaule* Koidz), "Shirage-Hime-Shiso."

Yield	0.3%
Components	Thymol (46%)
	Thymol Methyl Ether (12%)
	p-Cymene
	α-Thujene
	γ-Terpinene
	A Bicyclic Sesquiterpene

6. Oil of *Orthodon tenuicaule* Koidz (provisional term), "Hikage-Hime-Shiso."

Yield	0.3%
Components	Thymol (34%)
	Thymol Methyl Ether (16%)
	p-Cymene
	l-Bisabolene

7. Oil of *Orthodon grosseserratum* Kudo (*Mosla grosseserrata* Maxim.), "Hime-Shiso."

Yield	0.2%
Components	Thymol (20%)
	p-Cymene
	Methyl Eugenol
	Myristicin
	A Sesquiterpene

8. Oil of *Orthodon formosanum* Kudo (*Mosla formosana* Maxim., *M. lysimachiiflora* Hay), "Taiwan-Hime-Shiso."

Yield	0.18 to 0.28%
Components	Dillapiole (62%)
	Elemicin (2%)
	Carvacrol (9%)
	p-Cymene (4%)
	Carvacryl Ester (3%)
	α-Thujene
	Dipentene
	α-Caryophyllene
	l-Bisabolene
	A Sesquiterpene of the Cadalene Type

9. Oil of *Orthodon elemiciniferum* Fujita (supposed name), "Hime-Shiso-Modoki."

Yield	0.28%
Components	Elemicin (10–40%)
	Methyl Eugenol (25–60%)
	Thujone
	α-Caryophyllene

10. Oil of *Orthodon asaroniferum* Fujita (supposed name), "Inukoju-Damashi."

Yield	0.3%
Components	Asarone (25%)
	d-Limonene
	α-Caryophyllene
	Thujone
	l-Bisabolene
	Sesquiterpenes of the Cadalene Type

Section II

11. Oil of *Orthodon lanceolatum* Kudo (*Mosla lanceolata* Maxim., *M. leucantha* Hay), "Taiwan-Inukoju."

Yield	0.45 to 0.8%
Components	Cineole (60–80%)
	Limonene
	"Orthodene"
	α-Pinene
	d-Linaloöl
	α-Caryophyllene
	A Sesquiterpene of the Eudalene Type

12. Oil of *Orthodon punctulatum* Kudo (*Mosla punctata* Maxim.), "Inukoju."

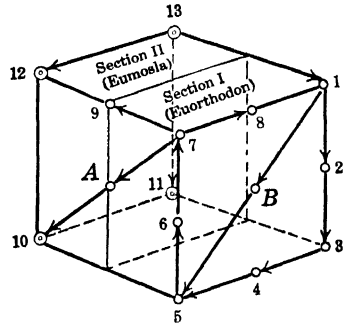
Yield	0.57%
Components	Thujone (75%)
	d-Sabinene (11%)
	d-Limonene (8%)
	α-Caryophyllene
	Sesquiterpenes of the Cadalene and Eudalene Types

13. Oil of *Orthodon linaloöliferum* Fujita (supposed name), "Oya-Inukoju."

Yield	0.37%
Components	*d*-Linaloöl (82%)
	d-Limonene
	Ocimene
	α-Caryophyllene
	Sesquiterpenes of the Cadalene Type

Fujita used the device of a hexahedron to illustrate the chemical classification of the oils belonging to the *Orthodon* group. Plotting every known *Orthodon* oil on the lines of the hexahedron, Fujita was able to demonstrate the directions of the botanical variations by means of their chemical components. Studying the figure on page 550, the reader will readily find the position of each of the thirteen *Orthodon* oils described above. As Fujita's investigations continue, new *Orthodon* oils will be discovered and can be placed in the hexahedron. Since this work is incomplete, the discussion of the *Orthodon* oils cannot be closed at the time of this writing. For example,

Fujita has described two *Orthodon* oils not mentioned above, viz., oil of *O. methylisoeugenoliferum* F. and oil of *O. pseudo-hirtum* F. On the hexahedron these are marked A and B. Both belong to Section I, *"Euorthodon."*



1. *Orthodon chinense* Kudo
2. *Orthodon hadai* Kudo
3. *Orthodon leucanthum* Kudo
4. *Orthodon perforatum* Ohwi
5. *Orthodon hirtum* Hara
6. *Orthodon tenuicaule* Koidz
7. *Orthodon grosseserratum* Kudo
8. *Orthodon formosanum* Kudo
9. *Orthodon elemiciniferum* Fujita
10. *Orthodon asaroniferum* Fujita
11. *Orthodon lanceolatum* Kudo
12. *Orthodon punctulatum* Kudo
13. *Orthodon linaloöliferum* Fujita

A. *Orthodon methylisoeugenoliferum* F.
B. *Orthodon pseudo-hirtum* F.

CUBIC MODEL OF ORTHODON SERIES

According to Fujita,[5] these two oils have the following composition:

(A) Oil of *Orthodon methylisoeugenoliferum* Fujita, "Nise-Hime-Shiso."

Yield	0.19%
Components	Methylisoeugenol (55%)
	l-Bisabolene (10%)
	α-Caryophyllene (15%)
	l-Copaene (20%)
	Benzaldehyde (1%)

(B) Oil of *Orthodon pseudo-hirtum* Fujita, "Shirage-Hime-Shiso-Modoki."

Yield	0.3%
Components	Carvacrol (48%)
	Thymol
	γ-Terpinene
	α-Caryophyllene

[5] *Ibid.* **65** (1944), 79, 220. *Chem. Abstracts* **41** (1947), 3585.

A few details should be added to the discussion of oil of *Orthodon perforatum* and oil of *Orthodon thymoliferum* as these oils possess some commercial interest.

Orthodon perforatum Ohwi (*Orthodon japonicum* Benth., *Mosla japonica* Maxim.) the so-called "Yama-Shiso," and *Orthodon thymoliferum* Kudo (*Mosla leucantha* Nakai, *Mosla thymolifera* Makino) the so-called "Ao-Yama-Shiso" grow wild in Japan.

About 1916, during World War I, they were cultivated first in the prefecture of Saitama near Tokyo, as a source of thymol. More recently the center of production has been moved to the prefecture of Ibaraki, which is adjacent to Saitama.

The seed is sown in the middle or toward the end of April. It germinates after three weeks; the plants are harvested in the middle of September when the grass has grown to a height of about 2 ft. and is flowering. The plants are dried under sheds and then steam distilled. One hectare yields about 3,700 kg. of dried grass. The yield of oil averages 1 per cent.

"Yama-Shiso" oil contains from 50 to 55 per cent of thymol which can be extracted [6] by means of a 5 per cent solution of caustic soda and regenerated by sulfuric acid. The crude thymol is purified by steam distillation and then crystallized from petroleum ether. By this method about 50 lb. of thymol are obtained from one hectare.

	Production of Dried Grass, Kg.	*Production of Oil, Kg.*
1940.....	21,440	216
1941.....	31,740	356
1942.....	33,240	320

After 1942, owing to the duress of the war, production was almost abandoned. After the war new plantings were started and at the time of this writing (middle of 1948) it is anticipated that in the district Ishioka (prefecture Ibaraki) the cultivation area comprises 2.2 hectares and that 6,600 kg. of dried grass will be harvested in the fall, which will yield about 66 kg. of oil, corresponding to about 30 kg. of thymol.

An oil of "Yama-Shiso" distilled by Hoshino [7] had these properties:

Specific Gravity at 15°.....	0.9154
Optical Rotation.....	+1° 0′
Refractive Index at 20°.....	1.4996
Acid Number.....	0.3
Ester Number.....	4.5

[6] Kariyone, *J. Pharm. Soc. Japan* (1920), 747.
[7] *J. Soc. Chem. Ind. Japan* **22** (1919), 557. *Chem. Abstracts* **13** (1919), 3278.

According to Fujita,[8] "Yama-Shiso" oil contains:

Thymol . . . . . 50 to 60%
p-Cymene . . . . . 30 to 35%
Moslene,[9] $C_{10}H_{16}$ (γ-Terpinene?)
α-Caryophyllene

OIL OF PATCHOULY

Essence de Patchouli *Aceite Esencial de Pachuli* *Patchouliöl*
Oleum Foliorum Patchouli

Introduction.—Our knowledge of the origin of patchouly oil for a long time has been vague and ambiguous. An important objective of the investigations undertaken by the author in British Malaya and Indonesia (the former Netherlands East Indies), therefore, was to clarify the former misconceptions associated with this oil.

The word "patchouly" seems to be derived from the Hindustan "pacholi." More than one hundred years ago precious Indian fabrics and shawls used to arrive in Europe, permeated with a strange odor which was considered characteristic and proof of oriental origin. It was only when the first shipment of dried patchouly leaves arrived in London, about 1844, that the long-sought secret of the mysterious scent was revealed. Soon, French manufacturers learned to perfume their homespun shawls with patchouly leaves in close imitation of the East Indian goods.

Botany.—There exist in the tropics several species of the *Labiatae* family with a patchouly-like odor. They serve mostly for the perfuming of shawls, carpets, and other woven materials; only one is actually used for the distillation of essential oil. The variations in the morphology of patchouly which are caused by soil and climatic conditions and the influence of cultivation seem to have rendered botanical classification difficult.

The patchouly plant was first described in 1845 by Pelletier-Sautelet, and named *Pogostemon patchouli.* In 1896, Holmes[1] identified it as *Pogo-*

[8] *J. Chem. Soc. Japan* **59** (1938), 931. *Chem. Abstracts* **32** (1938), 9393.
[9] Murayama, *J. Pharm. Soc. Japan* (1921), 769. *Chem. Abstracts* **16** (1922), 1568.
[1] *Pharm. J.* **56** (1896), 222; **80** (1908), 349.

stemon cablin Benth., a native of the Philippine Islands, the word "cablin" being derived from "cablam," vernacular name of the plant in the Philippines. The plant has also been described by Blanco in his *Flores de Filipinos* as *Mentha cablin.*

Today the true patchouly plant of commerce, *Pogostemon cablin* Benth. syn. *P. patchouli* Pellet var. *suavis* Hook., which serves for distilling the essential oil, is cultivated in British Malaya (Straits Settlements and Johore State) and more extensively in Indonesia (Northern Sumatra). The Malayan vernacular term "dhalum wangi" or "tilam wangi" means sweet or cultivated patchouly.

Pogostemon cablin Benth. has been grown experimentally and more or less successfully also in Madagascar, Réunion Island, the Seychelles Islands, and in Paraguay, where the author found it growing semiwild on an old, abandoned planting in the suburbs of Asunción.

Of late, patchouly has been cultivated also in the state of São Paulo (Brazil).

According to Finnemore: [2] "The leaves are two to four inches long and one and one-quarter to three and one-half inches broad. The margin is slightly lobed, and the lobes have crenate-serrate teeth (i.e., nearly equal-sided with curved edges), the lobes and apex of the leaf being obtuse. Hairs are abundant on the under surface along the ribs and give the leaf a pale appearance; they are not closely pressed to the leaf, but stand out a little."

Wild growing patchouly herb, which the natives sometimes mix with the cultivated leaves, is, according to Holmes,[3] a form of *Pogostemon heyneanus* Benth. In Malaya it is called "dhalum outan," "outan," meaning forest; it grows wild in Sumatra and Java between 1,000 and 2,000 m. altitude. *P. heyneanus* Benth., the so-called Java patchouly, is indigenous to India and often cultivated in gardens. It represents the only *Pogostemon* species which flowers; whence the Javanese term "dilem kembang," meaning flowering patchouly. The leaves are thinner, not lobed in the upper part and more distinctly and faintly serrate. Closely related to it is a variety which never flowers, and which has been grown for many generations in the gardens around Serang, in the province of Bantam, Java. Becker provisionally identified it as *Pogostemon hortensis.* Years ago, these "dilem" or Java patchouly varieties were distilled on a small scale, but the proper-

[2] "The Essential Oils," London (1926), 804.

[3] *Perfumery Essential Oil Record* **4** (1913), 369, 417. According to Index Kewensis, *Pogostemon patchouly* Pellet is identical with *Pogostemon heyneanus* Benth. from India and Burma, and with *Pogostemon cablin* Benth. from the Philippines.

ties of the oils were so different from those of the true *Pogostemon cablin* oil, and the odor so inferior, that production was abandoned.

Development of Patchouly Oil Production.—For many years, the bulk of patchouly oil was distilled in British Malaya, mainly on the island of Penang and in Singapore, Straits Settlements. Distillation was carried out with plant material cultivated originally on Penang and later largely in the state of Pahang and in the state of Johore, with Kluang and Segamat as centers. These leaves are frequently referred to abroad as "Penang patchouly" because *Pogostemon cablin* Benth. is known to have been cultivated in Penang since 1834. Today patchouly is no longer grown in Penang. Part of the dried leaf material was exported to Europe for distilling in modern essential oil factories, and the balance was processed in distilleries of Singapore, Wellesley, and Penang, and exported as Straits Settlements, Singapore, and Penang patchouly oil. On the other hand, the previously mentioned Java oil, distilled from a different plant variety, and quite inferior to true patchouly, never attained any commercial importance.

The production of patchouly oil took an entirely new turn when, at the beginning of this century, fairly important patchouly plantings were developed in the province of Achin or Atjeh (Sumatra, Indonesia). At first, all the leaf material was exported, sometimes directly to Europe but mainly via British Malaya, in particular via adjacent Penang and to a lesser extent via Singapore. As the cultivation of rubber trees in British Malaya attained ever-increasing importance and expanded rapidly, the small native owned patchouly plantings of British Malaya were greatly curtailed, so that patchouly distillers in Penang, Wellesley and Singapore had to rely more and more upon the dried plant material imported from neighboring Sumatra. However, the sharp decline in the price of rubber after 1919 again encouraged expansion of the patchouly plantings in British Malaya, with the result that Sumatra had difficulty in exporting its plant material. The year 1921 found the local growers of Achin on Sumatra with large stocks of dried patchouly leaves on hand; and, in order to alleviate this critical situation, the idea was conceived of distilling the accumulated plant material on the spot. The district government approached the Agricultural Experiment Station of Buitenzorg, Java, for guidance regarding the establishment of a local patchouly oil industry. Dr. Bobiloff was sent to Sumatra in an advisory capacity, and contributed greatly toward the new development. The industry was first controlled by the local governments, but with falling oil prices passed into the hands of natives and a few Chi-

nese. During the years prior to the outbreak of World War II, the new Sumatra industry had grown to such proportions that it represented then about 90 per cent of the world's total patchouly production; whereas British Malaya, which once held a monopoly, lost much of its former importance.

Trade of Leaves and Oil.—Thus, the province of Achin became not only the largest producer of oil but also the greatest exporter of dried leaf material. Prior to the conquest of Malaya by Japanese forces in 1941, ports of destination for the leaf material were Penang and Singapore in adjacent British Malaya, from where it was either transshipped to Europe and America or else used by the few remaining distilleries on the Malayan Peninsula for local distillation. It is impossible to ascertain to what extent the exports from British Malaya consisted of locally grown or imported Sumatra leaves.

During the years 1934–1940, the leaf exports from British Malaya averaged as follows:

About 35 per cent to the United States.
About 20 per cent to British India.
About 10 per cent each to France and Germany.
Some quantities to Hong Kong, Japan, Great Britain.

So far as the oil is concerned, production in Sumatra developed from a modest beginning to a yearly average of 15 to 20 metric tons or more. The export figures for oil from the Netherlands East Indies for 1936, 1937, and 1938 were about 13 metric tons, 22 tons and 17.72 tons, respectively. A small part of this oil was exported directly from the Achin ports, but the bulk was first shipped to Java and, after being passed upon by the Control of the Government Station in Buitenzorg, re-exported, together with the almost negligible quantities of Java oil, from the ports of Tanjong Priok and Sourabaya to foreign countries. The fact that the Sumatra oil was exported mainly via Java sometimes led to the erroneous belief that the oil had been distilled in Java, but the quantities of patchouly oil actually produced in Java have always been small.

The quantities of Sumatra patchouly oil in Table 2.8 were shipped from the Netherlands Indies during the last years prior to World War II.

The oil shipped directly from Sumatra went partly to Singapore, Wellesley, and Penang in British Malaya and was, in all probability, re-exported from there either as such or perhaps together with spot distilled oils. Thus, it is possible that the oils marketed as Penang or Singapore

TABLE 2.8

Destination	Quantity in Kg. Net		
	1938	1939	1940
PATCHOULY OIL SHIPPED FROM JAVA			
Holland	820	...	...
Holland, Option	300	256	...
Germany	460	...	...
Britain	...	600	2,726
France	2,838	3,965	1,418
France, Option	2,327	1,434	...
Italy	...	810	395
Total to Europe	6,745	7,065	4,539
United States	3,053	8,125	29,369
British India	1,567	937	1,807
Japan	3,138	394	98
Singapore	...	...	100
Australia	...	...	614
Other Non-European Countries	287	208	202
Grand Total	14,790	16,729	36,729
PATCHOULY OIL SHIPPED FROM SUMATRA			
Holland	250	...	...
France	430	350	...
France, Option	946	550	...
Britain	...	400	...
United States	...	...	100
Singapore	1,256	156	300
Other Destinations	50	100	100
Grand Total	2,932	1,556	500

oils were, in reality, Sumatra oils or mixtures of Sumatra oils with lots distilled in the Straits Settlements from leaf material mostly imported from Sumatra. The label "Penang" or "Singapore" should be permitted only for oils actually distilled in Singapore or Penang from plant material grown locally or in the neighboring Malayan province of Johore. The export of Singapore oil fluctuated rather widely and averaged several tons a year.

At the present writing, it is impossible to estimate the extent to which the Japanese occupation of British Malaya and Sumatra, during the war years, may have affected the production of patchouly leaf oil in those areas. Because of the internal strife in the Achin region, little news has come out about conditions there. It may be some time before normal interchange of leaf material and oil is re-established between British Malaya and Sumatra.

In the war years, the Seychelles Islands became large producers of the oil. Its quality does not equal that of the Malayan oil, but consumers in England and America have been forced to accept it as the only available type. Even prior to World War II the French possessions of Madagascar and Réunion Island, too, produced small quantities of patchouly oil which went mainly to France. The oil has moreover been distilled in the state of Mysore (India), mainly from imported leaf material, but such oil is used entirely for home consumption in India. During World War II, efforts were made to grow the patchouly plant in Mysore.[4]

Planting and Harvesting.—The patchouly plant thrives best in a damp and warm climate with evenly distributed rainfalls. It is quite a soil-exhausting plant and, therefore, requires fertile ground. Virgin jungle land gives best results. High, undulating land is most suitable, but the plant flourishes also in low altitudes and slightly moist soil, provided it is properly drained. In the state of Johore, British Malaya, there were about 400 to 500 acres of patchouly under cultivation in 1939, numerous small Chinese land holders cultivating the plant on lots ranging from one-half to one, rarely up to ten, acres. In many instances, these small patches resemble vegetable gardens around the native huts. Today there are few larger plantings left; but, should prices of patchouly oil go up, it would pay to renew the larger plantings.

Patchouly is propagated by stem cuttings which are first planted in nursery beds, if possible during the rainy season. In some cases, the cuttings are planted directly into the fields and shaded until established. During the early stages, the young plants must be protected carefully against

[4] M. N. Subba Rao and N. Nagesi Rao, "Oil of Patchouli," *Govt. of Mysore, Bd. of Ind. & Sci. Research* (1945). Cf. *Soap, Perfumery & Cosmetics* **18** (1945), 880.

too much sunshine and guarded against weed growth. They are, therefore, sheltered by coconut palm leaves and frequently weeded out. Shade and plenty of water are the chief requirements until the young plants are properly established. They remain in the nursery for about four weeks, when they are transplanted into the fields, usually during March. In preparation for the planting of patchouly, the natives burn and clear the jungle and allow the soil to cool for a few months.

Before transplanting, the field must first be "chunkled" (a changkol is a native hand hoe), with the rows 3 ft. apart, and a distance of 3 ft. between each plant in the rows. In good soil, growth is fairly rapid; the plants become heavily branched and attain a height of 3 ft. Constant weeding during the growing period and some light cultivating are well repaid. Manuring with stable dung will be advisable if the soil is not sufficiently rich. The first cutting takes place six months after planting, with another harvest six months later and so forth for two and even three years, all depending upon the soil, weather, and climatic conditions. Thus, two yearly harvests are possible until the planting must be renewed after the third year. On the plantings of Johore, the first cutting gives, roughly speaking, 10 piculs and finally 6 piculs per acre (1 picul equals 133.3 lb.) until the planting becomes exhausted after two or three years. In Sumatra the yields vary considerably, from 80 to 3,600 kg. of dried leaves yearly per hectare, according to the condition of the planting and the number of annual cuts. Patchouly is frequently replanted on the same ground, after fresh "chunkling," although crop rotation would, of course, produce much better results. Subsequent plantings on the same ground are accompanied by a marked deterioration in the crop, but here, as in so many instances, the Chinese and native growers are rather indifferent and pay little heed to proper selection of soil and advice on the part of the agricultural departments. It is quite possible that better plants, a higher yield of plants per acre, and a higher yield of oil could be obtained, if more efficient agricultural methods were employed.

After transplanting in March, the first cutting takes place during the rainy season in December and January, when the bush is well grown and from 2 to 4 ft. in height (the average being 3 ft.). The cutting should be done early in the morning or toward evening and not during the hot noon hours. All parts of the plant—i.e., roots, stems, branches, and leaves—contain essential oil, but in varying proportions. The oil from the root is of very high specific gravity and of subnormal quality. The oil from the stems, too, is inferior and, therefore, neither part of the plant is used

for distillation. De Jong [5] in Buitenzorg carried out systematic experiments distilling the different parts of the patchouly plant and arrived at the conclusion that the oil is contained mainly in the three top (youngest) leaves, and that the oil content in these leaves remains constant, even if the weight of the leaves increases. De Jong, therefore, recommended cutting the plants when they have five pairs of leaves and distilling only the leaves, the low oil content of the stalks making the latter unsuitable for distillation. Thus, only the tops are cut, for which purpose the natives use scissors or sharp knives. If the entire plant were cut, regrowth would take too much time and the interval between harvests would be too long for profitable production. Besides, the buyers of leaves reject material which contains too many inert stems. Depending upon the height of the bush, the length of the cut tops should range from 10 in. to 1½ ft. A stalk 10 in. long and about ⅛ in. thick, with all the attached leaves, is considered very good distillation material. The harvest must take place before the leaves turn brown.

Drying and Curing of the Leaves.—After cutting, the stems and leaves are spread out to dry in thin layers on a hard, dry surface, usually in front of the native huts or, more rarely, on concrete floors. In Sumatra, the native growers frequently use bamboo racks. Proper drying is of great importance for the quality of the leaves, as well as of the oil. During the process, the material should be frequently turned over by hand or with sticks in order to promote even and thorough drying and to prevent fermentation.

Drying is usually done directly in the sun, although shade from a shed with air freely circulating would be preferable. Sun-drying doubtless causes some loss of essential oil by evaporation and, furthermore, leaves dried too quickly become brittle and easily turn to dust, which is difficult to distill. On the other hand, when dried too slowly the leaves remain damp, and develop that disagreeable moldy odor which remains predominant and is imparted even to the oil. Depending upon sunshine and atmospheric humidity, drying requires about three days, when the leaves develop a strong and characteristic patchouly note which is much less noticeable in the fresh leaves. Careful growers spread their leaves upon grass mats and cover them during rain showers, or take them under sheds or inside the huts upon indication of coming rain. The same is done as a protection from dew. During the drying, it is most important to avoid fermentation which readily takes place if the leaves are not spread out but stacked up in wet condition. Rain showers may by sheer force throw particles of

[5] *Teysmannia* (1906), (1909). "L'huile Essentielle de Patchouli," *Rec. trav. chim.* **24** (1905), 309; **30** (1911), 211.

earth or dust upon the leaves while spread on the ground; this accounts in part for the small percentage of earth or little stones sometimes found in bales of dried patchouly. Improper drying is not always due to bad will on the part of the growers, but often to weather conditions beyond their control. Even well dried leaves, if stored loosely for a prolonged time, may, on account of prevailing atmospheric humidity, develop that moldy odor which is so objectionable. The best way, therefore, would be to press the completely dry leaves into bales immediately; slightly wet material when baled would soon start to ferment, which condition can be noticed by heat development inside the bales.

In British Malaya, the dried leaves are first cleaned of foreign matter and of the larger stalks, packed into gunny bags (old rice bags) containing 40 to 50 catties (1 catty is about 1⅓ lb.), and sold to native, usually Chinese, middlemen who either sell them to the few local distillers or bale them and sell the pressed bales of 175 to 220 catties to the exporters in Singapore and Penang. In Sumatra the dried leaves, packed loosely in jute bags, are either brought to the native distilleries for distillation or are dried once more, baled, and exported to Penang and Singapore. The local distillers of Achin in Sumatra, for financial reasons, usually rush distillation and employ mostly loosely packed leaf material. This fact may be one of the reasons for the different quality of Sumatra distilled oil as compared with the Singapore, Wellesley, and European oils which are distilled exclusively from baled and pressed leaf material. It seems quite possible, and this is an interesting thought, that the storage of the leaves during the long haul from Malaya to Europe has some influence upon the quality of the European distilled oils. Years ago, Dr. A. Hischmann, an expert on Java essential oils, distilled in Batavia patchouly leaves imported from Sumatra which had previously been baled for export and stored for a year or two. He obtained excellent oils which were almost identical with European distilled oils and proved that Achin leaves, if properly aged and distilled, yield oils equal to those from Johore leaves.

Before reaching the exporters, the leaf material sometimes changes hands several times. The exporters in Singapore or Penang ship the pressed bales to Europe or America, usually with a guarantee of a minimum content of 3 per cent volatile oil. The author was rather surprised to learn how little most of these exporters were informed about the origin of the leaf material which they bought from Chinese middlemen, although an intimate knowledge of the plantation, its location, its age, the working methods employed, and the honesty of the growers and the middlemen would seem to be of considerable help. Not knowing these facts, the exporters usually base their guarantee of a minimum content of 3 per cent volatile oil upon a

certificate issued by a public analyst. In order to be absolutely sure of best quality, the distiller should purchase sorted material directly from a grower well known to him. In this respect, the few distillers of Singapore who obtain their leaf material directly from plantings in neighboring Johore have the advantage over the distillers abroad.

Adulteration of Patchouly Leaves.—Patchouly leaf material is frequently adulterated, the Chinese small growers and middlemen being quite ingenious in adding foreign material to the patchouly bales. The author was told by a leading distiller in Singapore that the Chinese manage to incorporate up to 16 catties of earth, sand, and dust into a gunny sack holding 50 catties of dried leaves. This can be done by mixing fine dust with the leaves or by sprinkling muddy water over the leaves, with subsequent drying. Another method of adulteration is to spray water inside of the bales or to pack the leaves very early in the morning while they are still wet with dew. Turning the wet leaves over during the night also increases their weight because of adhering dust gathered from the ground. Moist leaves can be packed more easily but the contents of such bales will later ferment. Pressed bales heavier than 200 catties are to be regarded with suspicion because they may contain moisture. Another form of adulteration is to admix previously distilled leaf material which still contains a small percentage of oil (about one-quarter to one-half per cent). Such leaf material is more difficult to detect, except under the microscope which reveals cells ruptured by steam. Sometimes the growers and intermediaries use other foreign plant material of similar appearance for adulteration, e.g., the leaves of the wild-growing patchouly which, according to Holmes,[6] is a form of *P. heyneanus*, or the leaves of *Ocimum basilicum* L. var. *pilosum*, called "ruku" by the Malayans, or those of *Urena lobata* L. var. *sinuata* (*Malvaceae*), called "perpulut" in Malayan, or *Hyptis suaveolens*, etc.[7] Because of the very strong odor of the patchouly leaves which is imparted to admixed leaves, detection of this form of adulteration is difficult.

Fermentation of Patchouly Leaves.—There exists some confusion in literature as to whether patchouly leaves are fermented during or after the drying process. De Jong[8] carried out systematic experiments, distilling separately the fresh, dried, and fermented patchouly leaves. He arrived at the conclusion that it is not advisable to distill fresh leaves because they yield very little oil, the bulk of the oil then coming over only during a second distillation, after the leaves have been dried.[9] The reason is that the oil-

[6] *Perfumery Essential Oil Record* **4** (1913), 369, 418.

[7] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 901.

[8] *Teysmannia* (1906), (1909). "L'huile Essentielle de Patchouli," *Rec. trav. chim.* **24** (1905), 309; **30** (1911), 211.

[9] It is a well known fact that *fresh* plant material, in general, offers great difficulties as far as complete exhaustion by steam distillation is concerned (the Author).

containing cells are distributed partly over the surface and partly through the interior of the leaves, and distillation of the fresh leaves liberates mainly the oil of the cells located on the surface. Drying or fermenting results in a considerably higher yield of oil simply because the membranes of the cells become more permeable and all plant cells yield their oil content. Since both dried and fermented leaves give about the same quantity of oil, the theory of additional oil formation by fermentation may be disregarded. If, during distillation of fresh leaves, the steam pressure is increased or if superheated steam is employed, the oil yield rises considerably because more cell walls are ruptured and the oil is freed. If, prior to distillation, fresh plants are comminuted, the yield of oil also increases. Any possibility of enzyme action responsible for this higher yield was disproved by De Jong who boiled the leaves with water before distillation.

The findings of De Jong may be accepted as true in regard to yield of oil, but they leave some doubt as far as odor value is concerned. The leading distillers in Singapore, for instance, claim that while fermentation might slightly increase the yield, it has an undesirable effect upon the quality of the oil, causing a somewhat moldy odor. Therefore, they prefer to use leaf material which has been well dried without fermentation. It is a matter of dispute whether the slight wilting ("curing") during drying can actually be considered a process of fermentation.

While this seems to be the generally accepted opinion of the distillers in the Straits Settlements, the author was told by Mr. A. H. G. Blokzeijl, near Sourabaya in Eastern Java, who started in 1937 planting patchouly slips imported from Sumatra, that he first dries the leaves in the shade and then stacks them up for two to three days. During this process, which resembles the curing of tobacco, the temperature is measured and controlled. The resulting somewhat moldy odor must be eliminated by spreading the slightly fermented leaves in thin layers on bamboo hurdles and thoroughly airing them.

According to Meijer,[10] the patchouly leaves, when baled, contain about 17 per cent of moisture which results in a slight fermentation in the bales. This "curing," as it is called, causes a moderate rise in the temperature inside the bales and is probably responsible for the better quality of oils distilled from baled patchouly leaves, after the long transport to Europe or America. If the leaves have been more thoroughly dried, prior to baling, and contain only 12 per cent or less of moisture, fermentation inside of the bales will not take place.

Distillation.—The art of distilling patchouly involves considerable experience and is of paramount importance for producing a high grade of oil.

[10] Private communication by Dr. Th. M. Meijer, Laboratorium Voor Scheikundig Onderzoek, Buitenzorg, Java.

Each lot of leaves requires special distillation methods, according to its condition. A lot containing much stalk material must be treated differently from one consisting mostly of leaves. A lot with much dust resulting from too brittle leaves again requires a different treatment.

The leaves should be distilled by direct steam generated in a separate steam boiler. Low steam pressure does not easily yield the oil; hence, prolonged distillation will be necessary. This, however, usually gives oils of somewhat different quality from those obtained by high steam pressure. On the other hand, high steam pressure alone does not necessarily result in a better yield, although it may shorten the period of distillation. In a modern distillery it is advisable to interchange high and low steam pressure, thereby giving full range to the forces of hydrodiffusion which are so important in the distillation of dried plant material (cf. Vol. I of this work, p. 114).

Production of High-Grade Oil.—There exist no general and fixed rules by which a high-grade oil of patchouly can be obtained, the working methods depending upon the type of still employed and upon the condition of the plant material. It can only be said that too short distillation gives oils of too low specific gravity; whereas too high steam pressure or too long distillation may yield oils that contain resins of disagreeable odor. The difficulty lies in finding the optimum and the proper point at which distillation should be stopped. The extreme limits of distillation vary within 6 and 24 hr. Sometimes a second distillation, after discharging and recharging the leaf material, is advisable because it yields another fraction of oil, hydrodiffusion being, very likely, the reason. The oil should not remain too long in contact with water, but should be separated as quickly as possible. If this does not take place automatically in the Florentine flasks, special means must be resorted to. From all these considerations, it appears that the native distillers of Sumatra, working with more primitive apparatus, are not always able to produce as high a quality of oil as that produced in a modern distillery.

Freshly distilled oils have a somewhat "green" and harsh note which, however, changes considerably with time. Aging of the oil for a prolonged period will develop that full, rich, and almost fruity note for which the best grades of patchouly oil are renowned and so highly esteemed by expert perfumers.

Thus, several factors influence the quality of the oil; they may be summarized as follows:

1. The Quality of the Leaf Material.—

(a) The richest soil gives the best leaf material; the latter should contain few stalks. Good material yields about 3.5 per cent of oil.

(b) The plants should not be cut prematurely; yet the native growers are inclined to do so because they are usually in need of cash. Such plant material is too young and gives inferior oil.

(c) The first two or three cuttings on a newly started planting give better leaf material; the quality declines with subsequent cuttings.

(d) The leaves should be slowly, carefully, and well dried in the shade without fermentation or wetting during the drying.

(e) Plants originating from the states of Johore and Pahang (British Malaya) seem to give a somewhat better oil than those from neighboring Sumatra (Indonesia). Probably, there exist in Sumatra several varieties of patchouly, the botany of which is not yet fully established; some sections of Sumatra produce better leaf material than others. It is also possible that the natives collect not only the planted patchouly but also leaves growing wild on the edges of jungles or on old clearings. Labor in Sumatra is rather scarce, and this may be one of the reasons why Sumatra leaf material is not always carefully prepared. In general, it can be said that the quality of the Sumatra lots is irregular—sometimes excellent, sometimes inferior.

(f) The age of the leaves seems to have a marked influence upon the quality of the oil. The superiority of European and American distilled oils may be due to the long transport of the baled leaf material. The usually high specific gravity of these oils may be attributed to evaporation of the lower boiling constituents of the oil in the plants, quite likely also to oxidation and polymerization, affecting the properties and the quality of the oil. In British Malaya and especially in Sumatra, the producers often distill the plant material much too soon after drying; in fact, some of that leaf material is not baled at all but arrives in the distilleries loosely packed in sacks. This, of course, gives oils of different quality.

2. The Method of Distillation.—

(a) The steam pressure during distillation must be carefully regulated. It is advisable to alternate between higher and lower steam pressure.

(b) Prolonged distillation usually gives a higher yield and better quality of oil, provided the oil is not "burned." The most valuable parts of patchouly oil are contained in the higher boiling fractions obtained after prolonged distillation. Evidently, increased consumption of fuel adds to the cost of production, but the top qualities of oil merit higher prices.

3. Aging of the Oil.—Aging of the oil is of utmost importance. A patchouly oil several years old possesses a much finer and fuller odor than one freshly distilled.

Production in British Malaya.—There existed, in former years, quite a number of distilleries in Penang and Singapore but, as far as the author

could ascertain,[11] there is, at present, only one operating in the Province of Wellesley and two in Singapore. One, the most renowned and largest distillery in Singapore, is owned by a Chinese family. It consists of 12 stills arranged in two batteries and housed in two different buildings. The steam is generated in a separate steam boiler. Only dried leaf material is used for distillation. Wetting, according to the owners, merely has the advantage of easier packing into the stills; it requires longer hours of distillation but does not influence the quality or yield of the oil. Each still holds about two piculs of dried plant material. Distillation of one charge lasts from 20 to 24 hr., at the most. The stills of one battery are connected with one large condenser. The Florentine flask is enclosed in a special compartment, to which only the owners have access. The yield of oil should be at least 3 per cent, provided the plant material is normal. When fully operating, this distillery could produce several thousand pounds of oil per month.

The other patchouly distillery of Singapore is operated by an Englishman who is making every effort to produce a high grade of oil, paying special attention to procuring the best plant material, well dried and not fermented, from neighboring Johore State. During the author's visit to this distillery there were in operation three modern stills, one constructed in England, one in France, and one in Germany. The yield of oil was about 3.3 per cent. One of the stills was equipped for automatic cohobation of the distillation waters, which increased the oil yield to about 3.8 per cent. The owner of this distillery did not believe in prolonged distillation, preferring to distill for only 12 hr. which, in his opinion, gave oils of better color.

Production in Sumatra.—As has been pointed out, several varieties of patchouly probably grow in Sumatra today, although most of the oil is distilled from *Pogostemon cablin* Benth., perhaps mixed with small quantities of wild-growing patchouly. Dr. A. Hischmann of Batavia distilled large quantities of patchouly leaves originating from different districts in Sumatra and found that a variety grown in Pangkalan Brandan on the northeast coast yielded the best oils. However, numerous efforts to establish the botany of this variety were in vain.

The main producing regions in Sumatra are located on the northwest coast, in the province of Achin (Atjeh), though plantations are also found in the adjoining part of Sumatra's east coast (Langkat). Prior to 1941, the leaf material was exported principally via the ports of Tampat Toean, Tjalang, and Meulaba on Sumatra's west coast. As in British Malaya, the patchouly is grown on native or Chinese owned small patches and holdings, the larger plantings being more or less controlled by local rulers (rajahs).

[11] Latest information through the courtesy of the American Consul General in Singapore.



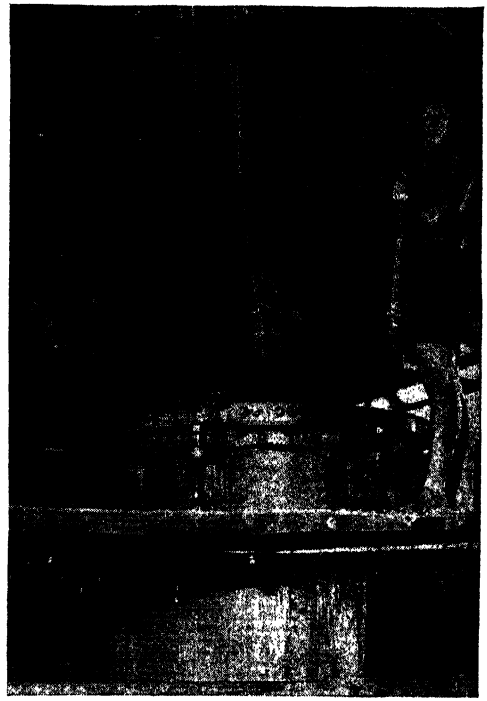


Above: A patchouly plantation in British Malaya.

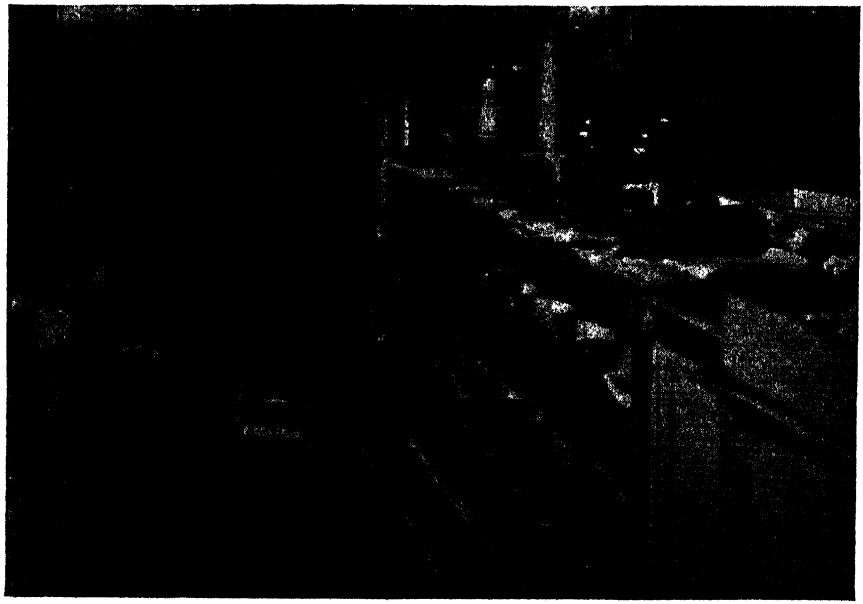
Left: Patchouly plants between rocks of limestone in Sumatra.

All photographs courtesy of Fritzsche Brothers, Inc., New York.

Right: A patchouly distillery in Sumatra: Removal of the spent leaf material.



Below: Filtration of patchouly oil in a distillery in Sumatra.



On the west coast of Achin and in Koeta Raja, in 1939, there were a number of small and medium sized patchouly oil distilleries, the most important ones being located—

In Lhokroet: a small European producer used direct fire distillation.

In Tjalang: a native distiller operated two distilleries. The stills were small and heated by direct fire.

In Meulaba: a native producer operated seven relatively large stills heated with direct steam.

In Tampat Toean: a native distiller operated thirteen large direct steam stills, whereas a Chinaman had a few small, direct fire stills.

In Bakongan: a native distiller operated seven small direct fire stills. He was the only one who moistened his leaf material 24-hr. prior to distillation.

The stills in Sumatra are constructed of iron, instead of copper, which gives oils of green color. Those heated by direct fire contain a false bottom (grid), so that the plant material is not in direct contact with the boiling water. Distillation lasts, as a rule, from 12 to 24 hr.

The Achin patchouly oils usually have a relatively low specific gravity, because of less careful selection of the plant material or, more likely, because most Achin patchouly oil is distilled in direct fire stills which operate with steam of low pressure. Another reason may be the condition of the leaf material, which is not baled previous to distillation, but packed loosely and carried in sacks to the distilleries. Having been stored for a few days in a warm and humid climate, these dried leaves often undergo slight fermentation.

Prior to 1941 a small part of the Sumatra oil was exported directly from the Achin ports, and the bulk was shipped first to Java and re-exported from there.

Production in Java.—We have already mentioned that, because of their inferior quality, the real Java patchouly oils are no longer produced. In former years, they were distilled from *Pogostemon heyneanus* Benth., or from *Pogostemon hortensis,* or from mixtures of both varieties. These oils, described in literature as Java or dilem oils, originated almost entirely from Serang in the province of Bantam where, since time immemorial, patchouly has been growing. *Pogostemon heyneanus* is the only form of patchouly known to flower. However, in Java some very good patchouly oils have been distilled (in small quantities) from the leaves of true *Pogostemon cablin* Benth., imported from Sumatra. A few planters imported cuttings of true patchouly from Sumatra or from the Straits Settlements and started plantations in Java. In most cases, however, it was found that after some time the plants deteriorated, especially in regard to oil formation. In a

few instances, this deterioration did not occur, but the reason remains unknown. Perhaps it is a question of altitude, of humidity, of shading, or of climatic or soil conditions. The best plant material was raised on the higher slopes of two volcanoes in eastern Java. The quantities of true patchouly oil actually distilled in Java amount to only a few hundred pounds annually. The principal planter in 1940 was Mr. A. H. G. Blokzeijl who had planted about 35 hectares on virgin soil, 1 hectare yielding about 15 kg. of oil.

Production in the Seychelles Islands.—Holdsworth-Haines [12] described in detail the methods of cultivating *Pogostemon patchouli* Pellet in the Seychelles Islands (around Mahé, Praslin and La Digue). Distillation is carried out mainly in direct fire stills and only in a few cases with direct steam. The yield of oil in both cases is about the same, but the oils differ slightly in regard to their constants. Calculated upon the dried leaf material, the yield of oil varies from 3½ to 5 per cent.[13]

A government decree stipulates that oils exported under the label of standard quality must conform to the analytical limits established and controlled by the government.

Export figures of Seychelles patchouly oil were 1,919 lb. in 1934; 5,702 lb. in 1945, the bulk of which went to England.

As was mentioned previously, the production of patchouly oil in the Seychelles Islands increased largely during World War II, when the Malayan and Sumatra oils were no longer available as a result of the Japanese occupation.

Production in Madagascar.—Insignificant quantities of patchouly oil were produced some years ago in St. Paul, Réunion Island, but the plantings since have been discontinued.

Madagascar produces only very small quantities, on the high plateaus near Lac Aloatra in the region of Moramanga. It is a rather primitive industry, distillation being carried out by small settlers and share croppers. The oil is usually shipped via Tamatave.

Nossi-Bé, a small island off the northern tip of Madagascar, also has started to experiment with the growing of patchouly, but only experimental quantities of oil have actually been distilled. The plants are propagated by slips in the shade of coffee trees; for harvesting, the tops of the plants are simply pinched off by hand. In the evening after the harvest, the leaves are spread on a cement floor and covered with a woolen cloth. The temperature rises somewhat and slight fermentation seems to soften the cell walls, facilitating distillation. This operation is repeated for three con-

[12] *Perfumery Essential Oil Record* **26** (1935), 171.

[13] According to the author's experience, a yield of 5 per cent seems unusually high.

secutive nights; but during the three intervening days the leaves are uncovered and spread out in the shade to dry.

Production in Europe and United States.—The best grade of patchouly oil undoubtedly is produced in the modern distilleries of Europe and America from plant material imported from British Malaya or Sumatra. Their superior quality can be explained by the more efficient methods of distillation in modern apparatus, higher steam pressure, etc., and especially by the condition of the plant material, which seems to improve greatly during the long transport in pressed bales. Such European or American distillates, properly aged, are undoubtedly the finest patchouly oils available.

Physicochemical Properties.—

I. Singapore Oils.—Four samples of genuine Singapore patchouly oils which the author secured in the leading Chinese distillery of Singapore had the following properties:

	Extra Special	*Special*	*Medium*	*Ordinary*
Specific Gravity at 15°/15°	0.991	0.980	0.971	0.968
Optical Rotation	Too dark	−56° 8′	−52° 0′	−49° 40′
Refractive Index at 20°	1.5128	1.5111	1.5100	1.5091
Saponification Number	14.0	13.1	10.3	8.4
Ester Number after Acetylation	27.1	23.3	23.3	17.7
Solubility	Soluble in 0.5 vol. and more of 90% alcohol	Soluble in 0.5 vol. and more of 90% alcohol	Soluble in 5.5 to 6 vol. and more of 90% alcohol	Slightly hazy in 8, clear in 9 vol. and more of 90% alcohol

Lots of genuine patchouly oils imported from Singapore and examined in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied within these limits:

Specific Gravity at 15°/15°	0.967 to 0.972, in one case 0.986
Optical Rotation	−49° 40′ to −55° 41′
Refractive Index at 20°	1.5090 to 1.5100
Acid Number	About 5.0
Saponification Number	5.6 to 10.7
Ester Number after Acetylation	16.8 to 21.5
Solubility	Soluble in 6.5 to 7 vol. of 90% alcohol, clear to cloudy with more

The properties of commercial Singapore oils usually fall within the limits of Sumatra oils, probably for the reason that in many cases so-called Singa-

pore oils are nothing but Sumatra distilled oils transshipped via Singapore under a Singapore label.

II. Sumatra Patchouly Oils.—The properties of Sumatra oils have been established, after mutual consultation between the Chemical Research Laboratory in Buitenzorg, Java, and the Trade Museum Division of Java. According to Koolhaas and Rowaan [14] they are:

Specific Gravity at 15°	0.950 to 0.990 (a high quality oil shows at least 0.970)
Optical Rotation	−40° 0′ to −72° 0′
Refractive Index at 20°	1.5060 to 1.5160
Acid Number	0.5 to 3.0
Ester Number	2.0 to 10.0
Solubility	Soluble in 1 to 10 vol. of 95% alcohol. (A good quality oil is soluble in 90% alcohol)

Genuine Sumatra patchouly oils imported and examined by Fritzsche Brothers, Inc., had properties varying within these limits:

Specific Gravity at 15°/15°	0.962 to 0.971
Optical Rotation	−48° 0′ to −54° 5′
Refractive Index at 20°	1.5072 to 1.5100
Saponification Number	3.4 to 7.5
Ester Number after Acetylation	9.1 to 22.4
Solubility	Soluble in 6.5 to 7.5 vol. and more of 90% alcohol. Occasional oils hazy to turbid in 10 vol. of 90% alcohol

III. Réunion Patchouly Oils.—Réunion oils imported some years ago and examined by Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 15°/15°	0.974 to 0.991
Optical Rotation	−57° 20′ to −65° 40′
Refractive Index at 20°	1.5095 to 1.5119
Saponification Number	6.5 to 16.3
Ester Number after Acetylation	15.9 to 23.3
Solubility	Soluble in 0.5 to 1 vol. of 90% alcohol, clear to cloudy with more

IV. Seychelles Patchouly Oils.—Before patchouly oils can be exported from the Seychelles Islands they must meet the following limits [15] imposed by the Seychelles government:

Specific Gravity at 20°	0.940 to 0.980
Optical Rotation	−43° 0′ to −68° 0′

[14] *Indische Mercuur* **60** (1937), 504.
[15] *Parfums France* **15** (1937), 297.

Refractive Index at 20°	1.505 to 1.510
Acid Number	0 to 5
Ester Number	0 to 9
Ester Number after Acetylation	7 to 28
Solubility	Soluble in 1 to 10 vol. of 90% alcohol

Several lots of patchouly oils from the Seychelles Islands examined by Fritzsche Brothers, Inc., during and after World War II had these properties:

Specific Gravity at 15°	0.962 to 0.966
Optical Rotation	−50° 44′ to −52° 15′
Refractive Index at 20°	1.5075 to 1.5095
Acid Number	0.9 to 1.9
Ester Number	1.8 to 8.2
Ester Number after Acetylation	12.0 to 16.4
Solubility at 20°	Soluble in 7.5 to 9 vol. of 90% alcohol, often with slight haze

The odor of these oils was not as characteristic and fine as that of the Singapore or Sumatra types, but this divergence might also have been caused by insufficient aging of the Seychelles oils which were in great demand during that period.

V. European Distilled Patchouly Oils.—Patchouly oils distilled in France under the author's direction, from imported plant material, had properties varying within the following limits:

Specific Gravity at 15°/15°	0.975 to 0.987
Optical Rotation	−54° 0′ to −65° 30′
Refractive Index at 20°	1.5099 to 1.5111
Saponification Number	3.3 to 9.3
Ester Number after Acetylation	17.7 to 22.4
Solubility at 20°	Soluble in 0.5 vol. and more of 90% alcohol

Gildemeister and Hoffmann [16] give somewhat wider limits for European distilled oil:

Specific Gravity at 15°/15°	0.966 to 0.995
Optical Rotation	−50° 0′ to −71° 0′
Refractive Index at 20°	1.507 to 1.513
Acid Number	Up to 5.0
Ester Number	2.0 to 12.0
Solubility	Usually soluble in 0.5 to 1.5 vol. of 90% alcohol; sometimes temporary opalescence with addition of alcohol. Many oils are soluble only in 4 to 6 vol.

[16] "Die Ätherischen Öle," 3d Ed., Vol. III, 903.

It is necessary to evaluate oil of patchouly by odor as well as by physico-chemical properties. The latter are in direct relation to the quality of the oil: a high specific gravity, high laevorotation, high refractive index, and good solubility indicate a good quality of oil.

A high specific gravity is associated with a high optical rotation; as the one increases, so does the other.

Adulteration.—Patchouly oil is frequently adulterated with cedarwood oil or, more cleverly, with the higher fractions of cedarwood oil, which are less pronounced in the typical cedarwood odor and, therefore, difficult to detect by olfactory test. In fact, the suspected patchouly oil must be left to evaporate for a few days on blotting paper before the faint cedarwood character becomes noticeable. The addition of cedarwood fractions has the effect of somewhat "sweetening" the patchouly note and, therefore, as a rule only the expert is able to detect it. The analyst will find indication of such addition in a slight lowering of the properties, especially of the solubility.

Chemical Composition.—Despite the commercial importance of patchouly oil and many attempts to elucidate its chemistry, relatively little is known about the principles which are responsible for the characteristic, strong odor of this oil.

The Schimmel chemists [17] found that about 97 per cent of the oil consists of compounds which have very little influence upon its odor. Of these, 40 to 45 per cent boil from 260°–280° and belong, therefore, to the sesquiterpene group. The balance seems to be composed of the so-called patchouly alcohol.

The presence of the following compounds has so far been established:

Benzaldehyde. Only traces are present, according to the Schimmel chemists.[18] Identified as semicarbazone m. 214°.

Eugenol. Benzoate m. 69°–70°.

Cinnamic Aldehyde. Semicarbazone m. 208°.

An Alcohol(?). Of rose-like odor, occurring in the fractions b_4 54°–95°.

A Ketone(?). The same fraction also contains a ketone yielding a semicarbazone m. 134°–135°.

Another Ketone(?). The above described ketone is accompanied by traces of another ketone possessing an orris-like odor.

Two Bases(?). Present in all low boiling fractions, imparting to them a strong, benumbing odor. When extracted from the oil with dilute sulfuric acid, a part of

[17] *Ber. Schimmel & Co.*, April (1904), 71; April (1905), 62.
[18] *Ibid.*

the bases had b_{3-4} 80°–130°, the other part b_{3-4} 135°–140°. The lower boiling base gave a very hygroscopic hydrochloride m. 105°–115°, not sharp.

The higher boiling base formed a hydrochloride m. 147.5°–148.5°; analysis pointed toward the empirical molecular formula $C_{14}H_{23}NO \cdot HCl$.

The presence of these amine-like compounds has frequently been observed by experimenters working with patchouly oil. Extraction with dilute mineral acid, followed by liberation with alkali and extraction with ether, gives a small amount of an oily substance having a very intense, not altogether pleasant odor. Furthermore, the odor of the oil deprived of these bases is greatly altered, becoming much softer and less characteristic of patchouly. These and other important odorous compounds occur in the lower boiling fractions, so that upon rectification of the oil care must be exercised to prevent their loss.

Two Sesquiterpenes(?). Fractionating a patchouly oil, von Soden and Rojahn [19] isolated two sesquiterpenes with the following constants:

(a) b_{750} 264°–265°, b_{3-4} 95°–96°, d_{15} 0.9335, α_D^{20} −58° 45′.

The compound added bromine and hydrogen bromide, and yielded a hydrochloride of oily consistency which did not solidify.

(b) b. 273°–274°, d_{15} 0.930, α_D +0° 45′.

A crystalline hydrochloride could not be obtained.

Patchouly Alcohol(?). The chemical composition and structural formula of patchouly alcohol, which in old oils sometimes precipitates as a crystalline deposit, has not yet been clarified. Montgolfier [20] established the empirical formula $C_{15}H_{26}O$; whereas Wallach [21] suggested the designation patchouly alcohol for the compound which formerly had been considered a camphor. According to Semmler and Mayer,[22] patchouly alcohol, m. 56°, b_8 140°, d_{20}^{65} 0.9924, α_D −97° 42′ (in chloroform solution), n_D^{65} 1.5029, is probably a saturated tricyclic tertiary alcohol. (The chromate of patchouly alcohol, according to Scholz,[23] melts at 117°–118°, not at 52°–53°, as claimed previously.)[24]

Losing water readily, patchouly alcohol forms the sesquiterpene patchoulene, b_{743} 252°–253°, b_{12} 112°–115°, d_{15} 0.9334, d_4^{20} 0.9296, α_D −36° 52′,[25] $[\alpha]_D^{20}$ −38° 5′, n_D^{20} 1.49835.

Patchoulene possesses a cedrene-like odor; its constitution has not yet been elucidated.

Azulene. Gladstone [26] reported the occurrence of azulene in the highest boiling constituents of patchouly oil.

A Sesquiterpene Alcohol. Pfau and Plattner [27] obtained from patchouly oil a sesquiterpene alcohol fraction b_{10} 130°–131°, d_{20} 0.9225–0.9245, α_D −45° 18′ to −46° 43′, n_D^{20} 1.5020 to 1.5030, which on dehydrogenation with sulfur yielded *S*-guaiazulene.

[19] *Ber.* **37** (1904), 3354.
[20] *Compt. rend.* **84** (1877), 88.
[21] *Liebigs Ann.* **279** (1894), 394.
[22] *Ber.* **45** (1912), 1391. *Ber. Schimmel & Co.*, April (1904), 74.
[23] Inaugural Dissertation, University Leipzig (1930). *Ber. Schimmel & Co.* (1931), 174.
[24] *Ber. Schimmel & Co.*, October (1908), 82, footnote.
[25] *Ibid.*, April (1904), 71; April (1905), 62. Cf. Simonsen, "The Terpenes," Vol. II (1932), 595.
[26] *J. Chem. Soc.* **17** (1864), 3. *Jahresber. Chem.* (1863), 545.
[27] *Helv. Chim. Acta* **19** (1936), 874.

Use.—Patchouly oil is one of the most important and valuable perfumers' raw materials. There is hardly a composition of fancy, and especially oriental, character that does not contain a good percentage of patchouly oil. It imparts strength, character, alluring notes, and lasting qualities. The oil is almost a perfume by itself.

Patchouly oil is equally indispensable in soaps, cosmetics, and incense.

The oil can truly be declared as essential, particularly in old, established perfume formulas of the French school.

SUGGESTED ADDITIONAL LITERATURE

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OIL OF PENNYROYAL

Introduction.—Although belonging to different genera of the *Labiatae* family, *Mentha pulegium* L., the Old World pennyroyal, and *Hedeoma pulegioides* (L.) Pers., the American pennyroyal, yield essential oils closely related in physicochemical properties, as well as in chemical composition. However, the American oil possesses a more pronounced mint-like odor, rather disagreeable. Both oils contain pulegone as the main constituent (85 to 92 per cent), the foreign (European and North African) oil usually containing more than the American type. Since pulegone is a very convenient base for the manufacture of synthetic menthol, oil of pennyroyal deserves consideration in any plan for producing synthetic menthol.

European and North African Pennyroyal Oil

Essence de Pouliot *Aceite Esencial de Poleo* *Poleiöl*
Oleum Menthae Pulegii

Mentha pulegium L., var. *eriantha* (according to Holmes) [1] grows wild and abundantly in the more humid and lower coastal regions of southern Spain (provinces of Huelva, Cadiz, Sevilla, and Malaga) and is distilled while in bloom during the summer months.

According to observations made by the author,[2] distillation of pennyroyal in Spain takes place in the type of field stills described under "Spanish Oil of Spike Lavender." In the case of pennyroyal the stills are usually 2 m. high and 1.6 or 1.8 m. wide, holding 70 or 90 arrobas (1 arroba = 11.5 kg. or 25 lb.) of plant material. Distillation of one batch (including charging, etc.) lasts altogether about 6 hr. and is completed when 190–240 liters of water have been distilled over.

The yield of oil from Andalusian pennyroyal amounts to approximately 1 per cent (8–9 arrobas of plant material yielding about 1 kg. of oil). This type of oil is the best produced in Spain, having a pulegone content of usually not less than 92 per cent.

Another and potentially very large producing region was opened only a few years prior to the outbreak of World War II, in Morocco. There, *Mentha pulegium* var. *villosa* Benth. (according to Miège) [3] also grows wild and very abundantly in several regions of the Riff Mountains, the Mid-Atlas, and the Saharan Atlas. The yield of oil varies from 1.25 to 2.0 per cent depending upon locality and season. The best oils originate from the regions Beni-Mellal du Tadla, Boulhaut, and Ouezzane (Riff). In Morocco the harvest takes place from the middle of May to the beginning of September.

No pennyroyal plantations exist in Spain or Morocco. The relatively low labor cost prevailing in those countries, especially in Morocco—where distillation of oil of pennyroyal is almost a family or tribal industry—permits production of the oil at low prices. Women and children collect the wild growing plant material and carry it to portable stills operated by the men. Obviously, the United States could never hope to compete with such a system and, therefore, efforts to produce the oil in this country by utilizing wild growing plants are doomed to failure. Domestic producers will have to overcome the handicap of high wages by raising pennyroyal on regular plantings and by utilizing machinery for sowing and harvesting.

[1] *Perfumery Essential Oil Record* **2** (1911), 254; **14** (1923), 235.
[2] "Spanish Essential Oils," *Am. Perfumer* **47**, December (1945), 49.
[3] Cf. Müller, *Parfumerie moderne* **33** (1939), 97. Naves, *Helv. Chim. Acta* **25** (1942), 732. Guenther, *Drug Cosmetic Ind.* **42** (1938), 304, 439.

Total Production.—Prior to World War II Spain produced annually and on the average 10 metric tons of oil of pennyroyal. Morocco used to produce a few tons per year, with a tendency toward an increase. During World War II production was very largely increased in Spain, as well as in Morocco, due to a heavy demand for the oil on the part of continental Europe (the oil was being used at that time as a starting material for the production of synthetic menthol). Demand has remained high even after the war. In 1947 Spain produced 27 metric tons of oil of pennyroyal; most of this supply was employed in Spain for the making of liquid (racemic) menthol. For 1948 the total was 30 metric tons.

Physicochemical Properties.—Shipments of genuine oils received by Fritzsche Brothers, Inc., from Spain and Morocco during the past years had properties which varied within the following limits:

Specific Gravity at 15°/15°	0.936 to 0.944
Optical Rotation	+15° 18′ to +23° 48′
Refractive Index at 20°	1.4829 to 1.4877
Pulegone Content	85.0 to 96.0%
Solubility	Soluble in 4.5 to 5.5 vol. of 60% alcohol, clear to hazy with more; occasionally opalescent to hazy in 4.5 to 5 vol. and more

The content of pulegone in oil of pennyroyal is usually determined by the neutral sulfite method. The figures thus obtained represent not only pulegone but also include certain other carbonyl compounds present.

Bennett [4] showed that the ketones in oil of pennyroyal react with the neutral sulfite solution much more slowly than other ketones occurring in other essential oils—carvone in oil of caraway seed or oil of dill, for example. Therefore, it is necessary, according to the same author, to shake the oil with neutral sulfite solution for about 3 hr. Otherwise, the figures obtained are too low. When assaying oil of pennyroyal, the laboratories of Fritzsche Brothers, Inc., New York, employ a hot neutral sulfite solution, the determination requiring about 4 hr. for completion.

Pinel [5] reported that the oil of *Mentha pulegium* L. distilled in Morocco is distinguished by its high pulegone content. The Moroccan oil, according to the same author, has these properties:

Specific Gravity at 15°	0.939 to 0.982 (occasionally 0.932 to 0.945)
Optical Rotation	Around +16° 30′ (occasionally up to +22° 33′)
Refractive Index at 20°	1.487 to 1.494

[4] *Perfumery Essential Oil Record* **9** (1918), 208.
[5] *Ann. chim. anal. chim. appl.* **23** (1941), 289. *Chem. Abstracts* **38** (1944), 3085.

Pulegone Content	89 to 97%
Solubility	Soluble in 1.5 to 2 vol. of 70% alcohol

When the outbreak of World War II severed the supply of natural menthol from Japan to continental Europe and when, for the same reason, European producers of synthetic menthol could no longer obtain Java citronella oil, Europe had to return to other, somewhat neglected sources for the manufacture of synthetic menthol, and particularly to oil of pennyroyal. As a result, the production of this oil, very suitable for the purpose, increased on the Iberian Peninsula to five or six times its prewar figure, when the oil was used almost entirely for the scenting of soaps. As Naves [6] pointed out, this increase became possible by exploiting not only new valleys in which the plant occurs abundantly, but also slopes and dry uplands on which a sparse growth of pennyroyal is intermingled with large proportions of other *Labiatae*, e.g., *Teucrium marum* L., *Nepeta cataria* L. (catmint), and others. The pennyroyal plants, unfortunately, were harvested in various stages of growth and with insufficient care. Furthermore, distillation was often carried out by unskilled hands and in apparatus ill adapted for the purpose. As a result, many parcels of oil with unusual and abnormal characteristics appeared on the market.

Naves [7] grouped these different types of Iberian (Spain and Portugal) pennyroyal oils into three classes, namely:

Normal type.—Oils produced prior to World War II exclusively from true *Mentha pulegium* L., growing in the low coastlands of Andalusia. (These normal oils are again being produced since the end of the war.)

Type A.—Oils produced during World War II, characterized by a low specific gravity, low refractive index, and either an abnormally high or abnormally low optical rotation. Fractional distillation reveals that the oils with a high optical rotation contain a high percentage of *d*-isomenthone, those with a low optical rotation a high content of *l*-menthone.

From numerous observations, it appears that this abnormality is caused by growth in dry and sunny places. The properties of oils produced in Portugal during periods of drought confirm this contention.

Type B.—Oils produced during World War II, characterized by a high specific gravity, high refractive index, and a low optical rotation which is caused by high content of two ketones not hitherto observed in essential oils, namely, piperitenone and isopiperitenone.

These compounds occur mostly in oils from young plants harvested in damp places.

[6] *Perfumery Essential Oil Record* **35** (1944), 221.
[7] *Ibid.*

Type C.—Normal oils, except for their somewhat low optical rotation. These oils probably represent mixtures of Types A and B.

Naves [8] reported the physicochemical properties for these types of Iberian pennyroyal oils given in Table 2.9.

TABLE 2.9

Properties	Normal Type	Type A	Type B	Type C
Specific Gravity at 20°	0.932 to 0.936	0.925 to 0.932	0.938 to 0.943	0.934 to 0.942
Optical Rotation	+18° 0′ to +23° 0′	+9° 0′ to +18° 0′ / +23° 0′ to +28° 0′	+13° 0′ to +20° 0′	+10° 0′ to +22° 0′
Refractive Index n_D^{20}	1.483 to 1.488	1.480 to 1.485	1.493 to 1.497	1.484 to 1.491
Dispersion of Refraction $(n_F - n_C) \times 10^4$	126 to 132	118 to 125	139 to 144	125 to 138
Ketone Content (Neutral Sulfite Method)	87 to 96%	76 to 88%	90 to 94%	76 to 86%
Ketone Content (by Oximation)	87 to 94%	86 to 95%	82 to 85%	82 to 92%

According to Naves [9] the different ketones present in the variant types of pennyroyal oils behave differently with a solution of neutral sodium sulfite. Menthone and isomenthone practically do not react; piperitenone reacts more slowly than pulegone. The reaction with sulfite should be carried out in a boiling water bath for 3 hr. with continual shaking—preferably mechanical (cf. above).

Under the conditions of oximation suggested by Stillman and Reed,[10] and slightly modified by Naves [11] (oximation for 6 hr. and with reflux of ethyl alcohol on a water bath), the oximation of pulegone, menthone, isomenthone and piperitone is practically quantitative, whereas that of piperitenone will be incomplete. This difference in results between the two methods (neutral sulfite and hydroxylamine) may be interpreted as follows: "A higher value by the hydroxylamine method will be proportional to the richness in menthone and isomenthone, except for the group C of oils. The lower results of the B oils indicate the richness in piperitenone. In oils of the C class the proportions of menthone and isomenthone on the one hand, and piperitenone on the other hand, are not in equilibrium and the sense of the difference shows which is the higher" (Naves).[12]

[8] *Ibid.*
[9] *Ibid.* Cf. *Helv. Chim. Acta* **26** (1943), 162, 172.
[10] *Perfumery Essential Oil Record* **23** (1932), 283.
[11] *Helv. Chim. Acta* **26** (1943), 164, 172.
[12] *Perfumery Essential Oil Record* **35** (1944), 221.

The same author suggested that a careful analysis of pennyroyal oil should comprise the determination of the specific gravity, optical rotation, refractive index, dispersion $n_F - n_C$, ketone content by both the neutral sulfite method and by oximation, and fractional distillation. Special importance should be given to the dispersion of refraction as determined in a Pulfrich instrument.

Naves [13] indicated the properties (given in Table 2.10) for the various ketones occurring in the above-described types of pennyroyal oils.

TABLE 2.10

	l-Menthone	*d*-Isomenthone	*l*-Piperitone	*d*-Pulegone	Piperitenone
b_{10}	82°–83°	83.5°–84.0°	96°–97°	94°–95°	106°–107°
d_{20}	0.8949	0.9002	0.9328	0.9370	0.9774
$[\alpha]_D^{20}$	−28° 18′	+95° 0′	−67° 48′	+22° 22′	±0°
n_C^{20}	1.44844	1.45083	1.48064	1.48268	1.52393
n_D^{20}	1.45082	1.45322	1.48420	1.48460	1.52942
n_F^{20}	1.45659	1.45902	1.49284	1.49544	1.54273
$(n_F - n_C) \times 10^4$	81.5	81.9	122.0	127.6	188.0

Before closing this discussion it should be pointed out that since the end of World War II the oils shipped from Spain and North Africa are again of the normal type, containing pulegone as chief constituent.

Chemical Composition.—The ketone forming the main constituent of oil of pennyroyal derived from *Mentha pulegium* L. was first identified by Beckmann and Pleissner [14] and named pulegone. Other constituents of the oil were later reported by Tétry,[15] but the most thorough examination of oil of *Mentha pulegium* L. was undertaken more recently by Naves [16] who examined normal and abnormal oils (see above) produced during World War II under variant conditions in Spain, Portugal, and Morocco. The constituents identified by Naves and by the earlier workers are listed below. In general it can be said that, with the exception of probably nepetalactone (the presence of which in an oil of pennyroyal seems to be due to contamination of the plant material with *Nepeta cataria* L.), all the constituents observed by Naves in the abnormal oils (types A, B, and C) are present

[13] *Ibid.*
[14] *Liebigs Ann.* **262** (1891), 1.
[15] *Bull. soc. chim.* [3], **27** (1902), 186.
[16] *Perfumery Essential Oil Record* **35** (1944), 221.

also in the normal oil, but in variant proportions. The difference between normal and abnormal oils, therefore, is of a quantitative order so far as the percentage of constituents is concerned. The quantity of menthone and isomenthone in the normal oils never falls below 2–3 per cent;[17] piperitenone and 1-methyl-cyclohexan-3-one can be completely absent; 3-octanol and Matsutake alcohol are always present. *In normal oils the ketone fraction consists almost entirely of pulegone.*

l-α-Pinene. Identified by Naves;[18] oxidation with potassium permanganate yielded pinonic acid, the semicarbazone of which melted at 201.5°–202°.

l-Limonene and Dipentene. Also identified by Naves[19] who prepared the tetrabromide m. 104°. Previously these terpenes had been observed by Tétry[20] in the lowest boiling fraction b. 170°–173° which was strongly laevorotatory.

d-Pulegone. According to Beckmann and Pleissner,[21] 80–92 per cent of the oil boils between 212°–216° at 760 mm. and consists chiefly of pulegone. Naves[22] identified *d*-pulegone by means of its semicarbazone m. 171°–171.5°, and of its phenyl-4-semicarbazone m. 142°–143°.

l-Menthone. The presence of this ketone in oil of pennyroyal was first reported by Tétry who prepared a semicarbazone m. 184°. Naves,[23] however, found only laevorotatory menthone in oil of pennyroyal.

d-Isomenthone. Naves[24] separated menthone and isomenthone by means of the hydrochlorides of their oximes, that of *d*-isomenthone melting at 129°–129.5°, and at 130°–131°.

Piperitone. Morani[25] had observed that the ketonic fraction of Sicilian pennyroyal oil (*Mentha pulegium* var. *hirsuta*) contains substantial quantities of *l*-piperitone. Naves,[26] investigating a Moroccan oil of pennyroyal (*Mentha pulegium* var. *villosa* Benth.) which was distilled from young plants, found that it contained 2–4 per cent of piperitones. He characterized *dl*-piperitone by the preparation of its α-semicarbazone m. 224°–225°.

In a somewhat later publication the same author[27] isolated piperitone from a fraction $b_{2.5}$ 82°, α_D −3° 6′ (0.3 per cent of the oil), which boiled between pulegone and piperitenone. He succeeded in preparing the *dl*-piperitone-4-phenylsemicarbazone m. 191°–192°, but not that of *l*-piperitone, although *l*-piperitone was probably present in the oil. Naves explains this by the ease with which optically active piperitones are racemized.

[17] Private communication from Dr. Y. R. Naves, Geneva.
[18] *Helv. Chim. Acta* **25** (1942), 744.
[19] *Ibid.*
[20] *Bull. soc. chim.* [3], **27** (1902), 186.
[21] *Liebigs Ann.* **262** (1891), 1.
[22] *Helv. Chim. Acta* **25** (1942), 738; **26** (1943), 172.
[23] *Ibid.* **26** (1943), 162.
[24] *Ibid.*, 167.
[25] *Ann. chim. applicata* **13** (1923), 37. *Rivista ital. essenze profumi* **7** (1925), 65.
[26] *Helv. Chim. Acta* **25** (1942), 738.
[27] *Ibid.* **26** (1943), 171.

Piperitenone (1,4[8]-*p*-Menthadien-3-one) and Isopiperitenone (1,8[9]-*p*-Menthadien-3-one). In the same (abnormal) oil Naves [28] observed two ketones, viz., piperitenone and isopiperitenone, which amounted to 24 per cent of this oil. (The same oil also contained 62–64 per cent of *d*-pulegone and 2–4 per cent of piperitones.) The fractions in which piperitenone and isopiperitenone were present had these properties:

$b_{2.5}$	97°
d_4^{20}	0.9738 – 0.9742
α_D	−2° 10′ to −2° 17′
n_D^{20}	1.5284 – 1.5288

The odor was less mint-like, weaker and more unpleasant than that of pulegone. Piperitenone yielded a 2,4-dinitrophenylhydrazone m. 184°–184.5° (recryst.).

Piperitenone readily isomerizes to thymol m. 50°–50.6°.

Menthol. According to Tétry,[29] about 10 per cent of the fraction b_{20} 100°–120° of pennyroyal oil consists of menthol which he identified by means of its phenylurethane m. 111°–112°.

In the course of his investigations Naves also observed a number of compounds which in the various types of pennyroyal oil occur in variant but small quantities, the normal type of oil containing traces only:

1-Methyl-3-cyclohexanone.

b_{732}	167°–168°
b_2	52°–52.5°
d_4^{20}	0.9155
$[\alpha]_D$	+12° 55′
n_D^{20}	1.4439

identified by means of its semicarbazone m. 178°–178.5°.

1-Methyl-1-cyclohexen-3-one.

b_{732}	171°–172°
b_2	53°–53.5°
d_4^{20}	0.9689
$[\alpha]_D$	±0°
n_D^{20}	1.4947

identified by means of its semicarbazone m. 198.5°–199°.

3-Octanol and Acetate. Naves [30] isolated the above-mentioned two ketones from the fraction b_2 50°–55° of a Portuguese pennyroyal oil, and from them separated, by borization, a secondary *d*-octanol b_2 53°–54°, d_4^{20} 0.8248, $[\alpha]_D$ +8° 44′, n_D^{20} 1.4277 which yielded an allophanate m. 182°–182.5°. Examining several other types of pennyroyal oil, the same author [31] found that this amylethylcarbinol b_{732} 176°–176.5°, $b_{2.2}$ 52°–53°, d_4^{20} 0.8246, $[\alpha]_D^{20}$ +7° 56′ (homogeneous), n_D^{20} 1.42682 occurs in the oil in variant proportions (0.2–1.0 per cent), free and as acetate, the acetate having these properties:

[28] *Ibid.* Cf. *ibid.*, 162. Cf. Naves and Papazian, *ibid.* **25** (1942), 984, 1023, 1046.
[29] *Bull. soc. chim.* [3], **27** (1902), 186.
[30] *Helv. Chim. Acta* **26** (1943), 168. Cf. Naves and Papazian, *ibid.* **25** (1942), 984, 1023, 1046.
[31] *Ibid.* **26** (1943), 1034.

b_{728}	176°–176.5°
b_{10}	74°
d_4^{20}	0.8654
α_D	−4° 23′ (laevorotatory!)
n_D^{20}	1.4168

n-1-Octen-3-ol (Matsutake Alcohol). In a later publication Naves [32] confirmed the occurrence of 3-octanol in oils of pennyroyal from the Iberian Peninsula and observed that these oils also contain octenols. He identified one of them as laevorotatory *n*-1-octen-3-ol (Matsutake alcohol) b. 175°–175.2°, $b_{3.5}$ 53°, d_4^{20} 0.8383, α_D −15° 15′, n_D^{20} 1.43675; it yielded an iodo-4′-xenylurethane m. 165°–166°. The odor of the alcohol was musty, reminiscent of forest humus.

1-Methyl-3-cyclohexanol. In various lots of oil Naves [33] also detected 1-methyl-3-cyclohexanol by first acetylizing the alcohols b_2 50°–55°, fractionating the acetates, and regenerating the alcohols $b_{5.6}$ 61°–62°, d_4^{20} 0.885–0.888, α_D −1° 6′ to −2° 2′, n_D^{20} 1.4461–1.4474. Oxidation with potassium bichromate yielded *d*-1-methyl-3-cyclohexanone which could be identified by the preparation of its *l*-semicarbazone m. 178°–178.5°, $[\alpha]_D^{27}$ −38° 11′ (c = 8.016 in acetic acid).

1,1,3-Trimethyl-4-cyclopentanone. In the course of further work on oil of pennyroyal, Naves [34] observed that it contains also a small quantity of optically inactive 1,1,3-trimethyl-4-cyclopentanone which he extracted from a terpene and alcohol fraction b. 155°–162° by means of the reagent P of Girard and Sandulesco. The regenerated ketone b. 159.5°–160.5°, d_4^{20} 0.8740, n_D^{20} 1.43075 yielded a semicarbazone m. 158.5°–159°, and a dinitro-2,4-phenylhydrazone m. 160.5°–161°.

A Lactone(?) $C_{11}H_{14}O_3$. According to Naves,[35] this compound is identical with that found by Sernagiotto [36] among the products of the autoxidation of pulegone.

Nepetalactone(?). Naves [37] reported about the occurrence of another lactone, with a very bitter taste, in oil of pennyroyal; it may be the nepetalactone discovered earlier in the essential oil of *Nepeta cataria* L. (catnip oil). This lactone was probably contributed to the oil of pennyroyal in question by the admixture of *Labiatae* other than *Mentha pulegium* L., to the distillation material.

Use.—See "American Pennyroyal Oil," below.

American Pennyroyal Oil
(Oil of Hedeoma)

Essence d'Hedeoma *Aceite Esencial de Poleo Americano*
Amerikanisches Poleiöl *Oleum Hedeomae*

Hedeoma pulegioides (L.) Pers., is an indigenous annual plant, 9 to 15 in. high, with a small branching fibrous root and quadrangular stem from

[32] *Ibid.*, **1992.**
[33] *Ibid.*
[34] *Ibid.* **27** (1944), **52.**
[35] *Perfumery Essential Oil Record* **35** (1944), **223.**
[36] *Gazz. chim. ital.* **47**, I (1917), 150.
[37] *Perfumery Essential Oil Record* **36** (1945), **121.**

which spring numerous slender erect branches. It flowers from June to October. The plant is common in the Eastern and Middle Western states, and in the South; and it thrives best in dry ground. Like *Mentha pulegium* L., American pennyroyal contains a volatile oil of pungent mint-like odor which can be isolated by steam distillation. American pennyroyal grows well on average upland soils and is frequently abundant on sandy or gravelly slopes. For field planting, Stockberger [38] recommends sowing the seeds in rows in the fall, not more than ¼ of an in. deep, since they rarely germinate if planted at a greater depth. The plants come up early in spring, and for best results clean cultivation and freedom from weeds are essential.

Early in summer, when the plants are in full bloom, they may be mowed. To prepare the herb for market the plants are dried, preferably in the shade and carefully packed immediately after drying. Removal of all large stems improves the quality of the product. The herb should be marketed promptly, since it deteriorates with age. For production of the volatile oil, the plants should be harvested when in full flower and distilled when dried. It is usually easier to distill herb material at clover dryness rather than in the green, fresh state. Less steam and a shorter distillation time are required when the plants have been properly dried.

According to Stockberger [39] returns from an experimental area indicate that a yield of about 1,200 lb. of dried herb per acre may be expected. The yield of oil varies from 15 to 30 lb. per acre. According to Gildemeister and Hoffmann,[40] distillation of flowering American pennyroyal gives about 0.6 to 1.0 per cent of oil.

Physicochemical Properties.—The same authors [41] indicate the following limits:

Specific Gravity at 15°/15°	0.925 to 0.940
Optical Rotation	+18° 0′ to +35° 0′
Solubility	Soluble in 2 vol. and more of 70% alcohol

The content of pulegone in American pennyroyal is usually somewhat lower than in the foreign variety (*Mentha pulegium* L.).

Chemical Composition.—The chemistry of American oil of pennyroyal was investigated by Habhegger [42] who identified pulegone as a principal constituent, by Kremers,[43] and later by Barrowcliff [44] who established the presence of:

[38] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. **663** (1935), 29.
[39] *Ibid.*
[40] "Die Ätherischen Öle," 3d Ed., Vol. III, 718.
[41] *Ibid.*, 719.
[42] *Am. J. Pharm.* **65** (1893), 417.
[43] *Proc. Am. Pharm. Assocn.* **35** (1887), 546. *Am. J. Pharm.* **59** (1887), 535. *Pharm. Rundsch. New York* **9** (1891), 130.
[44] *J. Chem. Soc.* **91** (1907), 875.

l-α-Pinene. Small quantities in the fraction b. 155°–165°. Identified as nitrolbenzylamine m. 122°, and as nitrosochloride m. 103°–104°.

l-Limonene and Dipentene. Small quantities in the fractions b. 165°–170° and 170°–180°. Preparation of the tetrabromides m. 104° and m. 124°, respectively.

1-Methyl-3-cyclohexanone. B. 167°–168°. Identified as semicarbazone m. 182°–183°. The oil contained 8 per cent of this ketone.

l-Menthone. B. 207°–208°. Identified as semicarbazone m. 184°–186°, and as oxime m. 58°–59°.

d-Isomenthone. B. 209°–210°. Semicarbazone m. 125°–126°. Identical with the dextrorotatory constituent of Beckmann's[45] "inverted menthone." According to the nomenclature of Aschan, this compound should be named *d*-isomenthone. The amount of *l*-menthone and *d*-isomenthone constituted about 50 per cent of the oil.

Pulegone. The main constituent b. 221°–222°. Identified as semicarbazone m. 171°. The oil contained about 30 per cent of pulegone.

A Sesquiterpene Alcohol(?). About 2 per cent of the oil consisted of a compound which distilled in the fraction b. 300°–310°. The nature of this sesquiterpene alcohol remains unknown; it yielded a sesquiterpene of these properties:

b.	270°–280°
d_{20}^{20}	0.8981
α_D	+1° 4′
n_D^{20}	1.5001
Mol. refr.	66.8

Formic Acid. Free and in ester form.

Acetic Acid. In ester form.

Butyric Acid. Free.

Isoheptylic Acid.

Octoic Acid. Free and in ester form.

Decylic Acid. Free and in ester form.

Salicylic Acid. Probably as methyl salicylate.

A Dibasic Acid(?) (in Ester Form). M. 83°–85°; probably it has the empirical formula $C_8H_{14}O_4$.

A Phenol(?). The oil also contained small quantities of a phenol which was not identified.

Use.—Pennyroyal is a gently stimulant aromatic.

The main use of the oil is in the scenting of soaps, and for the manufacture of synthetic menthol. This applies chiefly to the European and North African oils, as very little, if any, oil of pennyroyal is produced at present.

[45] *Liebigs Ann.* **250** (1889), 325, 334. *Ber.* **42** (1909), 847.

SUGGESTED ADDITIONAL LITERATURE

G. V. Pigulevski, "Russian Ethereal Oils," *J. Russ. Phys. Chem. Soc.* **51** (1920), 60. *Chem. Abstracts* **17** (1923), 3231.

I. L. Rosenthaler, "Microchemical Characterization of Essential Oils," *Pharm. Acta Helv.* **1** (1926), 117.

M. G. Cancer, "Results of Distillation of Wild Plants from Calabria," *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi* **14** (1939), 147. *Chem. Zentr.* II (1940), 2825.

OIL OF PEPPERMINT

Essence de Menthe Poivrée *Aceite Esencial de Menta Piperita*
Pfefferminzöl *Oleum Menthae Piperitae*

Botany, Habitat, and Range.—The question of ancestry of some of the mints, such as the spearmints, peppermints, and Japanese mint, is very complicated. They are evidently hybrids so complex that it is hazardous to guess their parentage. Ruttle[1] found that the *Mentha spicata* plants he examined could be regarded neither as a simple hybrid between *M. longifolia* and *M. rotundifolia*, as they were formerly held to be, nor as pure species. Because of the existence of numerous hybrids, the botanical nomenclature of peppermint, too, is confusing. Suffice it here to summarize the principal points of this complicated subject.

According to Millspaugh,[2] peppermint is a native of Mediterranean countries. As our cultivated *Mentha piperita* L. rarely develops seed, Bacon, Jenison and Kremers,[3] Bruckner,[4] and Bacon[5] came to the conclusion that it is a hybrid resulting from a cross between *M. viridis* L. and *M. aquatica* L. The former, according to Schürhoff,[6] is itself a hybrid of *M. sylvestris* L. and *M. rotundifolia* L.; therefore, *M. piperita* may be considered a triple cross between *M. sylvestris* L. × *M. rotundifolia* L. × *M. aquatica* L. This would seem important from the practical point of view: the odor and flavor of *M. piperita* L. improve as the plant approaches *M. aquatica* L., and as the plant departs from *M. viridis* L. which has a harsher odor. Theo-

[1] "Cytological and Embryological Studies on the Genus *Mentha*," Gartenbauwiss. **4** (1931), 428–468 (in German).
[2] *Medicinal Plants* **2** (1892), 116; publ. by J. C. Korstay & Co., Philadelphia.
[3] *J. Am. Pharm. Assocn.* **12** (1923), 1075.
[4] *Angewandte Botanik* **10** (1928), 87.
[5] *J. Am. Pharm. Assocn.* **17** (1928), 1094.
[6] *Arch. Pharm.* **267** (1929), 515.

retically it thus appears advisable to grow selected plants which contain a maximum of elements inherent to *M. aquatica* L. However, the varieties and strains of peppermint actually under cultivtaion are the result of natural crosses, since the plant has not yet been produced by controlled hybridization (see section on "Diseases," below).

Peppermint, naturalized in the United States from Europe, may be found growing wild in damp places from Nova Scotia to Minnesota, and south to Florida and Tennessee. It is extensively cultivated, as we shall see later, in southern Michigan, northern Indiana, Oregon, Washington, and Ohio, growing there in two commercially important forms, viz., the black or English mint, and the American mint. Differing somewhat in adaptiveness to the cultural conditions of this country, the two varieties yield our commercial American peppermint oil.

The form most extensively grown in the Middle West (main producing region of American peppermint oil) is the so-called English or black mint, *M. piperita* var. *vulgaris* L., originally brought from England. This plant gives a high yield of oil and is hardy, but not nearly so resistant to climatic inclemencies as the naturalized American. In regard to diseases and insect pests, the English variety is just as susceptible to anthracnose and root rot as the American. The square branching stems of English black mint are of dark green to deep purple color and bear opposite, broadly lance-shaped, slightly toothed leaves of deep green color, 1 to 2 in. long. The plant spreads by a system of branching, underground rootstocks, and grows to a height of 1½ to 3 ft. Small purplish blossoms, which flower from late July to early September, are borne in terminal spikes on the main stem and branches.

The so-called American mint, *M. piperita* L., was also introduced originally from Europe; it resembles the English or black mint, but has green stems and leaves of lighter green color. It is hardy, and makes a good, vigorous growth, but does not give a high yield of oil. For the latter reason this type of mint should gradually be eradicated from those commercial peppermint fields where it still exists, and be replaced with the higher yielding English or black mint.

In a recent study of the nomenclature and subdivisions of the *M. piperita* grown in the United States, Hocking and Edwards [7] arrived at the conclusion that, in accordance with the International Rules,[8] it would appear proper to designate the species as *M. piperita* L. *pro parte,* Hudson, in place of the customary *M. piperita* L., inasmuch as Hudson's proper identifica-

[7] *J. Am. Pharm. Assocn.* **33** (1944), 333.

[8] Briquet, John, et al., "International Rules of Botanical Nomenclature," 3d Ed. (1935), Article 47.

tion in 1762 preceded that of Linnaeus' amended description (Species Plantarum, 2d Ed., 1763). This is in line with the considered opinion of the most profound students of *Mentha.*

The so-called white mint, *M. piperita* var. *officinalis* L., is a smaller plant; being less hardy it is not grown on a commercial scale in the United States. Its principal producing regions are located around Mitcham (Surrey, England). The oil distilled from this variety enjoys a high reputation; in fact, it is considered the finest of all commercial peppermint oils. However, the quantities of oil distilled today from the white mint are almost negligible.

The native American wild mint, *M. canadensis* L., must not be mistaken for commercial peppermint. It grows commonly on moist soil along streams, and often invades peppermint plantings. Yield and quality of the oil are subnormal.

The varieties of peppermint grown at present in Russia, Bulgaria, Italy, Hungary, Germany, France, and other European countries are descendants mainly of the English black mint; they will be described in chapters on their respective oils.

Japanese mint oil, produced and consumed in very large quantities, must not be designated in the United States as a peppermint oil, according to a ruling of the U. S. Department of Agriculture. The Federal Food and Drug Act requires that products containing Japanese mint oil, whether natural or dementholized, must be labeled "flavored with corn mint" or "flavored with field mint." The Japanese oil is distilled from *M. arvensis* L. subsp. *haplocalyx* Briquet, var. *piperascens* Malinvaud (*M. arvensis* var. *glabrata* Holmes). This ruling of the U. S. Department of Agriculture, although attacked as inaccurate by some botanists, aims at protecting our domestic peppermint oil industry against destructive competition from the Japanese oil. Crude Japanese mint oil contains such a high percentage of menthol that the latter can be isolated by simply freezing the oil. Even the low-priced dementholized Japanese oil has a menthol content ranging from 40 to 50 per cent and is, therefore, widely exported to Europe. It would undoubtedly present a most serious threat to our American peppermint oil, were its employment for flavoring purposes permitted in this country. However, the Japanese oil possesses a somewhat bitter and harsh taste, due to the presence of certain not fully investigated constituents, which cannot be completely removed by rectification.

Occurrence of Oil in the Plant.—In all peppermints the volatile oil occurs in numerous minute glands on the upper and under surfaces of the leaves; the stems contain little oil. It is, therefore, advisable to develop plants of

very bushy growth. The volatile or essential oil may be obtained from the cut plant material by steam distillation.

American Peppermint Oil

History of the American Peppermint Oil Industry.—According to historical records,[9] the world's consumption of peppermint oil toward the end of the eighteenth century was only 2,000 to 3,000 lb., produced mainly in Mitcham (Surrey, England); it amounted to about 12,000 lb. in 1844 and approximately one million pounds in 1940, which figure, however, does not include the very large Japanese mint oil production.

The first peppermint plants grown in the United States originated from England. They were imported in sacks, with earth around the roots as protection, and planted about 1816 in Wayne County, New York. From Wayne County peppermint was introduced into Ohio and from there, in 1835, into Pigeon Prairie, in St. Joseph County, Michigan. However, the sandy soil of Pigeon Prairie resulted in excessive winter-killing, and the young industry moved to Indiana. It remained small as late as 1855. About that time, the merits of well decomposed peat or highly organic soils, commonly known as black muck, were recognized, and since then peppermint plantings have spread over southern Michigan, northern Indiana, and small sections in Ohio. Taking South Bend as the center, peppermint is grown today within a radius of approximately 150 miles. The principal producing centers in Michigan are St. Johns, Kalamazoo and Decatur, St. Johns being the most important. The main producing centers in Indiana are South Bend, North Judson, and Wolf Lake. Aside from these Midwest regions, peppermint is grown in Oregon—the center being Portland—and in nearby southern Washington, where mint cultivation is confined to sections of the Columbia and Yakima valleys. Washington and Oregon are favored by a temperate climate, and abundant land suitable for the growing of peppermint and an ample supply of water are available—all factors which contributed to the rapid development of the peppermint oil industry in these western states.

During 1946 the production of peppermint oil in the United States was divided approximately as follows: [10]

[9] See: Bell, *Pharm. J. & Trans.* **10** (1850–1851), 297. Stearns, *Proc. Am. Pharm. Assocn.* **7** (1858), 449.

[10] Private communication of Prof. N. K. Ellis, Purdue Univ., Lafayette, Ind. Cf. *U. S. Dept. Agr., Agricultural Marketing Service.* Ellis, Fawcett, Gaylord and Baldinger, "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941), 3.

States	*Planted Acreage*	*Yield of Oil per Acre (lb.)*	*Total Production of Oil (lb.)*
Indiana	18,000	26.4	654,000
Michigan	14,000	21.1	388,000
Oregon	9,000	44.0	403,000
Washington	4,200	49.0	189,000
California	600	27.0	24,000
	55,180		1,620,000

The average production from 1935 to 1944 was as follows:

States	*Planted Acreage*	*Yield of Oil per Acre (lb.)*	*Total Production of Oil (lb.)*
Michigan	18,220	27.3	510,000
Indiana	12,140	24.7	203,000
Oregon	2,970	41.4	126,000
Washington	1,660	43.4	71,000
California	580	42.4	23,000
Ohio	300	31.6	9,000
	35,870		942,000

In 1947 production figures of oil of peppermint in the United States were approximately 800,000 lb. in the Midwest and 700,000 lb. in the far West.

In 1948 Washington and Oregon produced 815,000 lb. of peppermint oil, the Middle West only 765,000 lb. The Far West thus exceeded the Middle West in total production. This changed state of affairs is a result largely of three factors:

1. Diseases—chiefly mint wilt [*Verticillium* (sp.)]—have greatly damaged the peppermint fields in the Middle West in recent years, and particularly those in Michigan. The plantations in Washington and Oregon, on the other hand, have been (at least up to the present) free of diseases, and are not yet affected by mint wilt.

2. Ecological factors in Washington and Oregon are generally more favorable to the cultivation of peppermint. There is an unlimited supply of water for irrigation, for example. (Every peppermint field in these states is irrigated, sometimes by overhead irrigation.)

3. Yield of oil per acre is considerably higher in the Far West than in the Middle West.

Peppermint plantations in Washington and Oregon have, in general, longer life-spans than those in the Middle West.

According to the Crop Reporting Board of the United States Department of Agriculture the acreage by states for peppermint in 1947 and 1948 was:

	1947	1948
Indiana	18,500	16,500
Michigan	13,500	10,000
Oregon	11,000	11,300
Washington	4,400	4,200
	47,400	42,000

Ohio and California also produce small quantities of peppermint oil. Production in European and other countries will be discussed later.

Soil Requirements, Planting, and Cultivating.—Details on the planting, cultivating, harvesting, and distilling of peppermint are given in a number of excellent papers by A. F. Sievers,[11] N. K. Ellis,[12] and O. Johnson and J. C. Snyder.[13] Equally interesting and thorough studies on peppermint oil production are those of N. K. Ellis, K. I. Fawcett, F. C. Gaylord and L. H. Baldinger,[14] and M. G. Smith and L. Robertson.[15] It will suffice to summarize here the principles of peppermint culture recommended by the above-named experts and observed by the author during field surveys in the Middle West.

Peppermint grows on a wide range of soils, but thrives best in deep, rich, well-drained, but not overdrained, irrigated, former swamp lands. Various types of muck or loamy upland soil are best suited. A fairly open texture permits easy root penetration. It is the same type of soil as is required by celery, onions, cabbage, and similar crops for strong and rapid growth. Rabak[16] reported that light, sandy, or loamy soils produce oils of higher menthol and ester content than heavier soils.

An optimum of growth and oil yield is obtained on nonacid soils—pH 6.0 to pH 7.5, with pH 5.0 to pH 8.0 as the wider limit. If natural wind barriers are nonexistent, windbreaks should be planted. The land should be cleaned as thoroughly as possible. The better fitted the soil, the cheaper it is to eradicate weeds after planting, careful weeding being one of the main prerequisites for producing a high quality oil. The ground is prepared by plowing in fall or spring, and disking and harrowing before planting. For fertilizing the soil, well-rotted stable manure or commercial fer-

[11] "Peppermint and Spearmint as Farm Crops," *U. S. Dept. Agr., Farmers' Bull.* No. 1555 (1929).

[12] "Mint Culture in Northern Indiana," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Circ.* No. 227 (1937).

[13] "Peppermint Oil Production in Washington," *State College of Washington, Pullman, Washington, Extension Bull.* No. 227 (1936).

[14] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941).

[15] "An Economic Analysis of the Production of Peppermint and Spearmint in Indiana," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 459 (1941).

[16] *U. S. Dept. Agr., Bull.* No. 454, Washington (1916).

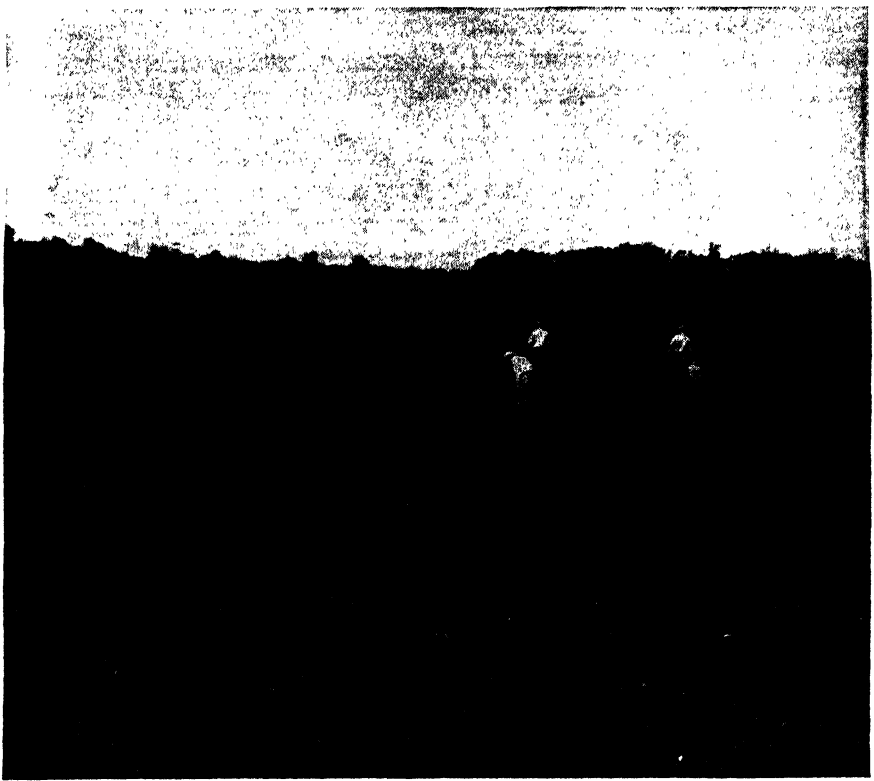
tilizers containing a high percentage of potash are recommended. According to Ellis and collaborators,[17] the physicochemical properties of peppermint oil are not affected by the application of fertilizer except as fertilizing affects the maturity of the plants. The yield of oil, however, is directly affected by the fertilizer. A mixture having a ratio of either one part of phosphate to two parts of potash, or equal parts of phosphate and potash, was most effective under the condition of their experiment. Commercial mixtures of these proportions would be 0–10–20, or 0–20–20. Three hundred pounds per acre gave the same results as 600 lb. per acre. Springer[18] reported that the yield of oil depends upon the quality of the soil and the fertilization, nitrogen-phosphor fertilizers giving the best results. The physicochemical properties and the chemical composition (content of total menthol, of ester menthol and menthone) are influenced not so much by fertilizers as by various degrees of drying, direct and prolonged exposure of the cut plant material to sunlight having the most unfavorable effect.

After the land has thus been prepared, furrows 5 to 6 in. deep and 30 to 42 in. apart are laid out. The most widely used method of growing peppermint is by propagation with rootstock. For this purpose roots from a previous year's planting are dug out during March, usually with the help of homemade machines, transformed plows, or potato diggers. From the data collected by Ellis and collaborators, it would appear that peppermint growers should prepare a special plot from which to take new plantings. This plot should be well fertilized, and cut at least by August 15th, under northern Indiana conditions. One acre so treated will plant ten acres. After adhering soil is shaken off, the roots are forked into piles and covered with earth, which keeps them moist until general conditions permit replanting. Little time should elapse between digging and replanting; the shorter this period the better the plants will develop. Most peppermint growers plant in the spring, but a few have learned to plant successfully during October and November. The planting is done by placing in the furrows selected runners overlapping one another and forming a continuous row. This may be accomplished by hand or by machines, some of the latter homemade. The furrows must be covered and the soil packed.

The roots begin to sprout in late April, the period depending upon weather conditions. Cultivation starts before the plants are up and is continued as long as possible to kill weeds. After horse- or tractor-drawn mint cultivators can no longer be used in the fields, due to the growth of the herb, the weeds must be removed by hand. Cultivation is continued for about forty-five days when the plants have approximately three-fourths matured.

[17] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941).
[18] *Botan. Arch.* **39** (1937), 102.

Peppermint planted during the previous fall or the spring of the same year is called "row mint," because the fields consist of clearly marked rows of plants. About 35 per cent of the present total mint acreage in the Midwest consists of "row mint." As the fields become older the rows overgrow, forming regular meadows. "Meadow mint," therefore, refers to fields two



Courtesy of Fritzsche Brothers, Inc., New York.

A peppermint field—"row mint"—in the United States.

years old and older. About 65 per cent of the total mint acreage consists of "meadow mint." The common practice is to keep a field in mint for three years, when its productivity declines. In order to restore the soil, the crop is then rotated with corn, potatoes or other suitable crops. However, some fields have been in mint for ten years and, in exceptional cases, even longer. The old mint plantings should be plowed under as late in the fall as possible, but before freezing sets in.

Thorough weed control of the mint fields is the most important requirement for obtaining a good yield and quality of oil. The presence of weeds

in the herb to be distilled would have a most harmful effect upon odor and flavor and make the oil unsalable. "Meadow mint" in its early stages may be worked by mint weeders (horse- or tractor-drawn cultivators). As the plants reach a growth of half-maturity, they become too large for mechanical cultivation and must thereafter be hand weeded; this is expensive, as the fields should be gone over every two weeks until the mint is matured and ready to be harvested.

Modern Farming of Peppermint.—What can be accomplished in the growing of peppermint by employing modern methods of agriculture has been



Courtesy of Richard Gumz Farm, North Judson, Indiana.

Loading peppermint in the field.

demonstrated by some of the largest and most successful producers of peppermint oil. One Indiana grower has cultivated as much as 2,000 acres of peppermint in a single year, producing over 80,000 lb. of oil. His fields are well drained to eliminate excessive moisture; in case of a dry spell, they may be irrigated by damming the ditches. Thirty to forty tractors are in operation day and night. The policy is to leave a field in mint for not more than two years. After the second year of mint, the field is changed to corn, potato, or onion; and in the third or fourth year it is again planted with peppermint. Evidently this program is costly because of labor expense, but the plantings are free of weeds, pests, and diseases. A comparison of these beautiful fields with those worked according to old-fashioned methods is most impressive. Progressive producers should be encouraged by a premium for their high-grade oil.

Harvesting.—Before describing the methods of harvesting, we might discuss briefly the development of oil in the cells as the plant matures.

Kleber [19] observed on American peppermint oils that the plant first develops menthone, which in later stages seems to be transformed into menthol. Bacon, Jenison, and Kremers [20] assumed that menthone and menthol originate by reduction of a previously formed menthenone. Rutovski and Travin,[21] studying Russian peppermint in the Experiment Station at Ogino, near Moscow, found that with progressive plant development the content of menthol increases, whereas that of menthone decreases. Their oils distilled from peppermint in various stages of development analyzed as shown in Table 2.11.

TABLE 2.11

Date	State of Vegetation	Menthol			Menthone (%)
		Ester (%)	Free (%)	Total (%)	
July 17–19.....	Long before blooming	8.21	39.67	47.88	13.04
Aug. 8.....	Without buds	7.25	44.85	52.10	...
Aug. 14.....	With buds	7.97	46.07	54.04	6.38
Aug. 31–Sept. 3....	Beginning of blooming	11.16	48.82	59.98	7.22
Sept. 17–18.....	Full bloom	13.04	46.33	59.73	1.43
Sept. 26–Oct. 3....	End of blooming	15.68	45.00	60.68	2.46

This is interesting insofar as menthone possesses a bitter, rather harsh odor, an excess of which is undesirable in peppermint oils of high quality. On the other hand, good commercial oils must have a high menthol content, the Pharmacopoeia prescribing a minimum of 50 per cent total menthol (free and as esters). Sardanovsky [22] found that the percentage of menthol in peppermint oil increases with progressing growth of the plant and attains a maximum near the end of the bloom.

Rabak [23] observed that oils from shaded plants contain less acid, ester menthol, free and total menthol than oils distilled from plants which had grown in full daylight. Sobolevskaya [24] arrived at similar conclusions: two-year old plants which had been exposed to normal light yielded oils

[19] *Ber. Schimmel & Co.*, April (1914), 79.
[20] *J. Am. Pharm. Assocn.* **12** (1924), 1075.
[21] *Riechstoff Ind.* **4** (1929), 124.
[22] *Farm. Zhurn.* (1929), 18. *Chem. Abstracts* **25** (1931), 4577.
[23] *U. S. Dept. Agr., Bull.* No. 454 (1916).
[24] *Trans. Sci. Chem. Pharm. Inst. Moscow* **19** (1928), 194. *Ber. Schimmel & Co.* (1929), 159.

containing 51 to 65 per cent of total menthol and only 2.5 to 5.3 per cent of menthone; whereas shaded plants yielded oils containing only 47 to 53 per cent of total menthol and 11.8 per cent of menthone.

These findings may explain why during prolonged spells of cloudy or rainy weather the content of menthol in peppermint remains low, whereas that of menthone will be high. However, workers at Purdue University, Lafayette, Indiana, are inclined to believe that this is purely a matter of plant maturity, shading or lack of sunshine merely delaying the growth. According to Baldinger,[25] the biogenetic process in the plant apparently synthesizes menthone as well as menthol, and a phytochemical reduction changes the former substance into the corresponding alcohol (viz., menthol), as the plant matures. The same author then ventured the opinion, but left it open to discussion, that the sum of the menthol and menthone percentage in American oil of peppermint is within the range of 75 to 85 per cent. At any rate, the percentages of menthone indicated above by Rutovski and Travin for Russian oils are much lower than those pertaining to American oils.

So far as the content of oil in the plant is concerned, Sardanovsky [26] reports that the leaves contain the most oil in the interval between inflorescence and opening of the blossoms. Mikhalov [27] concluded that the oil content in the leaves is a direct function of the mean temperature during the growth period, e.g., mint harvested in July contained 2 per cent of oil; that harvested in October only 0.6 per cent. The average yields from year to year follow the mean temperature of the growing season.

Ellis, Fawcett, Gaylord and Baldinger [28] undertook a detailed study to ascertain the stage of maturity at which to cut peppermint for maximum oil production and to determine when the physicochemical properties of the oil most closely approach the standards of the U. S. Pharmacopoeia. The stage of maturity is more difficult to judge under field conditions than in small plots, since plants at all degrees of maturity are found in the larger areas. In "row mint," however, maturity is more easily determined than in "meadow mint," because the plants develop more evenly. Ellis and collaborators [29] concluded that in most cases the yield of oil increases as the herb is allowed to approach maturity, i.e., full bloom. The data on chemical composition show a progressive increase in the percentage of total menthol and esters with delayed cutting.

[25] *Ind. Eng. Chem., Anal. Ed.*, **14** (1942), 15.
[26] *Farm. Zhurn.* (1929), 18. *Chem. Abstracts* **25** (1931), 4577.
[27] *Masloboino Zhirovoe Delo* (1929), No. 11, 63. *Chimie & industrie* **23** (1930), 1225. *Chem. Abstracts* **25** (1931), 4086.
[28] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. **461** (1941).
[29] *Ibid.*

In the opinion of these authors, there are two exceptions to cutting peppermint before maturity. One is when the plant is infected with anthracnose ("leopard spots"). In this case, the mint should be cut the moment it becomes apparent that the disease is seriously reducing the foliage. The second exception occurs when planting stock is to be taken, as the yield from plants decreases in accordance with the length of time the previous crop was allowed to stand before cutting.

From all observations it appears that, for practical purposes, harvesting should be done when the mint is in bloom in order to obtain the optimum oil yield and menthol content. The oil content decreases rapidly after full bloom as the foliage begins to fall. If cut late, the loss of oil is greater than if the crop is harvested prematurely but, as has been explained, in the latter case the content of menthol is subnormal and that of menthone too high for delicacy and sweetness of odor. It is important to time the cutting properly, as individual plants open at different times and the period of bloom extends over several days. On a large acreage it is advisable to start harvesting when the first bloom shows, in order to reap the last part of the crop while most plants are still in bloom. Naturally, the rules cannot always be strictly adhered to, as insects, diseases, or weather conditions may necessitate an earlier harvest. In fact, the period of the year in which the plants should be cut varies considerably with the weather. Blooming mints contain most oil during dry and warm weather. Cutting should be done early in the day. Shining globules of oil may be observed on the under side of the leaves when tilted in sunlight, indicating that the oil is well "up" in the leaves.

Studying the relationship of yield of oil from peppermint and the free menthol content of the oil, Ellis and Gaylord [80] observed that the oil content of the peppermint plant increases up to a certain point (the oil then contains about 45 per cent free menthol); and, if the plant is allowed to stand, the yield of oil decreases and the free menthol increases. In a comparatively short period of time, 10 to 15 days, the decrease may amount to as much as 30 per cent of the total yield of oil. Within the same period of time preceding the highest yield, the yield may increase from 10 to 15 lb. per acre, or as much as 30 per cent of the total yield. It is, therefore, very important to the grower to be able to estimate the right time to cut mint in order to obtain the highest yield of oil and menthol.

Experience has shown that the free menthol seldom exceeds 60 per cent but that the total menthol, which includes the free menthol as well as that combined in the form of esters, may be considerably greater than 60 per cent. The data obtained by Ellis and Gaylord show that the yield of oil

[80] *Proc. Am. Soc. Hort. Sci.* **45** (1944), 451.

rises and falls as the season advances, but that the content of menthol in the oil increases throughout the season.

From these data it may be concluded that, if the free menthol content of the oil is below 41 per cent, the peppermint is not ready for cutting. If the free menthol content is between 41–43 per cent, the peppermint approaches the stage of maximum oil yield and another sample of herb should be cut and distilled within 2 to 5 days. When the free menthol content equals or exceeds 45 per cent, the yield is probably near its maximum and the peppermint should be cut immediately.

Swift and Thornton [31] developed a simple and practical viscometric method for determining the content of free menthol in peppermint oil, and on that occasion found that there existed a direct relationship between the free menthol and the yield of oil.

A prolonged rainy spell may cause drooping of the plants in the fields or lodging, resulting in mold and loss of lower leaves with a subsequent inferior yield and quality of oil.

Since new mint matures later than old mint, it is possible to harvest the old fields before the new ones. Thus, "meadow mint" in the Middle West is cut from the middle of July to the middle of August, "row mint" during the latter part of August and early September. During some seasons it is possible to make two cuttings. However, the second harvest, known as "clippings," produces an inferior oil, generally of poor flavor, which must be sold as a second-rate product. A second cutting is not advisable unless the field is to be discontinued, because it generally ruins the stand and strength of a planting. Ordinary hay mowers, usually equipped with a short cutter bar, serve for cutting the mint which, on small fields, can also be cut by hand, using scythes.

Drying.—The cut mint is left in the swath to "cure" until about half dry. The time required for this process depends on the weather. Under favorable conditions the hay may be raked the following morning; sometimes the drying takes three or more days. Usually the mint is left in the fields for 48 hr. It is said that peppermint hay rained upon before distillation often gives a lower yield and a discolored oil. A possible explanation lies in the fact that wet mint is very difficult to distill and, in most cases, cannot be completely exhausted. The spread mint is turned over into windrows with side delivery rakes, later bunched into hay cocks like those made for drying clover hay, then loaded with hay loading equipment on trucks or wagons, and finally transported to the distilleries.

[31] *Horticultural Department, Mimeograph* No. 3, *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana* (1944).

Ellis [32] observed that the greatest loss of oil from cut peppermint hay takes place when high temperatures follow a rain, and when the cut hay is allowed to lie in the field for several days during a period of unseasonably high temperature. The oil may then be discolored, indicating, perhaps, oxidation of the oil. In this case also a loss in oil yield will result.

It is pertinent, at this point, to discuss briefly the reasons for drying the mint prior to distillation, as it might appear that exposure to direct sunlight for so many hours should result in considerable loss of volatile oil by evaporation. In fact, Jud [33] found that plants of the *Labiatae* family (lavender, balm, mint, rosemary, and thyme), when dried in direct sunlight, lost as much as 24 per cent of essential oil; dried in the shade they lost between 2 and 10 per cent. A temperature of 25°–30° C. was found most effective in preventing undue loss of oil. Rabak [34] reported oil losses of 50 percent by evaporation and advised against drying the harvested mints. Gildemeister and Hoffmann [35] expressed doubt about Rabak's findings; they ventured the opinion that oil losses as high as 50 per cent in Rabak's experiments may have been caused by improper handling of the plants during drying. One must beware especially of leaf shattering, which occurs easily with overdried plants and from which growers have suffered a great deal of loss. As a precaution, some growers load the dried material in the early morning when there is still some dew on the ground. Drying in the shade of well-aired barns or sheds seems preferable to drying in the direct sunlight of sweltering summer days in Indiana and Michigan, a practice against which Rabak warned. However, the quantities of peppermint arriving daily at the distilleries during the harvest period are so large that drying under sheds becomes simply impossible in large-scale operation. Furthermore, it is by no means proved, and is in fact doubtful, that the cut peppermint herb loses much oil by evaporation. Loss of oil during prolonged drying in the sun must probably be attributed to resinification, rather than to evaporation. The oil globules on the leaves appear to be encased in a resinous film or membrane; the oil does not evaporate unless this membrane is ruptured mechanically, or by high temperature (steam), or is exposed to the process of hydrodiffusion, which plays such an important role in the distillation of aromatic herbs, seeds, roots, wood, etc. The whole problem is rather complex and still open to discussion. One factor is clear: peppermint producers prefer to dry the plants for the simple reason that the dry mint is more economical to handle; it is lighter, less bulky, and

[32] Private communication of Prof. N. K. Ellis, Purdue Univ., Lafayette, Indiana.
[33] *Ber. schweiz. botan. Ges.* **50** (1940), 19. *Chem. Abstracts* **35** (1941), 6736.
[34] *U. S. Dept. Agr., Bur. Plant Industry, Bull.* No. 454, Washington (1916).
[35] "Die Ätherischen Öle," 3d Ed., Vol. III, 791.

yields the oil much more readily on distillation, consuming less steam, fuel, and time. Vinogradova, Markov, Kurdyumov and Rolik [36] reported that the consumption of steam for the distillation of fresh peppermint leaves is seven times greater than that for dried leaves.

Years ago, the opinion prevailed, and even today is occasionally heard, that drying ("curing") the plants increases the yield of oil, loss of weight by evaporation of water in the dried plants being, of course, considered in the calculation. According to Gildemeister and Hoffmann,[37] the fallacy of this assumption has been demonstrated by systematic and exact distillation experiments on a large scale. The explanation, in most cases, is that green plant material containing much moisture, such as freshly cut herbs, leaves, or grasses, presents considerable difficulty in distilling. Such material yields its oil slowly, necessitating longer hours of distillation and, hence a considerable waste of steam (five to seven times more) and time; occasionally it becomes necessary to interrupt distillation in order to draw off excess condensed water accumulated in the still. In most cases it is almost impossible completely to exhaust moist plant material by steam distillation, a fact often neglected in comparative distillation tests with freshly cut and with dried herb, leaf, or grass material. It is this factor in such experiments which sometimes leads to the faulty conclusion that the oil content increases with the drying and so-called curing of the plants. So far as odor quality of the oils from fresh and dried mint is concerned, that from the fresh plant is considered superior. It possesses a more delicate, sweeter fragrance, reminiscent of the flowering plant. One need only walk through a peppermint field during the harvest, pick one leaf from a blooming plant, another from a dried herb lying on the ground, and crush the two leaves between the fingers; the difference is striking. The scent of the dried leaf is flat, almost rough, compared with that of the green leaf.

As has been said, mint producers in the United States during past years have been inclined to dry their mint hay quite thoroughly prior to distillation, rendering the material easier to handle. They have been motivated by economy of operation rather than by striving for superior oil quality, which would entail greater cost. It should also be remembered that within the period of bloom and harvesting enormous quantities of plant material must be processed; longer distillation time would, therefore, necessitate greatly enlarged distillation equipment. The drying for so many hours in direct sunlight doubtless involves a substantial loss of oil, resulting from several factors—i.e., shattering of leaves, resinification, and perhaps evapo-

[36] *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Efirno-Maslichnoi Prom., Sbornik Rabot po Myate* (1939), No. 5, 82. *Khim. Referat. Zhur.* (1940), No. 2, 120. *Chem. Abstracts* **36** (1942), 2081.

[37] "Die Ätherischen Öle," 3d Ed., Vol. III, 791.

ration of oil. A comparison of the working methods employed in the Middle West with those followed in the peppermint fields of Europe shows that our growers in the past have been inclined to carry drying to excess. "Clover dryness" would probably be preferable. As a matter of fact, in recent years American peppermint growers are attempting to distill the hay before it is completely dry.

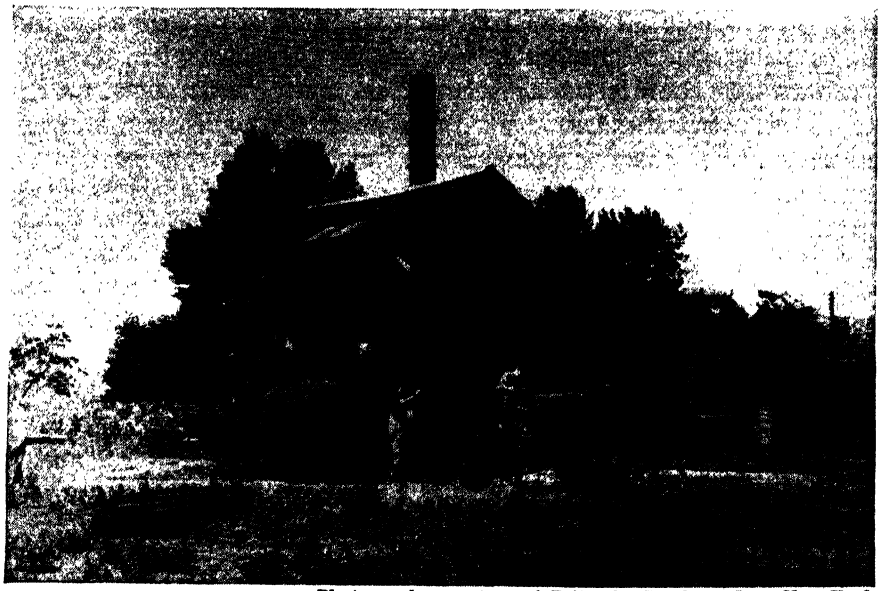
There is still another point to be considered in connection with drying the mint prior to distillation. Rabak [38] showed that oils distilled from freshly cut and from dried plants show marked differences in their physico-chemical properties. Schimmel & Co.[39] reported that peppermint oils distilled from freshly cut plants undergo considerable change upon aging. The specific gravity increases, the solubility in 70 per cent alcohol decreases; in other words, the oils partly and gradually resinify. The explanation is probably that the fresh mint contains certain volatile compounds which easily resinify; therefore, progressive resinification of the oil distilled from freshly cut mint is to be anticipated. If, on the other hand, the mint is permitted to dry, these compounds are oxidized or polymerized into resin, *while still in the plant*. Being nonvolatile constituents, the resins are not carried over into the oil by steam distillation. In fact, oils distilled from dried peppermint are more stable than those from fresh herb. It would not be surprising if this "polymerization" were caused by the oxidation of menthofuran, a constituent of peppermint oil which will be described in the section on "Chemical Composition."

Distillation.—Growers raising about 30 or more acres of mint usually possess their own distilleries; whereas smaller growers have their crop processed by a neighboring still owner. The typical American mint distillery consists of a shed holding two or four, or in a large outfit six and even more, stills (vats, tubs). The live steam is generated in a separate steam boiler. There are two types of boilers, viz., the so-called low-pressure boiler, which produces a quantity of steam but no measurable pressure, and the high-pressure boiler, which can carry a steam pressure of 100 lb. and more.

The still, vats, or tubs vary from 6 to 11 ft. deep and 6 to 9 ft. wide across the top, tapering slightly toward the bottom. The smaller sizes hold about 2,000 lb. of field-dried herb, which is hoisted from a truck or wagon into the still and tramped down. Steam is turned on to moisten the charge somewhat, so that it can be packed in more tightly, and then the cover is clamped down. Some stills operating with low steam pressure are equipped with water seals which allow for quicker closing and opening of the cover.

[38] *U. S. Dept. Agr., Bull.* No. 454, Washington (1916).
[39] *Ber. Schimmel & Co.*, April (1909), 77.





Photographs courtesy of Fritzsche Brothers, Inc., New York.

Distillation of peppermint in the United States.

Distillation of a batch requires in general 45 to 60 min., but longer if the plant material is wet.

The condensers are either of the old-fashioned worm type (a single tapering pipe, about 100 ft. long, doubled back and forth and cooled with water dripping from a tank above) or of the modern tubular type which is much more efficient, compact, and durable. Often two stills are connected to one



Courtesy of Fritzsche Brothers, Inc., New York.

Discharging of the spent plant material from a still in the United States.

condenser. Ellis, Fawcett, Gaylord and Baldinger [40] reported that condensers made of galvanized sheet metal become rusted (peppermint oil is generally slightly acid in reaction), and that much resinous matter collects on the interior during the process of distillation. When these coils can no longer be cleaned by steaming, the peppermint oil condensed in them will be discolored. It is, therefore, important to replace all rusted condensers with new galvanized coils, if uncolored oil is to be produced. Coils made of aluminum would be more satisfactory. Further details on distillation and equipment may be found in the previously cited papers of Ellis, of Johnson and Snyder, and especially in that of Sievers. The oil is finally separated in a receiver constructed on the principle of a Florentine flask and collected in cans or drums.

[40] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941).

Ellis and collaborators [41] found that 40 to 45 per cent of the peppermint oil comes over during the first 10 min. of distillation. The quantity of oil decreases as distillation progresses. Less than 10 per cent of the oil comes over during the last 15 min. of a 45-min. distilling period. The menthol and ester content, as well as the laevorotation, increase as distillation progresses; the content of menthone decreases. When distillation is carried to completion, the refractive indices of the last two oil fractions are higher than those of the oil fractions collected during the first 20 min. of the distillation period. If peppermint oil of fine quality (high menthol and ester content) is to be produced, sufficient time must be allowed for complete distillation, i.e., until the plant material is completely exhausted.

Yield of Oil.—Yield of peppermint oil per acre varies from 10 to 75 lb., on the average it is 24 or 25 lb.[42] Yield and quality of the oil depend a great deal upon the condition of the fields—age, absence of diseases, pests, weeds, etc. Ellis and Morris [43] reported from 23 to 48 lb. of oil per acre of "meadow mint," and from 10 to 58 lb. of oil per acre of "row mint" (muck soils with controlled water tables).

As far as yield of oil per weight of plant material is concerned, it depends entirely upon the state of dryness of the cut herb. It averages from 0.3 to 0.4 per cent but may be as high as 1 per cent.

Weeds.—Ragweed and smartweed are considered the worst offenders, adversely affecting odor and flavor of peppermint oil. Aside from those, pigweed, horseweed (fleabane, *Erigeron canadensis*), purslane, buttermold, Canadian thistle, lamb's-quarters, Indian hemp, and nettle are commonly present in peppermint fields. Ellis and collaborators [44] found that among all these weeds only the common ragweed (*Ambrosia elatior* L.) yielded a volatile oil, lighter than water, and in appreciable quantity. It possessed an offensive odor and taste. Chewing gum containing 1 per cent of ragweed oil in the flavoring compound was disagreeable to the taste and unsalable. The distillates obtained from the other weeds had characteristic odors ranging from the sickening aroma of buttermold and hemp to the hay-like odor of horseweed and smartweed. The distillates, however, lost much of their odor when exposed to the air for a few days.

The absence of weeds in well-kept "row mint" fields makes it seem logical that oil distilled from "row mint" should be superior in aroma to oil distilled from "meadow mint." It is very hard to keep the latter com-

[41] *Ibid.*

[42] These average figures apply to the Midwest; they are higher on the West Coast (see below).

[43] *Soil Science Society of America, Proceedings,* **10** (1945), 282.

[44] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941).

pletely free of weeds except by regular and thorough hand weeding, an expensive procedure.

Diseases.[45]—Mint anthracnose, commonly called "leopard spots," is caused by a fungus (*Sphaceloma menthae* Jenkins) and has done considerable damage to the fields, especially in Indiana. It produces characteristic lesions on peppermint, but has little effect on spearmint. Small, brown spots on young leaves are the first evidence of the disease. New shoots frequently become so heavily infested that they die outright. This blighting of the young shoots and partial defoliation of the plants reduces the oil yield. When setting out a new acreage, the use of infected plants for transplanting must be avoided. For control, frequent application of a 20–80 copper-lime dust or a copper-lime spray has been recommended.

Complete coverage of all plant material during plowing is recommended. At the present time, anthracnose is under control in the Midwest.

Peppermint wilt has done tremendous damage, resulting in a notable reduction of acreage in the Middle West. It is caused by a fungus *verticillium* (sp.), favored by a high soil temperature (70 to 80° F.) and low soil-moisture content. Soils with a water level of 18 to 20 in. depth are thought to be less susceptible to the disease. As the name of the blight indicates, the leaves turn yellow and dry up from the top; the plant becomes stunted and wilts downward until it dies. No control for the disease has yet been found, and once the ground is affected it can never again be used for the growing of peppermint (*M. piperita*). To prevent occurrence of the wilt, it has been suggested that no "meadow mint" be grown, "row mint" apparently being less easily affected. Experiments are now being conducted by various botanical institutes of Michigan and Indiana and at the U. S. Department of Agriculture Experiment Station in Beltsville, Maryland, in the hope of producing a resistant hybrid from peppermint and spearmint. The task is difficult, however, because of the sterility of mint and because the two mints bloom at different periods, so that cross fertilization in the fields cannot be achieved easily. Fertile peppermint plants (*Mentha piperita* L.) have lately been produced at the Purdue University Agricultural Experiment Station by the use of the drug colchicin. These plants have tetraploid characteristics and open up new possibilities in mint breeding.

Insect Pests.—A detailed paper on mint pests has been published by Purdue University's Agricultural Experiment Station.[46]

In a wet spring several minor pests, such as cutworms, wireworms, white

[45] Detailed information may be obtained through Dr. Ralph Caldwell, Dept. of Botany and Plant Pathology, Purdue Univ., Agr. Expt. Sta., West Lafayette, Indiana.
[46] *Circ.* No. 211.

grubs, grasshoppers and millipeds do considerable damage but do not constitute too serious a menace.

Much more serious are attacks by small white larvae of the mint flea beetle, feeding on the plant roots which they sap. Control measures must be applied at a time when most beetles are present and before eggs are laid. In normal seasons, this period is from July 20th to August 5th. If this conflicts with the harvest, it may become necessary to cut the mint a week or so early. The remedy is to dust the growing mint with calcium arsenate at the rate of 15 to 20 lb. per acre, or the mint stubble with a Paris green flour mixture at a 1 to 9 dilution. This is done during and after the harvesting season; if applied too late—for instance, when the crop is late—the results of dusting are practically nil. Standing mint, which has been dusted with calcium arsenate, should not be used as hay for animals after the oil has been extracted from it. "Row mint" seems to be less affected by the mint beetle than "meadow mint."

A mixture suitable for flea beetle and anthracnose control consists of 10 lb. of Paris green, 20 lb. of fresh monohydrated copper sulfate, and 70 lb. of hydrated lime, applied to the mint stubble at a rate of 15 to 20 lb. per acre. DDT is used for the control of beetles alone or may be incorporated with a fungicide for the control of anthracnose, but DDT must not be applied when the distilling time is approaching.

Weather Damage.—Strong winds during early spring, when the ground is dry, are likely to blow the muck soil away, expose the roots, and cause them to die. Early mint is easily killed by frost. Prolonged flooding of the soil will kill the roots.

Storage of Peppermint Oil.—If not stored properly, peppermint oil easily oxidizes and resinifies. Partly filled containers, poorly fitting corks, water in the oil, and warm temperatures in the storage room represent some of the factors which have a harmful influence upon the quality of the oil. Ellis, Fawcett, Gaylord and Baldinger[47] found that under such poor storage conditions peppermint oil undergoes certain physicochemical changes—such as a slight increase in optical rotation and menthone content, an apparent increase in menthol and ester content, and darkening of the oil. These changes can be explained by resinification which also causes discoloration of the oil. The resins thus formed react with potassium hydroxide; therefore chemical analysis shows an apparent, but not actual, increase in the menthol and ester content of such partly resinified oils.

[47] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941).

Ellis and collaborators [48] recommend that:

1. Peppermint oil be cooled and the moisture removed before being poured into the final storage containers.
2. The containers be new or clean and free from rust or accumulated resin, as the latter dissolves in the oil and discolors it.
3. The containers be full so that there is only a little air space left above the oil to allow for expansion. Galvanized drums holding about 400 lb. of oil are suitable; aluminum kegs holding 110 lb. of oil represent excellent storage containers.
4. The containers be well sealed and no air permitted to pass in and out of the drum, as this results in oxidation and resinification.
5. The oil be stored in a cool place. Less change takes place in the chemical and physical properties of peppermint oil, under cool storage condition, even when poor containers are used.

Baldinger, Ellis and Fawcett [49] reported that with the percentage of menthol as a criterion on which to base the efficiency of antioxidant action and to compare storage conditions, it was observed that cool-cellar storage is better than storage in an attic or in locations where extremes of temperature are likely. Sealed tin cans are more advantageous than clear-glass bottles stoppered with corks or with corncobs, or tin cans with cork stoppers.

The addition of 0.1 per cent of catechol is more effective as an antioxidant than hydroquinone in maintaining the original percentage of menthol. The chief disadvantage of either of these is probably the slight coloration produced, particularly in the older oils. This coloration is more noticeable in the case of the hydroquinone-protected samples, much less pronounced in the catechol-protected samples, and less noticeable still for both antioxidants in the samples stored in corked bottles and sealed tins. The slight coloration is not accompanied by a resinous odor which is very noticeable in unprotected oils. Baldinger, Ellis and Fawcett [50] therefore recommend that, wherever feasible, sealed containers, completely filled, be used for storing the oil, and that cool storage conditions be maintained at all times.

Redistillation and Rectification.—There is much confusion in the trade as to correct application of the two terms. The U. S. Pharmacopoeia specifies that "oil of peppermint be distilled with steam from the fresh overground parts of the flowering plant of *Mentha piperita* L. (fam. *Labiatae*),

[48] *Ibid.*
[49] *J. Am. Pharm. Assocn.* **33** (1944), 41.
[50] *Ibid.*

and rectified by distillation." This is quite clear. However, a good many brands of peppermint oil on the market are labeled "single distilled," "double distilled," "triple distilled," or "rectified," "twice rectified," or labeled with trade names, each indicating a certain quality as produced by a special rectification process. In fact, no definite rules exist, each essential oil house marketing a number of brands prepared by secret processes.

The term "and rectified by distillation," as used by the U.S.P., implies that the natural oil is either redistilled by blowing live steam through it, or that the natural oil is dry-distilled, usually *in vacuo*. Ellis and collaborators [51] showed that redistillation is practical, especially with old or discolored peppermint oils, as it removes resinous matter and yields oils of light color. They found that losses ranged from 4 to 22 per cent, the greatest loss occurring in the oils of darkest color. According to the same authors, the refractive indices and ester numbers are lower in redistilled oils, the menthol content higher in some cases, lower in others.

Rectification by distillation as prescribed by the U. S. Pharmacopoeia, however, aims at eliminating not only resinous matter, but also other undesirable substances contained in the natural oil. Since these compounds possess characteristic odors detrimental to the flavor, they must be removed. The most important of these objectionable substances is dimethyl sulfide, a colorless liquid of disagreeable odor and a very low boiling point (99° F.; 37.2° C.). Dimethyl sulfide can be removed from natural peppermint oil by drawing off and rejecting the small first fraction which also contains other compounds of little or questionable odor value. Some supply houses rectify their natural oils with live steam; others use dry vacuum distillation, heating the oil in the still through a steam jacket or through a closed steam coil. The main fractions represent the different brands of commercial rectified oils. They possess a much finer odor than natural oils and are 5 to 10 per cent higher in menthol, as the eliminated first and last fractions (residue) contain little, if any, menthol. Depending upon the equipment used (stills with fractionation columns) and the care exercised in the operation, the process of rectification involves an oil loss of 5 to 15 per cent; it may be even higher.

According to Varentsov,[52] best results in the rectification of peppermint oil are obtained by distilling with water. There exists a definite relation between the organoleptic value of the product and its physical properties.

[51] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941).

[52] *Trudy Vsesoyuz. Inst. Efirno-Maslichnoi Prom.* (1940), No. 8, 108. *Chem. Abstracts* **37** (1943), 3558.

The content of menthol increases and the odor of the oil improves as the specific gravity and optical rotation become higher; nevertheless it should be kept in mind that resinified oils also exhibit a high specific gravity and optical rotation.

Fundamental Points for Production of a High-Grade Peppermint Oil.—From the foregoing it appears that a number of precautions must be taken in order to attain a good yield of oil per acre and a high quality. To summarize:

1. The soil should be carefully prepared to eradicate all weeds.
2. The yield of oil is directly affected by the fertilizer. (See section on "Soil Requirements, etc.")
3. The plantings and fields must be thoroughly weeded, as certain weeds affect the odor and flavor of the oil.
4. Diseases and insect pests should be controlled from the moment their first symptoms appear.
5. The harvesting must be timed properly, the best period being at full bloom. Premature cutting gives oils of high menthone and low menthol content. Late cutting affects the yield of oil unfavorably. (See menthol test in section on "Harvesting.")
6. Excessive drying in the fields causes loss from shattering of the leaves, and evaporation and polymerization of volatile oil.
7. The distillation equipment must be in good condition, and free from rust and resin, which discolor the oil.
8. Distillation must be long enough to obtain oils of high menthol content.
9. After being freed of moisture, the oils should be stored in cool places, in clean containers, well filled and stoppered airtight.
10. Natural oils must be rectified in order to meet the requirements of the U. S. Pharmacopoeia.

Regarding West Coast peppermint oils, St. John, Vandecaveye, Buchanan, Click and Ownbey [58] arrived at some interesting conclusions, the most poignant features of which may be summarized as follows:

1. The cut mint hay should never be permitted to lie wet on the ground.
2. In the Middle West and west of the Cascade Mountains, the peppermint plant is harvested at an earlier stage of maturity than in the Ken-

[58] "Peppermint Oil Production in Southeastern Washington," *Monograph Circ.* No. 45, *Agr. Expt. Sta., Institute of Agricultural Sciences, State College of Washington, Pullman, Washington.*

newick area. Even if cut at an earlier date in the Kennewick area, the yield of oil per acre may still be twice that obtained in the Middle West. Data collected from experimental plots in 1946 show a progressively and rather sharply increasing yield of oil until the middle of August. Thereafter, the yield per acre ranged between 40 and 50 lb. per acre with a tendency toward a decrease. By August 1st, the yield was about 62 lb. per acre and by August 20th it fluctuated around 70 lb. per acre in the various fields.

3. Since the oil is contained in the leaves and not in the stems, any forcing of growth to a maximum (rank growth) by irrigation and fertilization will increase the yield of oil only if accompanied by an increase in leaves.

4. The hay should be cured for a comparatively short time only, perhaps 24 to 36 hr. Every effort should be made to prevent shattering and loss of leaves during harvest and handling.

5. In 1946, the oil from hay harvested at first bloom had a higher optical rotation than oil from hay cut at a later stage of maturity. Therefore, if buyers demand an oil of high optical rotation and high menthol content, it may be necessary to harvest at an early date. Even though the yield per acre will be less, it may still be twice, or more than twice, that obtained in the Middle West.

6. A second growth of mint harvested in October produced an oil high in rotation and menthol. The yield of oil from the second growth was about 20 lb. per acre, which is nearly equal to the average yield in the Middle West.

Determination of Volatile Oil in the Plant Material.—For assaying the amount of peppermint oil in a given sample of plant material, the regular Clevenger apparatus gives satisfactory results. A micro-analytical method, permitting the test of as little as 1 to 2 g. of plant material, has been described by Ullrich and Schneider.[54] By this method the content of menthol, ester menthol, and menthone in the oil can also be determined micro-analytically. The menthone is assayed by the use of hydroxylamine, and menthol plus menthone by oxidation of the former with chromic-sulfuric acid and determination as menthone. Esters are determined by saponification and titration of residual sodium hydroxide.

Physicochemical Properties of American Peppermint Oils.—Natural unrectified peppermint oils from the Middle West and the Pacific Coast states, examined in past years in the laboratories of Fritzsche Brothers, Inc., New York, had properties varying within the following limits:

[54] *Z. physiol. Chem.* **245** (1937), 181. *Chem. Abstracts* **31** (1937), 4055.

	Oils from Michigan and Indiana	*Oils from Oregon and Washington*
Specific Gravity at 25°/25°....	0.899 to 0.906	0.900 to 0.907
Optical Rotation.....	−19° 30′ to −27° 30′	−20° 10′ to −28° 8′
Refractive Index at 20°.....	1.4598 to 1.4640	1.4612 to 1.4631
Total Alcohol Content, Calculated as Menthol.....	45.6 to 61.2%	51.2 to 65.1%
Ester Content, Calculated as Menthyl Acetate.....	4.6 to 9.6%	3.1 to 9.2%
Ketone Content, Calculated as Menthone (Hydroxylamine Hydrochloride Method).....	14.3 to 30.5%	17.3 to 21.0%
Distillate up to 200°.....	7.0 to 18.2%	10.0 to 15.0%
Solubility at 25°.....	Clear to turbid in 2.5 to 3.5 vol. of 70% alcohol; opalescent to turbid with more	Clear to opalescent in 2.5 to 3.5 vol. of 70% alcohol; opalescent to turbid with more

The menthone content is in inverse proportion to the total menthol content.

All natural (country) oils were tested for the presence of alcohol; oils containing up to 2 per cent of alcohol have been observed.

Peppermint oils are subject to resinification, the extent of which may be determined by the evaporation residue. A normal amount is about 2 per cent.

Natural peppermint oils, received from producing regions, are pale yellow in color, and invariably contain water which should be eliminated right after arrival of a shipment.

The physicochemical properties of Midwest and West Coast oils do not appear to differ appreciably, except for the oils produced in the eastern part of Washington, a dry region with an average rainfall of less than 6 in. per year. The soil in eastern Washington is rich, deep lava ash and requires irrigation. According to Tornow and Fischer,[55] the (natural) oils produced there often have a specific gravity and a refractive index slightly above the limits specified by the U. S. Pharmacopoeia. However, these abnormalities can be corrected by rectification. The same (natural) oils, in addition, frequently possess an optical rotation below the U.S.P. limit. Rotations of only −10° have been observed, the average being −17°. This abnormality cannot be sufficiently corrected by rectification and, therefore, the rectified oil will not meet the U.S.P. requirements.

In regard to odor and flavor, the Midwest oils frequently show a considerable difference from the West Coast oils, the latter being sweeter, less

[55] *J. Am. Pharm. Assocn.* **37** (1948), 76.

pungent, and less "minty." It is a matter of personal choice as to which of the two types of oil should be preferred.

Gildemeister and Hoffmann [56] indicate the following properties for natural (unrectified) American peppermint oils:

Specific Gravity at 15°/15°	0.900 to 0.920
Optical Rotation	−18° 0′ to −34° 0′
Refractive Index at 20°	1.4600 to 1.4640
Total Menthol Content	48.0 to 65.0%
Ester Menthol Content	3.7 to 11.0%
Menthone Content	9.0 to 25.0%
Solubility	Soluble in 2.5 to 5 vol. of 70% alcohol, sometimes with slight opalescence or turbidity which increases with dilution

Years ago Rabak [57] reported that the content of menthol increases, whereas that of menthone decreases as the plant reaches the full blooming stage. Yet, many natural American oils contain less than 50 per cent of total menthol. Fritzsche Brothers, Inc.[58] examined numerous lots of natural Michigan oils produced during the 1916 harvest and came to the conclusion that only oils distilled in the late season met the U. S. Pharmacopoeia requirement in regard to total menthol content. On the other hand, the ester menthol content was above the minimum specification of the U.S.P.

Shipments Received	*Total Menthol* (%)	*Ester Menthol* (%)
Aug. 14 to Sept. 30	47.59	6.33
Oct. 3 to Nov. 13	49.55	7.02
Nov. 18 to Dec. 21	51.34	7.53
Average	49.23	6.87

Interesting data about the time of cutting, in relation to the yield and the physicochemical properties of Indiana peppermint oils, were given by Ellis, Fawcett, Gaylord and Baldinger [59] and are included in Table 2.12.

From this table it appears that in most cases the yield of oil increases as the herb is allowed to approach maturity. The data on chemical composition show a progressive increase in the percentage of total menthol and esters with delayed cutting. Only in two cases did the total menthol content meet the minimum requirement of the U. S. Pharmacopoeia (50 per cent) and both were in the late season. As has been pointed out, the U. S.

[56] "Die Ätherischen Öle," 3d Ed., Vol. III, 820.
[57] *U. S. Dept. Agr., Bull.* No. 454, Washington (1916).
[58] *Ber. Schimmel & Co.* (1920), 43.
[59] "A Study of Some Factors Affecting the Yield and Market Value of Peppermint Oil," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Bull.* No. 461 (1941).

TABLE 2.12

Time of Cutting	Yield in Pounds per Acre	Optical Rotation	Esters (%)	Menthol (%)
1938 (Row Mint)				
August 4	48.0	−20° 24′	2.99	36.48
August 13	...	−20° 0′	3.18	35.59
August 17	48.0	−20° 36′	4.09	41.37
September 19	56.0	−22° 24′	5.21	53.59
1939 (Meadow Mint)				
July 13	38.3	−23° 22′	2.99	31.51
July 24	46.7	−22° 52′	3.47	27.88
August 2	53.8	−25° 44′	3.95	42.12
August 17	61.0	−23° 9′	4.14	36.32
1940 (Row Mint)				
August 13	48.5	−20° 18′	3.38	37.1
August 22	54.5	−17° 30′	4.01	37.0
September 4	73.0	−21° 0′	5.23	49.6
September 17	76.9	−21° 48′	6.28	54.8
1940 (Meadow Mint)				
July 24	54.9	−24° 18′	4.43	41.3
August 2	66.8	−22° 0′	4.08	37.1
August 14	76.9	−22° 24′	4.53	40.4
August 22	98.0	−20° 48′	4.10	42.4

Pharmacopoeia requires that American Peppermint oil be rectified if it is to be marketed under the U.S.P. label.

Johnson and Snyder [60] reported that, although freshly cut mint may be used for distillation, it is much more economical to use the well-cured, dry hay. Exposure to rain lowers the yield and quality of oil. In order to obtain a maximum yield of oil, the harvesting should be done while the plants are in full bloom.

Analysis of Peppermint Oil.—A routine analysis of a peppermint oil should include the determination of the specific gravity, optical rotation, refractive index, total menthol content, ester content, menthone content, and solubility in 70 per cent alcohol. A test to distinguish between the oil of *Mentha piperita* and oil of *Mentha arvensis* will also be of value. For rectified oils a test for the absence of dimethyl sulfide should be included. Detailed procedures for these determinations and tests may be found in the

[60] *Wash. Agr. Expt. Sta., Extension Bull.* No. 227 (1936), 8.

chapter "The Examination and Analysis of Essential Oils, Synthetics, and Isolates," Vol. I of this work.

In connection with the assay for menthol, the findings of Baldinger [61] will be of interest. Baldinger observed that the saponification of acetylated peppermint oil does not proceed normally. This is probably due to the presence of menthyl isovalerate, an ester requiring considerable time for complete saponification. Baldinger suggests a slight excess of alkali and heating at 100°, at least for 1 hr.

Swift and Thornton [62] developed a rapid and simple viscometric method of determining free menthol in peppermint oil. The accuracy of the method is claimed to be sufficient for field purposes and should facilitate work in the breeding of mints for high menthol content, as the breeder will be able to make his own analyses. Since only small samples are required, the use of the viscometric method will materially lessen the number of plants to be grown before selections are made. However, application of this method is limited to fresh or well-preserved natural oils of normal composition; it is not applicable to oils of high resin content, because the resins greatly increase the viscosity of the oil.

Although not prescribed by the U. S. Pharmacopoeia, it is advisable for completeness' sake to determine the content of menthone in peppermint oils. As pointed out previously, menthone has a bitter taste and, therefore, an excessive menthone content is generally considered undesirable. For details see Vol. I of this work, p. 286.

Adulteration.—All peppermint oils should be submitted to a careful odor and flavor test in order to detect the presence of small quantities of spearmint oil. This may be considered a contaminant rather than an adulterant.

Adulteration with terpenes is occasionally encountered. The presence of added terpenes is indicated by abnormalities in the rotation, and by lowered specific gravity and total menthol content.

Recently, adulteration with phellandrene has been noted. This may be detected by examining the first 3 per cent of the oil, the so-called sulfide fraction. This fraction should be tested for phellandrene according to the method described in Vol. I of this work, p. 313.

Adulteration with water-soluble glycols has the purpose of increasing the apparent total menthol content of the oil. Both this addition and that of alcohol may be disclosed by washing the oil with salt solution and observing the decrease in the volume of the oil.

A frequently observed form of adulteration is that with synthetic menthol. No satisfactory method has been found up to the present time for proving such fraud. Addition of Japanese mint oil as adulterant may be

[61] *J. Am. Pharm. Assocn.* **27** (1938), 584.
[62] *Ind. Eng. Chem., Anal. Ed.*, **15** (1943), 422.

revealed by means of the color reaction described in Vol. I of this work, p. 343.

Addition of benzyl alcohol results in an abnormally high specific gravity and abnormally low optical rotation of the adulterated peppermint oil. According to Carles,[63] the benzyl alcohol is readily detected by converting it into benzylbromide, which has a pungent odor and an irritating action on the eyes. Carles recommends the following procedure:

"Four or 5 cc. of hydrobromic acid and 1 or 2 cc. of peppermint oil are placed in a test tube, together with a few boiling-chips. The test tube is then fitted with a stopper carrying a glass tube, and the liquid is cautiously heated to boiling for a quarter of an hour over a very small flame. Thereupon a strip of filter paper is impregnated with the peppermint oil which, as a rule, turns red. If benzyl alcohol was present, the paper gives off the characteristic, burning, lachrymal odor of benzylbromide. Occasionally it is necessary to rinse the paper lightly with water."

Adulteration with terpineol is also occasionally encountered. The presence of terpineol in an essential oil is usually disclosed by acetylation and subsequent fractional saponification. For details see Vol. I of this work, p. 336.

However, peppermint oil contains some menthyl acetate as a natural constituent; this is one of the very few esters which behaves in a manner similar to terpinyl acetate during fractional saponification. In order to detect terpinyl acetate the oil must, therefore, be fractionated. At atmospheric pressure terpineol has a boiling point quite close to menthol and menthone, but at reduced pressure terpinyl acetate is somewhat higher boiling than most of the acetylated alcohols or esters occurring as natural constituents in peppermint oil. It can be separated by fractionation in comparatively pure condition.

The method for detecting terpineol or terpinyl acetate in oil peppermint follows:

A 200 g. sample of oil peppermint is acetylated by refluxing for 1 hr. with an equal amount of acetic anhydride and 20 g. of anhydrous sodium acetate. The acetylated oil is washed and dried and subjected to fractional distillation at 10 mm. A pure acetylated peppermint oil will not give an appreciable fraction boiling above 103° at 10 mm. Terpinyl acetate, however, boils at about 108°–115° at 10 mm. Hence, if a fraction is obtained boiling at 105°–115° at 10 mm. it should be subjected to fractional saponification as described in Vol. I of this work, p. 336.

The terpinyl acetate can often be recognized in this fraction by its sweet and strong odor, reminiscent of bergamot and lavender. The free terpineol obtained after saponification can be separated and identified through the nitrosochloride m. 110°–113°.

[63] *Ber. Schimmel & Co.* (1930), 66.

Chemical Composition of American Peppermint Oil.—Most of the presently known constituents of American peppermint oil were identified by Power and Kleber.[64] Using a pure oil distilled in Wayne County, New York, from dried peppermint which was absolutely free of weeds (yield 0.67%, d_{15}° 0.9140, α_D —32° 0′, ester menthol 14.12%, free menthol 45.5%, total menthol 59.6%), these authors found that when fractionated at atmospheric pressure their oil had the following boiling range:

	Per Cent		*Per Cent*
Up to 200°	2.6	220°–225°	19.6
200°–205°	2.4	225°–230°	9.0
205°–210°	8.6	230°–235°	3.6
210°–215°	18.8	Residue	12.2
215°–220°	24.0		

By 1896, about seventeen constituents of American peppermint oil had been identified. Further contributions to our knowledge of the chemistry of this oil were made by the Schimmel chemists, by Kremers, and by Gordon (for literature references see below).

The following list enumerates the compounds which, so far, have been identified in American peppermint oil; they are listed approximately according to boiling points.

Acetaldehyde. The oil contains about 0.044 per cent. Oxidation yields acetic acid. Identified by Power and Kleber.[65]

Dimethyl Sulfide. Isolated by the Schimmel chemists.[66]

Isovaleric Aldehyde. The oil contains about 0.048 per cent. Oxidation gives valeric acid. Identified by Power and Kleber.

Free Acetic Acid. By Power and Kleber.

Isoamyl Alcohol (2-Methyl-4-butanol). Identified by Gordon[67] as α-naphthylurethane m. 61°.

Amyl Alcohol. Identified as acetate by the Schimmel chemists.[68]

α-Pinene (Inactive, Possibly a Mixture of *d*- and *l*-α-Pinene). Identified by the Schimmel chemists[69] as pinene nitrolpiperidine m. 118°, and as pinene nitrolbenzylamine m. 123°.

Free Isovaleric Acid. By Power and Kleber.

Phellandrene. By Power and Kleber as nitrite m. 100°.

[64] *Pharm. Rundschau, New York,* **12** (1894), 157.
[65] *Ibid.*
[66] *Ber. Schimmel & Co.,* October (1896), 61.
[67] *J. Am. Pharm. Assocn.* **16** (1927), 130.
[68] *Ber. Schimmel & Co.,* October (1896), 61.
[69] *Ber. Schimmel & Co.,* April (1894), 42. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 823.

Cineole. By Power and Kleber as hydrobromide compound, and as cineolic acid m. 196°.

l-Limonene. Also by Power and Kleber, as tetrabromide m. 104°.

Terpinene. Identified by Gordon [70] as nitrosite m. 150°–155°. in an oil distilled in Madison, Wisconsin.

d-Menthone. Investigating a dextrorotatory fraction of the same oil, Gordon [71] obtained menthone thiosemicarbazone m. 155°–157°, which indicates the presence of *d*-menthone.

l-Menthone. Isolated by Power and Kleber, through conversion into menthol.

l-Menthol. The main constituent of American peppermint oil, isolated by Power and Kleber.

A Menthenone. B. 215°–221°; mol. refr. 46.6, was found by Kremers.[72]

Menthyl Acetate. By Power and Kleber.

1-p-Menthen-3-one (Piperitone). As this ketone is present in Japanese mint oil, it was logical to assume its occurrence also in the American oil. In fact, Kremers [73] identified it as semicarbazone m. 215°, in the direct oil as well as in the cohobation water oil.

Menthyl Isovalerate. By Power and Kleber.

Menthyl Ester of an Acid $C_8H_{12}O_2$. By Power and Kleber.

Cadinene. First observed by Halsey.[74] Dihydrochloride m. 118°.

A Lactone, $C_{10}H_{16}O_2$. Observed by Power and Kleber, this compound m. 23° had an insipid odor somewhat reminiscent of borneol. The corresponding hydroxy acid crystallizes from petroleum ether in shining needles m. 93°.

Menthofuran [3,6-Dimethylcumarone-tetrahydride-(4,5,6,7)]. This interesting and important compound was first observed in Italian peppermint oil. (See section on "Chemical Composition of Italian Peppermint Oil.") More recently Bedoukian [75] isolated menthofuran from American peppermint oil after having freed the fraction α_D +15° 0′ to +20° 0′ of menthone by means of the semicarbazone and by distilling the residual oil. The menthofuran thus obtained had these properties:

b_{17}	92°–94°
d_{25}^{20}	0.930
α_D	+61° 0′
n_D^{25}	1.4657

The maleic anhydride addition product of natural menthofuran, after several recrystallizations from benzene, had a melting point of 133°–133.5°.

Menthofuran has also been identified by Schmidt [76] in the high boiling fractions of American, Russian, Bulgarian, and Italian peppermint oil (see below).

Under the influence of air and light, menthofuran is oxidized to an acid m. 186°,

[70] *Am. J. Pharm.* **99** (1927), 523.
[71] *Ibid.*
[72] *Am. J. Pharm.* **97** (1925), 663.
[73] *Ibid.*, 660.
[74] *Proc. Wisconsin Pharm. Assocn.* (1893), 90.
[75] *J. Am. Chem. Soc.* **70** (1948), 621.
[76] *Chem. Ber.* **80**, No. 6 (1947), 538.

which might partly explain the resinification of peppermint oils and the resulting increased acid content in resinified oils. Such oxidation might take place in the oil cells while the cut plants are left in the field to dry.

The above list of substances so far identified in oil of peppermint may give the impression that the chemical composition of the oil has been fairly thoroughly elucidated. However, comparatively little is known about those compounds which, although occurring in the oil in small quantities only (trace substances), are, nevertheless, chiefly responsible for its sweet odor and flavor, and distinguish it from the Japanese or Chinese mint oil (*Mentha arvensis*). The latter, despite its high content of menthol, possesses a somewhat bitter odor and flavor, noticeable particularly in the higher boiling fractions.

Schmidt [77] has only recently succeeded in identifying a few of these trace substances in the high boiling fractions of Russian, American, Bulgarian, and Italian oil of *Mentha piperita* L. He investigated the last runs of peppermint oil given in Table 2.13.

TABLE 2.13

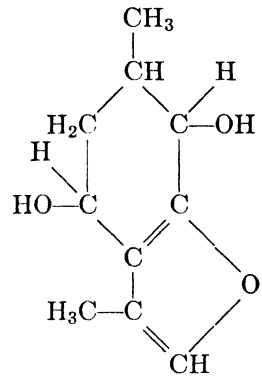
Last Runs of Peppermint Oil	d_{15}	α_D	n_D^{20}	Acid Number	Saponification Number	Saponification Number after Acetylation	Carbonyl Content, Calculated as $C_{10}H_{16}O$ (%)
Russian..	0.944	−19° 30′	1.48712	11.8	84	190	10.4
American.	0.939	−21° 48′	1.48172	4.2	49	180	11.4
Bulgarian	0.952	−18° 12′	1.49507	2.8	22	140	9.1
Italian...	0.937	−22° 24′	1.48402	2.8	21	173	9.5

Rectifying substantial quantities of American, Russian, Bulgarian, and Italian peppermint oil with live steam, Schmidt found that the spicy, agreeable odor, which contributes so greatly to the pleasant aroma of the total oil, is associated chiefly with the high boiling fractions.

In the Italian oil Schmidt identified benzaldehyde, after treatment of the high boiling fraction with hydrogen sulfite; but he expressed doubt about the occurrence of benzaldehyde in *genuine* Italian peppermint oil, because this oil is frequently adulterated with benzyl alcohol. Treating the last runs with sulfite-bicarbonate, Schmidt obtained carbonyl compounds with

[77] *Ibid.*

a carvone odor. Extraction of the free acids with sodium carbonate solution gave a mixture of fatty acids consisting chiefly of an unsaturated octylic acid. This acid occurs in the oil free and in ester form. Extraction of the last runs with potassium hydroxide solution yielded phenols consisting mainly of thymol and carvacrol. The potassium hydroxide solution also removed small quantities of a well crystallized substance m. 186°, which Schmidt originally considered to be a lactone, but which finally turned out to be an autoxidation product of menthofuran. This oxidation product has the following structural formula:



According to Schmidt, menthofuran, which previously had been identified only in the oil derived from the flowers of Italo-Mitcham peppermint oil, occurs in all *Mentha piperita* oils. The American oil seems to be especially rich in this constituent.

Menthofuran is present chiefly in the menthone-menthol fractions, being found in much smaller quantities in the last runs. The maximum optical rotation of menthofuran isolated from the menthol-menthone fraction was +93° 24′. An important constituent of peppermint oil, it exercises great influence upon the aroma of the oil.

After removal of the acids and phenols, the last runs were treated with boric acid, to isolate the alcohols by means of their borates. These alcohols consisted primarily of *l*-menthol and sesquiterpene alcohols $C_{15}H_{26}O$.

The portions of the high boiling fractions which did not react with boric acid were treated with semicarbazide, to isolate the carbonyl compounds. In addition to *l*-menthone, Schmidt identified a new constituent of peppermint oil, viz., jasmone $C_{11}H_{16}O$, and a sesquiterpene ketone $C_{15}H_{24}O$, of unknown constitution. The occurrence of jasmone in peppermint oil is interesting. The quantity present in the oil is very small (less than 0.1 per cent), but jasmone nevertheless exercises a considerable influence upon the odor and flavor of peppermint oil.

After removal of the carbonyl compounds, Schmidt isolated *l*-caryophyllene and another bicyclic, but dextrorotatory, sesquiterpene $C_{15}H_{24}$, from the residue. Caryophyllene had previously been identified in Japanese mint oil, but not in peppermint oil.

Cineole, which occurs in all oils of *Mentha piperita,* but not in Japanese *Mentha arvensis* oil, was identified by means of its resorcinol compound.

To summarize, Schmidt identified the following constituents in the high boiling fractions of Russian, American, Bulgarian, and Italian peppermint oil:

An Unsaturated Octylic Acid (Free and Esterified). Hydrogenation with Raney nickel yielded caprylic acid b. 237°–240°; amide m. 104°–105°.

Thymol. M. 49°.

Carvacrol. α-Naphthylurethane m. 281°.

Menthofuran. Identified by the above-mentioned autoxidation product m. 186°.

Sesquiterpene Alcohols $C_{15}H_{26}O$. These alcohols were not uniform and had these properties: b_{10} 128° to 150°, d_{15} 0.960 to 0.991, α_D −6° 12′ to +6° 24′, n_D^{20} 1.49554 to 1.50937, ester number after acetylation 106 to 151.

Jasmone. Identified by means of its semicarbazone m. 206°–208°.

A Sesquiterpene Ketone $C_{15}H_{24}O$. The fraction which contained 85 per cent of a ketone $C_{15}H_{24}O$ had these properties: d_{15} 0.9497, α_D +3° 0′, n_D^{20} 1.49980.

l-Caryophyllene. Identified by means of its hydrate m. 94°–95°.

A Bicyclic Sesquiterpene $C_{15}H_{24}$. The fractions containing this dextrorotatory sesquiterpene had these properties: b_9 116°–122°, d_{15} 0.922 to 0.929, α_D +2° 0′ to +26° 48′, n_D^{20} 1.50336 to 1.50753.

Cineole. Identified by the preparation of the cineole-resorcinol compound m. 81°.

Chemical Composition of the Cohobation Water Oil.—The oil obtained by redistillation (cohobation) of the distillation waters was investigated by Kremers [78] who, aside from the main constituent menthol, identified the following compounds:

Acetone. Apparently it is formed during distillation.

3-Methyl-1-cyclohexanone. B. 169°, d_{23} 0.915, n_D^{23} 1.4553. Identified as semicarbazone m. 180°. This compound is probably a cleavage product of pulegone.

Pulegone. Identified as semicarbazone m. 169°–170°. In order to isolate this ketone, Kremers first eliminated menthol, by freezing, from a menthone fraction. This fraction was diluted with alcohol and repeatedly shaken with a bisulfite solution. After six weeks, crystals separated from which a ketone could be regenerated. It possessed the properties of pulegone: b_{17} 105°–110°, n_D 1.484.

[78] *J. Am. Pharm. Assocn.* **10** (1921), 835. *J. Biol. Chem.* **52** (1922), 443. *Am. J. Pharm.* **97** (1925), 658.

1-*p*-Menthen-3-one (Piperitone). Identified as semicarbazone m. 215°. It is present in the cohobation water oil, as well as in the direct oil.

Russian Peppermint Oil

The beginning of the Russian peppermint industry dates back to the last century, when native varieties were distilled. Around 1895 the English black mint, *Mentha piperita* var. *vulgaris,* was introduced to the Ukraine, and planted in the Agricultural Experiment Station. Favored by the rich, black soil of that part of the U.S.S.R., the plantings were extended and steam distilleries erected. Around 1914 production reached about 20,000 lb. of oil. It was only during the ten years preceding World War II that the U.S.S.R. started to expand their potentially large peppermint industry. This long-range program was accompanied by scientific work in various agricultural experiment stations, and resulted in a tremendous increase of peppermint oil production, which, in 1939, reached about 330,000 lb. Exact figures are not available, but it may be estimated that about 190,000 lb. of oil were consumed domestically, and about 140,000 lb. exported. Thus, the U.S.S.R., before World War II, had become one of the world's greatest peppermint oil producers. Years ago, the Russian oil was considered somewhat inferior in quality, as it usually contained a substantial percentage of menthone, and only 45 to 50 per cent of menthol. Recently, however, considerable progress has been made. Strausz [79] claims that the Ukraine produces an excellent oil, containing 53 to 58 per cent of menthol, 10 to 14 per cent of menthones, and almost no resin. The top quality oils, however, originate from the regions north of the Caucasus; these oils contain 53 to 55 per cent of menthol, and only about 9 per cent of menthone. Their odor and flavor are sweet, strong, resembling Mitcham oils.

A discussion of the numerous investigations carried out in various experiment stations of the U.S.S.R. would lead too far; besides, the results in several instances are contradictory. Suffice it to mention the findings of only a few workers. Sardanovski [80] reported that the oil accumulates in the leaves, reaching its maximum in the period between the formation of blossoms and blooming. The menthol content of the oil increases as the plant matures, and attains its maximum toward the end of the blooming period. The ester content increases during the formation of blossoms, slightly decreases during bloom, and finally increases again. Leaves which have dropped and remained on the ground not more than two weeks, without fermenting, contain relatively small amounts of oil, but the oil is rich

[79] *Drug Cosmetic Ind.* **40** (1940), 290.
[80] *Pharm. J.,* Kharkov (1929), 124. *Ber. Schimmel & Co.* (1930), 67.

in menthol and esters. Rutovski and Travin [81] reported that the menthol content of the oil increases, whereas the menthone decreases, as the plant grows and matures. Tables proving this contention will be found in a previous section (see "American Peppermint Oil.").

Nilov and Ponta [82] reported that the percentage yield of peppermint oil decreases from the upper to the lower leaves. The specific gravity of the oil increases, the optical rotation decreases, and the percentage of combined menthol decreases from the lower to the upper leaves. The variations of the quantity of free menthol among the various levels of the leaves are insignificant and the quantity of menthol increases in the upper layers. There seems to be a tendency to a lower content of oil after late harvesting.

Physicochemical Properties.—Two samples of rectified Russian oils analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	I	*II*
Specific Gravity at 25°/25°	0.899	0.900
Optical Rotation	−25° 10′	−26° 45′
Refractive Index at 20°	1.4610	1.4610
Total Alcohol Content, Calculated as Menthol	55.2%	56.8%
Ester Content, Calculated as Menthyl Acetate	5.6%	6.6%
Ketone Content, Calculated as Menthone (Hydroxylamine Hydrochloride Method)	23.2%	23.8%
Solubility at 25°	Clearly soluble in 3 vol. of 70% alcohol	

Gildemeister and Hoffmann [83] indicate these properties for Russian peppermint oils:

Specific Gravity at 15°	0.902 to 0.909
Optical Rotation	−21° 0′ to −29° 15′
Refractive Index at 20°	1.459 to 1.472
Total Menthol Content	47.0 to 57.0%
Ester Menthol Content	3.1 to 12.5%
Menthone Content	21.0 to 25.4%
Solubility	Soluble in 2.5 to 3 vol. of 70% alcohol; a dilute solution is sometimes opalescent

[81] *Riechstoff Ind.* **4** (1929), 124.

[82] *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Efirno-Maslichnoi Prom., Sbornik Rabot Perechnoi Myate* (1939), No. 5, 104. *Khim. Referat. Zhur.* (1940), No. 2, 39. *Chem. Abstracts* **36** (1942), 1981.

[83] "Die Ätherischen Öle," 3d Ed., Vol. III, 854.

Chemical Composition.—The following compounds have been identified in Russian peppermint oils:

dl-α-Pinene. Identified by Schindelmeiser [84] as nitrosochloride m. 103°, and as nitrolpiperidine m. 118°.

l-Limonene. Identified by Andres and Andreef [85] in the fraction b. 173°–175° as tetrabromide m. 102°, as nitrosochloride m. 103°, and as dihydrochloride m. 49.5°–50°.

Dipentene. By Schindelmeiser [86] as tetrabromide m. 125°–126°, as nitrosochloride m. 103°, and as carvone oxime m. 92°–93°.

Cineole. Also by Schindelmeiser as hydrobromide compound m. 57°.

d- and *l*-Menthone. Schindelmeiser isolated a mixture of *d*- and *l*-menthone, in which the *l*-modification predominated; whereas in the mixture of menthones, as isolated by Andres and Andreef,[87] the *d*-modification predominated.

Menthol, Free and Esterified with Acetic and Valeric Acid. Identified by Andres and Andreef, as well as by Schindelmeiser.

Regarding further constituents of Russian peppermint oil, see the recent work of Schmidt cited in the section on "American Peppermint Oil—Chemical Composition."

Bulgarian Peppermint Oil

During the last years prior to World War II, Bulgaria became a very important peppermint oil producer. In fact, the rise of Bulgaria's peppermint industry from practically nothing to a strong position in Europe is remarkable. The beginning of peppermint production in that country dates back to about 1923, when some roots of Mitcham type black mint were introduced from Hungary. The venture failed, however, some years later. Only one farmer retained a few of the peppermint plants in his garden; their number was increased in the following years, and finally several acres could be planted. The world-wide economic crisis of 1929 to 1932 depressed the price of rose oil to such low levels that many discouraged Bulgarian rose growers started to look for more lucrative crops. Several farmers planted peppermint from the old plants which had been introduced several years before from Hungary, and distilled the oil. It proved to be of excellent quality, resembling the Italo-Mitcham type. From then on, the newly established industry developed rapidly and to such an extent

[84] *Apoth. Ztg.* **21** (1906), 927. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 854.
[85] *Ber.* **25** (1892), 609.
[86] *Apoth. Ztg.* **21** (1906), 927. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 854.
[87] *Ber.* **25** (1892), 609.

that in 1938 Bulgaria produced about 140,000 lb. of peppermint oil, two-thirds of which went to Germany, the balance to France and England. The oil has even been offered in the United States.

In the trade, the Bulgarian oil is also known as Bulgaro-Mitcham peppermint oil.

The producing regions are near Karlovo, between the rivers Struma and Tundzha. Peppermint is grown successfully also around Svistov on the Danube in northern Bulgaria and in the plain of Sofia.

The Bulgarian peasants being skilled gardeners, and the country offering soil and climatic conditions comparable to our Middle West, it is not surprising that Bulgaria produces an excellent quality of peppermint oil. In fact, the Bulgarian oil has a somewhat "American" character; it possesses a high menthol content (52 to 61 per cent) and can be classed with our best brands.

A sample of genuine Bulgarian peppermint oil analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 25°/25°	0.907
Optical Rotation	−19° 52′
Refractive Index at 20°	1.4629
Total Alcohol Content, Calculated as Menthol	55.2%
Ester Content, Calculated as Menthyl Acetate	5.5%
Solubility	Soluble in 3 to 3.5 vol. of 70% alcohol; opalescent to cloudy with more

In Simmons'[88] opinion, the Bulgarian oil is of very good quality, superior to the American oil and about equal to the Italo-Mitcham oil, which it also very closely resembles in regard to its properties.

Simmons reported these properties for eight samples of Bulgarian peppermint oil:

Specific Gravity at 15°	0.9102 to 0.9135
Optical Rotation	−18° 0′ to −22° 12′
Refractive Index at 20°	1.4614 to 1.4645
Total Menthol Content	52.0 to 59.3%
Menthol Ester Content	4.3 to 6.6%
Solubility	Soluble from 1 in 2.75 to 1 in 3.50 vol. of 70% alcohol

It is not known how far World War II has affected Bulgaria's peppermint industry, which had made such a promising start and attained a prominent position in Europe.

[88] *Perfumery Essential Oil Record* **31** (1940), 92.

Chemical Composition.—The chemical composition of Bulgarian peppermint oil undoubtedly closely resembles that of oils of other origin (cf. the recent work of Schmidt cited in the section on "American Peppermint Oil—Chemical Composition."

Italian Peppermint Oil

The modest beginning of Italy's peppermint oil industry dates back to about 1800, when only native varieties, e.g., *Mentha piperita* var. *piedmontese* were grown, and on a very small scale. The oil distilled from this plant was of inferior quality, not suited for export. About 1880, a French variety was imported from Grasse (A.M.) but, due to the cultural methods employed, became naturalized in Piedmont; the oil was of good quality, but the yield very inferior. In 1902, M. Honoré Carles, a French essential oil producer from Grasse (A.M.) visited the Po plain and perceived of the great possibilities that that fertile region offered for the cultivation of peppermint. Mr. Carles' subsequent work brought about fundamental changes, and such a prosperous development of the industry that he may be called the actual founder of Italy's modern peppermint oil industry. He introduced from England the Mitcham black mint, *Mentha piperita* var. *vulgaris*, and planted it on a large scale. Compared with the native mints and the white Mitcham, the English black mint is more resistant to climate, diseases, and pests; furthermore, it gives a higher yield of oil. The first harvest and distillation of Italo-Mitcham peppermint took place in 1903.

According to Carles,[89] the Po plain south of Torino is ideally suited for the growing of peppermint, because it possesses a fertile, alluvial topsoil (clay rich in silica) and a moist subsoil. The winters are cold, with snowfall; spring frosts are rare, the summers are warm and quite dry; the land is irrigated; and labor is abundant, very efficient, and comparatively low priced. The mint is grown by countless peasants, all members of their families participating in the cultivating and harvesting.

The producing regions are located in the fertile plains of Piedmont (Provinces of Torino and Cuneo) with Pancalieri, Vigone, Polonghera, and Mottura as centers, and in the Po delta (Province of Venetia and Ferrara) with Serravalle as center. In 1938, some fifty distilleries contained more than 200 stills, some being antiquated direct fire stills, others of modern construction. A few large distilleries were equipped with 6 to 8 efficient steam stills of 2,500 to 3,500 liters capacity, constructed either in Grasse

[89] "La Menthe et ses plantations," Pancalieri. The author is deeply grateful to Mr. J. M. Rodié, Chief Chemist of Méro and Boyveau, Grasse (A.M.), France, for much of the information contained in this section.

(A.M.), France or in Italy, according to plans drawn by experienced constructors in Grasse.

Italian peppermint is planted every spring from rootstocks. After harvesting and after rootstocks have been gathered for propagation purposes, the field is plowed under for other crops, left fallow during the winter, planted with wheat the following spring, and with maize or hemp for another year. Thus the crops are rotated, the same field being replanted with peppermint every third year. The plants are set out at a distance of 10 cm. in rows 15 cm. apart, fertilized with stable dung, and with nitrates in August. Harvesting takes place in August when the plants are 60 to 70 cm. high.

The plant material, after having been cut with scythes, is spread and left in the fields until slightly dried; in other words, it is distilled when "clover dry," not after excessive drying in the sun. To obtain a high quality of oil, the producers distill the herb as rapidly as possible, which precaution prevents hydrolysis of esters and alteration of other constituents by excessively long action of the passing steam.

The yield of herb per acre, as well as the yield of oil, varies considerably and depends upon weather conditions prevailing during the winter and spring and the period of harvest. According to Chauvet,[90] one hectare (2.47 acres) of Italian mint produces 15,000 to 25,000 kg. of herb, yielding 0.2 to 0.3 per cent of oil. On the average, one hectare of a peppermint planting in good condition yields about 40 kg. of oil (1 acre yields about 35 lb.).

Annual production of Italian peppermint oil has varied considerably from year to year since 1900. The banner year was 1926 with a production of about 100,000 kg. of oil. In normal years the production figures range from 25,000 to 50,000 kg. Obviously, World War II temporarily affected the production of this oil, but for 1947 more than 30,000 kg. of oil were reported.

Italian oils have been marketed under the label of Italo-Mitcham peppermint oils because the plant originally came from Mitcham. The main consumers before World War II were France, Germany, England and, of course, Italy. Rectified Italo-Mitcham oils enjoy a high reputation for quality. The odor is sweet, the flavor is mild, somewhat spicy.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[91] the properties of Italo-Mitcham oils vary within the following limits:

Specific Gravity at 15°.....	0.902 to 0.926
Optical Rotation.....	−2° 30′ to −27° 0′ (since 1910, not below −12° 51′)

[90] Private communication of Mr. Pierre Chauvet, Seillans (Var), France.
[91] "Die Ätherischen Öle," 3d Ed., Vol. III, 850.

Refractive Index at 20°	1.462 to 1.470
Acid Number	Up to 0.6
Total Menthol Content	43.0 to 67.0%
Ester Menthol Content	2.9 to 10.4%
Menthone Content	8.0 to 29.4%
Solubility	Soluble in 3 to 7 vol. of 70% alcohol; opalescent to turbid with more

According to Carles,[92] Italo-Mitcham peppermint oils have these properties:

Specific Gravity	0.906 to 0.912
Optical Rotation	−18° 0′ to −25° 0′
Total Menthol Content	47.0 to 57.0%
Ester Menthol Content	3.0 to 6.0%
Menthone Content	15.0 to 30.0%
Solubility in 70% Alcohol	Soluble in 3 and more vol.

Chemical Composition.—The chemistry of Italian peppermint oil has not been investigated as thoroughly as that of the American oils because it has probably always been assumed that its composition is fundamentally identical with that of American oils, both oils being derived from closely related plants.

Distilling fresh, blooming peppermint, Carles[93] obtained an oil from which he isolated a compound not previously observed in peppermint oil. The new constituent contained oxygen, showed a high specific gravity (0.965 at 15°) and strong dextrorotation (+88°). It was apparently not present in oils distilled from young plants before they had reached the blooming stage. On the other hand, the compound was isolated also from two oils distilled exclusively from flowers. These two oils had specific gravities (at 15°) of 0.9409 and 0.9364; optical rotations (at 20°) of +30° 10′ and +24° 40′. The high specific gravity and the dextrorotation of these oils permit the conclusion that the new compound is present mainly in oils distilled exclusively from flowers. It is apparently formed in the plants and gradually reaches a maximum (about 10 per cent of the oil) during the blooming period, disappearing as the menthol content increases. The compound was finally identified by Wienhaus and Dewein[94] as 3,6-dimethylcumaronetetrahydride-(4,5,6,7), and named menthofuran. Upon exposure to air menthofuran is oxidized to a colorless acid m. 186°.

[92] "La Menthe et ses plantations," Pancalieri. Courtesy Messrs. Benard et Honorat, Grasse (A.M.), France.

[93] *Parfumerie moderne* **22** (1929), 615.

[94] *Z. angew. Chem.* **47** (1934), 415.

Regarding other constituents of Italian peppermint oil, see the recent work of Schmidt cited in the section on "American Peppermint Oil—Chemical Composition."

English (Mitcham) Peppermint Oil

English or, as it is usually called, Mitcham peppermint oil still enjoys its reputation as the finest of all commercial oils. The English peppermint industry antedates that of other European countries, and of North America. Lately, however, English peppermint oil production has declined considerably in volume because of competition from the lower priced American, Russian, Bulgarian, and other peppermint oils, not to speak of the Japanese dementholized product. As a matter of fact, Mitcham produces only very small quantities of peppermint oil today.

Botany.—There are two types of English peppermint, viz., the black mint and the white mint.

Black mint (*Mentha piperita vulgaris,* or *Mentha piperita nigra* L. var. *Mitcham,* or *Mentha piperita* Huds. var. *officinalis* Sole forma *rubescens* Camus) [95] is, according to Schürhoff,[96] a triple hybrid *Mentha sylvestris* L. × *Mentha rotundifolia* L. × *Mentha aquatica* L. The stems have a purple color. It is a hardy plant, with a high yield. All the so-called Mitcham type peppermint oils produced in other parts of Europe, e.g., the Italo-Mitcham and the Franco-Mitcham oils, are derived from black English or Mitcham mint, the roots of which were originally introduced from Mitcham. The peppermint grown in the United States is also a descendant of English black mint, now acclimatized to our country.

The white mint, or white Mitcham mint (*Mentha piperita officinalis,* or *Mentha piperita* Huds. var. *officinalis* Sole forma *pallescens* Camus), is a smaller plant, more sensitive to inclement weather, climate, insects, and diseases. The stems have a lighter green color. White mint yields an extremely fine quality of oil, but the percentage of the yield is lower than that of the black mint. It used to be very popular but lately the plant is being replaced more and more by black mint.

Producing Regions.—The center of the English peppermint industry used to be Mitcham (Surrey), but the growth of London gradually suppressed agriculture around Mitcham, and the farms were converted into urban real estate. Today peppermint in England is grown and distilled in Lincolnshire and Cambridgeshire, and at Hitchin (Hertfordshire) and Long Melford (Suffolk).

[95] *Repts. Roure-Bertrand Fils,* October (1911), 3. *Ber. Schimmel & Co.,* April (1912), 98.
[96] *Arch. Pharm.* **267** (1929), 515.

Planting, Cultivating, and Harvesting.—Peppermint grows well in moist soils, excepting heavy clays. The ground must be thoroughly cleaned to eradicate weeds—which would spoil the flavor of the oil—and then well manured. Propagation is effected by means of suckers. These may be taken up in autumn, reared in cold frames, and planted out in spring; or they may be set out directly in the fields during the autumn. The latter method, however, involves some risk of loss in unfavorable seasons. The cuttings are set out by hand, about 1 ft. apart, and planted very firmly. One acre requires about 40,000 plants. The first year will bring only a small crop. The plantings must always be kept clean by hand weeding. A field is kept in mint for four years, after which it must be plowed up. If the plants are strong and the weather is dry, the crop can be harvested by moving machines; otherwise it has to be cut by hand. The cut plants are usually placed on mats and allowed to wilt before they are carted to the distilleries, but excessive drying must be avoided, to prevent loss of oil.

Distillation.—The semidried herb is charged into a still provided with a false bottom and a steam jacket, the water in the still being kept below the false bottom throughout the course of distillation. The procedure thus represents a typical case of water *and* steam distillation (see Vol. I of this work, pp. 120, 147) with resulting low steam pressure. The aqueous phase of the condensate is returned into the still during distillation (automatic cohobation). Distillation of one plant charge usually requires 6 hr. The slow low-pressure steam distillation of plant material which is only semi-dried (not fully dried) may well be one of the reasons for the fine odor and flavor of the English peppermint oil.

The yield of oil per acre ranges from 20 to 40 lb.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[97] the properties of Mitcham peppermint oils vary within the following limits:

Specific Gravity at 15°/15°	0.901 to 0.912
Optical Rotation	−21° 0′ to −33° 0′
Refractive Index at 20°	1.460 to 1.463
Acid Number	Up to 1.6
Total Menthol Content	48.5 to 68.0%
Ester Menthol Content	3.0 to 21.0% (3.0 to 8.0% in oils distilled from white mint and 13.0 to 21.0% in oils distilled from black mint)
Menthone Content	9.0 to 12.0% (determined only in a few cases)
Solubility	Soluble in 2.0 to 3.5 vol. and more of 70% alcohol; dilute solutions are in some cases more or less opalescent to turbid

[97] "Die Ätherischen Öle," 3d Ed., Vol. III, 844.

According to Parry and Ferguson,[98] the properties of genuine English peppermint oils, distilled from 1927 to 1935, from the same plantings and from the same plants, or their descendants, varied within these limits:

Specific Gravity	0.9035 to 0.9094
Optical Rotation	−22° 50′ to −29° 10′
Refractive Index	1.4591 to 1.4643
Total Menthol Content	42.4 to 64.1%
Ester Content, Calculated as Menthyl Acetate	2.3 to 6.2%
Menthone Content	29.2 to 42.1%

The difference between these figures and those of oils distilled in former years, especially in regard to menthol and menthone content, appears quite striking. An explanation might be that rainy weather prevailed during the growing seasons, or that the plants were cut much too early.

In a later publication, Parry and Ferguson [99] reported that the total content of menthol plus menthone in English peppermint oil has remained quite constant for the past few years. It varied between 80.7 and 82.5 per cent. As the content of menthol increases, that of menthone decreases.

Stafford Allen and Sons, Ltd., London,[100] in the course of years observed the following properties of English peppermint oils:

Specific Gravity at 15.5°	0.902 to 0.910
Optical Rotation at 20°	−18° 0′ to −30° 0′
Refractive Index at 20°	1.4600 to 1.4670
Acid Number	Usually below 1.0
Free Alcohol Content, Calculated as Menthol	48.0 to 61.0%
Ester Content, Calculated as Menthyl Acetate	3.0 to 8.0%
Solubility in 70% Alcohol at 15.5°	Soluble in 1 to 4 vol.; frequently opalescent on further dilution

Chemical Composition.—English peppermint oil has not been as thoroughly investigated as the American or Japanese oils, and there is no doubt that further work on English oils would reveal the presence of a number of constituents already identified in the other oils. So far, the following compounds have been found in English peppermint oil:

A Mixture of Pinene and Phellandrene(?). Flückiger and Power [101] isolated two laevorotating terpenes, b. 165°–170°.

A Mixture of Phellandrene and Limonene(?). Found by the same authors in the fraction b. 173°–176°.

[98] *Chemist Druggist* **124** (1936), 37.
[99] *Ibid.* **125** (1936), 408.
[100] Private communication (1948).
[101] *Pharm. J.* [3], **11** (1880), 220. *Arch. Pharm.* **218** (1881), 222.

Probably Cadinene. This dextrorotatory sesquiterpene was isolated from the oil by Flückiger and Power [102] as fraction b. 255°–260°.

Phellandrene. Identified by Umney [103] by the nitrite reaction of this terpene.

Menthol, Free and as Acetate and Isovalerate. Umney also found that the acids which are esterified with menthol are the same as those occurring in the American oil.

Genuine Mitcham oils are known by their sweet odor and strong flavor, the result of a high content of total and free menthol, and (usually) a low content of menthone and resins.

Aside from the Mitcham district, certain regions of Norfolk and Suffolk produce small quantities of peppermint oil. However, the climatic conditions of Norfolk and Suffolk are somewhat different from those of Mitcham, and their oils, although distilled from Mitcham plants, do not possess the same fine character as genuine Mitcham oils. Nevertheless, the odor and flavor of the Norfolk and Suffolk oils are excellent, sweet, strong, lasting, and compare well with American products.

French Peppermint Oil

Years ago, when the essential oil industry of Grasse (A.M.) experienced its greatest period of expansion and prosperity, Southern France produced substantial quantities of peppermint oil, which were absorbed by the domestic market. The decline of Grasse as the world's essential oil center, which was caused by many factors, also brought about a sharp reduction in the growing of peppermint. During the last years prior to World War II France produced only about 3,000 lb. of peppermint oil. The growing regions were located in the section between Cannes, Mandelieu, Pegomas, Auribeau, Grasse, and Villeneuve-Loubet, Pegomas with its rich alluvial soil being the center. Plantings existed also near Castellane and Barrême in the Département Basses-Alpes, and here and there in the Département Vaucluse. Details may be found in a publication by Rodié and Louveau.[104] In 1935, according to Niquet,[105] the region of Annot (Dépt. B.A.) produced about 240,000 lb. of fresh peppermint plants, which were distilled on the spot. Assuming an oil yield of 0.20 to 0.57 per cent, as is said to be obtained in France from fresh mint herb, this would mean from 480 to 1,370 lb. of oil.

The plant variety grown at present in Southern France was introduced from Mitcham; it is the English black mint, *Mentha piperita* Huds. var.

[102] *Ibid.*
[103] *Pharm. J.* **56** (1896), 123; **57** (1896), 103.
[104] *Editions Rev. Marques*, Paris (1931).
[105] *Parfumerie moderne* **30** (1936), 317.

officinalis Sole forma *rubescens* Camus, which is better yielding than the Mitcham white mint. The Grasse region possesses a large number of distilleries equipped for the processing of all kinds of aromatic plants; hence the distillation of peppermint presents no difficulties. The mint grown in the Départements Basses-Alpes and Vaucluse is processed in some of the lavender distilleries with which those regions abound.

Young rootstocks are planted from January to March; the harvest takes place in August. It is customary to renew the plantings annually.

The French producers prefer to distill the fresh plant material without drying, claiming that in this way they obtain an oil of superior aroma and fresher "bouquet." According to Ripert,[106] some distillers employ indirect steam with cohobation of the distillation waters; they believe that this process yields 10 to 20 per cent more oil, and that such oils contain 5 to 10 per cent more menthol than those distilled with direct steam.

For the duration of World War II France was cut off from its former supplies of foreign peppermint and mint oil and had to rely upon its own domestic production, which brought highly inflated prices. Attracted by these prices, numerous farmers in the region of Avignon, in the northern part of the Département Bouches-du-Rhône, in the Département Vaucluse, in the region south of Paris, and in the central part of France started peppermint plantings. Because of this development, the present annual production of French peppermint oil is probably larger than it was prior to World War II, but exact figures are very difficult to obtain.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[107] the properties of French peppermint oils vary within the following limits:

Specific Gravity at 15°/15°	0.910 to 0.927
Optical Rotation	−5° 0′ to −35° 0′
Refractive Index at 20°	1.462 to 1.471
Total Menthol Content	45.0 to 70.0%
Ester Menthol Content	4.0 to 21.0%
Menthone Content (1 determination only)	17.4%
Solubility	Some oils are soluble in 3.5 vol. of 70% alcohol; soluble usually in 1 to 1.5 vol. of 80% alcohol, opalescent to turbid with addition of more alcohol

These so-called Franco-Mitcham peppermint oils possess a fine, sweet and quite strong aroma.

[106] *Perfumery Essential Oil Record* **15** (1924), 181. *Office Nat. des Matr. Premières Veg. pour la Drog. et Parf.*, Paris (1926), No. 22. *Bull. Imp. Inst.* **24** (1926), 260.
[107] "Die Ätherischen Öle," 3d Ed., Vol. III, 847.

Chemical Composition.—The chemistry of French peppermint oils was investigated in the laboratories of Roure-Bertrand Fils.[108] The presence of the following compounds has been established.

Isovaleric Aldehyde. Identified as ammonia compound m. 56°–58°.

Isoamyl Alcohol. B. 132°; oxidation to isovaleric aldehyde. It is not known whether this alcohol occurs in the oil in its free or esterified state.

l-α-Pinene. B. around 155°; nitrosochloride m. 102°–103°.

3-*p*-Menthene(?). Presence not definitely established.

Cineole, *l*-Menthol, *d*-Menthone, Esters of Acetic Acid, and Valeric Acid. Were found in French peppermint oil also by Roure-Bertrand Fils.[109]

Argentine Peppermint Oil

The first experimental plantations of *Mentha piperita* in Argentina were undertaken about 1936, at first near Buenos Aires, later around Cordoba, and still later near Mendoza. The planting material was imported partly from England (Mitcham variety) and partly from Northern Italy (Italo-Mitcham variety). Commercial production of peppermint oil did not begin until 1940 when the outbreak of World War II brought a great local demand for the product, the imported oil then no longer being as readily available as in previous years.

Today, Argentina's new and expanding peppermint oil industry is located principally in the region of Mendoza, at altitudes ranging from 600 to 900 m. Due to the paucity of rain (about 6 in. per year), the land around Mendoza must be irrigated; but irrigated land here has always been expensive and in great demand. Most peppermint plantings in the Mendoza section, therefore, are small and quite widely scattered. In 1947, they covered about 600 hectares; the acreage, however, is on the increase. There are additional peppermint plantings, amounting to about 50 hectares, near Buenos Aires, and smaller fields north and south of Mendoza.

The following short description of peppermint oil production in Argentina applies to the region around Mendoza, where the bulk of the oil is distilled by several companies operating modern distilleries. In 1947 Argentina produced about 20 metric tons of peppermint oil, most of it being sold on the local market.

[108] *Repts. Roure-Bertrand Fils* (1909), 40. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 848.

[109] *Repts. Roure-Bertrand Fils* March (1900), 17. Charabot, *Bull. soc. chim.* [3], **19** (1898), 117.

In the Mendoza region, a new peppermint field is started from June to August. The first cutting takes place the following January; the second at the end of March. Therefore, two crops can be gathered per year, the second crop, however, being considerably smaller than the first. The first crop is cut with machines, the second by hand, with scythes, because the plants are much smaller. On large plantations, cutting begins just before the blooming stage in order to complete it while the flowers are still in full bloom. The cut plants are heaped up in the fields and left there for 12 hr. to dry. When distilled, the plant material will be about clover dry, the degree of dryness depending upon the weather, the distance over which the mint hay must be hauled to the distillery, and upon the capacity of the distillery; in small distilleries not all the plant material arriving from the fields can be processed immediately and may lie around for some time.

Distillation is carried out with direct steam, and lasts from 1 to 2 hr. for each batch, depending upon the condition of the plant material.

The yield of oil from the first crop ranges from 0.3 to 0.4 per cent, calculated upon the cut plant material. The yield of oil from the second crop amounts to 0.2 to 0.3 per cent only. The yield of oil per acre varies considerably and depends upon the condition of the soil, the amount of fertilizer used, irrigation, the weather, etc. Contingent upon these factors, the average yield per hectare is from 20 to 40 kg. of oil per year, including both harvests. A field can stay in mint for two to three years, and in some cases for a longer period, but then the crop must be rotated.

The crude oil of peppermint distilled in the Mendoza region is finally rectified; usually this is done in factories located in Buenos Aires.

Two samples of Argentina peppermint oil, one crude oil and one rectified oil, were analyzed in the laboratories of Fritzsche Brothers, Inc., New York, and had the following physicochemical properties:

	Crude Oil	*Rectified Oil*
Specific Gravity at 25°	0.905	0.902
Optical Rotation	−24° 10′	−22° 58′
Refractive Index at 20°	1.4650	1.4632
Total Alcohol Content, Calculated as Menthol	65.2%	58.3%
Ester Content, Calculated as Menthyl Acetate	7.3%	6.3%
Ketone Content, Calculated as Menthone (Hydroxylamine Hydrochloride Method)	19.0%	19.6%
Solubility at 25°	Soluble in 2.5 to 3 vol. of 70% alcohol. Opalescent in 10 vol.	

Both oils possessed a very pleasant and fine peppermint odor. Tests for dimethyl sulfide, and for the presence of oil of spearmint were negative.

Peppermint Oils of Other Origin

Aside from the countries mentioned above, peppermint oil is produced in Roumania, Hungary, Germany, Austria, Holland, Sweden, etc. However, the quantities are insignificant, and the oils are not considered important on the world market. We shall, therefore, discuss them only briefly.

Roumanian Oil.—About 1926 the Leo-Werke, Dresden (Germany), instigated the growing of peppermint on the rich, black soil around Kronstadt in Siebenbuergen (Roumania). The venture was successful because of the favorable climate, the high underground water level, and the nitrogen-containing soil of those regions. The mint grows luxuriantly, 1 hectare yielding about 55 lb. of oil. It possesses a fine and strong aroma, equaling the best American brands. According to Strausz,[110] the crude oil contains from 55 to 62 per cent of total menthol, 7 to 12 per cent of ester menthol.

Despite unfavorable weather conditions about 7,700 lb. of oil were produced in Roumania during 1938. The oil did not reach the world market, as it was absorbed by the above-mentioned Leo-Werke in Dresden, sponsors of the venture. According to Kopp,[111] the yield of oil from fresh herb in Roumania varies between 0.20 and 0.24 per cent.

The properties of Roumanian peppermint oils vary within the following limits:

Specific Gravity at 15°	0.9042 to 0.9113
Optical Rotation	−21° 10′ to −27° 9′
Refractive Index at 20°	1.4602 to 1.4618
Total Menthol Content	50.0 to 65.8%
Free Menthol Content	46.7 to 50.3%
Ester Menthol Content	3.3 to 12.5%
Menthone Content (Lab. Distilled Oils Only)	7.9 to 10.1%
Solubility	Soluble in 2.7 to 3 vol. of 70% alcohol

Simmons [112] reported that an output of as high as 10,000 kg. per year has been reached, but no substantial lots of the Roumanian oil have ever been shipped to the United Kingdom or to America.

The Roumanian oil is of a quality similar to the Bulgaro-Mitcham oil, which it resembles also in physicochemical properties.

[110] *IV Congrès Inter. des Plantes Medic. et des Plantes à Essences*, Paris (1931), 270. *Ber. Schimmel & Co.* (1933), 49.
[111] *Pharm. Zentralhalle* **71** (1930), 577.
[112] *Perfumery Essential Oil Record* **31** (1940), 92.

Hungarian Oils.—Some years ago, the author [113] made a study of peppermint production in Hungary and found that most of the mint grown in that country was sold as dried drug. Only a small quantity of the production in the districts of Nyiregyháza, Kalocsa, and in the Valley of the Zala was converted into oil.

The first harvest takes place in July; if the weather permits, there is a second harvest in September, and occasionally even a third at the end of October or beginning of November. The first cutting gives the highest yields of plants and oil; successive cuttings yield less oil, but these oils are higher in menthol content.

The plants are dried in the swath for about 24 hr., until they lose about two-thirds of their moisture content. Depending upon the state of dryness, distillation of the plant material lasts from 1 to 2 hr. Calculated on the dried herb, the yield of oil ranges from 0.8 to 1.65 per cent, and averages from 1.0 to 1.2 per cent. One acre produces at least 15 lb. of oil, and normally 22 to 31.5 lb.

The properties of Hungarian peppermint oils, according to the author's findings,[114] range within the following limits:

Specific Gravity at 15°	0.9014 to 0.9063
Optical Rotation	−14° 25′ to −27° 31′
Refractive Index at 20°	1.4610 to 1.4769
Total Menthol Content	48.00 to 71.37%
Ester Menthol Content	5.07 to 12.8%
Menthone Content	7.40 to 14.11%

According to Rom,[115] peppermint oils distilled in Hungary from 1934 to 1937 had properties which varied within these limits:

Specific Gravity at 20°/4°	0.8894 to 0.9135
Optical Rotation	−15° 0′ to −38° 30′
Refractive Index	1.4600 to 1.4655
Total Menthol Content	36.2 to 56.3%
Ester Content, Calculated as Menthyl Acetate	4.4 to 9.9%

The Hungarian oil is of very fine quality, resembling the Mitcham type, as the plants cultivated in Hungary are of the black Mitcham variety. In 1938 Hungary produced almost 6,000 lb. of oil, most of which was exported to Germany.

German Oils.—Production of peppermint oil in Germany, like that in Holland, Scandinavia, Poland, and Yugoslavia, is insignificant. Suffice it to

[113] *Am. Perfumer* **36** (April 1938), 36.
[114] *Ibid.*
[115] *Kisérletügyi Közlemények* **42** (1939), 93. *Chem. Abstracts* **33** (1939), 7485.

mention that Schimmel & Co.[116] reported yields of oil from fresh herb as varying between 0.14 and 0.15 per cent, and from dried mint about 0.26 per cent.

Polish Oils.—According to Borkowski,[117] *Mentha piperita* L. is cultivated in various regions of Poland. The menthol content was found to meet the requirements of the Polish Pharmacopoeia, although the physical properties deviated. Borkowski suggested using the oil for the production of natural menthol.

Moroccan Oils.—During the years of World War II, when France, including her North African possessions and protectorates, could no longer import peppermint oils and Japanese mint oil, considerable efforts were made to develop a new peppermint industry in Morocco. Certain areas are eminently suited to the growing of peppermint—e.g., the plain of Rharb with its fertile alluvial top soil and moist subsoil. In that section actual production of peppermint oil in 1946 reached about 5,000 kg., with a considerable future increase in prospect. Other favorable regions lie to the south of Tiflet and Khemisset, with Maaziz as the center. Plantings are being developed at present on those rich black muck soils, the planting material consisting of Franco-Mitcham peppermint, imported from France and Algeria. The quality of the oil has been very good, resembling that of the Italian oils. The long experience of the French colonists in growing aromatic plants, the fertility of parts of Morocco, as well as the low cost of labor still prevailing in Morocco, will undoubtedly benefit this latest development in the world's peppermint oil industry.

Brazilian Oils.—During World War II when Brazil had difficulties in obtaining her share of imported drugs and essential oils that country started to develop plantations of *Mentha piperita* L. The plantings laid out in the States of Santa Catarina and São Paulo were intended primarily for the obtaining of dry peppermint leaves, which in Brazil are used for the making of teas. Part of the harvested peppermint was converted into essential oil, the production not exceeding 1,000 kg. Methods of cultivation resemble those of *Mentha arvensis*. A field yields on the average three cuts per year. The main difficulties the growers had to encounter consisted in weeds, which in the third year of the planting rendered the yield almost unprofitable. Once American and European peppermint oil is again exported freely, the Brazilian peppermint growers will have little, if any, interest in continuing their plantations of *Mentha piperita* L.

[116] *Ber. Schimmel & Co.* (1939), 66.
[117] *Acta Polon. Pharm.* **2** (1938), 263. *Chem. Abstracts* **36** (1942), 2684.

World Production and Use of Peppermint Oil

Total World Peppermint Oil Production.—According to Strausz,[118] the total production of peppermint oil in various countries during 1938 was distributed as follows:

	Pounds
United States	732,000
Soviet Russia	330,000
Bulgaria	143,500
Italy	77,000
China	10,100
Hungary	8,800
Roumania	7,700
England	5,000
France	4,400
All Other Countries	10,000
	1,328,500

Use.—Oil of peppermint is one of the most popular and widely used essential oils. It is employed for the flavoring of pharmaceuticals and oral preparations—such as tooth pastes, dental creams, and mouth washes—in cough drops, chewing gums, confectionery, and alcoholic liqueurs. So far as medicinal value is concerned, the oil is generally preferred to menthol for internal use, because of its more pleasant taste. Oil of peppermint is an excellent carminative and gastric stimulant. To a stimulating effect in the alimentary canal, it adds an antiseptic and local anesthetic influence.

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JAPANESE MINT OIL

(Oil of *Mentha arvensis* L., subsp. *haplocalyx* Briquet, var. *piperascens* Holmes, or forma *piperascens* Malinvaud)

"Oil of Cornmint" *"Oil of Fieldmint"*

Botany.—There exists considerable confusion regarding the botanical nomenclature of wild and cultivated Japanese mint. The opinion of some botanists that the Japanese plant is not a true peppermint has been attacked by others as incorrect. Schürhoff [1] believes that the parent plant of Japanese mint (*Mentha canadensis* D.C. var. *piperascens* Holmes) is a hybrid between *Mentha arvensis* L. and *Mentha aquatica* L. Japanese mint has also been classified as *Mentha arvensis* var. *piperascens* Malinvaud or Holmes, and the closely related Chinese plant as *Mentha arvensis* var. *glabrata* Holmes, or *Mentha canadensis* var. *glabrata* Gray. They are not of the same species as American and European peppermints. Freeman [2] indicated the chief differences between true peppermint (*Mentha piperita*) and Japanese mint (*Mentha arvensis* var. *piperascens*) as follows:

"Japanese mint is a perennial herb spreading by rootstocks which creep along the ground or just under the surface and root at the nodes. The erect stems of mid-

[1] *Arch. Pharm.* **267** (1929), 515.

[2] See: Sievers and Lowman, "Commercial Possibilities of Japanese Mint in the United States as a Source of Natural Menthol," *U. S. Dept. Agr., Tech. Bull.* No. **378** (1933), 5.

summer, 1 to 3 ft. in height, are usually branched and bear flower clusters in the leaf axils. This differs from peppermint, *Mentha piperita,* which bears its flowers in more or less interrupted, terminal, usually leafless, spikelike panicles. The stems of Japanese mint are covered with soft white hairs, as are the leaves and calyxes. Peppermint is usually glabrous throughout, and if hairs are present they are sparse and are mostly near the nodes at the lower part of the stems. The leaves of Japanese mint are lanceolate and broad-lanceolate with triangular blunt teeth. The leaf is gradually acuminate at the base with a margin extending nearly to the base of the petiole. The leaf of peppermint is similar, but differs in having sharper acuminate teeth, and the base is acute or abruptly acuminate with the petiole scarcely margined. Peppermint rarely, if ever, produces seed in the United States, while Japanese mint produces seed freely."

The full botanical name of Japanese mint is *Mentha arvensis* L., subsp. *haplocalyx* Briquet, var. *piperascens* Holmes, or forma *piperascens* Malinvaud. This name should always be used when referring to the plant as growing or being cultivated in Japan, because *Mentha arvensis* L., "Cornmint," is circumpolar in the Northern Hemisphere. The oils of other species and varieties occurring in Japan do not contain sufficient menthol to warrant commercial interest. The Japanese Department of Agriculture warns the growers against cross-hybridization with local wild varieties and advises them to improve their mint plantings by a number of measures. There exist several forms of mint as cultivated in Japan. The principal and most widely grown form "Aka Maru" is distinguished by a reddish-violet stem and gives the best yield of oil with the highest menthol content.

Historical Development.—The mint plant has been known and grown in Japan since antiquity. According to tradition, about 1,700 years ago Enzan, a Japanese priest, on his return from China brought along tea and mint and planted them in the vicinity of Kyoto. The oldest record of mint oil as a product of medicinal value is contained in *Ishin-Ho,* a book of prescriptions published about 984 by Tamba Yasuyori who recommended the employment of this oil in eye washes. The early production of mint oil, however, served exclusively for domestic consumption. About 1870, a substantial acreage of mint was planted in the prefecture of Yamagata, in the northern part of Japan's main island, and owing to the increased production in Yamagata the first lots of menthol were exported in 1883. Some years later, in 1892, trial plantations were undertaken in the Sapporo district on the island of Hokkaido (north of Japan's main island) and then transferred to the province of Kitami, also on the island of Hokkaido. In the course of years this development led to the dominant position which Japan enjoys in regard to mint oil and menthol. At about the same time (1892–1895) plantations of mint were also started in the so-called "San-Bi" district located in the southwestern part of Japan's main island. This "San-Bi" district ("San-Bi" meaning three B's) is composed of Bizen and

neighboring Bitchu—which two districts form the prefecture of Okayama—and adjoining Bingo which is part of the prefecture of Hiroshima. In 1894 the production of natural mint oil in Japan was distributed approximately as follows:

	Kin
Prefecture of Yamagata	60,000
District of "San-Bi"	10,000
Island of Hokkaido (Kitami)	1,000

During the years of 1887–1897 the prefecture of Yamagata was the principal producer of Japanese mint oil. Since then, however, the center of production has shifted repeatedly—first toward the "San-Bi" district and, more recently, toward Hokkaido. About 1900 the "San-Bi" district produced 80 per cent of Japan's total output of mint oil and Hokkaido 20 per cent, whereas from 1912 up to the present time Hokkaido has been producing 75 to 80 per cent and the "San-Bi" district 20 to 25 per cent of Japan's mint oil.

In its early days of development the methods applied in Japan for the separation of menthol from the natural mint oil were rather primitive and the quality of the menthol exported was often poor. Due to impurities present and the low melting point that may result from them, the menthol did not always withstand changes in climate and temperatures during the long transport abroad. In 1888, however, the modern method of separating the menthol crystals from the natural oil in brine or in a freezing mixture was developed and introduced, partly in collaboration with Mr. Cooking, a British engineer living in Yokohama, and recrystallized menthol was exported for the first time by Keisuke Kobayashi. When the first lot of snow-white menthol crystals arrived in London the incredulous consignee is said to have refused the shipment, believing it was not a natural product.

Gradually the production of mint oil and menthol developed into one of Japan's most important industries, and by 1914 the output amounted to half of the world's total production. Prior to World War II, mint oil and menthol were among Japan's principal exports, a large part of the world's demand being supplied by Japan. In politically and economically normal times, Japanese menthol holds a strong position on the world market, because Japanese mint oil can be produced cheaper and contains much more menthol than the American or European oils. However, Japanese dementholized mint oil is inferior in odor and flavor and can compete with the American and European peppermint oils only on account of its low price. As far as crystallized natural menthol is concerned, Japan prior to the last war enjoyed practically a monopoly on the world market, although the competition of synthetic menthol has been increasingly felt. The latter,

however, presents no serious threat to Japan because acreage of the quickly growing mint could be increased any time and, if necessary, the price of natural menthol could be lowered.

Producing Regions.—There exist in Japan two main mint producing regions:

1. *Province of Kitami* on the island of Hokkaido, Northern Japan.

About 80 per cent of Japan's mint oil is produced here. The harvest lasts from September to the beginning of October. Average free menthol content of the crude oil ranges from 65 to 67 per cent.

2. *District of "San-Bi,"* Southwestern Japan.

About 20 per cent of Japan's mint oil is produced in this section. There are three harvests yearly—June, August, and October. Menthol content of these oils is usually above 70 per cent.

The "San-Bi" District used to produce much larger quantities, but it has suffered from prolonged droughts and from typhoons in 1937.

The bulk of Japan's mint oil at present is produced on the island of Hokkaido, with the "San-Bi" district second (actually not more than 18 per cent)—the prefecture of Yamagata having fallen to the fifth rank.

The following statistics [3] show the acreage of mint under cultivation during 1940 in the various parts of Japan:

Prefecture	*Cultivated Area (hectares)*	*Quantity of Dried Herb Harvested (metric tons)*
Hokkaido	13,087.5 (93%)	15,938.1 (79%)
"San-Bi" District		
Okayama	721.9 (5%)	3,030.6 (15%)
Hiroshima	129.9 (0.9%)	551.9 (2.7%)
Kumamoto	60.2	310.1
Yamagata	19.7	79.6
Kagawa	18.3	126.7
Ibaraki	13.7	25.7
Kagoshima	11.6	31.5
Gifu	6.1	9.7
Saitama	5.8	13.8
Others	15.2	44.9
	14,089.9	20,162.6

Influence of Climate upon Yield and Quality.—The northern parts of Japan generally have fewer harvests per year, and the mint plants yield

[3] The author is greatly obliged to Mr. Shoichi Kusunose, President, and to Mr. Seiichiro Higo, Manager, of Suzuki Menthol Co., Kobe, Japan, for this and other information contained in this monograph.

less oil. The yield of oil from mints grown in Hokkaido averages 1.3 per cent, from plants grown in Hiroshima and Okayama 1.6 per cent. The latter two prefectures produce, per acre, almost three times as much oil as Hokkaido.

Table 2.14 [4] shows temperature (in centigrades) and rainfall in those regions.

TABLE 2.14

Region	Average Winter Temperature	Lowest Winter Temperature	Average Summer Temperature	Highest Summer Temperature	Average Yearly Temperature	Average Yearly Rainfall
Hokkaido.....	−5.5°	−23°	15.5°	32°	5.5°	95 cm. (38 in.)
Hiroshima and Okayama....	3.5°	−6.5°	24.5°	36.5°	14.6 to 18.1°	106.5 cm. (42 in.)

The bulk of Japanese mint oil is produced under climatic conditions resembling those of sections of North America. Climate and soil influence not only the size of the crop but also the quality, and particularly the menthol content of the oil. It is claimed that the mint oil produced in the Prefectures of Hiroshima and Okayama contains more free menthol but less menthone than that produced in Hokkaido, while the percentage of menthyl esters is about the same. Hiroshima and Okayama thus produce the best quality of oil. The following table shows the relative constitution of oils produced in the various regions:

	Free Menthol	*Menthone*	*Menthyl Esters*
Hokkaido.....	65 to 67%	16 to 18%	4 to 5%
Yamagata [5].....	About 73%	About 8%	About 5%
Hiroshima and Okayama....	75 to 79% and higher	6 to 9%	4 to 5%

Shinosaki, Nagasawa, and Makino [6] have reported that the mint oils produced in the Hokkaido district usually contain twice as much menthone and sulfite-reacting substances as the products from the Okayama district, which, on the other hand, contains 10 per cent more menthol than the

[4] *Ber. Schimmel & Co.* (1919), 41.

[5] Some years ago, when production in that section was still active.

[6] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **7**, No. 15 (1927), 1. *Chem. Abstracts* **21** (1927), 1690.

former. The sulfite-reacting portion of the high boiling fraction is mainly 1-*p*-menthen-3-one (piperitone).

Thus, *Mentha arvensis* grown in different regions yields oils of different quality. When cultivated in other countries the plant sometimes, but not always, retains its high menthol content. During 1922 to 1936, Sievers and Lowman [7] carried out experiments on the behavior of *Mentha arvensis* var. *piperascens* Malinvaud when cultivated in the United States. Their investigation showed that a satisfactory oil can be obtained, especially in California, where two to three crops a year could be gathered. From 1923 to 1936, the total menthol content of the oils investigated by Sievers and Lowman varied from 77.43 to 86.56 per cent, the free menthol from 67.4 to 76.34 per cent, and the ester menthol from 7.24 to 17.41 per cent. The menthol content of the plants showed no general decline. Several attempts have been made to raise *Mentha arvensis* ("Cornmint") in Oregon, but the plant does not seem to survive the damp winters which cause root rot.

According to Sievers and Lowman,[8] *Mentha arvensis* when grown in various parts of the United States—e.g., in California and Virginia—yielded about 30 lb. of oil per acre, the latter containing, on an average, 80 per cent of total menthol. On favorable soil with good cultural practices, 50 to 60 lb. of oil may be obtained, while on the poorer upland soils yields below the average must be expected. In those regions where climatological conditions make more than one cutting possible, relatively larger yields should be obtained. The extremely low price of imported Japanese menthol which prevailed before World War II gradually discouraged the planting of *Mentha arvensis* in the United States; new efforts were made during the war years but now the problem again is beset with uncertainty.

Planting and Cultivating.[9]—*Mentha arvensis* is cultivated largely on hillsides, although the crop will be richer in menthol when planted on low lying fields and rotated with wheat or beans. Fertile, well-drained soil, and a climate with little rain during the harvesting period are considered ideal. A good sandy soil, rain in the spring, and ample sunshine in summer produce a high menthol content.

For planting, root cuttings are taken from old but still vigorous plants. After plowing and hoeing of the field, the selected young, juicy roots, cut into 3 or 4 in. pieces, are planted in rows 18 to 20 in. apart. In Okayama and Hiroshima the planting is done in the late fall (end of November to

[7] *J. Am. Pharm. Assocn.* **26** (1937), 286. See in this connection also "Commercial Possibilities of Japanese Mint in the United States as a Source of Natural Menthol," by Sievers and Lowman, *U. S. Dept. Agr., Tech. Bull.* No. 378 (1933).

[8] *Ibid.*

[9] See in this connection also "Japanese Peppermint," Naojiro Inouye, from the Laboratory of Professor Edward Kremers, Madison, Wisconsin. *Ber. Schimmel & Co.*, October (1908), 205.

beginning of December), and to a limited extent also in spring. On the island of Hokkaido, the planting is carried out twice a year, once in spring (end of May) and once in fall (middle of September to end of October). Fertilizing and careful weeding are essential.

The maximum yield of oil is obtained in the second and third year after planting; then it diminishes. During the fourth year the yield usually falls to such unprofitable levels that replanting becomes necessary. It is advisable to rotate the crop, preferably with *Leguminosae*, before replanting on the same field. Because of soil conditions, the fields of certain districts must be replanted at the end of each year.

Harvesting.—The number of harvests per year varies in different mint growing districts. The prefectures of Hiroshima and Okayama (near Kobe), which are the main producing centers of southwestern Japan, have three harvests a year—one in June, one in early August, and one in October–November. In the prefectures of Niigata and Yamagata, Central Japan, only two yearly crops can be gathered—one in early July and one in October. Further north the harvests are less frequent; in Hokkaido, for instance, only one (September to October) takes place annually.

Harvesting requires special care, because improper methods might seriously lower the quality of the oil. The day should be bright and cutting should not start before the dew has disappeared. The most suitable period is the moment when the buds are still tight but ready to bloom out—usually from 9 A.M. to 3 P.M. Rutovski and Travin,[10] two Russian investigators, found that the menthol content increases with the growth of the plant, whereas the percentage of menthone decreases.

Menthol seems to occur mainly in the leaves, very little residing in the stems. The dried herb material consists of 35 per cent by weight of leaves and 65 per cent of stems. Distillation tests have shown that 88 per cent of the oil occurs in the leaves, and only 12 per cent in the stems. On bright summer days the menthol can be seen on the leaves in the form of powdery, fine crystals which disappear toward evening and do not reappear until the sun is well up the next day. For this reason, the harvesting should take place on bright, hot days when the sun is high above the horizon.

The cut plants are immediately tied in bundles, hung in the open air or under sheds and dried. Drying takes from ten days in summer to thirty days in fall, the best state of dryness being ⅓ to ¼ of the weight of the fresh plant, i.e., not completely crisp. In other words, 100 kg. of fresh herb are dried until they weigh only 25 to 30 kg. Care is taken to prevent the leaves from falling off during the drying process. Some growers dry the plants in the sun, but this is considered unsatisfactory because of oil loss

[10] *Riechstoff Ind.* **4** (1929), 124.

due to resinification and evaporation. Besides, there is the danger of damage from storms. The bundled herb material must not be allowed to ferment.

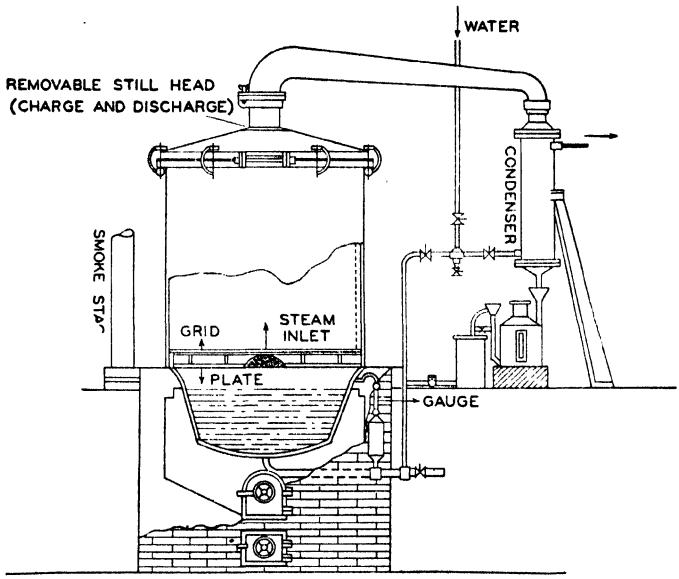
Japan's mint oil producing units are usually small, operated by individual growers, the construction of large, modern distilleries having been found too costly. The limited size of the Japanese stills does not permit immediate processing of the large amounts of plant material accumulated during the height of the harvest. If stacked up in wet condition, the plants would soon ferment and deteriorate. Partly dried, the plants can await distillation until the capacity of the small stills allows it.

Distillation.—The herb material is distilled in rather primitive stills scattered throughout the producing regions and owned by the grower-distillers, who sell the natural, crude oil to large firms. These firms operate modern plants equipped for separating and recrystallizing the menthol and for rectifying the residual oil.

The field distillers employ several types of apparatus, some of them antiquated:

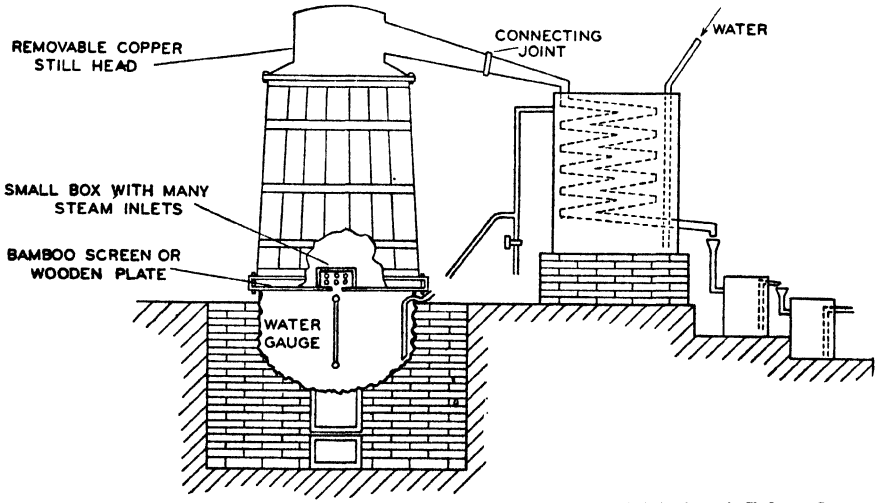
1. The so-called "box" stills. They are somewhat more efficient in regard to capacity than the "barrel" stills (see below). However, initial cost of installation is higher, because of the difficulty of making the wooden boxes steam tight.
2. Many producers employ stills made of wooden barrels. They are somewhat cheaper to install but hold less plant material.
3. There exist also regular metal stills such as are generally used for the distillation of aromatic plants. The steam is generated in a separate steam boiler. Much progress has been made in replacing the old-fashioned Japanese mint stills with modern equipment.

When distilling by the "box" method, two or more wooden boxes with bottoms removed are stacked on top of an iron kettle filled with water. A perforated grid separates the kettle from the lowest box. The boxes, 1.3 m. high and 1.2 m. wide, are filled with mint herb, and all crevices sealed with cloth or clay. From the top of the uppermost box a metal gooseneck leads spirally into the condenser. The water in the kettle is heated to the boiling point, and steam carries the vaporized essential oil into the condenser to be cooled and reliquefied there. Although this method permits handling a comparatively large quantity of herb at one time, it is rather difficult to distribute the steam evenly through the boxes and to prevent its escape through the joints. For this reason, the "box" stills have been replaced, almost entirely, in Japan, by "barrel" stills.



Courtesy of Dr. Teikichi Hiraizumi, Tokyo, Japan.

Japanese metal still, designed by Hokkaido Industrial Research Laboratory.



Courtesy of Dr. Teikichi Hiraizumi, Tokyo, Japan.

Japanese barrel still, designed by Ninomiya, Industrial Research Laboratory, Okayama. When the bamboo screen is used, the box with the steam inlets is unnecessary.

Distillation in "barrel" stills proceeds as follows: A bamboo screen is placed on top of the water kettle which has a diameter of about 1 m. A large wooden barrel, 1.2 to 1.5 m. high, bottom removed, is filled with 200 to 400 kg. of herb, and placed on the screen. From the top a spiral pipe leads to the condenser.

Distillation by either the "barrel" or the "box" method requires approximately 3 to 6 hr., depending on the size of the boxes or the barrel. Repeated distillation of the same plant material is often necessary in order to extract all the oil. In modern stills constructed of metal and heated with coal, distillation of one batch can be completed in 3 hr. Ninomiya [11] distilled 300 kg. of dried mint herb and reported the data in Table 2.15.

TABLE 2.15. DISTILLATION OF 300 KG. OF DRIED MINT HERB

Length of Distillation	Quantity of Oil (kg.)	Percentage of the Total Oil	Quantity of Coal Used (kg.)	Content of Menthol in Fraction (%)
First 40 minutes	3.6	63.36	12.56	45
Second 40 minutes	1.0	24.28	12.56	63
Third 40 minutes	0.35	6.18	12.56	66
Fourth 40 minutes	0.35	6.18	12.56	72
Two hours and 40 minutes	5.3	100.00	50.24	Average 52

The exhausted and sun-dried herb material is used to feed horses.

Prior to World War II, the natural (crude) oil was shipped to the refineries in Kobe and Yokohama for the extraction of menthol.

Yield of Oil.—Regarding the yield of oil per acre and the percentage of oil from the dried herb material, the average figures given in Table 2.16 have been received recently by the author.[12]

These figures, however, pertain to normal, prewar years. Since World War II, the yields have declined substantially, due mainly to lack of fertilizers. In Hokkaido, for instance, the yield of oil per hectare is at present only 25–30 kg., and similar reductions have been observed also in other mint producing regions of Japan.

[11] *Repts. Ind. Research Lab., Okayama Prefecture,* No. 9. Through courtesy of Dr. T. Hiraizumi, Tokyo.

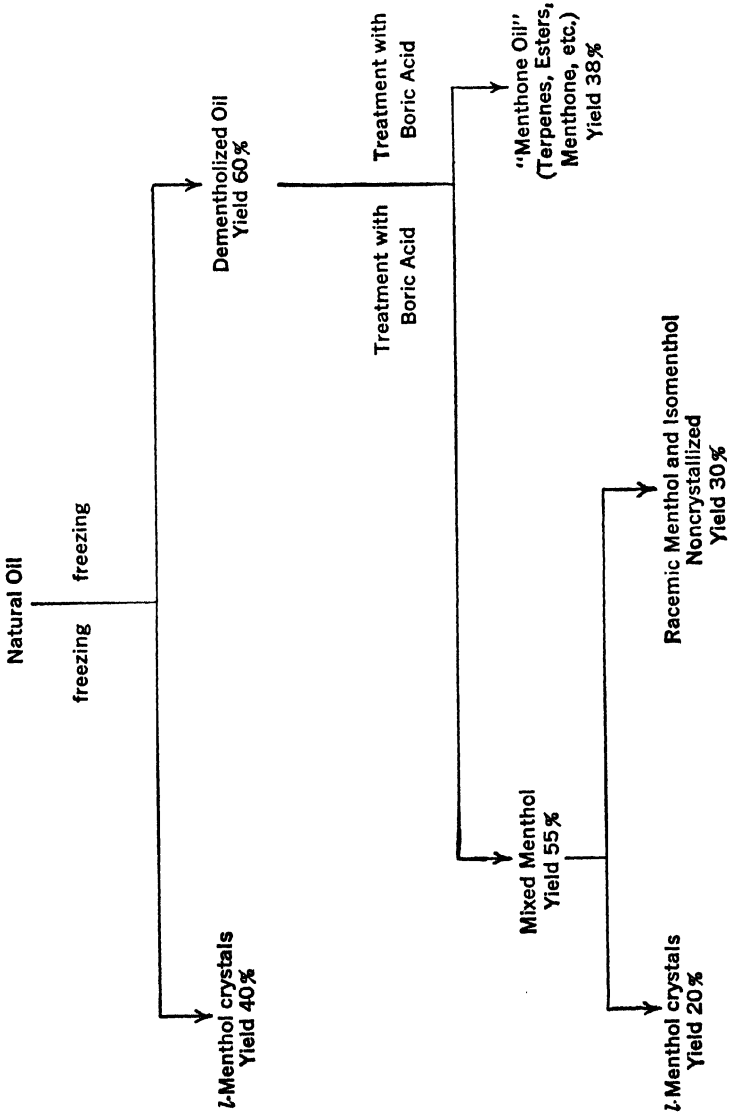
[12] Courtesy of Mr. Shoichi Kusunose, President, and Mr. Seiichiro Higo, Manager, of Suzuki Menthol Co., Kobe, Japan.

TABLE 2.16. YIELD OF MINT OIL IN JAPAN

Producing Region	Average Annual Temperature in °C.	Yield of Dried Mint Herb per Hectare (kg.)	Quantity of Oil per Hectare (kg.)	Yield of Oil from Dried Herb (%)
Hokkaido (Kitami)	5.5	3,000	39.0	1.30
Yamagata Prefecture	12.9	5,060 (1st crop 2,250 2nd crop 2,810)	64.7	1.28
"San-Bi" District		6,750 (1st crop 1,500 2nd crop 2,250 3rd crop 3,000)	108.0	1.60
Oda (Okayama Prefecture)	14.6			
Fukayasu (Hiroshima Prefecture)	18.1			

Isolation of Menthol and Rectification of the Residual Oil.—On cooling to a low temperature, natural (crude) mint oil yields from 40 to 50 (usually 40) per cent of *l*-menthol crystals, and from 50 to 60 (usually 60) per cent of partly dementholized mint oil, the ratio varying with the free menthol content of the natural (crude) oil. This process of isolating the menthol crystals is carried out in well-equipped plants owned by the well-known mint oil and menthol concerns of Japan. For this purpose the natural oil is first freed from moisture, filtered, and poured into metal containers 15 x 60 x 90 cm. in dimension; these are placed into a freezing mixture for about 24 hr. The dementholized oil is then drawn off through a drain cock at the bottom of the container, whereas the menthol crystals remaining in the vessel are dissolved in a solvent, with warming, and recooled in a specially constructed tank. The recrystallized menthol is then left to dry at normal temperature for several days in a kiln where any adhering solvent or oil may evaporate.

The so-called dementholized Japanese mint oil is by no means entirely free from menthol; as a matter of fact it still contains about 50 per cent of menthol (*l*-menthol, racemic menthol, isomenthol, etc.) and, therefore, possesses considerable usefulness for the flavoring of many kinds of preparations—e.g., mouth washes, tooth pastes, and pharmaceutical products. Prior to World War II it enjoyed wide sales in Europe, particularly in Germany, France, and Great Britain. Sales to France and Germany were effected mostly via the London market.


Natural Oil
freezing
freezing
l-Menthol crystals
Yield 40%
Dementholized Oil
Yield 60%
Treatment with
Boric Acid
Treatment with
Boric Acid
"Menthone Oil"
(Terpenes, Esters,
Menthone, etc.)
Yield 38%
Mixed Menthol
Yield 55%
Racemic Menthol and Isomenthol
Noncrystallized
Yield 30%
l-Menthol crystals
Yield 20%

The United States Pharmacopoeia does not recognize the Japanese mint oil as a true peppermint oil—only the oil distilled from *Mentha piperita* L. meets its requirements—and therefore the Japanese mint oil (crude or dementholized) cannot be used in official medicines of the United States. In fact, this oil may not be imported into the United States unless labeled "Oil of *Mentha arvensis* or Cornmint Oil," and indication must be given to the authorities as to its ultimate use.

The dementholized oil has been exported from Japan in two grades:

1. As crude dementholized oil. Shipments of this grade to the United States have been under the name of "cornmint oil."
2. As thrice rectified dementholized oil, exported mainly to Scandinavia.

More recently efforts have been made at the Kitami factory on the island of Hokkaido toward a more complete recovery of menthol crystals from the natural (crude) oil, by applying the boric acid method to the dementholized oil, after freezing of the natural oil (see diagram on page 651).

Considering a yield of 40 per cent of *l*-menthol crystals from the natural oil and a yield of 20 per cent of *l*-menthol crystals from the dementholized oil, the total yield of *l*-menthol crystals from the natural oil is, therefore, 52 per cent—in other words, substantially higher than that obtained by mere freezing of the natural oil (40 per cent).

American and European Versus Japanese Mint.—*Mentha piperita* is said to be hardier and more resistant to insects and diseases than *Mentha arvensis*. The latter does not stand up very well in the cold winter climate of the American Middle West. The first crop of *Mentha piperita* is usually larger than that of *Mentha arvensis*, but then growth slows up and the second yield is smaller than the first. In odor and flavor the true peppermint oil is superior to the Japanese mint oil, for which reason the former is preferred for flavoring tooth pastes, chewing gums, and confectionery. The Japanese oil has a strong, herby odor and somewhat bitter, pungent taste. Its chief advantage lies in its higher menthol content; hence it is used chiefly for the production of menthol crystals.

Total Production of Natural Mint Oil in Japan; Export of Menthol and Dementholized Oil.—Statistics from 1935 to 1945 are given in Table 2.17.

Prior to its entry into World War II, Japan used to supply about 70 per cent of the world's total consumption of menthol and dementholized mint oil, the balance being furnished mainly by China. Owing to Japan's strong position in regard to the production of natural menthol and dementholized mint oil, it is to be expected that Japan soon will start a comeback in this industry.

TABLE 2.17

Year	Total Production of Natural Mint Oil (kg.)	Exports of Menthol Crystals (kg.)	Exports of Dementholized Oil (kg.)
1935	499,680	309,420	323,100
1936	711,060	295,380	346,740
1937	806,520	374,520	379,680
1938	886,740	233,100	291,780
1939	644,460	268,920	332,040
1940	312,480	58,740	95,640
1941	172,200	131,040	64,080
1942	152.940	69,300	81,000
1943	150,240	24,000	24,000
1944	138,000	0	0
1945	84,000	...	...

Packing.—Menthol as well as mint oil is shipped in 5-lb. tins, one dozen to a case. The packing is done by hand. Due to the availability of cheap labor, machinery is used only to a small extent.

Producers' Associations and Cooperatives.—Some years prior to World War II Japan's five largest producers of menthol combined in an association known as S.K.Y.N.T., a name derived from the first letters in the names of the member companies:

1. Suzuki Menthol Co., Kobe
2. Kobayashi, Kobe
3. Yazawa, Kobe
4. Nagaoka, Kobe
5. Tase, Yokohama

With the exception of Messrs. Tase, in Yokohama, all the companies had their main offices in Kobe, the chief shipping port of menthol and mint oil.

These firms purchased more than 80 per cent of their oil from the small grower-distillers, and produced only a small portion from plants raised on their own fields. They rectified the natural oil in their refineries, and sold the isolated menthol either directly abroad or to exporters in Japan. It is a fact that in past years about 80 per cent of the trade and export of Japanese dementholized mint oil and menthol were handled through speculators and that prices in New York were, therefore, often lower than those quoted in Japan.

Before closing this section a few words should be added about producers' associations and cooperatives which have been playing an important role in Japan's mint oil and menthol industry. In 1933, Hokuren, a powerful agricultural cooperative in Hokkaido, extended its activities to mint oil, purchasing the natural (crude) oil from its members, refining it, and also selling it to the S.K.Y.N.T. In August 1947, however, this cooperative was reorganized, price controls ceased, and the trade in menthol was freed. At the same time the Hokkaido Mutual Society of Agriculture (Hokkaido Nogyo Kyodo Kumiai) was founded and now guarantees produce prices to its member growers. The plant of this corporation is located in the city of Kitami (formerly called Nōkkeushi), Province of Kitami, Island of Hokkaido, right in the center of Hokkaido's mint growing region. This fac-

TABLE 2.18

Properties	Natural Oil		Dementholized Oil	
	G. and H.	Shinozaki	G. and H.	Shinozaki
Specific Gravity at 24°–25°	0.895–0.902	0.8997–0.9011	0.895–0.907 [a]	0.8991–0.8998
Optical Rotation (α_D)	−29° 0′ to −42° 0′ [b]	−37° 11′ to −37° 29′ [c]	−20° 20′ to −35° 0′ [b]	−27° 56′ to −29° 7′ [c]
Refractive Index	1.460–1.463 [b]	1.4590–1.4595 [c]	1.459–1.463 [b]	1.4588–1.4614 [c]
Congealing Point	−5° to −28°	−15.75° to −18°	...	...
Ester Menthol Content	3–6%	4.74–5.01%	4–15%	8.64-9.47%
Total Menthol Content	69–91%	78.24–82.78%	46–68% Mostly 48–55%	60.59–62.10%
Acetylated Menthol Content	...	6.01–6.36%	...	10.96–12.02%
Menthone Content	...	11.85–13.75%	21–34%	27.09–33.29%
Terpene Content	...	4.10–6.61%	...	3.57–8.49%
Acid Number	2.0	1.1–2.1	2.0	...
Ester Number	...	17–18	...	31–34
Yield of Menthol by Freezing	...	56.48–65.56%	...	...
Solubility	Soluble in 2 to 3 vol. and more of 70% alcohol		Soluble in 2.5 to 4 vol. and more of 70% alcohol	

[a] At 15° C.
[b] At 20° C.
[c] At 25° C.

tory, the largest of its kind in Japan, is well equipped for the rectification of natural mint oil, as well as for the isolation and recrystallization of menthol. Members of the S.K.Y.N.T., as a matter of fact any merchant, can now freely purchase menthol and dementholized oil from this organization.

During World War II, the factories of the S.K.Y.N.T. and other menthol refineries in Kobe and Yokohama were badly damaged, but it seems quite probable that at least some of these plants will be repaired soon, which would mean an early revival of the menthol industry on Japan's main island.

Physicochemical Properties of Japanese Mint Oil.—According to Gildemeister and Hoffmann,[13] and Shinozaki,[14] the properties of natural and dementholized oils vary within the limits shown in Table 2.18.

Chemical Composition.—Because of its importance, Japanese mint oil has been subjected to numerous investigations in the course of the past seventy years. Almost all of the constituents listed below have been confirmed by Shinozaki et al.[15] who carried out a thorough research on the chemical composition of this oil.

l-α-Pinene. Found by Duncan and Short [16] in a fraction (1 per cent) of dementholized Japanese mint oil.

Furfural. Garratt [17] estimated that the oil contains about 0.018 per cent of furfural. The same author also devised a color reaction, based upon the presence of furfural in Japanese mint oil, by which it is possible to detect additions of Japanese mint oil to peppermint oils.[18]

l-Limonene. The α-pinene fraction contained also *l*-limonene which had already been identified in Japanese mint oil by Murayama,[19] and by the Schimmel chemists.[20] Tetrabromide m. 104°–105°.

Camphene. According to Shinozaki and Nagazawa.[21]

d-3-Octanol (*d*-Ethyl-*n*-amyl Carbinol) $C_2H_5CH(OH)C_5H_{11}$. Identified in the forerun by the Schimmel chemists.[22]

[13] "Die Ätherischen Öle," 3d Ed., Vol. III, 836.
[14] *J. Chem. Ind. Japan* **22** (1919), 296. *Chem. Abstracts* **13** (1919), 1896.
[15] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **10,** No. 5 (1929); **11,** No. 9 (1930); **11,** No. 10 (1930); **18,** No. 10 (1938).
[16] *J. Soc. Chem. Ind.* **50** (1931), 198T.
[17] *Analyst* **60** (1935), 369.
[18] In the experience of Fritzsche Brothers, Inc., this test is not reliable.
[19] *J. Pharm chim.* [7], **1** (1910), 549.
[20] *Ber. Schimmel & Co.,* April (1912), 100.
[21] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **10,** No. 5 (1929). *Chem. Abstracts* **23** (1929), 4298.
[22] *Ber. Schimmel & Co.,* April (1912), 100.

l-Menthone. A compound of the empirical molecular formula $C_{10}H_{18}O$ which was evidently *l*-menthone had already been observed by Beckett and Wright.[23] Its presence was later confirmed by Shinozaki and Nagazawa.[24]

d- and *dl*-Isomenthone. Reported by the same authors.[25]

d-Neomenthol. Pickard and Littlebury [26] found that Japanese mint oil contains very small quantities of this compound, b_{16} 98°, d. 0.90, $[\alpha]_D$ +19° 41′. According to Zeitschel and Schmidt,[27] b. 212°, d_{15}^{15} 0.903, α_D +17° 42′; phenylurethane m. 108°.

l-Menthol. The main constituent of the oil. Had been observed years ago by Beckett and Wright.[28]

1-*p*-Menthen-3-one (Piperitone). This rather unimportant constituent was isolated by means of the sulfite method by the Schimmel chemists.[29]

A Sesquiterpene(?). Beckett and Wright [30] found in the fraction b. 245°–255° a compound which consisted probably of an impure sesquiterpene mixed with menthol. Shinozaki and Nagazawa [31] found a sesquiterpene in a fraction b. above 240°. Duncan and Short [32] reported the occurrence of a dextrorotatory sesquiterpene in Japanese mint oil.

Caryophyllene. The same authors mention also the presence of caryophyllene in the same fraction (1 per cent) of a dementholized oil.

A *dl*-Sesquiterpene Alcohol. Occurs, according to Shinozaki and Nagazawa,[33] in the fraction b. above 240°.

β,γ-Hexenyl Phenyl Acetate. This ester possesses a characteristic and lasting odor. Walbaum [34] found it in the fraction b. 250°–310°. Saponification of this fraction with alcoholic potassium hydroxide gave phenyl acetic acid, and β,γ-hexenol. The alcohol had the following constants: b_9 55°–56°, d_{15} 0.8508, α_D −0° 10′, n_D^{20} 1.4803. Continuing Walbaum's [35] investigations of the acids as formed by saponification of the high boiling esters in Japanese mint oil, Walbaum and Rosenthal [36] found considerable quantities of liquid acids which are combined with hexenol and menthol. Some of them possess a strong, animal-like odor. One of these acids is α,β-hexenic acid.

[23] *J. Chem. Soc.* (1876), I, 3. *Jahresber. Chem.* (1876), 397.
[24] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **11**, No. 9 (1930). *Chem. Abstracts* **25** (1930), 172.
[25] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **10**, No. 5 (1929). *Chem. Abstracts* **23** (1929), 4298.
[26] *J. Chem. Soc.* **101** (1912), 109.
[27] *Ber.* **59** (1926), 2298.
[28] *J. Chem. Soc.* (1876), I, 3. *Jahresber. Chem.* (1876), 397.
[29] *Ber. Schimmel & Co.*, October (1910), 79.
[30] *J. Chem. Soc.* (1876), I, 3. *Jahresber. Chem.* (1876), 397.
[31] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **11**, No. 9 (1930). *Chem. Abstracts* **25** (1930), 172.
[32] *J. Soc. Chem. Ind.* **50** (1931), 198T.
[33] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **11**, No. 9 (1930). *Chem. Abstracts* **25** (1930), 172.
[34] *J. prakt. Chem.* [2], **96** (1918), 245.
[35] *Ibid.*
[36] *Jubiläums Ber. Schimmel & Co.* (1929), 205.

α,β-Hexenic Acid. Analysis of the silver salt. The identity was confirmed through synthesis of this acid.

Other Fatty Acids, Saturated and Unsaturated. In the higher boiling fractions of the acid mixture, Walbaum and Rosenthal [37] noticed other fatty acids, saturated and unsaturated, which, however, were not further identified.

An Acid, $C_{10}H_{21}COOH$. One of these acids has the empirical molecular formula $C_{11}H_{22}O_2$. It is present in the fraction b_4 160°. Esterification with methyl alcohol gave a methyl ester of the following constants: d_{15} 0.9719; n_D^{20} 1.44129; acid number 0; ester number 280. The ester is, therefore, probably $C_{10}H_{21}COO \cdot CH_3$.

An Acid, $C_{11}H_{17}COOH$. This acid was isolated from the fraction b_4 156°–157°. Analysis of the silver salt.

An Acid, $C_{14}H_{23}COOH$. In the fraction b_4 170°–180°.

It was surprising to Walbaum and Rosenthal that none of the high boiling fatty acids, isolated by them, possessed the characteristic animal odor, the carrier of which they were trying to isolate. On the contrary, the animal odor disappeared with continued fractionating.

Formic Acid, Acetic Acid, Isovaleric Acid, Caproic Acid, Free(?) and Esterified. Were identified by Shinozaki and Nagazawa [38] in the fraction b. above 240°, of Japanese mint oil.

Menthofuran(?) [3,6-Dimethylcumarone-tetrahydride-(4,5,6,7)]. Was found by Carles [39] in Italian peppermint oil and identified by Wienhaus and Dewein.[40] Possibly this compound is present also in the Japanese oil.

Tanaka [41] reported the following quantitative composition for a dementholized Japanese mint oil:

Ethyl Amyl Carbinol, Isovaleraldehyde } traces

Isovaleric Acid 0.3%

Total Hydrocarbons 12.6% (*l*-Limonene 9.8% and *p*-Menthene 1.5%, the latter probably being 4(8)-*p*-Menthene)

Total Ketones 33.6% (*l*-Menthone 32.3% and Piperitone 1.3%)

l-Menthol 37.3%

l-Menthyl Acetate 8.5%

[37] *Ibid.*
[38] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **11**, No. 10 (1930). *Chem. Abstracts* **25** (1931), 172.
[39] *Parfumerie moderne* **22** (1929), 615.
[40] *Z. angew. Chem.* **47** (1934), 415.
[41] *J. Chem. Soc. Japan* **50** (1929), 546. *Chem. Abstracts* **25** (1931), 5507.

Chemical Composition of Cohobation (Water) Oil of Japanese Mint.—Kremers [42] examined the cohobation (water) oil of *Mentha arvensis* grown in the United States. As main constituent, it contained pulegone (bisnitrosopulegone m. 83°), but no menthol, which seems abnormal. Jenison and Kremers [43] found large quantities of pulegone and *l*-limonene in an oil distilled from *Mentha arvensis*, grown in Wisconsin. Since they were unable to identify other constituents in the oil it is very likely that the oils investigated by these workers originated from a plant variety other than *Mentha arvensis* var. *piperascens* Holmes.

Chinese Mint Oil

Compared with Japanese mint oil, the Chinese product is of minor importance. In China, the mint plant has been known to grow wild for thousands of years, particularly on the north and south banks of the Yangtze River, near Kiukiang, between Nanking and Hankow. A thousand years ago Chinese physicians knew about the use of the dried mint plant in cooling beverages. The Chinese mint oil industry began fifty to sixty years ago when herb material growing wild around Chi-An and Nan-Chang (Province of Kiang-Si) was collected, dried, and shipped to Canton for distillation. Neither the quantity nor the quality of the oil thus produced, however, met the requirements of China at that time, and substantial amounts of mint oil had to be imported from Japan.

Regarding the development of mint cultivation in China there exist two versions:

1. In 1913/1914 Wang Li-Shen imported some mint roots from Japan and planted them experimentally near Tai-Chang and Chia-Ting (Province of Kiang-Su).
2. In 1927 some roots of wild growing herb were transplanted from Chi-An (Province of Kiang-Si) to Tai-Chang and Chia-Ting (Province of Kiang-Su).

At any rate it is certain that the first mint plantations in China were started in Tai-Chang and Chia-Ting, and from there cultivation spread to Nan-Tung and Hai-Meng in 1931, and to the island of Chung-Ming in 1935. Today, the growing regions of Chinese mint are around Nan-Tung and Hai-Meng, both located on the north bank of the Yangtze River; around Chang-Show, Tai-Chang, and Chia-Ting on the south bank of the

[42] *J. Am. Pharm. Assocn.* **10** (1921), 834.
[43] *Ibid.* **14** (1925), 495.

river, northwest of Shanghai; and on the island of Chung-Ming in that great river where it flows into the China Sea. All these places are north and northwest of Shanghai and quite near that great Chinese metropolis, with the result that Shanghai has become the center of the Chinese mint oil and menthol industry. In 1926 the Yung-Sheng Menthol Co. was established in Shanghai and Mr. Takasu Imagawa, an engineer of the Suzuki Menthol Co. in Kobe, Japan, was invited to come to Shanghai to introduce modern methods of distilling the oil and extracting and refining the menthol. Adapting the technique of Japan, the Chinese mint oil and menthol industry progressed rapidly and substantially, and has been exporting directly abroad from the following concerns in Shanghai: Yung-Sheng Co., Hsin-Hua Co., Hua-Sheng Co., Chung-Hua Co., Yao-Hua Co., and Ta-Hua Co.

On the occasion of a visit to Shanghai in 1939, the author inspected several of these concerns and found them well equipped for the extraction of menthol by freezing of the natural oil.

The author also learned that in China the mint is grown as a yearly crop to obtain a maximum yield of leaves. During the spring, root cuttings are planted into well-prepared fields, and after a few weeks the young plants begin to develop. When the mint attains a height of about 3 ft., the upper part is cut and "cured" in the sun. The dried lower (woody) parts serve as fuel for the stills. Distillation is carried out in some quite modern and efficient stills of Japanese design, but mostly as a family and village industry in primitive stills of Chinese make, resembling those employed in the distillation of cassia leaves and star anise. These small stills hold only about 15 kg. of dried herb and require 6 hr. for the completion of one operation. (In Japan the still capacity is 60 to 350 kg. of herb material—one charge of 60 kg. being distilled in 3 to 4 hr.)

There are two mint harvests in China per year—one at the end of June and one in September; in the Province of Kiang-Si, however, only one harvest takes place in September. Often the June harvest, after thorough drying of the herb, is held over and distilled together with the September crop.

The yield of oil derived from the summer crop varies from 1.3 to 2 per cent, whereas that of the fall crop averages 2 per cent. This relatively high yield is probably caused by the advanced dryness of the herb.

It is claimed that the oil derived from the summer harvest yields about 45 per cent of crystalline menthol, while that of the fall harvest yields about 55 per cent of crystalline menthol.

It is very difficult to obtain recent and reliable production figures for Chinese mint oil and menthol—World War II and the ensuing troubles in

China having greatly confused the picture. The following statistics,[44] however, will give a good picture of this industry as it operated during the last prewar year:

Cultivation Area in China (1940)

	Hectares
Tai-Chang, Chia-Ting	110
Hai-Meng	3,950
Nan-Tung	2,250
Chung-Ming Island	1,120
Chi-An	560
Hangchow	10
	8,000

Production of Natural Mint Oil[44a] in China (1940)

		Kilograms
Province of Chang-Su	Tai-Chang, Chia-Ting	1,400– 2,000
	Hai-Meng	50,000– 55,000
	Nan-Tung	27,000– 33,000
	Chung-Ming Island	14,000– 21,000
		92,400–111,000
Province of Kiang-Si	Chi-An	7,000
	Hangchow (Cheking Prefecture)	140
	Total about	100,000–110,000

Exports of Chinese Mint Products (1940)

	Pounds	
1. Crystallized Menthol		
To United States	270,000	(64%)
Germany	30,000	(8%)
South Sea Islands	60,000	(14%)
Europe (via Hong Kong)	60,000	(14%)
	420,000	
2. Dementholized Mint Oil		
To Germany	90,000	(28%)
South Sea Islands	120,000	(36%)
Europe (via Hong Kong)	120,000	(36%)
	330,000	

Before closing this section, it should be mentioned that the island of Taiwan (Formosa) also is a potential producer of mint oil; as a matter of

[44] The author is deeply obliged to Dr. T. Hiraizumi, President of Takasago Chemical Industry Co., Ltd., Tokyo, for this information.

[44a] Natural oil, containing menthol before separation.

fact in the years preceding World War II Formosa annually produced an average of 80,000 lb. of natural mint oil. Most of the oil was handled by the official Taiwan Chemical Industry Co., and was converted into menthol crystals and dementholized oil. Lately, however, the mint growers have replaced mint with essential food crops, and the cultivation of mint on the island of Taiwan has declined to a point where it no longer can be considered of any commercial importance.

Physicochemical Properties of Chinese Mint Oil.—According to Gildemeister and Hoffmann,[45] the properties of Chinese mint oil vary between the following limits:

	Complete Oil	*Dementholized Oil*
Specific Gravity at 15°/15°	0.8990 to 0.9091	0.9018 to 0.9090
Optical Rotation	−30° 2′ to −37° 32′	−26° 18′ to −29° 7′
Refractive Index at 20°	1.46012 to 1.46469	1.46092 to 1.46281
Total Menthol Content	70.5 to 87.4%	62.5 to 67.6%
Ester Menthol Content	1.6 to 7.3%	7.8 to 11.1%
Menthone Content (Hydroxylamine Method)	8.9 to 12.3%	Around 15.0%
Solubility in 70% Alcohol	Soluble in 2.5 to 3 vol., occasionally opalescent with more alcohol	Soluble in about 3 vol., opalescent with more alcohol

The physicochemical properties as well as the odor of the Chinese oils closely resemble those of the Japanese product.

Possibilities of Producing Mentha arvensis in the United States

Prior to World War II, the United States and the rest of the world were entirely dependent upon Japan and China for their supply of natural menthol. During the war the problem arose whether natural menthol could be extracted in this country from domestically grown *Mentha arvensis*. A detailed study made by Sievers and Lowman,[46] some years ago, may serve as a guide for any such venture. For completeness' sake, we shall mention here the most important conclusions of Sievers and Lowman.

Mentha arvensis grows and spreads through numerous underground runners, and therefore requires, for normal development, a deep soil, rich in humus and retentive of moisture, but well drained. Light, loose soils which dry quickly, and heavy clay soils, are equally unsuitable for the culture of Japanese mint. Favorable types are muck land, sandy loam river-bottom land, and well-cultivated loamy upland.

[45] "Die Ätherischen Öle," 3d Ed., Vol. III, 866.

[46] *J. Am. Pharm. Assocn.* **26** (1937), 286. See in this connection also "Commercial Possibilities of Japanese Mint in the United States as a Source of Natural Menthol," by Sievers and Lowman, *U. S. Dept. Agr., Tech. Bull.* No. 378, August (1933).

Propagation is usually carried out by means of runners, in the same way as the American peppermint is propagated. Another method of propagating is by vegetative cuttings. These are made from the herbaceous portion of the plant in much the same way as other vegetative cuttings. They are rooted in sand and are then transferred to pots, or set directly in the field. *Mentha arvensis* produces seed rather freely, and the plant may be propagated by this means, but the method is unsatisfactory and does not produce plants uniformly true to type.

The harvesting should take place when the plants are as nearly as possible in what is usually called the full blooming stage. The cut herb may be distilled immediately, or allowed to wilt for some time in the field, according to the practice followed with American peppermint and spearmint herb. It may be left in the swath until ready to be distilled, or raked into windrows after a period of wilting, and then placed in cocks like hay for further curing. It should not be allowed to dry enough to become brittle, because when handled in that condition many of the leaves will be lost, thus reducing the oil yield. The yield of oil from thoroughly air-dried leaves was 2.2 per cent, from the stems 0.083 per cent, and from the whole herb (calculated) 1.36 per cent.

From the tables given by Sievers and Lowman, it can be observed that in all cases the drying of the herb had the effect of increasing the percentage of menthol present as esters. The total menthol content appears also to be slightly greater in the oils distilled from the dried herb. On the whole, the results indicate that drying of the herb does not have any important influence on the character of the oil. This fact makes it possible for a large grower to handle his crop at a somewhat lower cost. The capacity of his distilling equipment need not be so large; the weight of the material hauled is considerably less, and economies in distillation are possible through lower fuel consumption. Whatever procedure is adopted, it is necessary at all times to avoid excessive loss of leaves through shattering, for reasons already stated.

The distilling of *Mentha arvensis* may be carried out exactly like that of American peppermint.

The yield of oil from *Mentha arvensis,* when grown in the United States, averages 30 lb. per acre provided the mint is in good condition. This is similar to the yield obtained from American mint.

Mentha arvensis has been attacked on the Pacific Coast, especially in California, by a form of mildew which causes severe loss of leaves. The other important disease of *Mentha arvensis* is a rust fungus which likewise attacks the leaves and causes them to drop, thus greatly reducing the yield of oil. There exist apparently no practical means of controlling either the

mildew or the rust. Regions in which these are severe year after year are not adapted to the growing of *Mentha arvensis*. The best procedure is to cut the crop before the damage becomes excessive.

Menthol can be separated from oil of *Mentha arvensis* by using the apparatus described in the section on Japanese menthol. After the outbreak of World War II, the production of Japanese mint in the United States was taken up rather extensively, but it has to be seen whether the United States, even by the adoption of very modern agricultural methods (mechanized planting, cultivating, and harvesting) can ever compete with the Japanese product, once the latter is again freely available.

Mint Species Growing Wild in Japan

Aside from the previously described *Mentha arvensis* L., subsp. *haplocalyx* Briquet, var. *piperascens* Holmes which is cultivated extensively in Japan (see the monograph on "Japanese Mint Oil"), there also exist in Japan four mint species which grow wild but which are not exploited commercially. For the sake of completeness they should be mentioned here at least briefly.

1. *Mentha arvensis* Benth., subsp. *haplocalyx* Briq., var. *sachalinensis* Briq. The Japanese name is Ezo, or Kusa Hakka, or Inu (= dog) Hakka. The volatile oil contains 20 to 30 per cent of pulegone.

2. *Mentha viridis* L., var. *crispa* Benth. The Japanese name is Oranda, or Chirimen, or Midori, or Ao Hakka. The oil contains 50 per cent of carvone.

3. *Mentha japonica* Makino. The Japanese name is Hime Hakka. The oil contains 60–70 per cent of menthone.

4. *Mentha sylvestris* L., var. *pubescens* Koch. The Japanese name is Ke-Hakka.

Suggested Additional Literature

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A. F. Sievers, M. S. Lowman, and Mabel L. Ruttle, "Investigations of the Yield and Quality of the Oils from Some Hybrid and Tetraploid Mints," *J. Am. Pharm. Assocn.* **34** (1945), 225.

Ya. Ya. Makarov-Zemlyanskiĭ, "Extraction of Menthol from Mint Oil," U.S.S.R. Patent 65,823, February 28, 1946. *Chem. Abstracts* **41** (1947), 5264.

BRAZILIAN MINT OIL

Introduction.—As has already been pointed out in the monographs on "Oil of Peppermint" (*Mentha piperita* L.) and "Japanese Mint Oil" (*Mentha arvensis*), the former does not lend itself to the isolation of menthol because it contains only 50 to 55 per cent of this terpene alcohol. The Japanese and Chinese mint oils distilled from *Mentha arvensis,* on the other hand, contain 80 to 85 and even 90 per cent of menthol and, therefore, represent the most economical source for the extraction of natural menthol.

In the years prior to World War II the United States imported annually about 500,000 lb. of menthol from Japan and the adjacent parts of China. In fact, for many years Japan held a monopoly on this product, which forms an important constituent of many pharmaceutical preparations. With the outbreak of World War II, imports of *natural* menthol from Japan and Japanese occupied China ceased and existing stocks in the United States were soon used up. Moreover, when oil of citronella, heretofore shipped in large quantities from Java, became unavailable, the most important source for the preparation of *synthetic* menthol could no longer be relied upon.

It was thus a great relief to the American pharmaceutical industries when, in 1941–1942, Brazil appeared on the market with offers of natural menthol, extracted from Brazilian-grown *Mentha arvensis* var. *piperascens* Holmes, (forma *piperascens* Malinvaud). In fact, the production of menthol from this plant on a large scale represents one of the most remarkable developments in the essential oil industry of the Western Hemisphere during the years of World War II.

The plant was introduced to São Paulo by one of the numerous Japanese immigrants who landed in Brazil soon after the great earthquake in Tokyo in 1923. Almost 200,000 settlers and sharecroppers of Japanese descent live in the State of São Paulo today, forming closely-knit colonies and communities. Their activities have been mainly agricultural. In some sections, as permanent settlers, they have exercised a beneficial influence upon the development of the countryside. In other sections, however, they have been only sharecroppers—owning no land, emigrating with their families into undeveloped areas where they burned the jungle—raised a few quick-growing crops without regard to fertilization, built no permanent homes, and after a few years of hard toil left the exhausted land to start again on virgin soil in some other section of the country.

Japanese settlers for the first time planted *Mentha arvensis* about 1936 on the Fazenda São Bartolomeu in Paraguassú (State of São Paulo). Despite many difficulties, caused particularly by the activities of speculators, the cultivation of *Mentha arvensis* for the purpose of menthol extraction has proceeded, at first slowly, but then rapidly, reaching its highest development during the war years, particularly in 1945. As the old stocks of menthol in the United States were consumed the acreage of *Mentha arvensis* and the production of menthol in Brazil increased steadily. At times the industry assumed a strongly speculative character which left some producers with great profits, but others with heavy losses. As prices advanced, and as the prospects of great profits became brighter, an ever larger number of planters and speculators invested their capital in the cultivation of *Mentha arvensis*. This condition resulted in highly inflated prices not only of the land suited for this crop, but also of wages, land rents, and cultivation expenses. Large sections of virgin forest and jungle were converted into plantations of *Mentha arvensis*, villages sprang up in places which previously had not even been explored, an element of gambling was visible everywhere, reminding the visitor of the California gold rush days in 1849. Unfortunately, the majority of the planters had started their fields of *Mentha arvensis* without sufficient "know-how" and often with borrowed money. It was inevitable that despite the high prices then prevailing considerable losses were encountered, due to the general increase in cost of production—and even more to the fact that the planters had not figured on the great sensitivity of the *Mentha arvensis* plant to spells of drought.

The following statistics will give an idea of the trend of production of natural (complete) oil of *Mentha arvensis*, menthol, exports of menthol, and prices of menthol in the years 1941 to 1948:

	Production in Metric Tons			
Year	*Natural Oil*	*Menthol* [1]	*Exports of Menthol (metric tons)*	*Prices of Menthol per Kg., F.O.B. Santos (cruzeros)*
1941.....	5	...	...	...
1942.....	100	60	50	...
1943.....	150	70	80	...
1944.....	300	160	150	720
1945.....	1,200	500	570	105
1946.....	300	250	400	220
1947.....	150	180	300	280
1948.....	200	120	136	340

[1] Not all of the natural (complete) oil of *Mentha arvensis* was always processed for the extraction of menthol.

It should be mentioned here that the bulk of the natural (complete) oil of *Mentha arvensis* is shipped from the producing regions in the interior to the city of São Paulo, where most of the producers of menthol are located. The latter, the so-called "crystallizers," extract the menthol from the oil by a process of freezing, the details of which will be explained in a following section. Some of the factories are of large capacity and surprisingly modern. Much capital has gone into their construction. A number of them are operated by competent European chemists, others by Japanese who had gathered the necessary experience in their mother country.

In the beginning, the newly established industry suffered a great deal from the unreliability of many of the field brokers who purchased the natural (complete) oil from the Japanese growers and distillers in order to supply it to the manufacturers of menthol; many a contract remained unfulfilled. As the industry became better established, the larger manufacturers of menthol organized their own plantations of *Mentha arvensis*, and distilled their own oil, which forced many of the unreliable field brokers out of business.

At present it can be said that the production of oil of *Mentha arvensis* and of menthol has developed into a well-established industry in Brazil and that the cultivation of the crop in certain sections of the State of São Paulo has become part of the regular agricultural program of the planters, particularly of the Japanese settlers. *Mentha arvensis* is no longer grown as a single crop, but is now planted, along with maize, rice, cotton, and peanuts, on patches of land which are most suited to its growth. The production of menthol has concomitantly assumed a more permanent and sound character. Nevertheless, the whole future of the industry will depend greatly upon importance of the Japanese and Chinese oils of *Mentha arvensis* and of menthol which dominated the world market up to 1940. Being a quick-growing plant, *Mentha arvensis* can easily be propagated, and the planting acreage rapidly increased, whenever such increase is warranted for economic reasons.

Producing Regions.—Encouraged by the prospect of extraordinary profits, the cultivation of *Mentha arvensis* has been tried in almost every part of the State of São Paulo and in neighboring states, in every altitude and on every type of soil. After years of experimenting, however, it has been found that the only areas economically suitable for this purpose are the tropical-subtropical, virgin forest and jungle zones located on the upper Sorocabana Railroad, in that vast triangle formed by the junction of the Rio Paraná and Rio Paranapanema, along the railroad between Araguassú and Presidente Prudente. The most important centers of production here are Presidente Prudente and Santo Anastácio. In these regions the altitude

averages 250 to 400 m., and the mean temperature during the day and during the rainy season 30° C. Such virgin soil, rich in humus, loose, and somewhat sandy in texture, supplies ideal conditions for the cultivation of *Mentha arvensis*. The soil has been built up by decaying matter in the course of thousands of years. It remains remarkably fertile for six or eight years, despite intensive cultivation, after which its fertility declines as a result of excessive planting, erosion, and sunburn. The general program is to plant corn, cotton, and rice, interspersed with *Mentha arvensis* during the years of fertility and then to turn the exhausted land into pasture for cattle.

In all other zones, including the purely tropical and very moist lowlands around Santos, the cultivation of *Mentha arvensis* is feasible but not sufficiently profitable at normal menthol prices.

In 1944 more than 3,500 alqueires (about 22,000 acres) were planted with *Mentha arvensis*, but in 1947 this acreage had shrunk to only one-quarter of the above figure.

Climatic and Soil Conditions.—The growth of the mint plant, the yield of essential oil, and the chemical composition of the latter (content of menthol!) are greatly influenced by soil, climatic, and weather conditions.

As has been pointed out, the fertile virgin forest soil of the warm regions of the River Paraná in the State of São Paulo, at an altitude of 250 to 400 m., offers the most favorable conditions for the cultivation of mint. Aside from a rich humus soil the most important factor in securing an abundant crop is ample and regular rainfall during the period of growth, which extends from October to March (summer in São Paulo). The cultivation of *Mentha arvensis* is always beset by one great hazard, viz., a period of drought may cause withering of the plants and complete crop failure, even in the richest of soils. This fact explains the great fluctuations in the quantity of mint oil produced and in the prices of mint oil and menthol.

In compact, loamy sand soils of low humus content, and in the moist soils of the lowlands, the mint does not thrive well, even if a great amount of fertilizer has been applied. The pH of the soil plays only a subordinate role.

Planting and Cultivating.—After the virgin forest or jungle has been cut down and burned over, root cuttings (5 to 6 cm. long, with 3 to 4 knots) are laid into shallow holes, 50 cm. apart, dug irregularly with a pickax. The earth is then stamped down, filling the hole and covering the plant material with a layer of soil at least 5 cm. deep. The root cuttings should be taken from selected, healthy plants, absolutely free from rust, and one to two years old. As they do not keep for a long time, they should be fresh, not

dry and blackened. The most appropriate time for planting is at the beginning of the rainy season, which extends from the end of August to the end of September (São Paulo's spring).*

Some growers prefer to propagate *Mentha arvensis* with young plants raised in nursery beds, 1.0 to 1.5 m. wide and about 20 m. long, consisting of fresh, fertile soil, rich in organic matter, and laid out like any vegetable bed. These nurseries are set up from June to August (São Paulo's winter) so that the young plants are ready for transplanting in September. For transplanting, the young plants are carefully dug out when they have grown to a height of 10 to 15 cm. The transplanting should be performed on cloudy or rainy days, when the soil is very damp.

When establishing a mint plantation on former jungle or virgin forest land, the burned-over soil is not further prepared. Plowing, for example, would be impossible because of the many felled logs lying around. The only form of cultivation applied, up to time of harvest, consists in the removal of sprouts from roots of old trees and bushes which have been cut down and burned over. Any barren spots in the mint plantings are filled in. In newly opened regions weeds need not be feared, at least for the first few years after the ground has been burned over.

However, when planting mint on old, previously cultivated land, the ground must be prepared by repeated plowing and harrowing, by eradicating all weeds, and by fertilization. Then shallow furrows are dug, the root cuttings placed into the furrows and covered with earth. To assure a better exposure to the sun, the rows are laid out in an east-westerly direction. One-year-old fields ("row mint") can be weeded mechanically, but two-year-old plantings on which the mint has closed in ("meadow mint") must be weeded by hand. All this obviously causes a great deal of expense and, therefore, *Mentha arvensis* today is grown in Brazil almost exclusively on newly opened virgin soil where only a minimum of cultivation is required (see above).

Harvesting.—Once the plants have developed and reached the flowering stage, they are harvested, the cutting being done with sickles. The cut herb is left on the ground to wilt and to dry partially, and then is hauled to the distilleries, usually on oxcarts. Some growers prefer to bundle the cut plants and suspend the bundles under a shed until the material is fully dried. This procedure makes it possible to carry out distillation at a later date, which is more convenient for the producer. It may happen, however, that during very wet spells in the course of the rainy season the herb will undergo a slight fermentation which develops a moldy odor in the plant.

* The author is greatly obliged to Mr. João Dierberger, São Paulo, for much of the information contained in this section.

The oil distilled from such material will be of low grade and deficient in regard to menthol.

Mint planted in September can be harvested for the first time in January —provided the rainfalls have been regular—and for the second time in March–April. Occasionally a third, but small, harvest is possible in June–July. Only in exceptional cases are the plants left in the same soil more than two years, because the soil tires of mint, the fields "burn out" in spots, and after two years rust diseases make their appearance. It is then more economical to start a new mint plantation elsewhere, and to rotate the crops on the old field.

Depending upon the fertility of the soil, the regularity of the rainfall, and the age of the planting, 1 hectare of mint yields from 2,000 to 15,000 kg. of herb material, which on distillation yield 20 to 150 kg. of essential oil. Owing to the great sensitivity of *Mentha arvensis* to drought, and to the irregularity of rains in the zones where mint is planted, it often happens that the mint fields are blighted, and that the crop is reduced to an unprofitable level.

Diseases.—Aside from the above-mentioned rust, Brazilian mint plants are almost free from diseases and insect pests. Rust can be prevented by changing the location of the planting frequently (crop rotation), and by destroying the fungus (*Puccines menthae* Pers.). For this purpose the root cuttings, prior to planting, are steeped for 10 min. in water of 45° C. If a field shows signs of rust the time of harvest has to be advanced, so that the disease cannot come to full development; the plants should then be cut close to the ground. Any field afflicted by rust must be cut long before the arrival of the rainy season, since winter rust is the more violent form of rust.

Distillation.—Some of the field stills employed in Brazil for the distillation of mint oil are small and rather primitive, others much larger and modern in construction. The smaller stills are usually heated with direct fire. A typical distillation post comprises several stills. Wood cut from the jungles and vast forests serves as abundant and low-priced fuel.

In the more primitive stills, distillation of one charge lasts about 6 hr., 2 hr. of which are required to get the steam up. More advanced stills, operated with live steam from a separate steam boiler, complete a charge in much less time.

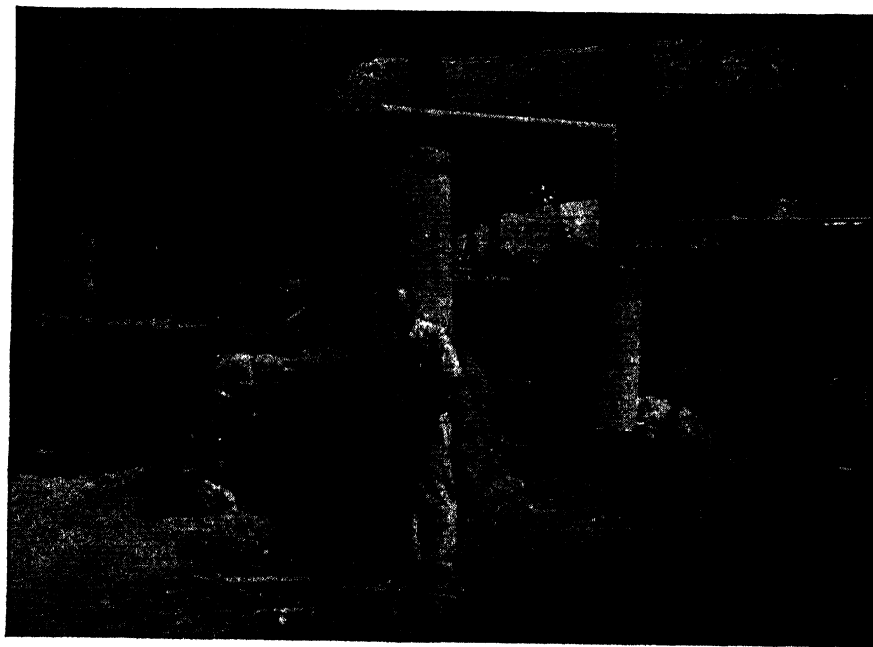
The crude oil, which usually contains dust, water, and mucilaginous matter, is collected in cans, and without further purification (filtration) sold to middlemen and field brokers.

Menthol Content of the Mint Oil.—The menthol content of the complete (natural) oil depends upon the time of the plant harvest and also upon the prevailing weather. Exposure to sunlight seems to increase the yield of oil



Courtesy of Fritzsche Brothers, Inc., New York.

A mint distillery in São Paulo, Brazil.



Courtesy of Fritzsche Brothers, Inc., New York.

A field still for the distillation of mint in São Paulo, Brazil.

and its menthol content. Depending upon soil and weather conditions, the first cutting produces oils containing 65 to 75 per cent of menthol, the second cutting oils of about 85 per cent, the third cutting oils containing 70 to 75 per cent of menthol. The average menthol content ranges from 78 to 80 per cent for oils from the higher lands, and amounts to about 87 per cent for oils from warm and humid lowlands.

Physicochemical Properties of the Complete Brazilian Mint Oil.—Since Brazil does not permit export of the complete mint oil, few, if any, such samples have been examined in the United States.

According to Berzaghi,[2] The Instituto de Pesquisas Tecnologicas in São Paulo analyzed thirty-one lots of crude mint oil which had properties varying within the following limits:

Specific Gravity at 25°	0.876 to 0.898
Optical Rotation	−29° 12′ to −42° 48′
Refractive Index at 20°	1.4577 to 1.4695
Total Menthol Content	65.2 to 88.9%
Ester Content, Calculated as Menthyl Acetate	4.5 to 18.9%

Of these thirty-one samples, twenty-three contained more than 80 per cent of total menthol.

The color of the oil, according to Berzaghi [3] depends upon several factors, for instance, the time of harvest and the condition of the plant material. Oils distilled from flowering mint possess a golden or yellow color, whereas those distilled from mint in the preflowering period are of darker color. Oils distilled from plants after the flowering period usually possess a somewhat greenish-yellow color. Fresh (green) plant material yields oils of a more intense color than dried herb.

Hoffmann [4] reported these properties of (complete) Brazilian mint oil (several samples):

Specific Gravity at 25°	0.895 to 0.899
Specific Optical Rotation	−35° 0′ to −41° 0′
Refractive Index at 20°	1.4590 to 1.4601
Total Menthol Content	70 to 90%
Ester Content	Above 5%

Chemical Composition.—The chemistry of Brazilian mint oil has been assumed to resemble that of the mint oil produced in Japan, which, according to Benezet, Igolen and Garnero [5] is composed of:

[2] Caetano Berzaghi, "Cultura da Menta para Producão de Óleo e Mentól," a brochure edited by the Dept. Agr., State of São Paulo.

[3] *Ibid.*

[4] *Anais assocn. quim. Brazil* **4** (1945), 99. *Chem. Abstracts* **40** (1946), 6214.

[5] *Perfumery Essential Oil Record* **38** (1947), 242.

Hydrocarbons. *l*-Limonene, α-pinene, camphene, caryophyllene, two unidentified sesquiterpenes.

Alcohols. Menthol, neomenthol, ethyl amyl carbinol (3-octanol), β,γ-hexenol (in the form of phenyl acetate, 1.4 per cent of the oil), a sesquiterpene alcohol.

Ketones. Menthone, menthenone, *d*- and *l*- isomenthones.

Aldehydes. Furfural.

Acids. Formic, acetic, isovaleric, caproic, pelargonic(?), and probably unsaturated acids.

To study the composition of Brazilian mint oil (*Mentha arvensis* D.C. var. *piperascens* Malinvaud), Benezet et al.[6] fractionated 1,535 kg. of a dementholized oil (d_{15}^{15} 0.8938, α_D −32° 5′, n_D^{20} 1.4588, free menthol 44.7 per cent) at 5 mm. pressure and recovered 209.5 kg. of first runs which were treated with 8 kg. of boric acid. The temperature of the mass was maintained at 160° for 3 hr. The substances which did not combine with the boric acid were then distilled off *in vacuo*, eliminating thereby 137 kg. of terpenic products. Distillation was stopped when the temperature of the mass reached 160°. The distillation residue containing the borates of the alcohols was saponified by steam distillation over 150 kg. of a 15 per cent sodium hydroxide solution. The totality of the alcohols thus obtained on distillation *in vacuo* yielded 3.2 kg. of low boiling portions (set aside for chemical investigation), and 17.1 kg. of ethyl-*n*-amyl carbinol (3-octanol). Fractionation and further study of the low boiling portions enabled Benezet, Igolen and Garnero[7] to identify these compounds:

Methanol(?). By characteristic color reactions.

Ethanol. By preparation of its 3,5-dinitrobenzoate m. 93.5°, and its α-naphthylurethane m. 79°.

n-Butanol. By preparation of the corresponding compounds m. 63° and m. 69°–70°, respectively.

Isoamyl Alcohol (Isobutyl Carbinol) and Some *n*-Amyl Alcohol (*n*-Pentanol). Oxidation with a 5 per cent potassium permanganate solution yielded methylethylacetic acid (identified as *p*-bromophenacyl ester m. 51°–52°), and isovaleric acid (identified as *p*-bromophenacyl ester m. 68°).

3-Hexen-1-ol. (d_{15}^{19} 0.8390, n_D^{19} 1.4365), identified by preparation of its α-naphthylurethane m. 72°. The 3,5-dinitrobenzoate yielded two series of crystals m. 39°–40° and 30°–31°, respectively.

n-Hexanol(?) and 3-Methyl-1-Pentanol(?). Oxidation (with a 5 per cent solution of permanganate at 0°) of the fraction containing 3-hexen-1-ol enabled Benezet et

[6] *Ibid.*

[7] Private communication by Établissements Antoine Chiris, Grasse (A.M.), France. *Ind. Parf.* **3** (1948), 353.

al. to isolate saturated hexyl alcohols (b_{732} 150°–151°, d_{15}^{15} 0.822, n_D^{16} 1.4197), apparently a mixture of 3-methyl-1-pentanol and *n*-hexanol.

d-Ethyl-*n*-Amyl Carbinol (3-Octanol). This alcohol (b_{732} 174°–175°, d_{15}^{18} 0.8275, α_D +6° 20′, n_D^{19} 1.4280) was obtained, as mentioned above, by saponification of the borates and was regenerated from its acetate. Identified by preparation of its α-naphthylurethane m. 81°.

Benezet, Igolen and Garnero did not find any vinyl-*n*-amyl carbinol in Brazilian mint oil.

Adulteration.—Adulteration of the complete mint oils by the field distillers occasionally has been observed. Sometimes they use cottonseed oil for this purpose; or they partly dementholize the oil by letting it crystallize during spells of cold weather and by pouring off the liquid oil which they sell then as complete (natural) mint oil.

Extraction of Menthol.—The first lots of Brazilian menthol were prepared on a very small scale, and in most cases without any previous experience, the apparatus used for the purpose consisting of simple ice cream freezers. The industry thus developed from a simple beginning, a house industry, so to speak. Today it has reached quite surprising proportions, some of the larger plants being equipped with very modern apparatus. The principle of menthol extraction consists of three steps, viz., formation of menthol crystals by freezing of the complete oil, removal of the crystals from the residual oil by centrifuging, and drying of the crystals.

The complete (natural) oil, after arrival from the interior, should be clarified prior to cooling (freezing) as it usually contains some water and mucilaginous impurities which prevent ready formation of the menthol crystals. For this purpose some producers filter the oil, others centrifuge it in Sharples or De Laval supercentrifuges, whereas others rectify it in vacuum stills. The latter process offers several advantages: the crystals of menthol form easier if a part of the complete oil is removed as foreruns, and the menthol crystals will possess a finer odor and flavor, not being contaminated with the bitter tasting, high boiling constituents of the complete oil; furthermore, the remaining oil can be sold as *rectified* dementholized oil.

A. Crystallization.—The purified complete oil is slowly and gradually cooled to progressively lower temperatures whereby menthol crystals form in each operation. The freezing process usually comprises three steps: the first at about +14° C., the second at +10° C., and the third at −5° C. Every producer follows his own ideas in this respect and uses certain modifications; this applies equally to the equipment.

The freezing plant proper consists of three tanks cooled with brine solution, or of numerous cells, such as used for the making of ice blocks, im-

mersed into three tanks in which cold brine solutions of different temperature circulate. However, some manufacturers employ large refrigerator compartments, usually three, and therein freeze the oil in tin cans. The larger plants are equipped with regular freezing rooms, each cooled to the proper temperature. Gradual and slow cooling permits the formation of larger and more regular crystals; otherwise it would be difficult to separate the residual dementholized oil from the intricate meshwork of crystals.

B. Separation of the Menthol Crystals from the Dementholized Oil.—This is performed by first decanting the remaining liquid oil from the crystals and by centrifuging the crystals in large centrifuges, rotating at a speed of about 1,200 rpm. Some operators wash the crystals during this process by pouring small quantities of water into the centrifuge.

C. Drying of the Menthol Crystals.—The centrifuged crystals are spread upon trays in large compartments or special rooms and for approximately 36 hr. dried in a slow current of air at a tempertaure of about +26° C. This operation must be undertaken very carefully, as a too fast air current or too high temperature would result in considerable losses of menthol by evaporation; whereas insufficient drying would leave the crystals too wet. Traces of adhering oil may lower the melting point of the menthol crystals below that prescribed by the U. S. Pharmacopoeia for *l*-menthol (41° to 43° C.). Some Brazilian menthol producers recrystallize their menthol, which process yields a product of very pure odor, free from traces of adhering oil, but consisting of only small, needle-like crystals.

Yield of Menthol and Dementholized Mint Oil.—The yield of menthol evidently depends upon the menthol content of the original complete oil and upon the efficiency of the freezing operation. Most manufacturers aim at a maximum yield of menthol, without much consideration for the menthol content of the residual, partly dementholized oil. Yields of menthol by mere freezing vary from 40 to 50 per cent; they are usually 50 per cent of the total oil. Higher yields of menthol can be obtained by first saponifying the menthol esters in the complete (natural) oil and by reducing the menthone to menthol with metallic sodium, or by other methods. A few of the larger and better equipped factories resort to such chemical means in addition to the regular freezing and thereby obtain dementholized oils which are chemically quite differently composed than those resulting from mere freezing. It is, therefore, not surprising that the dementholized Brazilian oils offered on the market are of widely different quality. When placing orders for dementholized Brazilian mint oils, the buyer should always inquire as to how the oil was prepared and base his contracts upon a definite minimum menthol content. He should also test his samples for the content of esters and menthone.

Reduction of Menthone to Menthol in Mint Oil.—Borisyuk and Regilyant [8] reported that the menthone contained in peppermint oil can be catalytically hydrogenated to menthol, thereby enriching the oil with menthol. A solvent such as ethyl alcohol may be used, or the enrichment of the oil with menthol can be effected without a solvent. The reduced oil is practically colorless and has a pleasant odor.

For instance, 30 cc. of oil were hydrogenated for 5 hr. at water-bath temperature with hydrogen (velocity 8–10 liters per hour) and with 2–3 per cent of nickel oxide as catalyst. When working with ethyl alcohol as solvent, the free menthol content could be raised about 5 per cent higher than when working without solvent.

Physicochemical Properties of Dementholized Mint Oil.—A sample of dementholized Brazilian mint oil examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.894
Optical Rotation	−32° 5′
Refractive Index	1.4600
Total Alcohol Content, Calculated as Menthol	54.5%
Ester Content, Calculated as Menthyl Acetate	20.9%
Ketone Content, Calculated as Menthone (Hydroxylamine Hydrochloride Method)	26.8%
Solubility	Soluble in 3.5 vol. of 70% alcohol, slightly hazy in 10 vol.

According to Simmons,[9] samples of Brazilian mint oil submitted a few years ago had a high ester content (calculated as combined menthol) ranging from 12 to 15 per cent, and a total menthol content of nearly 60 per cent. More recently the Brazilian shippers seem to have endeavored to standardize the oil at about 50 to 55 per cent of total menthol. Good average samples at the present time should show the following figures:

Specific Gravity at 15°	0.895 to 0.905
Optical Rotation	−26° 0′ to −31° 0′
Refractive Index at 20°	1.459 to 1.463
Total Menthol Content	Minimum 50%
Free Menthol Content	Usually above 40%
Combined Menthol Content	10 to 15%
Solubility	Soluble in 1 to 3.5 vol. of 70% alcohol; occasionally 1 to 2 vol. of 80% alcohol are required

[8] *Farmatsiya* (1940), No. 4, 5. *Chem. Abstracts* **35** (1941), 2676.
[9] *Perfumery Essential Oil Record* **38** (1947), 264.

Simmons [10] also reports about efforts on part of the Brazilian shippers to reduce the high ester content of the Brazilian mint oil (a) by repeated rectification and (b) by saponification, in order to render it more similar to that from other countries. Three samples of oils thus treated had these properties:

	(*a*)	(*a*)	(*b*)
Specific Gravity at 15°	0.8942	0.898	0.9096
Optical Rotation	−23° 24′	−25° 18′	−23° 36′
Refractive Index at 20°	1.4579	1.460	1.465
Total Menthol Content	52.3%	59.6%	58.3%
Ester Content (Combined Menthol)	3.7%	6.1%	11.2%

Simmons could not explain why rectification was more successful in reducing the ester content than saponification.

SUGGESTED ADDITIONAL LITERATURE

Carlos Stellfeld, "A Hortela Pimenta Japonesa" (Japanese Peppermint), *Tribuna Pharmaceutica* (Curitiba, Brasil) **9** (1941), 1, 23, 61, 89, 103.

Ottilio Guernelli, "How Menthol Is Produced and Industrialized," *Química* (Rio de Janeiro) **1** (1945), 190. *Chem. Abstracts* **41** (1947), 4893.

OIL OF SPEARMINT

Essence de Menthe Crépue *Aceite Esencial de Yerbabuena*
Krauseminzöl *Oleum Menthae Crispae*

Botany, Habitat, and Range.—The nomenclature of the plant from which the different commercial spearmint oils are distilled is complicated and confusing; the vernacular term "spearmint" comprises a number of types possessing the well-known odor and flavor of this popular mint. The United States and Great Britain raise several varieties of *Mentha spicata* Huds. (*M. viridis* L.), e.g., *M. spicata* Huds. var. *tenuis* (Michx.) Briq. in North America, and *M. spicata* Huds. var. *trichoura* Briq. in England. *M. spicata* Huds. var. *crispata* (Schrad.) Briq. is cultivated in Germany, and *M. verticillata* L. var. *strabala* Briq. in the U.S.S.R.

In this section we shall confine ourselves chiefly to North American spearmint, since the United States produces most of the world's output of

[10] *Ibid.*

this oil. Like peppermint, our American spearmint has been naturalized from Europe; several varieties may be found growing wild in waste places and marshes from Nova Scotia to Utah, and south to Florida. It is now cultivated extensively in the northern counties of Indiana, especially around South Bend, Bremen, and Goshen; furthermore, in the southern counties of Michigan, especially around Kalamazoo, Niles and Decatur. Before spearmint is planted, any wild mint growing in the neighborhood must be exterminated, as the latter yields an oil of inferior quality. In the Middle West, 16,900 acres of spearmint were under cultivation in 1948, compared to 14,300 acres in 1947. Indiana's acreage in 1948 was 11,300, against 9,800 in 1947; and Michigan's acreage was 5,600 in 1948, against 4,500 acres in 1947. Total production of spearmint oil in the Middle West amounted to about 280,000 lb. in 1946 and 360,000 lb. in 1947; it was substantially higher in 1948, which year was a banner year. Experimental plantings of spearmint have recently been made in Oregon and Washington.

Spearmint resembles peppermint but does not grow quite as tall; spearmint stems are not so long as those of peppermint, but they stand more erect. The lance-shaped leaves are longer, narrower, lighter green in color, and either without stems, or with only very short ones. Instead of being thick and blunt, the flowering spikes are more sharply pointed, long and narrow; thence the designation spearmint. The characteristic odor and flavor of spearmint are caused by its volatile or essential oil, which can be obtained by steam distillation of the leaves and flowering tops.

Two types of spearmint are grown in Michigan and Indiana: the so-called native American or common, and the so-called Scotch or Highland spearmint. It is claimed that the former possesses greater hardiness, being more resistant to bad weather, diseases, and insect pests. Scotch spearmint was introduced to this country about 1910. Less hardy than the native type, it is more easily destroyed by frost. The great advantage of the Scotch spearmint lies in its higher yield of oil per acre; in some instances, the increase in yield is said to be 50 per cent. Scotch spearmint has been cultivated since at least 1910, and still appears to be true to type. Some users prefer oil distilled from the Scotch variety; others, oil from the American variety. The greater part of the acreage now is devoted to the Scotch variety.

Planting, Cultivating, and Harvesting.—The growing of spearmint resembles that of peppermint and has been described most competently by Sievers,[1] and Ellis.[2] Suffice it here to describe only the main points.

[1] "Peppermint and Spearmint as Farm Crops," *U. S. Dept. Agr., Farmers' Bull.* No. 1555, Washington (1929).

[2] "Mint Culture in Northern Indiana," *Purdue Univ., Agr. Expt. Sta., Lafayette, Indiana, Circ.* No. 227, February (1937).

Spearmint may be grown in a wide range of soils, loamy upland soil or various types of muck (characteristic of drained, but not overdrained, former swamp lands) being most suited. The ground is prepared as for corn or other grain crops, i.e., by plowing, disking several times, harrowing, dragging with a planker, and fertilizing. The better fitted the soil, the cheaper it is to eradicate weeds after planting. The planting is done mainly by hand and usually takes place either from October to November, or in the spring. The rows are spaced 36 to 42 in. apart. The rootstocks are laid overlapping one another in furrows, and soil is dragged over them. Many acres of spearmint are propagated annually by means of young plants. It is claimed that this method has certain advantages; for instance, the fields may be cultivated right after transplanting. During late June and July, the young plants reach a height of 6 in., and are then transplanted with a cabbage planting machine.

As in the case of peppermint, the growers recognize two stages of spearmint plantings, namely, the "row mint," which consists of one-year-old plantings, and the "meadow mint," which consists of fields two or more years old. "Meadow mint" may be weeded in the early stages by machines resembling the common harrow, but later, as it grows higher, all weeding must be done by hand. Although a spearmint ("meadow mint") planting may last from five to six years, experienced growers rotate in a three-year cycle, because after that the yield of oil per acre becomes uneconomical. In a few sections spearmint has been grown successfully for twenty years but this, of course, is exceptional. The crop should be rotated with corn, potatoes, or onions before mint is replanted. Generally speaking, the growing of spearmint is a much less hazardous undertaking than that of peppermint, the latter plant being more susceptible to diseases and insect pests. The greatest dangers to spearmint plantings are early frost and strong winds during early spring.

Like peppermint, spearmint contains a maximum amount of oil during the flowering stage, which lasts several days. The harvesting should be done on dry, warm days but this rule cannot always be followed, adverse weather conditions sometimes requiring a premature harvest. After maximum bloom, the oil content decreases rapidly. "Meadow spearmint" flowers in late July and early August; whereas "row spearmint" reaches that stage about a month later. The plants are cut with a mowing machine and left on the ground to dry for 48 hr. or longer, depending upon the weather. The drying must not progress far enough to make the leaves too brittle as handling of the hay would result in a considerable loss of leaves by shattering. The dried material is raked, bunched, loaded on wagons with a hay loader or pitchforks, and hauled to the distilleries.

Distillation.—Spearmint is distilled in much the same way as peppermint, in a number of small and medium sized distilleries scattered throughout the producing regions. Large-scale growers possess their own distillation equipment; the smaller ones have the hay "custom distilled" by still owners. The average distillery contains a high-pressure boiler developing almost 80 lb. of steam pressure, or a low-pressure boiler that develops almost no pressure, but only a volume of steam—furthermore, two or four galvanized sheet metal tubs, a condenser for each tub, oil separators built like Florentine flasks, water pumps, and hoists for charging and discharging the herbs from the tubs. The tubs are from 6 to 11 ft. deep and 6 to 8 ft. wide. The hay or herb material is moistened by steam and tramped into the tubs prior to closing the tubs for distillation.

Yield of Oil.—Distilling a 3,000 lb. charge requires 35 to 50 min. and yields about 20 lb. of oil. This yield is slightly higher than that of peppermint. One acre of spearmint may yield from 35 to 40 lb. of oil.

Quality of Oil.—There is very little difference between spearmint oils distilled from "row mint" and "meadow mint." At any rate, the difference is even less pronounced than that between "row peppermint" and "meadow peppermint" oils.

Over a number of years, the analytical laboratories of Fritzsche Brothers, Inc., have observed a gradual change in the odor and flavor of freshly distilled spearmint oils received from the producing regions in Indiana and Michigan. The difference was particularly marked when these oils were compared with samples of previous years. It is true that spearmint oil improves with age, one-year old lots being finer and more characteristic in odor and flavor than freshly distilled oils. Nevertheless, the difference in the quality of the freshly distilled oils was so pronounced that the consuming trade reacted to it. Observers in the field offered the explanation that there has been a gradual change in the Scotch spearmint under continued cultivation. The latter is no longer planted in Indiana and Michigan, roots for new plantings now being taken from fields in which Scotch spearmint has become naturalized.

Ellis and Baines [3] expressed the opinion that in the asexual propagation of Scotch spearmint there is very little likelihood of mutations occurring on a large enough scale to account for changes in the plant type, particularly in the absence of the propagation of individual plant selections by growers. More likely the yearly variations in the quality of spearmint oil are due to seasonal factors, and possibly cultural conditions, such as time of harvest, weeds, drainage, etc.

[3] Private communication of Prof. N. K. Ellis and Dr. R. C. Baines of Purdue University, Lafayette, Indiana.

Physicochemical Properties of American Spearmint Oils.—Genuine oils received and analyzed by Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 25°/25°	0.919 to 0.933
Optical Rotation	−50° 15′ to −60° 10′
Refractive Index at 20°	1.4851 to 1.4899
Carvone Content (Neutral Sodium Sulfite Method)	57.0 to 71.5% (usually 60 to 65%)
Solubility at 25°	Soluble in 1 vol. of 80% alcohol; hazy to turbid with more

Crude spearmint oil often contains heavy metals, which can be removed readily by the usual method of treating the oil with tartaric acid.

Since about 1939, the laboratories of Fritzsche Brothers, Inc., have on numerous occasions observed the presence of organic sulfides in shipments of unquestionably genuine spearmint oil. This has been determined by the test for dimethyl sulfide as outlined in Vol. I of this work, p. 311. The presence of dimethyl sulfide in spearmint oils, not observed in former years, decreases their odor and flavor value, imparting a harsh, musty effect which previously was absent. No satisfactory explanation has yet been given for the presence, during recent years, of dimethyl sulfide in spearmint oils. It might be possible that some spearmint fields contain weeds of peppermint which are not eradicated in the regular process of weeding. Such an explanation does not seem quite satisfactory, as spearmint is a much stronger plant than peppermint, and undoubtedly would crowd out any peppermint weeds. It would take a great deal more than a stray plant here and there in a field to account for the presence of dimethyl sulfide in spearmint oils to the extent indicated. It is possible, of course, that some growers are perhaps somewhat negligent in removing such peppermint, especially since it is not as easily noticed as other more conspicuous plants would be. But the fact that peppermint does not thrive in direct competition with spearmint is a reason for questioning this explanation. What adds to the confusion is the fact that these sulfides occur in spearmint oil more frequently in some years than in others.

A sample of spearmint oil produced in Oregon and analyzed in July 1948 by Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°/25°	0.923
Optical Rotation	−55° 4′
Refractive Index at 20°	1.4852
Carvone Content (Neutral Sulfite Method)	63.0%
Solubility	Soluble in 1 vol. and more of 80% alcohol

The properties and odor of this oil were normal. It should be noted that this oil from the West Coast did not give a positive test for dimethyl sulfide.

In evaluating spearmint oil, consideration should be given to resinification, which readily takes place in this oil. In normal oils the specific gravity and carvone content are in direct proportion. If an oil shows a high specific gravity and a carvone content lower than should correspond to this high gravity, resinification is indicated. A harsh odor and flavor, characteristic of such oils, confirm the suspicion.

Chemical Composition.—The earliest investigations on the chemistry of spearmint oil date back more than a century; the results, however, were of little value. Gladstone [4] first isolated carvone, the main constituent of spearmint oil, but assigned to it the misnomer menthol. In the course of numerous subsequent investigations, the following compounds were isolated from spearmint oils of different origin.

l-Carvone. Identified by Flückiger,[5] and by Beyer.[6] Kremers and Schreiner [7] found that American spearmint oil contains about 56 per cent of carvone.

A Terpene. B. 160°–167.5°; occurs in the American oil, according to Trimble.[8]

A *l*-Rotatory Hydrocarbon. B. 168°–171°, according to Beyer.[9]

l-Limonene and probably *l*-Pinene. According to Power.[10] That *l*-limonene actually occurs in American spearmint oil was later confirmed by Nelson,[11] who identified *l*-limonene as nitrosochloride and by conversion to carvone oxime m. 71°–72°.

l-Phellandrene. Elze [12] identified this terpene as nitrosite m. 105°–105.5°, in the lowest boiling fraction of the residual oil, after carvone had been eliminated. Nelson [13] later confirmed Elze's contention.

Acetic Acid, Valeric Acid* Esterified with Dihydrocuminyl Alcohol. Upon further investigation of the above-described carvone-free, residual oil, d_{15} 0.917, α_D −28° 0′, Elze [14] found that it contained 18 per cent of ester, calculated as acetate of dihydrocuminyl alcohol. Fractionation gave a first fraction containing *l*-phellandrene (see above) and another fraction possessing a pronounced spearmint odor. The saponification liquor of the last-named fraction contained acetic and valeric acid; whereas 15 per cent of the alcoholic portion consisted of dihydrocuminyl alcohol: d_{15} 0.9539, α_D −30° 15′; naphthylurethane m. 146°–147°.

[4] *J. Chem. Soc.* **25** (1872), 1.
[5] *Ber.* **9** (1876), 473.
[6] *Arch. Pharm.* **221** (1883), 283.
[7] *Pharm. Rev.* **14** (1896), 244.
[8] *Am. J. Pharm.* **57** (1885), 484.
[9] *Arch. Pharm.* **221** (1883), 283.
[10] "Descriptive Catalogue of Essential Oils," Fritzsche Brothers, Inc., New York (1894), 33.
[11] *U. S. Dept. Agr., Bur. Chem., Circ.* No. 92.
[12] *Chem. Ztg.* **34** (1910), 1175.
[13] *U. S. Dept. Agr., Bur. Chem., Circ.* No. 92.
* The presence of the *n*-valeric acid ester is questionable; it appears more likely that the ester was that of *iso*valeric acid.
[14] *Chem. Ztg.* **34** (1910), 1175.

Since the characteristic odor of spearmint disappeared when the oil was saponified, Elze came to the conclusion that dihydrocuminyl acetate is the carrier of the typical spearmint odor. That this ester actually possesses a strong spearmint-like odor had previously been pointed out by Walbaum and Hüthig.[15]

Investigating a genuine American spearmint oil—

d_{25}^{25}	0.9290
α_D^{25}	−52° 10′
n_D^{25}	1.4866
Ester Number	12.4
Ester Number after Acetylation	36.4
Carvone Content	66.0%
Solubility	Soluble in equal parts of 80% alcohol

—which had been distilled in Michigan from selected plant material, Nelson [16] found that the American oil did not contain any dihydrocuminyl acetate, but the acetate of dihydrocarveol, an ester of very characteristic spearmint odor. (Years ago Blumann and Zeitschel [17] had reported that carveol acetate, too, has a typical spearmint odor.[18]) Saponifying and subsequently fractionating American spearmint oil, Nelson identified dihydrocarveol in the fraction b_{10} 100°–115°.

Dihydrocarveol Esterified with Acetic Acid. Possibly also Butyric Acid, Caproic Acid, and Caprylic Acid. The alcohol was isolated by heating with succinic anhydride at 125°, and was identified as dihydrocarveol through its constants, also by oxidation to dihydrocarvone, semicarbazone m. 200°–201°, oxime m. 88°–89°.

A Solid Acid(?). Aside from these acids, Nelson [19] found that American oils contain also 0.1 per cent of a solid acid m. 182°–184°.

Dipentene and Cineole. Occur in German spearmint oil, according to Haensel.[20]

Use.—Oil of spearmint finds wide application, especially in the flavoring of chewing gums and lately also of tooth pastes. This oil does not possess the medicinal virtues of peppermint oil; consequently, only about one-tenth of the total mint acreage in the United States is devoted to spearmint cultivation.

Chemical Composition of Russian Spearmint Oil.—The Russian oil differs from American, English and German spearmint oils in regard to its carvone content (low) and its content of linaloöl and cineole (high). The odor of the Russian oil is not nearly as pronounced as that of the American type.

[15] *J. prakt. Chem.* **71** (1905), 472.
[16] *U. S. Dept. Agr., Bur. Chem., Circ.* No. 92.
[17] *Ber.* **47** (1914), 2623.
[18] According to the author's experience, one of the components of spearmint oil greatly responsible for its characteristic odor is either an aldehyde or a ketone. The boiling point and the behavior of this compound to bisulfite are very similar to those of carvone which makes its separation rather difficult.
[19] *U. S. Dept. Agr., Bur. Chem., Circ.* No. 92.
[20] *Chem. Zentr.* I (1907), 1332.

Investigating a Russian spearmint oil, the Schimmel chemists [21] identified the following constituents:

l-Linaloöl. The oil contained about 50 to 60 per cent of this terpene alcohol. It was isolated from the fraction b. 196°–200°, α_D^{17} −17° 37′. Oxidation gave citral; identified as citryl-β-naphthocinchoninic acid m. 197°.

Cineole, ca. 20%. About 20 per cent of the oil consisted of a fraction b. 170°–175°, α_D^{17} −24° 54′. Reaction with iodol gave a crystalline addition product m. 113°.

Limonene(?), ca. 20%. The same fraction yielded a nitrosochloride m. 100°, probably limonene nitrosochloride.

l-Carvone. Identified in the highest boiling fraction as hydrogen sulfide compound m. 210°–211°. Russian spearmint oil contains only 5 to 10 per cent of carvone.

According to Kusner and Grinberg,[22] a Russian spearmint oil produced in the Ukraine contained 56 to 65 per cent of cineole and linaloöl, 12 to 13 per cent of carvone, and some limonene.

It appears not unlikely that some of the differences in the physicochemical properties and the flavor of oil of spearmint produced in different countries is due to varietal differences as mentioned under "Botany, Habitat, and Range."

Chemical Composition of Japanese Spearmint Oil.—Nagasawa,[23] investigating Japanese oil of *Mentha viridis* L. var. *crispa* Benth., established the presence of *l*-carvone by the preparation of its semicarbazone m. 162°–163° and its oxime m. 72°–73°. The various derivatives which Nagasawa obtained by catalytic hydrogenation confirm the occurrence of *l*-carvone in Japanese spearmint oil.

OIL OF *MENTHA AQUATICA* L.

Mentha aquatica L.[1] grows wild in many sections of Europe, especially in the southern part, e.g., in Sicily. The physicochemical properties of the various oils described in literature differ considerably except those distilled in Sicily.

[21] *Ber. Schimmel & Co.*, April (1898), 28.
[22] *J. Applied Chem. U.S.S.R.* **8** (1935), 1221. *Chem. Abstracts* **30** (1936), 6129.
[23] *Repts. Imp. Ind. Research Inst., Osaka, Japan* **19**, No. 4 (1938). *Chem. Abstracts* **34** (1940), 219.
[1] According to Index Kewensis identical with *Mentha citrata* Ehrh.

La Face [2] reported on a Sicilian oil (yield 0.03 per cent):

Specific Gravity	0.955
Optical Rotation	+44° 36′
Refractive Index	1.4895
Acid Number	0.56
Saponification Number	72.8
Saponification Number after Acetylation	87.73
Solubility	Soluble in 0.6 vol. of 85% alcohol

Rovesti [3] investigated two Sicilian oils distilled from flowering *Mentha aquatica* L. (yield 0.310 per cent and 0.325 per cent) and reported the following properties:

	I	*II*
Specific Gravity at 15°	0.941	0.931
Optical Rotation at 15°	+16° 48′	+10° 27′
Refractive Index	1.4882	1.4821
Combined Alcohol Content, Calculated as Menthol	6.45%	9.30%
Total Alcohol Content, Calculated as Menthol	28.70%	36.65%
Ketone Content, Calculated as Carvone (Determined as Oxime)	17.10%	21.20%
Solubility in 70% Alcohol	Soluble in 5.5 vol.	Soluble in 2.1 vol.

Romeo and Giuffré [4] distilled the dried herb of Sicilian *Mentha aquatica* L. and obtained 0.8 per cent of an oil with these properties:

Specific Gravity at 15°	0.9671
Optical Rotation at 20°	+39° 55′
Refractive Index at 20°	1.4883
Ester Number	63.40
Ester Content, Calculated as Menthyl Acetate	22.41%
Saponification Number after Acetylation	155.7
Free Alcohol Content, Calculated as Menthol	28.53%
Total Alcohol Content	46.19%
Ketone Content, Calculated as Menthone	0.77%

Carvone is the only compound which has actually been identified in Italian *Mentha aquatica* oil, but the oil probably also contains menthol, menthyl acetate, menthyl valerate, pulegone, and menthone.

[2] *Rivista ital. essenze profumi* **4** (1922), 64. *Ber. Schimmel & Co.* (1923), 52.
[3] *Profumi Italici* **3** (1925), 177.
[4] *Ann. chim. applicata* **17** (1927), 83.

An oil distilled in Tyrol and examined by Schimmel & Co.[5] had the following properties:

Specific Gravity at 15°/15°	0.9416
Optical Rotation	+24° 0′
Refractive Index at 20°	1.48218
Ester Number	18.7
Ester Number after Acetylation	44.8
Total Alcohol Content, Calculated as Menthol	12.9%
Solubility	Soluble in 10 vol. of 80% alcohol, with slight turbidity

The oil possessed a not disagreeable, slightly mint-like odor.

Oil of *Mentha aquatica* has not attained any commercial importance.

OIL OF BERGAMOT MINT
(*Mentha citrata* Ehrh.)

Mentha citrata Ehrh.,[1] a hybrid between *M. aquatica* L. and *M. viridis* L. and commonly called bergamot mint, is a native of Europe, but has also been cultivated in the United States, e.g., in New Jersey, Florida, and Ohio. Experimentally it has been grown by the United States Department of Agriculture [2] at Arlington Farm, where about 30 lb. of oil were obtained per acre.

The oil distilled from this plant possesses an agreeable odor of linalyl acetate, reminiscent of lavender rather than bergamot. Schimmel & Co.[3] reported a yield of 0.2 per cent of oil from young, not flowering, fresh plants, growing probably wild, in Florida.

Physicochemical Properties.—Kremers,[4] Rabak,[5] and Lehn and Fink[6] reported properties of this oil which have been compiled by Gildemeister and Hoffmann[7] as follows:

[5] *Ber. Schimmel & Co.* (1932), 45.
[1] According to Index Kewensis, *Mentha citrata* Ehrh. is identical with *M. aquatica* L.
[2] *Am. Perfumer* **18** (1924), 556.
[3] *Ber. Schimmel & Co.*, April (1904), 98.
[4] *J. Biol. Chem.* **52** (1922), 439.
[5] *Am. Perfumer* **5** (1910), 192.
[6] *Parfumerie moderne* **18** (1925), 205. *Ber. Schimmel & Co.* (1926), 72.
[7] "Die Ätherischen Öle," 3d Ed., Vol. III, 874.

Specific Gravity at 15°	0.916 to 0.924
Optical Rotation	−7° 0′ to −8° 0′
Refractive Index at 20°	1.4582 to 1.4598
Acid Number	Up to 8.0
Ester Number	94.0 to 211.0
Ester Content, Calculated as Linalyl Acetate	33.0 to 74.0%
Ester Number after Acetylation (One Determination Only)	224.0
Solubility	Soluble in 1.5 to 2 vol. of 70% alcohol and in 5 vol. of 60% alcohol

Two oils distilled during 1927 in Michigan and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

	I	*II*
Specific Gravity at 15°/15°	0.905	0.903
Optical Rotation	−8° 24′	−8° 49′
Ester Content, Calculated as Linalyl Acetate	43.9%	43.9%
Solubility	Soluble in 2 vol. and more of 70% alcohol	

Chemical Composition.—Our knowledge of the chemistry of this commercially unimportant oil is rather vague. Kremers [8] reported the presence of the following compounds:

Linaloöl. Identified as phenylurethane m. 64°–65°.
Linaloöl occurs in the oil principally as

Linalyl Acetate. The main constituent, which is accompanied by

Another Ester(?). In small quantities.

A Free Acid(?).

An Aldehyde(?). Of rather unstable nature.

Use.—Oil of bergamot mint has not attained any importance despite efforts to push its use. It would seem that because of the scarcity of imported lavender and bergamot oil during World War II, oil of bergamot mint should have been produced in the United States, but the shortage of labor probably prevented a revival of the small production of former years.

Suggested Additional Literature

R. C. Roark, "Oil of *Mentha citrata*," *J. Am. Pharm. Assocn.* **2** (1913), 839.
H. Carrevon, "Oil of *Mentha citrata*," *Parfumerie moderne* **19** (1926), 243.

[8] *J. Biol. Chem.* **52** (1922), 431.

OIL OF *MENTHA ROTUNDIFOLIA*

Distilling the fresh tops of *Mentha rotundifolia*, which grows wild in Portugal, Costa and do Vale [1] obtained 0.059 to 0.097 per cent of essential oil which had these properties:

Specific Gravity at 15°	0.960–0.975
Specific Optical Rotation at 13°	−24° 0′
Refractive Index	1.475–1.484
Ester Number	101–133
Ketone Content, Calculated as Menthone	1.84%

Oil of *Mentha rotundifolia* consists largely of esters and free alcohols, with small amounts of pinene and limonene present.

The oil has not attained any commercial importance.

OIL OF PERILLA

Essence de Perilla *Aceite Esencial de Perilla* *Perillaöl*
Oleum Perillae

Botanical Classification.—There exists considerable confusion, in literature, regarding the botanical nomenclature of the plant (colloquially called "Shiso") from which the volatile oil of perilla is actually distilled in Japan. According to Furukawa,[1a] there are several "Shiso" plants growing wild and being cultivated in Japan but of those listed below only the first one yields genuine perilla oil, which contains 40 to 55 per cent of perillaldehyde, the chief and most characteristic constituent of the commercial oil:

1. *Perilla frutescens* Brit. var. *crispa* Decne. forma *viridis* Makino (colloquially called "Ao-Shiso")
2. *Perilla frutescens* Brit. var. *crispa* Decne. forma *crispa* Makino ("Chirimen-Shiso")

[1] *Bol. escola farm. univ. Coimbra Portugal* **5** (1945), 90. *Chem. Abstracts* **42** (1948), 3908.

[1a] Private information from Dr. Seiji Furukawa, through the courtesy of Dr. Teikichi Hiraizumi, Toyko.

3. *Perilla frutescens* Brit. var. *crispa* Decne. forma *viridis-crispa* Makino ("Chirimen-Ao-Shiso")

4. *Perilla frutescens* Brit. var. *crispa* Decne. forma *purpurea* Makino ("Aka Shiso"). This plant is widely cultivated in Japan and used to impart color to preserved plums.

5. *Perilla citriodora* Makino ("Lemon-Shiso"). According to Kondo and Yamaguchi,[2] and Suzuki,[3] the oil distilled from this plant contains perillene and about 59 per cent of citral.

6. *Orthodon perforatum* Ohwi ("Yama-Shiso")

7. *Orthodon thymoliferum* Kudo ("Ao-Yama-Shiso")

Although colloquially called "Shiso" these two last-named plants differ widely from perilla plants and yield a volatile oil which contains about 50 per cent of thymol.

One more plant should be mentioned here, viz., *Perilla frutescens* Brit. (*Perilla ocymoides* L.), which in Japan is called "Egoma" and which grows wild in Japan, China, and India. The seed contains about 40 per cent of a fatty, fast drying oil which serves as food and as a constituent of oriental lacquers, instead of linseed oil. The plant is not used for distillation purposes as the volatile oil contains no perillaldehyde.

To conclude, for the distillation of commercial perilla oil, only *Perilla frutescens* Brit. var. *crispa* Decne. forma *viridis* Makino, a white-flowering annual labiate, is employed. In Japan, it grows wild and is also cultivated. The fresh or dried aromatic leaves and flowering tops of this plant are used widely as a condiment in oriental dishes. The odor and flavor are peculiar, cumin-like, rather pungent.

Producing Regions.—Formerly the producing regions were located in Okayama and Saitama (on Japan's main island) but lately production has shifted to the Kitami district on Hokkaido (Japan's northern island) which incidentally is now also the main producing section for mint oil (*Mentha arvensis*).

Planting and Harvesting.—On the main island the seed is sown in the middle of April, on Hokkaido island toward the end of May. The methods of planting and cultivating closely resemble those employed for mint (*Mentha arvensis*).

On the main island the harvest takes place from the middle of September to the beginning of October, on Hokkaido in November.

Under normal conditions, 2.5 acres yield 40 to 50 lb. of perilla oil, but in the years following the conclusion of World War II the yield of oil

[2] *J. Pharm. Soc. Japan* **446** (1919), 263. *J. Chem. Soc.* **116** (1919), 492.
[3] *J. Pharm. Soc. Japan* **56** (1936), 841. *Chem. Abstracts* **33** (1939), 552.

decreased by about one-half, due to lack of fertilizers and to poor seed material (see also below).

Distillation and Yield of Oil.—The harvested plants (leaves and flowering tops) are tied into bundles, hung under sheds, and dried for about two weeks. The stills are of the same type as those used for the distillation of mint oil; some stills serve for the production of perilla oil as well as of mint oil. One thousand pounds of dried perilla herb yield from 1 to 1.5 lb. of volatile oil.

Physicochemical Properties.—Genuine lots of perilla oil imported from Japan and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 15°/15°	0.923 to 0.938
Optical Rotation	−73° 10′ to −96° 32′
Refractive Index at 20°	1.4971 to 1.5048
Acid Number	1.0 to 1.5
Saponification Number	Around 40.0
Aldehyde Content, Calculated as Perillaldehyde (Hydroxylamine Hydrochloride Method)	39.2 to 54.8%
Solubility	Soluble in 0.5 vol. and more of 90% alcohol

A high optical rotation is associated with a high aldehyde content, perillaldehyde being strongly laevorotatory.

Toward the end of, and in the years right after, World War II, the content of perillaldehyde (about 40 to 55 per cent in normal oils) began to decrease and fell to 5 per cent in some lots of oil. Japanese experts have attributed this decrease to the fact that many planters in the Kitami region of Hokkaido purchased their seed material (derived probably from hybrid plants) from seed producers located in the southern parts of Hokkaido, or on Japan's main island. Unless planters collect their seed material from their own fields, it is very difficult to distinguish genuine perilla seed from hybrid seed. Lately, however, efforts have been made to remedy this defect and to return to normal oils.

Chemical Composition.—We owe our knowledge about the chemistry of perilla oil (*Perilla frutescens* Brit. var. *crispa* Decne. forma *viridis* Makino) mainly to the Schimmel chemists,[4] who found that perillaldehyde is the main constituent of this oil.

α-Pinene. Only small quantities, according to Furukawa and Tomizawa.[5]

l-Limonene. The Schimmel chemists[6] reported the presence of about 9 per cent of *l*-limonene in perilla oil; identified by means of the tetrabromide m. 104°.

The structural relationship between *l*-limonene and perillaldehyde is evident.

[4] *Ber. Schimmel & Co.*, October (1910), 136.
[5] *J. Chem. Ind. Japan* **23** (1920), 342. *Chem. Abstracts* **14** (1920), 2839.
[6] *Ber. Schimmel & Co.* (1921), 35.

Perillaldehyde (Dihydrocuminaldehyde). Perilla oil contains about 50 per cent of perillaldehyde, b_{750} 235°–237°, b_9 104°. The odor of perillaldehyde is similar to that of cuminaldehyde. It can be isolated from the oil by the neutral sodium sulfite method.

The aldehyde is strongly laevorotatory, α_D −146° 0′.[7]

A Compound(?) m. 128°. From the fraction b_4 114°–116° the Schimmel chemists isolated colorless long needles m. 128° which possessed a characteristic celery- and parsley-like odor. The small quantity available did not permit further identification.

Distilling fresh perilla herb in different states of maturity, Furukawa and Tomizawa [8] found that the content of aldehydes increases as the stage of flowering progresses, whereas the content of esters decreases correspondingly. On the other hand, for oils distilled from dried plant material the opposite holds true. In order to split the glycosides present in the green parts of the plant and to obtain a good yield of oil, it is necessary to conserve the enzymes by drying the plants at low temperature.

As has been pointed out, there exists considerable confusion in literature regarding the botany of the plant from which perilla oil is distilled. The previous part of this monograph describes the commercial perilla oil, distilled from *Perilla frutescens* Brit. var. *crispa* Decne., forma *viridis* Makino. It possesses a high laevorotation.

Yuoh-Fang-Chi [9] reported that the alcoholic extract from leaves of what he believed to be *Perilla nankinensis* Decne.,[10] on steam distillation yielded a volatile oil which contained a ketone, but no perillaldehyde.

Goto [11] described an oil distilled from a Manchurian *Perilla frutescens* Brit. (the fresh herb yielded 0.01–0.07 per cent oil) which contained perilla ketone $C_{10}H_{14}O_2$, semicarbazone m. 98°–99°. The oil crystallized on cooling and melted at 14°. It had an optical rotation of +0° 30′, and a specific gravity d_{22}^{22} 0.8708, and was therefore very different from the commercial perilla oil.

More recently, Sebe [12] investigated an oil distilled from *Perilla frutescens* var. *viridis* Kudo which grows wild in Formosa, and identified perilla ketone as the principal constituent of this oil.

Our discussion of the chemical composition of perilla oil would not be complete without a short reference to the extremely sweet taste of one of the two stereoisomeric oximes of perillaldehyde. Furukawa and Tomi-

[7] See also Semmler and Zaar, *Ber.* **44** (1911), 52.
[8] *J. Chem. Ind. Japan* **23** (1920), 342. *Chem. Abstracts* **14** (1920), 2839.
[9] *J. Chinese Chem. Soc.* **2** (1934), 315. *Chem. Abstracts* **29** (1935), 2659.
[10] This plant was probably *Perilla frutescens* Brit. (the Author).
[11] *J. Pharm. Soc. Japan* **57** (1937), 77. *Chem. Zentr.* II (1937), 2082.
[12] *J. Chem. Soc. Japan* **64** (1943), 1130. *Chem. Abstracts* **41** (1947), 3785.

zawa [18] prepared the *α-anti*-aldoxime and the *β-syn*-aldoxime of this aldehyde and found that the former is 2,000 times as sweet as sugar, 4 to 8 times as sweet as saccharin, whereas the *β-syn*-aldoxime is not sweet at all. The Japanese Government permits the use of this compound for the sweetening of tobacco, as a replacement for maple sugar or licorice. Consequently, the demand for it has increased to such an extent that in Japan efforts are being made to synthesize perillaldehyde from pinene.

Total Production.—For the same reason the demand for oil of perilla in Japan has increased in the course of the past years, especially since about 1940. The peak of production was reached when 3,000 kg. of oil were produced in one year. Due to the cultural factors explained above, production has fallen off since the end of World War II. In 1948 it amounted to 500 to 600 kg. of oil from 125 to 150 acres then under cultivation.

Use.—Oil of perilla is a flavoring agent used sparingly in exotic table sauces and in confectionery of oriental character. If blended skillfully, oil of perilla gives interesting and peculiar flavor notes in dentifrices. The oil possesses a strong antiseptic action and is used as an antimildew agent. The chief application of perilla oil in Japan, however, is as a base for the preparation of the above-described sweetening agent.

THE PYCNANTHEMUM OILS
(Oil of Mountain Mint)

Introduction.—There exist in North America at least three species of *Pycnanthemum,* commonly called mountain mint, the most important probably being *Pycnanthemum incanum* Michx. All three species possess a mint- and pennyroyal-like odor, due to the presence of pulegone.

I. Oil of Pycnanthemum incanum Michx. (Koellia incana [Michx.] Baill.—Clinopodium incanum L.)

This mint, commonly called hoary mountain mint, calamint, or wild basil, occurs in North Carolina. Two oils distilled there in 1942 and 1943, and analyzed in the laboratories of Fritzsche Brothers, Inc., had the following properties:

[18] *J. Chem. Ind. Japan* **23** (1920), 342. *Chem. Abstracts* **14** (1920), 2839.

	I	*II*
Specific Gravity at 15°/15°	0.940	0.937
Optical Rotation	+18° 37′	+15° 8′
Refractive Index at 20°	1.4862	1.4900
Acid Number	2.8	2.3
Saponification Number	8.4	8.2
Ketone Content, Calculated as Pulegone	76.2%	78.5%
Solubility	Opalescent in 4.5 vol. and more of 60% alcohol	Hazy in 6 vol. and more of 60% alcohol

These oils possessed an odor similar to European pennyroyal, but less pronounced in pulegone character and more mint-like.

The Texas Engineering Experiment Station, Agricultural and Mechanical College of Texas, distilled an oil of *Pycnanthemum incanum* Michx. which was analyzed by Fritzsche Brothers, Inc., New York, in 1943:

Specific Gravity at 15°/15°	0.934
Optical Rotation	+16° 20′
Refractive Index at 20°	1.4836
Pulegone Content	91.7%
Solubility at 20°	Soluble in 6 vol. and more of 60% alcohol

The high pulegone content of the oil is interesting. This type of oil could undoubtedly replace the imported pennyroyal oil.

The above-named station [1] advised that propagation of this plant in field rows would yield sufficient tonnage to make commercial production feasible. Indications are that tonnage increases in the second and third year.

So far, oil of *Pycnanthemum incanum* Michx. has not attained any commercial importance.

II. Oil of Pycnanthemum lanceolatum Pursh. (Koellia lanceolata [Pursh.] O.K.—Thymus virginicus L.)

The odor of this oil also resembles that of pennyroyal. The plant grows wild in North America, especially in Virginia, for which reason it is commonly called Virginia mountain mint. In the dried state it yields on the average 2.2 per cent of volatile oil.

Physicochemical Properties.—The oil has been described by Miller,[2] Barker,[3] Correll,[4] and by Alden [5] who found the following properties:

[1] Private communication.
[2] *Pharm. Experiment Sta., Univ. Wisconsin, Circ.* No. 2 (1918).
[3] *Am. J. Pharm.* **66** (1894), 65.
[4] *Pharm. Rev.* **14** (1896), 32.
[5] *Ibid.* **16** (1898), 414.

Specific Gravity at 15°	0.918 to 0.936
Specific Gravity at 25°	0.9017 (one oil only)
Optical Rotation	−0° 34′ to +11° 5′
Refractive Index at 16°	1.4881 (one oil only)

Chemical Composition.—The above-named workers reported the presence of the following compounds:

Dipentene. The lowest boiling constituents (about 20 per cent) probably contain dipentene: nitrosochloride m. 104°, nitrolbenzylamine m. 105°–106° (instead of 109°–110°), nitrolpiperidine m. 140°–141° (instead of 152°).

Pulegone. Identified as oxime m. 117°–118°, and as semicarbazone m. 169°–170°.

Carvacrol. According to Correll, the oil contains from 7.0 to 9.0 per cent of carvacrol: dicarvacrol m. 145°–147°, sulfonic acid m. 56°–57°. Miller reported that the oil contains from 14.5 to 58 per cent, on the average 25 per cent of carvacrol: nitrosocarvacrol m. 152°–153°.

Geraniol.

Thujone. Presence probable; semicarbazone m. 175°–176°.

According to Kir'yalov,[6] the essential oil of *Pycnanthemum lanceolatum* Pursh. distilled from the inflorescence in the Experimental Station of the Agriculture Institute of Voronezh (U.S.S.R.) contained these compounds:

70–75% *l*-menthone
10–15% pulegone (probably *d*-)
About 5% terpenes

When distilling the whole plant, Kir'yalov obtained an oil composed of

25–30% *l*-menthone
45–50% *d*-pulegone
5–7% terpenes

Menthone probably is synthesized in the inflorescence. In spite of previous reports, carvacrol, geraniol, and β-thujone were not detected.

Kir'yalov recommended the essential oil of *Pycnanthemum lanceolatum* Pursh. for employment in tooth powders or pastes, and for the preparation of menthol. In the United States the oil has not attained any commercial importance.

III. Oil of Pycnanthemum muticum (Michx.) Pers.

The plant is commonly called short-toothed mountain mint. Distilling the air-dried herb, Werner[7] obtained a yield of 1.5 per cent of oil possessing a mint- and pulegone-like odor.

[6] *J. Applied Chem. U.S.S.R.* **12** (1939), 290. *Chem. Abstracts* **33** (1939), 6526.
[7] *Am. Perfumer* **24** (1929), 473.

Physicochemical Properties.—Werner [8] reported these properties:

Specific Gravity	0.9250 to 0.9266
Optical Rotation	+12° 2′
Refractive Index	1.4807

Foote and Torres [9] distilled three different lots of *Pycnanthemum muticum* (Michx.) Pers. at Gainesville and at Clewiston, Florida, and obtained oils with these properties:

Specific Gravity at 20°/20°	0.9320 to 0.9326
Specific Rotation at 20°	+22° 13′ to +23° 19′
Refractive Index at 20°	1.4837 to 1.4845
Pulegone Content	87.3 to 90.2%

Chemical Composition.—According to Werner [10] the oil contains:

62.0 to 71.0% pulegone
8.0% menthone
15.0% menthol
Terpenes
Sesquiterpenes
β-Thujone(?)
Formic acid
Acetic acid
A nonvolatile acid

In addition to the constituents identified by Werner,[11] Foote and Torres [12] established the presence of limonene.

The oil has not attained any commercial importance.

IV. Oil of Pycnanthemum pilosum, Nutt.

According to Chilquist, Gilmour and Jannke,[13] *Pycnanthemum pilosum* Nutt. has been cultivated near Atlantic, Iowa, for bee pasture. On distillation the fresh herb yielded 0.95 per cent of a volatile oil with a strong odor suggesting the presence of pulegone.

The physicochemical properties of the oil distilled in 1945, 1946, and 1947 varied within these limits:

Specific Gravity at 25°	0.9225 to 0.9378
Specific Optical Rotation at 25°	+11° 54′ to +14° 30′
Refractive Index at 25°	1.4690 to 1.4795
Saponification Number	15.5 to 38.0
Free Alcohol Content (Calculated as $C_{10}H_{20}O$)	4.37 to 10.90%

[8] *Ibid.*
[9] *J. Am. Pharm. Assocn.* **31** (1942), 72.
[10] *Am. Perfumer* **24** (1929), 473.
[11] *Ibid.*
[12] *J. Am. Pharm. Assocn.* **31** (1942), 72.
[13] *J. Am. Pharm. Assocn.* **38** (1949), 204.

Ester Content (Calculated as Acetate of $C_{10}H_{20}O$)	5.48 to 13.44%
Phenol Content	3.1 to 7.5%
Ketone Content (Sodium Sulfite Method)	33 to 51%

The ketones consisted chiefly of pulegone, identified by means of its oxime m. 124°.

The aqueous cohobate was shown to contain an alcohol and an aldehyde or ketone.

The oil has not attained any commercial importance.

OIL OF ROSEMARY

Essence de Romarin *Aceite Esencial de Romero* *Rosmarinöl*
Oleum Rosmarini

Botany.—*Rosmarinus officinalis* L., a native of Mediterranean countries, is a small evergreen shrub esteemed since antiquity for its pleasant, slightly camphoraceous odor. The leaves and flowering tops contain a volatile oil which can be isolated by steam distillation.

The erect stems are divided into numerous long, slender branches bearing many sessile, opposite leaves, about 2.5 cm. long, smooth and green on the surface, woolly, whitish, and glandular beneath. The flowers appear as pale blue verticillasters. Because of their aromatic taste, the leaves are employed as condiment in the seasoning of European dishes and sauces, especially those of France and Italy. They are also considered emmenagogue and gently stimulant. Upon aging, the leaves lose part of their oil and become progressively odorless.

The botany of rosemary is rather complicated, as there exist, according to Turrill,[1] several species of the genus *Rosmarinus*, with a number of varieties and forms:

Rosmarinus officinalis L. var. *genuina* Turrill. Occurring in most Mediterranean countries, the Canary Islands, the Azores, and Madeira.

R. o. var. *genuina* forma *erectus* Pasq. Occurring in the same countries and islands.

[1] *Kew Bull.* (1920), 105. *Ber. Schimmel & Co.* (1923), 146.

R. o. var. *genuina* forma *humilis* Ten. Occurring in Italy, Dalmatia, and probably elsewhere.

R. o. var. *genuina* forma *albiflorus* Bég. Occurring in Italy, Dalmatia, and probably elsewhere.

R. o. var. *rigidus* Car. et Saint Lag. Occurring in Southern France, Italy, and Spain.

R. o. var. *angustifolius* Guss. Occurring in Southern France, Italy, and Corsica.

R. o. var. *latifolius* Bég. Occurring in Southern France and Italy.

R. o. var. *pubescens* Pamp. Occurring in Tripoli.

R. o. var. *pubescens* Pamp. forma *roseus* Pamp. Occurring in Tripoli.

R. laxiflorus de Noé. Occurring in Algeria and Spain.

R. lavandulaceus de Noé. Occurring in Algeria.

R. tournefortii de Noé. Occurring in Algeria.

The existence of these varieties and forms of *Rosmarinus officinalis* might explain the fact that rosemary oils of varied geographic origin possess somewhat variant physicochemical properties. However, such variations might also be caused by local conditions of soil, climate, altitude, exposure to sunlight, and by the season of harvesting—i.e., summer or winter. So far as Spanish rosemary oil is concerned, botanists at the University of Sevilla [2] do not doubt that the rosemary growing in Spain is of the same variety everywhere, and they attribute the difference in the physicochemical properties of the Spanish oils to local conditions. The regions of Murcia and Almeria possess a warmer climate than Granada and Jaén, especially during winter.

Habitat, Range, and Occurrence.—Rosemary grows wild and abundantly in lime soil, over extended areas, on arid, sunny mountain slopes, especially in Spain, Dalmatia, Tunisia, Morocco, and Southern France. The price of the oil distilled from wild plants has always been low; therefore, rosemary is not cultivated, except for ornamental purposes.

Rosemary oil was originally produced in Southern France but the industry there has almost completely disappeared, although it experienced a temporary revival during the Spanish Civil War (1936–1939).

Quite some years ago, Dalmatia became a large producer of the oil. However, during World War I, Dalmatia (then part of Austria-Hungary) suffered from labor shortage and could not export to Allied countries; Spain, where rosemary grows in great abundance, then started distillation in increasing quantities, assuming gradually a leading position. Spain's monopoly lasted until the outbreak of civil war in 1936, when a shortage of the Spanish oil and high prices encouraged Tunis and Morocco to produce

[2] Private communication by Mr. Ramon Bordas, Sevilla.

rosemary oil on a limited scale. Today the bulk of rosemary oil again comes from Spain, with Dalmatia, Tunis, and Morocco exporting smaller quantities.

Spanish Rosemary Oil

Producing Regions.—Rosemary is distilled chiefly in the provinces of Murcia and Albacete, the centers of production there being Lorca, Murcia,



Courtesy of Fritzsche Brothers, Inc., New York.

Field distillation of rosemary oil in Spain.

Cieza, Caravaca, Calasparra, Tazona, Socovos, Hellin, and especially Campo de Lorca—the headquarters of several large farmer-distillers. Other producing sections, supplying much smaller quantities, but of superior quality, lie in the provinces of Granada and Jaén.

Plant Collection and Distillation.—In Spain rosemary oil is produced largely between March and July, but in the event of a heavy demand, the oil is distilled also during the winter in the province of Murcia. The collection and distillation of the plant material is carried out as described in the section on "Oil of Spike Lavender." As a whole, the production of Spanish rosemary oil thus resembles that of Spanish spike lavender, except for the fact that the bulk of rosemary oil is not produced by the exporters through their own organizations but by a great number of peasant-operators, who carry on distillation throughout the year, aside from their regular agricultural activities. Since these peasants do not count their own or their

families' labor, the exporters can buy the oil from them cheaper than they could produce it through their own distilling organization.

Yield of Oil.—During the summer months 12 arrobas (1 arroba = 11.5 kg. or about 25 lb.) of plant material yield about 1 kg. of oil; but during the winter months 20 arrobas of plants are required per kilogram of oil. The yield thus varies from about 0.725 per cent in summer to 0.435 per cent in winter.

Physicochemical Properties.—As was pointed out in the chapter on Botany, the properties of Spanish rosemary oil vary according to producing region.

Samples of authentic oils which the author collected in the provinces of Murcia and Albacete, Spain's chief rosemary producing regions, had the following properties:

	Lorca	*Cieza*	*Calasparra*
Specific Gravity at 25°/25°	0.898	0.896	0.896
Optical Rotation	−0° 32′	−2° 14′	−2° 27′
Total Alcohol Content, Calculated as Borneol	10.4%	10.6%	10.9%
Ester Content, Calculated as Bornyl Acetate	2.6%	2.8%	2.8%
Solubility	Clearly soluble in 5.5 to 6 vol. of 80% alcohol and more	Clearly soluble in 6 to 7 vol. of 80% alcohol and more	Soluble in 10 vol. of 80% alcohol with slight turbidity

Not all of these genuine oils were completely soluble in 10 volumes of 80 per cent alcohol. Therefore, they did not quite meet the specifications of the U.S.P. XIII.

Authentic samples collected by the author in the other, less important producing regions of Spain, viz., Jaén and Granada, had the following properties:

	Jaén	*Granada*
Specific Gravity at 25°/25°	0.898	0.898
Optical Rotation	+4° 53′	+4° 47′
Total Alcohol Content, Calculated as Borneol	14.8%	15.1%
Ester Content, Calculated as Bornyl Acetate	2.8%	2.9%
Solubility at 25°	Soluble in 6 and more vol. of 80% alcohol	Clearly soluble in 10 vol. of 80% alcohol

These properties fell within the specifications of the U.S.P. XIII.

The quantities of rosemary oil produced in the provinces of Jaén and Granada represent only about 15 to 20 per cent of the total amount pro-

duced in Spain. Yet, the Jaén and Granada oils have been in considerable demand because of their better physicochemical properties.

From information secured by the author while surveying the production of Spanish rosemary oil, it appears that oils distilled during the winter months are generally less soluble than those distilled in summer. Furthermore, plants collected from slopes with southern exposure give oils of better solubility than those gathered from hills facing the north.

Genuine lots of Spanish rosemary oil imported during past years and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties which varied between the following limits:

Specific Gravity at 25°/25°	0.893 to 0.910
Optical Rotation at 25°	−0° 58′ to +11° 30′
Refractive Index at 20°	1.4682 to 1.4712
Ester Content, Calculated as Bornyl Acetate	1.0 to 3.9% (in an exceptional case as high as 5.4%)
Total Alcohol Content, Calculated as Borneol	8.7 to 15.6%
Solubility	Soluble in 4.5 to 5 vol. of 80% alcohol; many genuine oils turbid in 10 vol. of 80% alcohol

Few lots of genuine Spanish rosemary oils fall within the limits of the U.S.P. XIII. Therefore, it is advisable that the specifications of the U.S.P. be revised accordingly.

Adulteration of Spanish Rosemary Oil.—In past years oil of rosemary was frequently adulterated with oil of turpentine, but lately more "efficient" products have been employed for this purpose—e.g., certain fractions of camphor oil, oil of pine steam distilled, eucalyptus oil terpenes, and fractions resulting from the manufacture of terpineol. Using these various products skillfully, the adulterator has little difficulty in arranging the properties of his oils in such a way that they will meet regular routine tests.

Total Production of Spanish Rosemary Oil.—From 1931 to 1935, the annual total production of Spanish rosemary oil varied from 60,000 to 150,000 kg. Production fell off considerably with the outbreak of the Spanish Civil War in 1936, until it amounted to only about 10,000 to 12,000 kg. per year. Since the end of hostilities in Spain production has been increasing again, reaching 60,000 kg. in 1946, 35,000 kg. in 1947, and about 55,000 kg. in 1948.

French Rosemary Oil

Quite some years ago rosemary oil was produced in Southern France, particularly in the Départements Var, Drôme, Vaucluse, and Bouches-du-Rhône. Wild growing plant material cut from the surrounding hillsides

was distilled in small portable stills, such as were then used for the production of lavender oil. According to Blin [3] the yield of oil in these old-fashioned stills was low, amounting to about 0.125 per cent. Larger and more modern direct steam stills, holding 1,200 to 1,500 kg., gave better yields, ranging from 0.38 to 0.5 per cent oil.

Blin reported that rosemary, which is very sensitive to cold weather, was at some time also *cultivated* in Southern France. It can be propagated by seed, cuttings, or layers in fall. The planting takes place in March and April; two to three years later the plants can be cut; this should be done during the flowering period. The leaves yield the best quality of oil; for this reason the woody material is removed from the plants prior to distillation.

Physicochemical Properties of French Rosemary Oil.—According to Gildemeister and Hoffmann [4] the properties of French rosemary oil vary between the following limits:

Specific Gravity at 15°/15°	0.900 to 0.920
Optical Rotation	Up to +13° 10′, in isolated cases slightly laevorotatory
Refractive Index at 20°	1.467 to 1.472
Ester Content, Calculated as Bornyl Acetate	1.0 to 4.9%
Total Alcohol Content, Calculated as Borneol	8.0 to 11.3%
Solubility	Usually soluble in 1 to 8 vol. of 80% alcohol

The shortage of labor resulting from the Civil War in Spain caused the production of Spanish oils to fall off considerably from 1936 to 1939, and this fact gave some impetus to a revival of the former French production.

Paulet and Vacquier [5] reported on the occurrence of two types of rosemary in La Garrigue (Langedoc)—viz., one with blue-violet flowers and dark green leaves, the other with white flowers and green-yellow leaves. Most of the plants growing wild in that region were hybrids of the two types. Graafland [6] declared the two types morphologically identical; yet the odor of the oils obtained from the two types differed markedly.

An oil distilled by these authors from plants growing near Matelettes, at 300 m. altitude, and 30 km. from the seacoast, had the following properties:

Specific Gravity at 15°	0.9135
Optical Rotation	+15° 24′
Solubility	Soluble in 75% alcohol

[3] *Parfumerie moderne* **10** (1917), 24, 44.
[4] "Die Ätherischen Öle," 3d Ed., Vol. III, 627.
[5] *Parfumerie moderne* **31** (1937), 211.
[6] *Ibid.*, 213.

An oil distilled from plants growing near Couvent de Mourgues, at 250 m. altitude and 28 km. from the seacoast, had these properties:

Specific Gravity at 15°	0.912
Optical Rotation	+12° 9′
Solubility	Soluble in 1 vol. of 80% alcohol

Different from these oils was one distilled from plants growing near La Paillade which had the following properties:

Specific Gravity at 15°	0.909
Optical Rotation	+5° 15′
Solubility	Soluble in 1.8 vol. of 80% alcohol

All these oils were distilled during January and February, the yield being about 0.4 per cent. The odor of the first two oils was much finer than that of Spanish oils.

Dalmatian Rosemary Oil

Producing Regions.—*Rosmarinus officinalis* L. grows wild and profusely over wide areas on the arid mountain slopes of the Dalmatian Islands, especially on Lesina (Hvar in Serbo-Croat), Lissa (Vis), Brazza (Brac), Solta, and Cherso. On Lesina, rosemary occurs only in the western section, rarely east of Gelsa. Main producing centers on that island are near the villages of Brusje and Grabje, where the peasants, some years ago, organized cooperatives for distilling the oil.

The rosemary shrub grows to a height of about 3 ft. and forms part of the hardy, rugged vegetation on the calcareous summits and slopes of the Karst Mountains, the top soil of which was washed away centuries ago by erosion, after excessive deforestation. This typical Karst vegetation, also referred to as "macchia," still finds sustenance where less hardy plants perish through summer heat and drought.

Rosemary blooms from fall to spring, but most luxuriantly in May and June. Seen from the distance, at that period, entire mountain slopes sometimes appear to radiate delicately bluish hues. The cutting of rosemary takes place from the end of August to the end of September, quite some time after the blooming period.

Collection of Plant Material.—The wild growing plants form part of the communities' property, the right of harvesting being yearly auctioned off to the highest bidder. In order to preserve the wild plant growth, Government regulations provide that each section may be exploited every third year only, with a two years' respite between the harvests.

The actual collecting is done by the female population of the villages, who cut the twigs with sickles, taking care not to injure the plants. The twigs are clipped according to the development and age of each shrub, to spare the weaker plants and permit them to recuperate.

The cut material is carried to the villages and dried until the leaves fall off the twigs. In literature, this process has occasionally been referred to as fermenting or curing, but actually it means only drying to facilitate removal of the leaves from the twigs; it is sometimes concluded by a light threshing.

Distillation.—Distillation is carried out by a great number of peasants and a few cooperatives, in portable stills, some of them small and primitive and resembling the old-fashioned Bulgarian rose stills of Turkish origin. These stills are charged with 80 liters of water and 30 kg. of leaves; the twigs deprived of the leaves serve as fuel for the fire beneath the stills. Distillation lasts 2 to 3 hr. The yield of oil amounts to about 1.5 per cent.

There are also larger stills, holding up to 1,500 kg., which are more modern in design and are heated with direct steam from a separate steam boiler. Distillation in these stills lasts only 1½ hr., and the yield is usually somewhat higher—up to 2 per cent, and occasionally even slightly above 2 per cent.

Physicochemical Properties of Dalmatian Rosemary Oil.—The fact that in Dalmatia only the leaves of the rosemary shrub are distilled is probably the chief cause for the finer odor of the Dalmatian oils, as compared with Spanish oils, which are distilled from the overground parts, including the woody twigs. This fact *might* also be responsible for the difference in the properties of Spanish and Dalmatian oils. The latter are more soluble in 80 per cent alcohol and possess dextrorotation, whereas most Spanish oils show laevorotation. The Dalmatian oils thus usually conform with the specifications of the U.S.P.; as a matter of fact the first specifications established for the U.S.P. were based entirely on French and Dalmatian oils, Spanish oils being practically unknown at that time.

Gildemeister and Hoffmann [7] suggested the following limits for Dalmatian rosemary oil:

Specific Gravity at 15°/15°	0.894 to 0.913, mostly above 0.900
Optical Rotation	+0° 43′ to +5° 53′, only in very rare cases higher
Refractive Index at 20°	1.466 to 1.468
Acid Number	Up to 0.7
Ester Content, Calculated as Bornyl Acetate	1.8 to 7%

[7] "Die Ätherischen Öle," 3rd Ed., Vol. III, 627.

Total Alcohol Content, Calculated as Borneol	8.4 to 14.3%
Solubility	Usually soluble in 1 to 8 vol. of 80% alcohol

Samples of genuine oils collected by the author in Dalmatia and oils imported and analyzed by Fritzsche Brothers, Inc., had properties varying within these limits:

Specific Gravity at 25°/25°	0.899 to 0.904
Optical Rotation at 25°	+2° 6′ to +2° 38′
Ester Content, Calculated as Bornyl Acetate	2.3 to 4.2%
Total Alcohol Content, Calculated as Borneol	10.5 to 11.8%
Solubility	Usually soluble in 2 vol. and more of 80% alcohol; some oils slightly turbid with more

Total Production of Dalmatian Rosemary Oil.—Prior to World War I Dalmatia formed part of the Austrian-Hungarian Empire, its population of forty millions offering a good domestic market for this oil. Dalmatia was then Austria-Hungary's "balcony on the Adriatic," and the Government did much to encourage production of rosemary and other essential oils. Experimental plantings were started, the organizing of cooperatives was sponsored, and finally rosemary oil was adopted by the Austrian Pharmacopoeia as denaturant of alcohol—which measure boosted the employment of this oil considerably. Before World War I Dalmatia produced yearly about 20,000 kg. of oil. This figure, since the disintegration of that empire, has fallen to less than half. It was only during the years of the Spanish Civil War (1936–1939) that substantial quantities of Dalmatian rosemary oil were again exported. The principal shipping ports for Dalmatian rosemary oil are Trieste and Spalato (Split).

Tunisian Rosemary Oil

A few years prior to World War II, Tunisia (North Africa) began production of substantial quantities of rosemary oil, which was of excellent quality and found ready acceptance on the world market. Annual production then amounted to 30,000 to 40,000 kg.; this figure probably would have increased had the war not interrupted production. The producing regions became battle fields, and many stills were destroyed. According to Fatter,[8] 25,000 to 30,000 kg. of oil were produced in 1946. Total production was 23,000 kg. in 1947, and 19,000 kg. in 1948.

[8] Private communication by Mr. Lucien Fatter, Carthage, North Africa.

Botany, Range, and Habitat.—The only species of *Rosmarinus* exploited in Tunisia for its essential oil is *R. officinalis* L., which embraces several forms and distinct varieties, their morphological structure differing according to the soil and climate in which they grow. The linear species, *R. officinalis* L., bears pale, purplish-blue flowers; the varieties *flexuosus* and *laxiflorus,* white flowers. The plant grows wild and abundantly over vast areas of Tunisia's coastal ranges, and especially in the low mountains of central Tunisia, where it occurs in the form of dense bushes and tufts about 18 in. high. On the calcareous soils of the plateaus and plains of more than 400 m. altitude rosemary covers large sections and grows all year round.

Plant Collection and Distillation.—Tunisia's rosemary oil industry is managed by French colonists. The manual work, however, is done by the Arab natives, who cut the plant material and haul it—using camels and donkeys, or carts—to the distilleries. These latter are also manned by Arabs. The harvest is conducted all the year round (except for the rainy season) and reaches its peak in May and June. In July the work usually slows down, as the native labor is temporarily occupied with the harvest of staple and food crops.

Field distillation posts consist of two or more stills, usually constructed of galvanized sheet metal, and having a capacity of about 3,200 liters. Most field stills are of the direct fire type; some, however, are operated with steam generated in a separate steam boiler. Steam distillation is supposed to produce a better quality of oil.

Distillation is centered in Djebel Serdj (Ousseltia), Medjez el Bab, Pont du Fahs, Kairouan and Bou Arada—all of which areas lie southwest and south of Tunis (these names are familiar to the veterans of the campaign in Tunisia!).

Yield of Oil.—The yield of oil depends upon the way the plant material has been cut. The oil glands are located in the leaves; hence the less woody parts that the plant material contains, the better will be the quality of oil. The yield also varies with the season. The highest yields are obtained in March and April. Gutkind [9] reported an average yield of 1 per cent, whereas Trabaud [10] speaks of 0.3 to 0.5 per cent.

Physicochemical Properties.—Two samples of genuine Tunisian rosemary oil submitted by Gutkind [11] to Ernest J. Parry, and analyzed by the latter, had these properties:

[9] Private communication of Mr. Felix Gutkind, London, England.
[10] *Drug Cosmetic Ind.* **44** (1939), 566.
[11] Private communication of Mr. Felix Gutkind, London, England.

	I	*II*
Specific Gravity at 15.5°	0.9165	0.9164
Optical Rotation	+2° 10′	+2° 40′
Refractive Index at 20°	1.4701	1.4693
Ester Content, Calculated as Bornyl Acetate	2.9%	2.0%
Free Borneol Content	11.0%	11.4%
Total Borneol Content	13.1%	12.9%
M.p. of *o*-Cresol Complex in B.P. Cineole Limit Test	42.1° C.	42.2° C.
Cineole Content	41.4%	40.8%
Solubility at 20°	Sol. in 1.1, up to 10 vol. of 80% alcohol	Sol. in 3 vol., up to 10 vol. of 80% alcohol

Various lots of Tunisian rosemary oil distilled in 1938 had the following properties:

Month of Production	*Spec. Grav. at 15.5°*	*Optical Rotation*	*Refractive Index*	*Solubility*
January	0.907	+3° 18′	1.469	Soluble
February	0.909	+3° 12′	1.468	in 1–4
March	0.911	+3° 27′	1.467	vol. and
April	0.915	+2° 18′	1.469	more of
May	0.916	+4° 12′	1.467	80%
June	0.917	+5° 12′	1.471	alcohol
July	0.918	+4° 6′	1.470	
August	0.919	+2° 30′	1.471	
September	0.919	+3° 12′	1.470	
October	0.918	+2° 42′	1.469	
November	0.910	+3° 12′	1.468	
December	0.908	+3° 12′	1.469	

According to Trabaud,[12] the ester content (calculated as bornyl acetate) is highest (3.9 per cent) in spring and early summer, and lowest (1 per cent) in winter. In the opinion of the same author, the time of the harvest, as well as the state of the plants at the moment of distillation, has little effect on the physicochemical character of the oil. For example, an oil (*I*) distilled in February at the height of the flowering season and an oil (*II*) distilled in July when the plants were dry had these properties:

	I	*II*
Specific Gravity at 15°	0.9156	0.9136
Optical Rotation	+3° 04′	+2° 48′
Refractive Index at 20°	1.4683	1.4681

[12] *Drug Cosmetic Ind.* **44** (1939), 566.

	I	*II*
Acid Number	0.3	0.3
Ester Content	0.65%	0.65%
Total Alcohol Content, Calculated as Borneol	12.4%	11.65%
Solubility in 85% Alcohol	Soluble in 0.8 vol. and more	Soluble in 0.7 vol. and more
Solubility in 80% Alcohol	Soluble in 1.6 vol., turbid with more	Soluble in 1.3 vol., turbid with more

The odor of Tunisian rosemary oil is finer—less camphoraceous than that of the Spanish oil.

Shipments of Tunisian rosemary oil received and analyzed by Fritzsche Brothers, Inc., New York, had properties which varied within the following limits:

Specific Gravity at 25°/25°	0.911 to 0.912
Optical Rotation	Average +4° 15′
Refractive Index at 20°	Average 1.4693
Ester Content, Calculated as Bornyl Acetate	1.3 to 1.6%
Total Alcohol Content, Calculated as Borneol	Average 15%
Solubility at 25°	Clearly soluble in 1 vol. and more of 80% alcohol

The total borneol content of these oils was somewhat higher than that of Spanish, Dalmatian, and French oils. The odor was very fine.

Moroccan Rosemary Oil

Rosemary grows abundantly and wild in Eastern Morocco on the left banks of the Muluya River, especially around Midelt and Debdu. Distillation can be carried out all year round, and large quantities of oil could be produced, lack of water for distillation being the only obstacle in some regions.

During the author's visit to Morocco in 1937, this industry was in its infancy, but showed possibilities of considerable expansion (see also "Moroccan Thyme Oil").

Distillation of one charge of plant material (overground parts) in the field stills employed in Morocco lasts 3½ hr.; the yield of oil is said to range from 0.3 to 0.4 per cent.[18]

An oil (*I*) distilled under the author's supervision and another oil (*II*) examined in 1946 had the following properties:

[18] This seems rather low as compared with the yield obtained in Spain, Dalmatia, and other countries of production (the Author).

	I	*II*
Specific Gravity at 25°/25°	0.905	0.912
Optical Rotation at 20°	+0° 14′	+1° 6′
Refractive Index at 20°	1.4690	1.4660
Ester Content, Calculated as Bornyl Acetate	1.6%	2.0%
Total Alcohol Content, Calculated as Borneol	10.3%	10.1%
Solubility	Soluble in 1.5 vol. of 80% alcohol, turbid in 10 vol.	Soluble in 1 vol. of 80% alcohol, opalescent in 10 vol.

The solubility does not fully meet the requirement of the U.S.P. XIII (see also physicochemical properties of "Spanish Rosemary Oil"). The odor of the oils was excellent.

As has been said, the young Moroccan rosemary oil industry may some day develop into a serious competitor of Spain, many factors, such as abundance of plant material and low priced labor, being in its favor.

Russian Rosemary Oil

Rosemary oil has also been produced, at least experimentally, in the U.S.S.R.

Rutovski and Vinogradova [14] reported that such oils had entirely different properties according to the regions:

	I	*II*
	Oil from the Crimea	*Oil from the Caucasus*
d_{20}^{20}	0.8954	0.9364
α_D	−9° 20′	+3° 3′
n_D^{20}	1.4727	1.4735
Ester Number	7.68	19.45
Ester Number after Acetylation	35.5	77.77
Solubility	Soluble in 0.2 vol. of 90% alcohol	Soluble in 0.1 vol. of 90% alcohol

Italian Rosemary Oil

According to Fayaud,[15] rosemary grows abundantly on the Mediterranean (western) shore of the Italian mainland from Piombino to Rome, and on the Adriatic (eastern) shore in the provinces of Campobasso, Foggia, and Bari, furthermore on Sicily and Sardinia. The oils distilled on the western shore resemble those of Southern France; the oils from the eastern

[14] *Riechstoff Ind.* (1926), 219. *Ber. Schimmel & Co.* (1927), 91.
[15] *Parfumerie moderne* **32** (1938), 163.

provinces resemble those of Dalmatia, being characterized by a somewhat more camphoraceous odor.

The properties of oils distilled in the province of Grosseto (western coast) varied within the following limits:

Specific Gravity	0.894 to 0.915
Optical Rotation	−2° 0′ to +13° 0′ [16]
Refractive Index at 20°	1.465 to 1.470
Ester Number	5 to 20
Solubility	Soluble in 10 vol. of 80% alcohol, and in 1 vol. of 90% alcohol

The difference in the properties of Italian oils is probably the result of botanical variations of the plant material. (Cf. section on "Botany—Rosemary Oil.")

Oils produced on the Italian mainland, Sicily, or Sardinia have seldom been exported; they are consumed locally.

Chemical Composition and Use of Rosemary Oil

Chemical Composition.—To the author's knowledge no chemical investigation has ever been carried out on Spanish rosemary oil, but oils of Dalmatian, Italian, and French origin have been examined by various workers.

The following constituents have been identified in rosemary oil:

α-Pinene. Investigating an oil of own distillation (Dalmatian leaf material), Gildemeister and Stephan [17] found that α-pinene occurs in the fraction b. 156°–158°, probably as a mixture of the *d*- and *l*- form. Pinene was characterized through the preparation of its nitrolbenzylamine derivative m. 122°–123°.

Camphene. Treating the fraction b. 160°–162° with glacial acetic acid–sulfuric acid mixture and saponifying the product of reaction, the same authors obtained isoborneol m. 211°–212°. It was possible to reconvert isoborneol into camphene m. ~50°. The low rotation of the camphene fraction suggested that this compound is present in the oil as optically inactive camphene.

Olefinic Terpenes(?). Gildemeister and Stephan [18] also reported that rosemary oil probably contains some olefinic terpenes such as occur in oil of bay.

Cineole. Investigating an oil of Italian origin, Weber [19] isolated cineole from the fraction b. 176°–182° as dihydrochloride compound. Cineole was characterized by the preparation of dipentene tetrabromide m. 123.5°–124°, and of dipentene dihydroiodide m. 78.5°–79°.

According to Traetta and Papocchia,[20] Pellini and Morani,[21] and Puxeddu.[22] the cineole content of Italian rosemary oil ranges from 17 to 32 per cent.

[16] Original gives 130° (by error) (the Author).
[17] *Arch. Pharm.* **235** (1897), 586.
[18] *Ibid.*
[19] *Liebigs Ann.* **238** (1887), 89.
[20] *Ann. chim. applicata* **18** (1923), 326.
[21] *Ibid.*, **18** (1923), 97.
[22] *Ibid.*, **15** (1925), 170.

Dipentene(?). When conducting gaseous hydrogen chloride through an ethereal solution of the fraction b. 171°–176°, Weber, as mentioned, obtained dipentene dihydrochloride m. 49°–50°. This compound may have originated from cineole or from dipentene. Since the fraction b. 171°–176°, according to analysis, contained substantial quantities of terpenes, it is possible that the dihydrochloride was formed from dipentene.

Camphor. Observed in rosemary oil [23] first by Lallemand.[24] Later, de Montgolfier [52] showed that the camphor present in rosemary oil [26] consisted of a mixture of the *d*- and *l*- modification.

Pellini and Morani [27] reported that an oil distilled in Sicily contained about 17 per cent of camphor.

Rutovski and Vinogradova [28] found *l*-camphor m. 175°–176° in a rosemary oil from the Caucasus.

Borneol, Free and as Acetate. Borneol was first observed in French rosemary oil by Bruylants [29] who isolated it, together with camphor, from the higher boiling fractions. Gildemeister and Stephan [30] determined the borneol content of two oils by acetylation and found 16.8 per cent and 18.8 per cent, respectively. These authors, however, assumed that the oil contained no other alcohols, geraniol, or linaloöl, for example.

Borneol is present in rosemary oil in free form and as bornyl acetate (2–7 per cent).

Haller [31] suggested separating camphor from borneol by heating the mixture with succinic acid, and converting borneol into the acid succinic ester.

According to Haller, both camphor and borneol occur in rosemary oil [32] as a mixture of the two optical isomers.

A Sesquiterpene (Caryophyllene?). Haller also reported the occurrence, in the high boiling fractions, of a sesquiterpene, probably caryophyllene. This was characterized by the preparation of the nitrosochloride m. 165°–166°, and the nitrosate m. 156°.

Use.—Oil of rosemary serves in certain medicinal preparations and as an ingredient in rubefacient liniments.

The bulk of rosemary, however, is used for the scenting of soaps and technical products, and for the denaturing of alcohol. The oil is useful also in room sprays and inhalants.

Because of their somewhat harsher note and usually lower price, the Spanish and Moroccan oils lend themselves more advantageously to use in

[23] Origin of the oil not indicated in the original literature.
[24] *Liebigs Ann.* **114** (1860), 197.
[25] *Bull. soc. chim.* [2], **25** (1876), 17.
[26] Origin of the oil not indicated in the original literature.
[27] *Ann. chim. applicata* **13** (1923), 97.
[28] *Riechstoff Ind.* (1926), 219. *Parfums France* **6** (1928), 112.
[29] *J. pharm. chim.* [4], **29** (1879), 508. *Pharm. J.* [3], **10** (1879), 327. *Jahresber. Chem.* (1879), 944.
[30] *Arch. Pharm.* **235** (1897), 586.
[31] *Compt. rend.* **108** (1889), 1308. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 633.
[32] Origin of the oil not indicated in the original literature.

soaps and technical preparations, whereas the usually higher priced Dalmatian oil, with its finer, more delicate odor is preferred for the flavoring of all kinds of food products, meats, sausages, soups, table sauces, etc. The Dalmatian oil thus replaces the dried leaves as condiment. Selected lots of Tunisian and Spanish oils may be used for the same purpose.

Suggested Additional Literature

A. M. Burger, "Production of Rosmarin Oil in Dalmatia," *Riechstoff Ind.* **6** (1931), 169.

A. Fernandez Costa, "Essential Oil of *Rosmarinus officinalis*," *Noticias farm.* (Portugal) **5** (1939), 317. *Chem. Abstracts* **33** (1939), 7487.

M. G. Cancer, "Results of Distillation of Wild Plants from Calabria," *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi* **14** (1939), 147. *Chem. Zentr.* II (1940), 2825.

D. C. Grove, "Assay of Peppermint, Rosemary, and Sandalwood Oils," *J. Assocn. Official Agr. Chem.* **24** (1941), 465.

J. Jud, "Investigations Concerning the Drying of *Labiatae*," *Ber. schweiz. botan. Ges.* **50** (1940), 19. *Chem. Abstracts* **35** (1941), 6736.

L. Palfray, "Catalytic Hydrogenation with Recording of Temperature and Pressure. Application to Natural Esters and Essences," *Bull. soc. chim.* **7** (1940), 439. *Chem. Abstracts* **36** (1942), 2840.

Louis Girard, "Present Status of the Question of Concretes and Concrete Absolutes," *Ind. parfum.* **2** (1947), 183, 217, 257. *Chem. Abstracts* **41** (1947), 7671.

Lucien Trabaud, "Le Romarin. Production Mondiale, Caractères de l'Essence," *Ind. Parfum.* **3** (1948), 139.

OIL OF SAGE

Essence de Sauge *Aceite Esencial de Salvia de Dalmacia* *Salbeiöl*
Oleum Salviae

Botany.—*Salvia officinalis* L. is a hardy perennial low shrub or subshrub with a quadrangular branching stem, carrying opposite, decussate leaves, characteristic for all members of the *Labiatae* family. The leaves of *Salvia officinalis* are of grayish-green color, occasionally tinged with red or purple. The flowers are blue; the fruits consist of black nutlets, borne in open cups, the dry postfloral calyx.

The highly aromatic leaves, after drying, are widely employed for the seasoning of poultry stuffings, ground meats, soups, sausages, and canned

foods. The volatile oil, to which the plant owes its flavor and aroma, may be obtained by steam distilling the leaves.

Of the several types of *Salvia officinalis*—which differ from one another chiefly in size and color of their flowers and in flavor—that growing wild in Dalmatia possesses the finest and most characteristic aroma. The occurrence of a wide range of varieties, botanically not well distinguished, has been one of the main difficulties encountered in attempts to grow in the



Courtesy of Bureau of Plant Industry, Soils & Agricultural Engineering, United States Department of Agriculture.

Salvia officinalis.

United States a type of *Salvia officinalis* containing a volatile oil the odor and flavor of which is identical with that of the imported Dalmatian sage. Climatic and soil conditions, as well as methods of harvesting, contribute to the difficulties of producing the desired type of plants in the Western Hemisphere. In fact, among numerous samples of domestic sage oils, the author found only a few which were fully equal in odor quality to oils imported from Dalmatia. *Salvia leucophylla,*[1] which grows wild in California, contains a good percentage of camphor and cineole, and has a strong odor indicative of these constituents. However, if the leaves of *Salvia leucophylla* are ground and allowed to stand for a period of time, the odor of cineole and camphor fades, leaving a residual note suggestive of Dalmatian sage.

Aside from the different varieties of *Salvia officinalis,* there are several

[1] After Index Kewensis identical with *Audibertia nivea* Benth.

other species of *Salvia,* the leaves of which have sometimes been used as adulterants of imported Dalmatian sage; for instance, Spanish sage (*Salvia lavandulaefolia* Vahl.) and Greek sage (*Salvia triloba* L.) with its broader, thicker, shorter and more woolly leaves. The odor of these perennials resembles rosemary and spike lavender, with a harsh camphoraceous "by-note."

The so-called Cyprus sage, which originates from the island of Cyprus in the eastern Mediterranean, may be a form of *Salvia officinalis,* but is of inferior quality.

Dalmatian Sage Oil

Habitat and Range.—*Salvia officinalis* L., the true Dalmatian sage, grows spontaneously in the form of low bushes and tufts on the bold, rocky, barren and sunny hillsides of the Dalmatian Islands and adjacent coast of the Adriatic Sea. Before World II part of this island world belonged to Italy, part to Yugoslavia. Important producing centers are the island of Cherso and the island of Veglia (known in Yugoslavia as Krk). In San Martino di Cherso alone about 2,000 kg. of sage oil were produced annually in the years preceding World War II.

Harvesting.—The plants attain a height of 2 ft. Cutting is a rather tedious and delicate task, as not all leaves are desirable. If not cut properly, the plant is likely to perish; hence, harvesting machines are not employed.

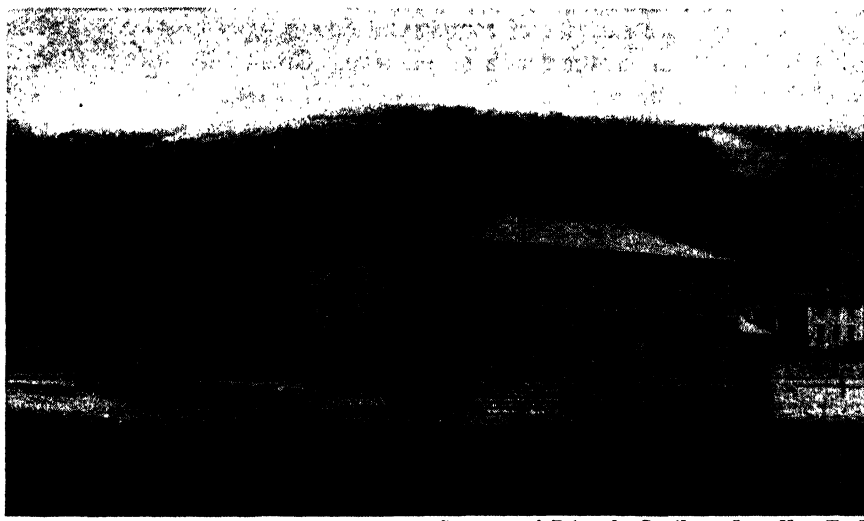
The Dubrovnik district produces the best type of aromatic sage plant. In that region harvesting starts early in June, as soon as the plants are large enough, and continues through the dry weather up to the beginning of September. Some shippers accept no sage leaves after the rains start. The harvesters, mostly women and children, collect the leaves by hand, like the tea pickers in Japan. Young plants that have not reached the flowering or seeding stage contain the largest amount of oil and the finest aroma. The leaves are placed on large canvas sheets, are thoroughly dried. and carefully stored in bags. The material is finally transported to Dubrovnik where some of the shippers have large warehouses. There the leaves are checked and assorted, to eliminate any foreign matter before the final packing for export. These precautions enable the exporters of Dubrovnik to ship the best quality of leaves.

In other districts of Dalmatia it is customary to cut the whole plants with small sickles and to dry them on the ground in the open. When dried, the tops are broken off, or the plants are stripped. This method, however, produces large amounts of stems and foreign matter, to which the U. S. Department of Agriculture objects.

Some of the collected plants are distilled locally for their essential oil, which in late years has increasingly replaced the leaves for the flavoring of packed food products. The bulk of the plant material is further dried, and the leaves are carefully removed and assorted into different grades for export.

Nine pounds of fresh leaves give about 2 lb. of dried leaves.

Distillation.—The production of sage oil is of comparatively recent date. Before 1914 not more than 300 to 500 kg. of sage oil per year were distilled



Courtesy of Fritzsche Brothers, Inc., New York.

An essential oil distillery in San Martino di Cherso, Dalmatia.

in San Martino di Cherso; most of this went to Germany and only very little directly to the United States. At that time sage oil was produced on an almost experimental basis by some of the larger progressive Dalmatian distillers. The intention then was to seek new oils, aside from the well-established rosemary oil. During World War I the main distillery in San Martino di Cherso was taken over by the Austro-Hungarian government, and the oil produced there (about 1,600 kg.) was used in field hospitals. After the war, particularly during 1921 and 1922, the market showed a greater interest in Dalmatian sage oil, essential oil houses in Germany purchasing about 1,500 kg. During 1927–1928 the United States started to buy this oil; exports from Dalmatia to the United States then reached about 5,000 kg., whereas the demand from Germany decreased considerably.

Since oil of sage requires careful distillation, it is now produced almost exclusively in well-equipped plants, and only a slight quantity in primitive

stills. Distillation of the dried plant material is carried out with live steam, a charge requiring about 1 hr.

Yield of Oil.—At the beginning of the harvest the yield of oil runs as high as 2.0 per cent, but it decreases toward the end of the harvest to about 0.7 per cent, the average yield being 1.4 per cent.

Three samples of official sage, when distilled by the Clevenger method, yielded 1.2, 1.1, and 1.3 per cent of volatile oil, according to a report of the American Pharmaceutical Association Laboratories.[2]

Youngken and Vander Wyk [3] obtained oil yields of 1.75, 1.50, and 1.64 per cent from three samples of commercial *Salvia officinalis* leaves, when using the Clevenger method with an oil trap. Greek sage leaves (*Salvia triloba*) yielded 2.37 per cent oil.

Clevenger [4] reported yields of 1.2 to 2.3 cc. of oil per 100 g. of Dalmatian sage leaves (*Salvia officinalis*), whereas Greek sage leaves (*Salvia triloba*) yielded 2.1 to 2.6 cc. of oil per 100 g. of leaves.

Physicochemical Properties.—Genuine Dalmatian sage oil has a strongly aromatic, somewhat spicy, odor and flavor. The quality of Dalmatian sage oil is determined mainly by its thujone content, a high percentage of thujone indicating a good quality. By evaluating the oil according to thujone content, the trade distinguishes between two types of Dalmatian sage oil, viz., the so-called "high test oils" and the "low test oils."

Genuine Dalmatian sage oils imported by Fritzsche Brothers, Inc., and analyzed in their New York laboratories had properties which varied within these limits:

	A. "High Test Oils"	*B. "Low Test Oils"*
Specific Gravity at 15°/15°....	0.915 to 0.923	0.921 to 0.927
Optical Rotation.....	+8° 10′ to +28° 56′	+4° 0′ to +11° 42′
Refractive Index at 20°.....	1.4571 to 1.4639	1.4647 to 1.4680
Ester Content, Calculated as Bornyl Acetate	1.6 to 4%, in one case 6.2%	2.2 to 4.9%
Total Alcohol Content, Calculated as Borneol.....	6.9 to 16.0%	11.6 to 15.0%
Ketone Content, Calculated as Thujone (Hydroxylamine Hydrochloride Method).....	41.6 to 61.2%	22.0 to 39.7%
Solubility.....	Clear to turbid in 3.5 to 8.5 vol. and more of 70% alcohol. Occasional oils not clearly soluble in 10 vol. of 70% alcohol	Clear to turbid in 7.5 to 10 vol. of 70% alcohol

[2] *Bull. Natl. Formulary Comm.* **8** (1939), 93.
[3] *Ibid.* **7** (1939), 273.
[4] *J. Assocn. Off. Agr. Chem.* **22** (1939), No. 3, 683.

An Italian oil of *Salvia officinalis* described by Morani [5] had the following properties:

Specific Gravity at 15°	0.91948
Optical Rotation at 25°	−11° 38′
Refractive Index at 15°	1.4758
Ester Content, Calculated as Bornyl Acetate	2.51%
Total Alcohol Content, Calculated as Borneol	13.04%
Solubility	Soluble in 9.5 vol. of 80% alcohol

This oil was distilled from *Salvia officinalis* grown in the littoral (Italian) regions of the Mediterranean. Like the type of oil from the eastern shores of the Mediterranean attributed to *Salvia triloba*, the oil investigated by Morani was laevorotatory and thus differed from the regular oil of *Salvia officinalis* produced in Dalmatia.

According to the same author,[6] the oil consisted of:

	Per Cent
Terpenes	15.0
Ketones (α-Thujone and *dl*-Camphor)	31.5
Cineole	15.0
Free Alcohols (*l*-Borneol and Probably *dl*-Borneol)	11.2
Esters	2.3
Sesquiterpenes	20.0

Morani [7] furthermore showed that the chemical composition of sage oil exhibits marked differences according to whether the oil is obtained in spring and summer from the flower heads alone or from the whole flowering plant, or in winter from the nonflowering plant.

The oils contained:

	Distilled from Whole Flowering Plant in Summer (%)	*Distilled from Whole Nonflowering Plant in Winter* (%)
Cineole	32.0 to 35.0	13.0 to 20.0
Sesquiterpenes	About 30.0	About 20.0
Borneol	9.0 to 14.0	7.5 to 12.0
Camphor and Thujone	5.0 to 10.0	20.0 to 32.0
Terpenes	?	About 15.0
Esters	2.0	2.2 to 3.7

[5] *Rivista ital. essenze profumi* **10** (1928), 99, 125. *Ber. Schimmel & Co.* (1929), 83. Cf. *Nuovi Ann. Agr.* **7** (1928), 25. *Chem. Abstracts* **24** (1930), 2235.

[6] *Ibid.*

[7] *Ibid.*

If Morani's findings are correct, the winter oil is of higher quality than the summer oil, thujone being the most important constituent of sage oil and largely responsible for its characteristic odor and flavor.

According to Clevenger,[8] the oil distilled from true *Salvia officinalis* L. is distinguished by its dextrorotation, whereas the oil from Greek sage (*Salvia triloba*) is laevorotatory (−4° 6′ to −21° 0′).

The laevorotation of oil of *Salvia triloba* was confirmed by Luisi [9] who reported these properties for an oil distilled in Sicily:

Specific Gravity at 16.5°	0.9123
Optical Rotation	−12° 0′
Refractive Index at 18°	1.4735
Ester Content, Calculated as Bornyl Acetate	3.55%
Total Alcohol Content, Calculated as Borneol	15.65%
Ketone Content (as $C_{10}H_{16}O$)	9.95%
Cineole Content	25.0%
Solubility	Soluble in 1 vol. of 80% alcohol

Chemical Composition.—The following compounds have been identified in Dalmatian sage oil:

Salvene $C_{10}H_{18}$. A hydrocarbon b. 142°–145°, d_{20} 0.800, α_D −1° 40′, n_D 1.4438, was obtained from the foreruns of sage oil after repeated distillation over metallic sodium and called "salvene" by Seyler.[10] These first fractions consisted of 1 to 2 per cent of the total oil and boiled below 155° at 760 mm. Oxidation of salvene with potassium permanganate yielded almost quantitatively an acid, probably β-tanaceto ketonic acid (β-thuja ketonic acid), the semicarbazone of which melted at 204°. Salvene is probably a dihydrotanacetene.

Seyler postulated for his "salvene" a formula which is now known to be that of *thujane*. The actual constitution of "salvene," therefore, remains doubtful.

d-α-Pinene. Wallach [11] converted the fraction b. 156°–158° into dipentene (tetrabromide m. 124°–125°), and the nitrosyl chloride compound of the fraction into nitrosopinene m. 130°,[12] thereby identifying the hydrocarbon in question as *d*-α-pinene. It seems that pinene occurs in sage oils as a mixture of the two optical isomers, one or the other predominating.

Cineole. Isolated as hydrobromide from the fractions b. 174°–178° by Wallach.[13]

d-β-Thujone. Identified as semicarbazone m. 174° by Wallach.[14]
and

l-α-Thujone. Identified as semicarbazone m. 186° by Wallach.[15]

[8] *J. Assocn. Off. Agr. Chem.* **22** (1939), No. 3, 683.
[9] *Boll. sta. sper. ind. essenze* **6** (1931), 110. *Chem. Abstracts* **26** (1932), 1707.
[10] *Ber.* **35** (1902), 550.
[11] *Liebigs Ann.* **227** (1885), 289.
[12] *Ibid.* **252** (1889), 103.
[13] *Ibid.*
[14] *Ibid.* **336** (1904), 270.
[15] *Ibid.*

Thujone is the main constituent of Dalmatian sage oil. Isolated from the fraction b. 198°–203°, it was originally called salviol by Muir and Sugiura.[16] Semmler [17] thought that salviol might be identical with thujone or tanacetone. The Schimmel chemists [18] showed that the corresponding compounds isolated with bisulfite from oil of sage, thuja, tansy, and wormwood are identical. Wallach [19] obtained the same derivatives from thujone, tanacetone, salviol, or absinthol and thereby proved that these compounds are actually identical.

Borneol. Acetylizing the fractions b. 205°–215°, Schimmel and Co.[20] found that they contained about 8 per cent of an alcohol possessing the empirical molecular formula $C_{10}H_{18}O$. Treatment with benzoyl chloride and saponification of the benzoic ester yielded a compound resembling borneol m. 204°, $[\alpha]_D$ +0° 23′ (in 10 per cent alcoholic solution).

d-Camphor. Oxime m. 118°. Aside from borneol, the Schimmel chemists [21] later identified *d*-camphor in sage oil. An even larger quantity of *d*-camphor is present in the oil obtained by cohobating the distillation waters.

Oleoresin Sage.—After steam distillation, the residual plant material still contains some nonvolatile constituents of considerable flavor value. Therefore, the plants are sometimes extracted with hot water after steam distillation, and the aqueous extracts are concentrated. About 20 per cent of concentrated extract is thus obtained, calculated upon the plant material. This oleoresin may be used in conjunction with the corresponding essential oil in the flavoring of all kinds of food products.

Adulteration.—The most common adulterant of Dalmatian sage oil is thujone, which can be isolated from the much lower priced American cedar leaf oil (*Juniperus virginiana* L.). Since thujone is also the main constituent of Dalmatian sage oil, such additions are difficult to prove by mere routine analysis.

Use.—The volatile oil of *Salvia officinalis* L. is employed as a convulsant, resembling in its action oil of wormwood but less powerful.

The bulk of sage oil, however, is used for the flavoring of table sauces, of canned and packed foods, soups, meats, and especially sausages, thereby replacing the bulkier and less uniform dried leaves.

Today, Dalmatian sage oil is one of the most important flavoring oils.

American Sage Oil

Introduction.—During the years of World War II, the Western Hemisphere was completely cut off from its former supply of dried sage leaves

[16] *J. Chem. Soc.* **37** (1880), 678.
[17] *Ber.* **25** (1892), 3350; **27** (1894), 895.
[18] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 694.
[19] *Liebigs Ann.* **286** (1895), 93.
[20] *Ber. Schimmel & Co.*, October (1895), 40.
[21] *Ibid.*, October (1907), 82.

and sage oil in Dalmatia. Since these products have always been important ingredients in the flavoring of all kinds of foods, especially packed meats and sausages, considerable efforts were made during World War II to cultivate the true *Salvia officinalis* in various parts of the United States. In general, sage is comparatively easy to grow, except in very dry and warm regions; and once established it persists for several years. Many attempts to this effect ended in failure as the odor and flavor of the domestically grown herb was usually quite inferior to the product formerly imported from Dalmatia. Owing to the pioneer work of the United States Department of Agriculture, some growers finally succeeded in producing an excellent quality of true sage (*Salvia officinalis*) which in flavor and appearance is quite equal to the Dalmatian product. However, cost of production in the United States is high, and, therefore, the dried leaves have found their way mainly into the meat packing houses for flavoring purposes and cannot be used for oil distillation except on a small scale.

Producing Regions.—According to Crooks and Sievers,[22] sage withstands winter temperatures down to 0° F., and even below, provided some protection is offered by snow or a covering of leaves or straw. Temperature and rainfall in the cornbelt states are more or less ideal for sage culture. Regions with high summer temperatures and long dry periods are not conducive to good growth and a good quality of sage. Even in cold, moist regions of the northern United States, where winters are severe enough to winterkill, sage may be grown as an annual, although profits from such a crop would be doubtful, even with unusually high prices.

Sage grows well in the regions from Wisconsin south to central Georgia, and throughout the eastern coastal states. In the extreme northern parts of the United States, especially where the land is not well drained, too much winterkilling occurs for sage to become a perennial crop. An excessively hot, dry climate usually develops a product of inferior quality.

Salvia officinalis is now being grown mainly in the State of Washington, near Wapato, and on the sloping hills along the coast of the Pacific southwest, especially around Tarzana, California, where conditions of soil and climate are similar to those in Dalmatia. As the work involves a great deal of hand labor, Mexicans are employed.

Soil.—Sage grows in a wide range of fertile soils, provided they are well drained and sufficiently supplied with nitrogen. The best soil, however, is a rich, clayey loam. The plant does not thrive so well on a very light, sandy soil, as the earth is easily splashed to the lower leaves by rain. The leaves are covered by a layer of very fine hair, in which the sand is retained to such an extent that the product may be unsuited for market.

[22] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 31.

Good drainage is very important if sage is cultivated as a perennial. An abnormal amount of moisture in the soil during freezing weather results in excessive winterkilling in the cold climate of the northern states.

Planting, Cultivating, and Harvesting.—Stockberger [23] recommends that for cultivation on a large scale the seeds be sown in early spring, in rows from 2 to 3 ft. apart. When well up, the plants are thinned to stand about 12 in. distant in rows. Seedling plants have a tendency to produce narrow leaves; hence, the broad-leafed varieties, which do not flower readily, are said to be the most desirable as they give a larger yield of leaves. Since the plants rarely set seed, they are usually grown from cuttings, which may be obtained from seed houses having their own propagating gardens. Cuttings set as early in the spring as weather conditions will permit, usually give a large crop. In the north, the plants should be protected in winter by a mulch of manure. Sage may also be grown as a second crop, after early vegetables.

A fair crop of leaves may be harvested the first season, and much larger ones for five or six years following. Only one picking should be made the first year, after which two or three pickings may be made in a season, provided climate and weather permit the plants to survive. If a product of fine quality is desired, the leaves are picked by hand and dried in the shade; drying in the sun is not recommended. Sage leaves are apt to turn black while drying; therefore, the moisture must be removed continually until they are fully dried. A cheap grade may be obtained at lower cost by cutting the plants with a mower, the cutter bar of which is set high enough to exclude woody stems. The dried herb should be marketed promptly, since it loses flavor strength rapidly with age.

According to Sievers,[24] the growing of sage from seed usually results in a mixture, as *Salvia officinalis* occurs in a wide range of types. The Bureau of Plant Industry Station in Beltsville succeeded in selecting from an experimental crop of seedlings a number of types which had a very good flavor, whereas others were suggestive of camphor or turpentine. Thus, the proper way to grow sage, if a uniform and good quality is desired, is to make cuttings from a desirable type and eliminate thereafter all other forms found among the seedlings.

Dafert and Mauerer [25] planted *Salvia officinalis* on a fertile, humus-poor, loess-loam soil, in which the plants were spaced at intervals of 25, 30, 40, and 45 cm. In the first crop, the yield of plants decreased with increase of spacing, probably because of the decrease of shading effect upon

[23] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935), 31.
[24] Private communication from Mr. A. F. Sievers, *U. S. Dept. Agr.*, Beltsville, Maryland
[25] *Z. landw. Versuchw.* **26** (1923), 101. *Chem. Abstracts* **18** (1924), 2784.

the young vegetation. In the second crop, while the plant yield per individual was greater with the wider spacing, the yield per unit of area was less; the closest spacing gave the highest oil content.

Crooks and Sievers [26] recommend planting sage in rows 2 to 3 ft. apart, the plants spaced 6 to 12 in. in the rows. Seeding may be direct to the field, or the plants may be started in coldframes or greenhouses and transplanted in the early spring. The cost and availability of the seed and the importance of getting a maximum crop the first year are determining factors in deciding upon the method to be used. If sown directly in the field, the seed should be planted about ¾ in. deep in the early spring, as soon as the ground is warm enough for germination. The plants are later thinned to the desired spacing. The first year crop, by this method, would be very light. By sowing the seed in a coldframe or hotbed, the seedlings could be transplanted to the field by hand, or set by an ordinary transplanting machine, such as is used for tobacco or any vegetable crop. One pound of good viable seed, grown in a coldframe, should produce from 12,000 to 20,000 seedlings, which are sufficient to plant an acre with ordinary spacing. Cultivation should be light and thorough; weeds should be kept from the field because the final, dried product must be free of any foreign matter that might give an undesirable flavor.

Only the leaves and small stems of the sage plant are prepared for market, either by handpicking, or by cutting with a mower and stripping the leaves from the stem. Both methods involve considerable hand labor, but it seems likely that cutting with a mower and then hand stripping to remove the dried stems would prove much more economical from the standpoint of labor involved.

Investigating the drying of *Labiatae*, Jud [27] came to the conclusion that drying in direct sunlight may cause a loss of essential oil as high as 24 per cent, shade drying loses from 2 to 10 per cent of oil. A temperature of 25°–30° may be considered best, both for preventing undue loss of oil, and for giving a product of good appearance. Shed drying in a common tobacco drying barn is advisable. The drying may be hastened by a slow fire.

According to The Herb Society of America,[28] sage will grow on a wide range of soils, heavy moist soil producing greater yields but leaves of somewhat inferior flavor. High gravelly soils tend to produce a high quality leaf, but are not recommended for direct seeding. Divisions and transplants, however, will take hold and thrive on gravelly soils. Sage very

[26] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 31.
[27] *Ber. Schweiz. botan. Ges.* **50** (1940), 19. *Chem. Abstracts* **35** (1941), 6736.
[28] *Sage Rept., Bull.* No. 4 (1943), Boston, Mass. Cf. Snyder, "The Americanization of the Sage Crop," *Spice Mill* **68**, No. 3 (1945), 38.

conceivably could be grown on side hill pasture land that is grazed by cattle or sheep, thus offering additional revenue for marginal land.

If planted from seed, direct seeding in the field is the least expensive. New turned sod or weed infested land should be avoided. A 12-hr. soaking of seed hastens germination. It is advisable to mix a few quick germinating seeds with sage, e.g., radish, for definition of rows and early cultivation. Thinning of plants to one per foot is advisable by the second year. Once the plant is established and additional acreage desired, division of plants will yield quicker and larger crops.

If a high quality leaf is desired, within the range of high yield, past tests indicate the following: a pH range of 6.2 to 6.4—acid phosphate at the rate of 500 lb. to the acre with a side dressing of hen manure, 1 ton per acre; horse manure, 1½ tons; cow manure, 3 tons to the acre. If these forms of manure are not available, a 5-10-5 commercial fertilizer at the rate of 700 lb. to the acre can be used. This commercial fertilizer should preferably derive at least ½ of its nitrogen from organic sources.

Cultivation is necessary and desirable for first year seedlings. If weeds can be subjugated the first year, one thorough early cultivation on two-year and older plants should be sufficient, provided a good heavy mulch can be applied afterward to discourage weed growth and conserve moisture.

If machines are to be used for harvesting, the plants necessarily must be kept at a low growth, which can be done by frequent cuttings.

Hand shearing, however, allows for a better selection of tip growth and less woodiness in the final product. As was pointed out in the 1942 Sage Report of The Herb Society of America, the gray tip growth gives the best quality leaf, and appears after the blossom period is over. Although there has been a tendency by the buyers to accept the inferior lower growth along with tip growth, such will not be the case when the war shortages are relieved and more attention is paid to quality leaf.

As to how late in the season it is possible to cut without plant injury, or how close to the ground the plants may be cut before going into the winter: these factors do not seem to make too much difference. However, a hard freeze will destroy the qualities of aroma and taste of the leaf, and the plant should have at least 6 in. of growth left above ground.

Sage will withstand average winter conditions, 15° F. below zero, but will be subjected to winterkill when the temperature goes below 15° below zero, or when the plants are continually exposed to cold winter winds. Even after winter dieback, the sage plant shows a remarkable ability to recuperate and, in the event of winter dieback, should be pruned to within 4 in. of the ground.

Yield.—According to Crooks and Sievers,[29] the yield in the first year is affected by many factors, although approximately 200 to 600 lb. of dried sage leaves per acre may be expected. Much would depend upon getting good seedlings planted early in the spring and upon favorable growing conditions in the early part of the season. Under advantageous conditions, the second year should yield from 1,500 to 2,000 lb. by making 2 or 3 cuttings of the crop.

According to Stockberger,[30] returns from experimental areas indicate that with a good soil a yield of 2,000 lb. or more of dried tops per acre may be expected. In case leaves only are harvested, the yield will be proportionately less.

Consideration of U. S. Production.—Much has been said and written, during World War II, in favor of growing sage as a highly remunerative domestic crop. Crooks and Sievers[31] give an unbiased and interesting account of the pros and cons which must be considered before starting on any such venture.

The following aspects favor domestic sage production:

1. Considerable cash income could be realized by American farmers if the 1,500,000 lb. of sage consumed yearly in this country were all produced here. Approximately 1,500 acres would be required. To this must be added another 500,000 to 600,000 lb. of sage which formerly entered the United States as distilled oil.
2. With high prices and good growing conditions, it should be possible to realize some profit from the first year's crop in addition to defraying the cost of establishing the crop.
3. Small meat packing houses throughout the country are usually interested in the local production of sage and would probably take a supply, even at a price somewhat higher than that for which foreign sage could be delivered in times of normal trade.
4. Sufficient acreage is available for the production of a domestic crop.
5. Sage can be grown in connection with some other crops, such as tobacco, and possibly hops, in order to make use of equipment now at hand, thus reducing the need of a large immediate investment. This equipment would consist largely of hotbeds, transplanting machinery, and some form of drying barns or sheds.
6. Under ordinary conditions, sage is a hardy plant, and probably would not be seriously affected by disease or insect enemies.

[29] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 31.
[30] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935), 31.
[31] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 31.

Opposed to these favorable factors are some which tend to limit the domestic production of sage:

1. Sage, grown as a crop, involves a considerable amount of hand labor. Unless low-priced labor can be obtained, it is likely that the cost of growing and harvesting domestic sage would be far higher than the price ordinarily paid for imported sage. The nature of this crop makes complete harvesting by machinery unlikely. Also, small, widely scattered plantings hinder the development and use of economical labor-saving machinery.

2. There exist many varieties of sage. Their identity is not well established and great variations occur, even within a single variety. This condition has resulted in the offer of products which lack uniformity, and which are undesirable in regard to odor and flavor. In fact, some discrimination against certain types of domestic sage has developed.

Physicochemical Properties of American Sage Oil.—The numerous samples distilled experimentally in the laboratories of Fritzsche Brothers, Inc., from all kinds of so-called American sage plants did not come up to the standard of Dalmatian oils and, therefore, need no further description.

Three oils of good quality, however, were distilled from plant material grown near Wapato in the State of Washington. The yield of oil ranged from 0.6 to 1.0 per cent. The oils had the following properties:

	I	*II*	*III*
Specific Gravity at 15°	0.922	0.926	0.925
Optical Rotation	+4° 28′	+4° 56′	+4° 30′
Refractive Index at 20°	1.4699	1.4637	1.4650
Ester Content, Calculated as Bornyl Acetate	4.3%	3.3%	6.0%
Total Alcohol Content, Calculated as Borneol	13.0%	...	...
Ketone Content, Calculated as Thujone (Hydroxylamine Hydrochloride Method)	35.4%	46.6%	46.7
Solubility	Soluble in 1 vol. and more of 80% alcohol	Soluble in 1 vol. and more of 80% alcohol	Soluble in 5.5 vol. and more of 70% alcohol

The odor and flavor of these oils compared favorably with that of the Dalmatian product.

Suggested Additional Literature

F. Berger, "Sage Leaves," *Pharm. Zentralhalle* **84** (1943), 203. *Chem. Abstracts* **38** (1944), 5043.

J. Small, "Sage," *Food* **13** (1944), 43. *Chem. Abstracts* **38** (1944), 1809.

F. Caujolle and F. Franck, "Pharmacodynamic Actions of Essential Oils of Clary Sage (*Salvia sclarea* L.) and Condiment Sage (*S. officinalis* L.)," *Compt. rend. soc. biol.* **139** (1945), 1109. *Chem. Abstracts* **40** (1946), 7390.

Heber W. Youngken and E. Warren Heaps, Jr., "Studies on the Leaf of *Salvia leucophylla*," *J. Am. Pharm. Assocn.* **37** (1948), 284.

OIL OF CLARY SAGE

Essence de Sauge Sclarée *Aceite Esencial de Salvia Moscatel*
Muskateller Salbeiöl *Oleum Salviae Sclareae*

Salvia sclarea L., a perennial native to Mediterranean countries, grows wild in Southern France, North Africa, parts of Italy, and also on the Crimean peninsula in the U.S.S.R. Years ago it was occasionally planted in the vineyards of Germany, where it has now turned wild. The green parts of the plant, and especially the flowering tops, contain an essential oil of delightful odor, somewhat wine-like and reminiscent of ambergris. The German term "Muskateller salbei" probably arose from this resemblance to wine. The oil can be isolated by steam distillation of the flowering tops and leaves of the plant or by extraction with volatile solvents.

For the production of oil, clary sage is now chiefly cultivated, the wild growing plants being too scattered for collection, except during periods of great demand and high prices. For years Southern France was the principal supplier of this oil, but about 1932 the U.S.S.R. appeared on the market with very large offerings and such low prices that the French producers were practically driven out of business. Experiments in growing clary sage have been conducted successfully in Calabria, in Roumania, in England, and in the United States (Puget Sound). Limited quantities of oil are also produced in Hungary. The principal supplier of clary sage oil at present is the U.S.S.R., the oil being distilled in the Crimea and probably in the Ukraine. Southern France still continues to produce a very high-quality oil, superior to the Russian.

French Clary Sage Oil

Producing Regions.—Oil of clary sage is produced principally in the South of France, viz., in the Départements of Alpes-Maritimes (near Grasse, Pégomas, Vence), Basses-Alpes (near Barrême, Valensole), Drôme, Vau-

cluse, and Bouches-du-Rhône. The most important region is in the Département of Var (near Montauroux, Fayance, Seillans, Bargemon, Figamières, and Lorgues).



Courtesy of M. Pierre Chauvet, Seillans (Var), France.
A clary sage plant.

Range and Habitat.—Clary sage prefers a dry calcareous soil, high elevations with ample sunshine, and a few good rain showers in spring. Under those conditions the plant gives the best yield of oil and an oil of superior quality. Rich, moist, or irrigated alluvial soil in the lowlands develops tall plants with much stalk and relatively little flower material, and hence a low yield of oil.

Planting, Cultivating, and Harvesting.—Most of the clary sage plantations of Southern France are small, patch plantings, so to speak, undertaken by individual farmer-producers.

The seed is planted in a nursery, usually during spring; in the following fall the seedlings are set out 2 ft. apart, in rows 2 ft. distant. The planting should be well exposed to sunshine. The elevations and the calcareous soil on which lavender thrives are well suited also for clary sage. There it develops two to three times as much essential oil as on rich alluvial soil in low altitudes. Fertilization is not necessary. Deel and Deel [1] recommended a soil with a pH of about 4.5. Simple cultivating and two or three hoeings per year are sufficient. The following summer yields a small harvest, the next summer a full one, amounting to about 5,000 kg. of plant material per hectare.

A planting in rich soil does not last more than two to three years; a planting in poor, dry soil sometimes lasts five to six years, giving a normal yield up to the last year. From then on the yield falls off rapidly, and a new plantation must be started in a different locality.

The harvesting takes place in July, or sometimes in the beginning of August, during the late flowering period. The plants are cut with sickles, like lavender. The farmers selling their harvest (by weight) to the distillers tend to cut as low as possible, thereby including much woody stalk material which contains no essential oil. The distillers, on the other hand, prefer to purchase only the flowering parts.

In years of exceptionally good weather a second harvest can be obtained in October, but it gives an inferior yield of plants and essential oil. The growers located near Grasse sell their plant material to the large distilleries in that town, whereas those in more remote regions usually do their own distilling in the type of stills employed also for lavender.

Distillation.—Clary sage should be distilled fresh; otherwise a considerable amount of volatile oil is lost by evaporation, or (more likely) by resinification. In a modern distillery, live steam from a separate steam boiler is injected, for about an hour or longer, into stills of 500 liters capacity charged with 100 kg. of plant material. The process is completed when about 500 liters of distillation water (plus the essential oil) have distilled over. The woody stalks should be cut off prior to distillation, as the distilling of only the flowering tops and leaves saves considerable steam. Distillation must not be stopped prematurely, for the high boiling last runs contribute greatly to the quality of the oil.

Yield of Oil.—The yield of clary sage oil is subject to wide fluctuations. It depends upon climatic and weather conditions, the location and soil of

[1] *Bull. soc. chim.* [4], **39** (1926), 946.

the planting, and the condition of the plant material, i.e., its degree of dryness, the preponderance of woody stalks or leaves and flowering tops, etc.

In southern France, for instance, the author obtained 0.15 per cent of oil from plants which came from poor ground in high altitudes (Barrême, B.A.), but only 0.07 per cent from plants which originated from fertile soil in low altitudes (Pégomas, A.M.). Distillation of material from the same planting in 1930 yielded 0.10 per cent, in 1931 0.14 per cent of oil.

Chiris [2] found that the oil content of cultivated plants increases as they mature, attaining a maximum (0.12 to 0.15 per cent) from the period of flower withering to that of seed ripening.

According to the same source the flowering tops contain much more oil than the stalks and green leaves.

Experimenting with cultivated Roumanian clary sage, Kopp [3] found:

	Per Cent
Oil in the Flowering Tops	0.15
Oil in the Entire Overground Parts	0.017
Oil in the Leaves	0.0021
Oil in the Dried Flowering Tops and Leaves	0.14
Oil in the Chaff and Stalks after Removing the Seed	0.18–0.28

According to the author's own experience, clary sage should be cut during the late flowering period; it should be distilled as fresh as possible and after removal of excessive stalk growth.

Physicochemical Properties.—Genuine French clary sage oils analyzed in the New York laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 15°/15°	0.900 to 0.910
Optical Rotation	−11° 22′ to −32° 38′
Refractive Index	1.4613 to 1.4700
Ester Content, Calculated as Linalyl Acetate	54.0 to 70.2%
Evaporation Residue	5.3 to 13.1% (one lot as low as 1.6%)
Solubility	Soluble in some cases in 1 vol. of 80% alcohol, opalescent with more. In most cases, however, soluble in 0.5 vol. of 90% alcohol, clear to turbid with more

A high-grade clary sage oil is characterized by a typical odor reminiscent of ambergris, especially during the last stages of evaporation. Such oils possess a high evaporation residue, a high specific gravity, and a high laevorotation. Oils possessing a low optical rotation and a low evapora-

[2] *Parfums France* **7** (1929), 149.
[3] *Pharm. Zentralhalle* **69** (1928), 677.

tion residue usually exhibit a better solubility than the high-grade oils. In other words, a good clary sage oil is not very soluble.

Chiris [4] examined two oils of clary sage, one distilled from the flowering tops, the other from the whole overground parts.

	Oil from the Flowering Tops	*Oil from the Overground Parts*
Specific Gravity at 15°	0.9275	0.9335
Optical Rotation at 24°	−23° 36′	−42° 4′
Acid Number	2.24	1.68
Ester Content, Calculated as Linalyl Acetate	66.64%	42.63%

The oil distilled from the stalks and fresh leaves had the most characteristic clary sage odor and contained a strongly laevorotatory compound of high specific gravity. The oil distilled exclusively from the flowers had a higher ester content than that distilled from the whole plants.

Igolen [5] examined oils distilled from clary sage grown on dry soil in Argeville (Southern France) and reported the following properties:

Specific Gravity at 15°	0.8975 to 0.9110
Optical Rotation	−7° 0′ to −20° 0′, in most cases −8° 18′ to −11° 0′
Refractive Index at 20°	1.4648 to 1.4658
Ester Content, Calculated as Linalyl Acetate	49.0 to 67.9%
Ester Number, after Cold Formylation	238.9 to 259.7
Solubility	Mostly soluble in 3.0 to 5.0 vol. of 70% alcohol, turbid with more

These figures differ from those indicated in literature, especially in regard to optical rotation and solubility.

Russian Clary Sage Oil

About 1932 the U.S.S.R. suddenly offered large quantities of clary sage oil on the market. When the supply was found to exceed the demand, Amtorg Trading Corporation, New York, the official representatives of the U.S.S.R., substantially reduced the price of the oil, hoping to stimulate consumption. This, however, did not take place, the demand of clary sage oil being limited even at low cost. The principal effect of this policy was a

[4] *Parfums France* **7** (1929), 149.
[5] *Ibid.* **12** (1934), 34.

reduced production of the French oil, which no longer could compete with the Russian product.

Since then the U.S.S.R. has been regularly shipping clary sage oil to the United States. Comparatively little is known about the regions of production in the U.S.S.R., except that *Salvia sclarea* grows wild on the Crimean peninsula and is also planted in Southern Russia.

Gunko [6] experimented with Russian clary sage and reported that the oil yield, calculated upon dried plant material, changes according to period of harvest:

	Per Cent
Dropping of the Flowers	0.30
Ripening of the Seed	0.41
Complete Maturity of Seed	0.48
Dropping of the Seed	0.19

According to Strepkov,[7] the volatile oil contained in the racemes (inflorescence) of *Salvia sclarea* upon drying in the shade decreases after 3 hr. to 67.0 per cent, after 6 hr. to 45.1 per cent and after one month to 37.7 per cent of the original oil content. Drying in the sun causes a decrease of the volatile oil to 46.4 per cent in 3 hr. and to 38.0 per cent in 6 hr. The oil in the leaves first decreases while drying in the shade, but after ten days increases to a maximum, and after two months falls to a minimum of 63.0 per cent. During the drying process the quantity of free acids and esters and the specific gravity of the oil increase.

During the development of the plant, the maximum oil content of the racemes is attained by the end of the blossom period, and then abruptly decreases (in the lactic maturity of the seeds). The oil content varies during the course of day and night, reaching a maximum about midnight and a minimum in the early afternoon. The formation of free acids during the period from beginning of blossom to full development appears to coincide with the formation of volatile oil. The curves of the acid number have two minima and two maxima in the state of lactic and beginning of growth maturity of the seeds; the curve represents a reflection of the curve of the volatile oil number.

Gaponenkov [8] reported that the oil is contained largely in the flowers, the least quantity being in the stalks. During the second year the plants reached a maximum oil content toward the end of the flowering period (0.305 and 0.335 per cent yield). The ester content of these oils, calculated

[6] Mem. of the 3rd Convention of the Botanists of the U.S.S.R. (1928). *Bull. Applied Botany, Genetics & Plant Breeding* **21** (1928–1929), 343. *Ber. Schimmel & Co.* (1930), 57.

[7] *Botan. Arch.* **39** (1938), 166. Through *Chem. Abstracts* **33** (1939), 315.

[8] *Sovietskaya Pharmacya* **6** (1935), 31, No. 4. *Ber. Schimmel & Co.* (1936), 46.

as linalyl acetate, was 58.09 and 77.00 per cent. In the third year the plants attained a maximum oil content at full seed maturity (0.396 and 0.410 per cent yield); the oil had then an ester content of 61.29 per cent.

Physicochemical Properties.—Two lots of genuine Russian clary sage oil examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

	I	*II*
Specific Gravity at 15°/15°	0.900	0.903
Optical Rotation	−11° 22′	−15° 20′
Refractive Index at 20°	1.4573	1.4612
Ester Content, Calculated as Linalyl Acetate	71.2%	65.7%
Evaporation Residue	1.6%	6.4%
Solubility	Soluble in 3 vol. and more of 70% alcohol	Soluble in 1 vol. of 80% alcohol, turbid with more

Two Russian clary sage oils examined by Schimmel & Co.[9] had the following properties:

	I	*II*
Specific Gravity at 15°	0.9066	0.8916
Optical Rotation	−21° 40′	−24° 21′
Refractive Index at 20°	1.46737	1.47348
Ester Content, Calculated as Linalyl Acetate	60.4%	29.1%
Solubility	Soluble in 1.4 vol. of 80% alcohol, turbid with more	Soluble in 1 vol. of 80% alcohol, turbid with more

An oil distilled on the Crimean peninsula was described by Rutovski and Gusseva:[10]

Specific Gravity at 20°/20°	0.9249
Optical Rotation	−10° 15′
Refractive Index at 20°	1.4719
Acid Number	2.43
Ester Number	173.94
Solubility	Soluble in 0.9 vol. of 80% alcohol and in 0.1 vol. of 90% alcohol

Italian Clary Sage Oil

Salvia sclarea L. grows wild also in Sicily and Calabria, but too scattered to permit collection and distillation at competitive prices. The soil

[9] *Ber. Schimmel & Co.* (1931), 44.
[10] *Riechstoff Ind.* 7 (1932), 65.

and climate of Southern Italy are very favorable for cultivation of this plant, but commercial lots of clary sage oil have not yet been exported.

According to Sorgonà Luisi [11] Italian clary sage oils distilled in Calabria during 1939 from the flowering tops had properties varying between these limits:

Specific Gravity at 20°	0.8930 to 0.8990
Optical Rotation at 21°	−15° 12′ to −29° 3′
Refractive Index at 20°	1.4675 to 1.4710
Acid Number	0.61 to 1.20
Ester Number	104.50 to 129.60
Saponification Number	105.18 to 130.80
Ester Content, Calculated as Linalyl Acetate	36.58 to 45.34%
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	60.20 to 68.81%
Solubility	Soluble in 0.60 to 1.20 vol. of 85% alcohol

Italian oils described by Rovesti [12] had the following properties:

Specific Gravity at 15°	0.8658 to 0.9130
Optical Rotation	−9° 31′ to −34° 43′
Refractive Index at 20°	1.4692 to 1.4818
Ester Content, Calculated as Linalyl Acetate	34.62 to 54.88%
Free Alcohol Content, Calculated as Linaloöl	4.34 to 23.48%
Combined Alcohol Content, Calculated as Linaloöl	27.20 to 43.12%
Solubility	Soluble in 0.8 to 1.1 vol. of 80% alcohol

Hungarian Clary Sage Oil

In Hungary clary sage is cultivated in several sections of that country west of the Danube River. It is also grown in several sections of Czechoslovakia which are populated by Hungarians, and which, after being occupied by Hungary during World War II, were returned to Czechoslovakia after the war. These plantations of clary sage (which is used entirely for the production of oil) amounted to about 30 hectares in 1944. The oil has been marketed largely in West-European countries.

According to a survey made by the author,[13] the seed is sown in outdoor

[11] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi* **15** (1940), 6. *Chem. Abstracts* **36** (1942), 4970.

[12] *Rivista ital. essenze profumi.* **10** (1928), 122. *Ber. Schimmel & Co.* (1929), 65.

[13] "Hungarian Essential Oils," *Am. Perfumer* **36**, March (1938), 48.

beds during spring or summer; the seedlings are transplanted in fall to the field, and planted 50 cm. apart in rows 60 cm. distant. The plants should be harvested toward the end of the flowering period, when flowers remain only on the small lower branches. A plantation lasts two to three years; because of high mortality in the third year, new plantings must be started. The plants are cut with sickles, and sufficiently high to exclude the leafless lower stalk material which contains no essential oil.

Under favorable conditions, one *kataster joch* (1.422 acres) produces about 3,500 kg. of plant material. The yield of essential oil ranges from 0.056 to 0.169 per cent. One *kataster joch* yields from 2.5 to 6.0 kg. of oil.

Physicochemical Properties.—The properties of Hungarian clary sage oil range within the following limits: [14]

Specific Gravity at 15°	0.9072 to 0.9328
Optical Rotation	−13° 28′ to −28° 18′
Linalyl Acetate Content	60.0 to 83.0%
Solubility	Usually soluble in 1 vol. of 90% alcohol, but marked opalescence and separation of crystals with more alcohol

The odor of Hungarian oils is very fine and closely resembles that of the best French oils.

An oil distilled under the author's supervision in Tihany had the following properties:

Specific Gravity at 15°/15°	0.907
Optical Rotation	−14° 40′
Refractive Index	1.4617
Ester Content, Calculated as Linalyl Acetate	71.2%
Evaporation Residue	4.4%
Solubility	Soluble in 1 vol. of 80% alcohol; opalescent in 3 vol. and more

English Clary Sage Oil

Clary sage is cultivated also in England but on a small scale only. The oil is of excellent quality, highly appreciated by connoisseurs.

The following properties have been reported: [15]

Specific Gravity at 15.5°	0.904 to 0.915
Optical Rotation at 20°	−16° 0′ to −53° 0′
Refractive Index at 20°	1.469 to 1.492
Acid Number	0.5 to 1.8

[14] Courtesy of Dr. Jules de Bittera, Budapest.
[15] Courtesy Messrs. Stafford Allen & Sons, Ltd., London. Private communication.

Saponification Number	98 to 164
Ester Content, Calculated as Linalyl Acetate	34% to 53%
Solubility	Not entirely soluble in 1 to 10 vol. of 90% alcohol

Due to labor conditions, the oil produced in England has always been expensive.

Chemical Composition and Use of Clary Sage Oil

Chemical Composition.—The first investigation on the chemistry of French clary sage oil was undertaken by Roure-Bertrand Fils [16] who identified linalyl acetate and linaloöl as the main constituents. Later, Rutovski and Gusseva [17] examined Russian clary sage oil.

The presence of the following compounds has been established:

l-Linalyl Acetate. Linaloöl was identified as phenylurethane m. 64°–65° by Rutovski and Gusseva.

Applying Glichitch's method of cold formylation,[18] the Chiris chemists [19] found that two oils of own distillation contained 53.27 per cent and 38.71 per cent of linalyl acetate, respectively.

Linaloöl. Identified by Roure-Bertrand Fils [20] as phenylurethane m. 65°.

The Chiris chemists [21] found that their two oils contained 32.56 per cent and 39.18 per cent of free linaloöl, respectively.

l-Nerolidol. After saponification and repeated fractionation of the oil, Rutovski and Gusseva [22] isolated from Russian clary sage oil a compound, the constants of which resembled those of *d*-nerolidol, except for the laevorotation. Oxidation gave an aldehyde with constants similar to those of farnesal, except for the rotation. Preparation of a semicarbazone m. 133°–134°.

The presence of the laevorotatory form of nerolidol in an essential oil was thus established for the first time.

Acetate of *l*-Nerolidol. According to the same authors, *l*-nerolidol occurs in clary sage oil also as an acetic ester.

A Sesquiterpene(?) (β-Santalene?). Rutovski and Gusseva reported that Russian clary sage oil contains a bicyclic sesquiterpene with constants resembling those of β-santalene: b_{4-5} 105°–110°, d_{20}^{20} 0.8916, α_D −33° 18′, n_D^{20} 1.4930, mol. refr. 66.51.

[16] *Repts. Roure-Bertrand Fils,* April (1908), 10. *Ber. Schimmel & Co.,* October (1908), 89.
[17] *Riechstoff Ind.* **7** (1932), 65, 78.
[18] *Compt. rend.* **177** (1923), 268. *Bull. soc. chim.* [4], **33** (1923), 1284.
[19] *Parfums France* (1924), 263.
[20] *Repts. Roure-Bertrand Fils,* April (1908), 10. *Ber. Schimmel & Co.,* October (1908), 89.
[21] *Parfums France* (1924), 263.
[22] *Riechstoff Ind.* **7** (1932), 65, 78.

Use.—Oil of clary sage is a valuable perfumers' raw material which enables them to achieve unique and pleasant tonalities. The oil blends especially well with lavender and bergamot, and also with jasmine. It imparts to a composition a delightfully rich, rather unique top note and, because of its lasting ambergris-like evaporation residue, helps in the fixation of an odor.

Clary sage oil has also found employment in flavors, especially wine bouquets. Some of the most famous brands of old Rhine wine possess a characteristic clary sage-like top note which to a certain degree can be imitated by this interesting oil.

Concrete and Absolute of Clary Sage

Concrete.—Instead of being distilled, the flowering tops of clary sage can be extracted with volatile solvents, usually petroleum ether, according to methods described in Vol. I of this work, p. 200. It is best to remove stalks and leaves previous to extraction, as the chlorophyll would impart too much color to the final product. One hundred and eighty pounds of flowering tops yield about 1 lb. of clary sage concrete. Because of its insolubility in alcohol, the concrete cannot be employed as such in alcoholic solutions. However, it is useful in soaps, creams, powders and other preparations which do not require solubility in alcohol. The flower waxes present in the concrete act in these cases as a natural fixative. Because of the much higher yield obtained by extraction with volatile solvents, the concrete can be produced at lower prices than the distilled oil.

The concrete has a full and soft, natural odor which blends beautifully with lavender, labdanum, and pine.

Absolute.—In order to obtain the alcohol soluble absolute, the concrete is treated several times with strong alcohol, the alcoholic solution is cooled, filtered, concentrated and processed in the usual way. The concrete yields about 50 per cent of absolute, the balance consisting of odorless plant waxes and other insoluble matter. The absolute is a semisolid mass, alcohol soluble and of very fine, soft, typical clary sage-like odor. It can be used to great advantage in alcoholic perfumes, lotions, and other preparations and, like the concrete, blends with lavender, labdanum, pine, and many other scents.

Over the distilled oil the absolute possesses the advantage of high fixative qualities, its odor by far outlasting that of the distilled oil. The mellow, lasting fragrance, in conjunction with a relatively moderate price, makes absolute of clary sage one of the most interesting perfumers' raw materials.

The fixation value of the absolute is due to high boiling constituents, such as sclareol and sesquiterpene alcohols which are not present (or only in small quantities) in the distilled oil. Because of their high boiling points these compounds are not carried over by steam distillation and probably remain in the residual plant material. This may also be the reason why the yield of distilled oil is much smaller than that of the absolute.

Chemical Composition.– The chemical composition of the concrete and absolute of clary sage was investigated by Volmar and Jermstad [23] who found that the absolute oil contained 21.8 per cent of volatile constituents, 28 per cent of a sesquiterpene alcohol $C_{15}H_{26}O$, and 42.2 per cent of sclareol. More recently Ruzicka and collaborators [24] succeeded in elucidating the configuration of sclareol.

The presence of the following compounds has been established:

Linalyl Acetate. The volatile constituents of the extract consisted of about 80 per cent of linalyl acetate, and

Linaloöl. Twenty per cent of linaloöl.

Cedrene(?). The absolute also contained small quantities of a compound with the constants of cedrene: d_{15} 0.9123, α_D^{15} −40° 6′, n_D^{20} 1.5122.

A Sesquiterpene Alcohol(?) $C_{15}H_{26}O$. It had the following constants: d_{15} 0.9841, α_D^{20} +24° 47′, n_D^{20} 1.5138.

Sclareol [25] $C_{20}H_{34}(OH)_2$. A crystalline, odorless and tasteless diterpene alcohol possessing the following constants: m. 104°–105°, b_1 182°, $[\alpha]_D^{20}$ −6° 7′ (in absolute alcohol).

OIL OF SPANISH SAGE

Essence de Sauge Espagnole *Aceite Esencial de Salvia Española*
Spanisches Salbeiöl

The oil distilled from *Salvia lavandulaefolia* Vahl. (= *S. hispanorum* Lag.) must not be confused with that from *Salvia officinalis* L. growing in Dalmatia, or with the oil from *Salvia sclarea* L. cultivated in Southern

[23] *Compt. rend.* **186** (1928), 517, 783. See also Rovesti, *Notizr. chim. indr.* **3** (1928), 12. *Chem. Zentr.* I (1928), 2467.
[24] *Helv. Chim. Acta* **21** (1938), 366; 25 (1942), 621.
[25] For further details regarding this compound see the section on "Diterpenes" in Vol. II of this work, p. 127 (Table of Diterpenes).

France and Southern Russia. According to Box,[1] the colloquial term for *Salvia lavandulaefolia* in Spain is "Salvia fina."

Producing Regions.—*Salvia lavandulaefolia* occurs wild in the Spanish provinces of Granada, Murcia, Almeria, and Jaén, the main producing center of the oil being Granada.

Collection of the Plants and Distillation.—The collection of plant material and its distillation closely resemble those employed with Spanish spike lavender. The period of distillation extends from May to October.

Ten arrobas (1 arroba = 11.5 kg. or about 25 lb.) of plant material yield about 1 kg. of oil; in other words the yield of oil is about 0.88 per cent. Distillation of one charge requires 4 hr.

Physicochemical Properties.—The physicochemical properties of Spanish sage oil vary considerably with soil, climatic, and weather conditions.

Samples of genuine Spanish sage oils, obtained by the author in various producing regions, and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	Spec. Grav. at 15°/15°	*Optical Rotation*	*Total Alcohol Content*[2] (%)	*Ester Content*[3] (%)	*Solubility at 20°*
Murcia	0.935	+22° 33′	27.8	15.3	Not clearly soluble in 10 vol. 70% alcohol; clearly soluble in 1 vol. 75% alcohol up to 10 vol.
Maria (Almeria)	0.933	+20° 57′	23.9	12.6	Insoluble in 70% alcohol; clear in 1.5 to 3 vol. 75% alcohol; soluble in 1 to 2 vol. 80% alcohol, opalescent with more
Almaciles (Granada)	0.936	+23° 42′	23.0	13.4	Insoluble in 70% alcohol; soluble in 1.5 to 3.5 vol. of 75% alcohol; soluble in 1 to 3 vol. of 80% alcohol, opalescent with more
Jaén	0.918	−3° 35′	16.9	7.5	Insoluble up to 10 vol. of 70 and 75% alcohol; soluble in 1 to 1.5 vol. 80% alcohol, opalescent with more

[1] *Pharm. Ind.* **9** (1942), 273. *Ber. Schimmel & Co.* (1942–1943), 60.
[2] Calculated as linaloöl.
[3] Calculated as linalyl acetate.

It is interesting to note that oils distilled in the province of Jaén differ in regard to physicochemical properties and odor from those distilled in Murcia, Almeria, and Granada.

Spanish sage oil has a pronounced camphoraceous odor with a by-note of cineole.

Adulteration.—Spanish sage oil is sometimes adulterated with oils of camphor, or eucalyptus, steam distilled pine oil, or with fractions of these oils.

Total Production.—Total yearly production of Spanish sage oil, previous to the outbreak of the Spanish Civil War in 1936, varied from 4 to 7 metric tons. During this war production fell off considerably. In 1946 about 10 tons of sage oil were distilled in Spain, 4 tons in 1947, and 8 tons in 1948.

Chemical Composition.—The chemistry of Spanish sage oil was investigated by Dorronsoro.[4]

Fractionating an oil originating from the province of Granada, Dorronsoro obtained, at 710 mm. pressure, the following fractions.

	Per Cent		*Per Cent*
164°–170°	9.5	190°–203°	8.0
170°–180°	38.0	203°–205°	25.0
180°–190°	15.3	Residue	4.0

Dorronsoro established the presence of the following constituents:

Pinene(?) and Dipentene(?). The melting point of pinene nitrosochloride and pinene nitrolbenzylamine did not remain constant on recrystallization, which indicates the presence of another terpene, possibly dipentene.

Camphene(?). Presence probable. The fraction b. 170°–180°, when treated with potassium permanganate gave a white substance m. 135°–136°, evidently camphene-camphoric acid.

Cineole. Identified as resorcinol compound. The oil contained a large amount of cineole.

Linaloöl. Linaloöl was characterized by oxidation to citral.

Linalyl Acetate
Linalyl Isovalerate } Part of linaloöl occurs in the oil as acetate and as isovalerate.

d-Camphor. M. 178°; oxime m. 120°.

Use.—In Spain sage oil is occasionally employed for adulterating spike lavender oil. When exported it serves primarily for the scenting of soaps, usually in combination with lavender, spike lavender, and rosemary.

[4] *Mem. acad. cienc. exactas Madrid,* **29** (1919). Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 698.

SUGGESTED ADDITIONAL LITERATURE

J. Small, "Sage. A Pocket Lens Study," *Food* **13** (1944), 43.
Obdulio Fernández and Juan Abeniacar, "Essential Oils of Spanish Sage," *Farm. nueva Madrid* **12** (1947), 161, 215. *Chem. Abstracts* **42** (1948), 5613.

OIL OF *SALVIA CARNOSA* DOUGL.

Salvia carnosa Dougl. (after Index Kewensis identical with *Audibertia incana* Benth.) is, like *Salvia leucophylla* Greene, an American plant, growing wild in western North America.

White and Jenkins [1] reported that distillation of the unground leaves of air-dried *Salvia carnosa* collected in the vicinity of Reno, Nevada, yielded 3.46 per cent (weight to volume) of a volatile oil having these characteristics:

Specific Gravity	0.9209
Specific Rotation at 25°	+2° 50′
Refractive Index	1.4705
Acid Number	1.62
Saponification Number	48.27
Ester Number	46.65
Ester Number after Acetylation	42.55
Solubility at 25°	Soluble in 1 vol. of 85% alcohol and in 12 vol. of 80% alcohol

The same authors [2] identified in the oil a compound of the molecular formula $C_{19}H_{26}O_4$ which they named carnosol. The molecule contains two phenolic hydroxyl groups and an unidentified ester group. The results of zinc dust distillation followed by dehydrogenation with sulfur strongly indicate the presence of an octahydrophenanthrene nucleus.

The oil has not attained any commercial importance.

[1] *J. Am. Pharm. Assocn.* **31** (1942), 33.
[2] *Ibid.*, 37.

THE *SATUREIA* OILS

("SAVORY OILS")

Introduction.—There exist two species of *Satureia,* viz., *S. hortensis* L. and *S. montana* L., possessing a pronounced thyme-like odor and flavor. Both are employed as culinary herbs. The oils of the two plants are closely related in chemical composition; they can be obtained by steam distillation of the flowering herb.

OIL OF *SATUREIA HORTENSIS* L.

Essence de Sariette *Aceite Esencial de Ajedrea* *Bohnenkrautöl*

Description, Habitat, and Range.—*Satureia hortensis* L., our "summer savory" or garden type, is largely cultivated, although it grows wild to some extent. An annual, it is less developed than *S. montana.* Its stalks are herbaceous, covered with soft and linear leaves. The branches are frequently of reddish color. Flowers of the garden savory are whitish, dotted with red, growing in a bouquet from the summit of the branches.

The seed is sown annually in light soil, at the end of April in Northern France and at the end of February–March in Southern France. It begins to sprout after about one week or a little longer. The harvest takes place during the flowering season.

According to Slessman,[1] seed should be sown, ¾ lb. per acre, in rows about 12 in. apart. The seed sprouts very slowly, and requires intense cultivation and two hand weedings. Savory is ready for harvest when flowers commence to bloom.

Yield per Acre.—Slessman reports a yield of about 6 U. S. tons of clover-dried plants per acre which, in turn, give a little more than 26 lb. of oil (about 0.21 per cent).

Distillation.—The plant material is charged into a still, live steam generated in a separate steam boiler is injected, and the oil separated in a Florentine flask. Fresh flowering *Satureia hortensis* yields about 0.1 per cent of oil.

[1] Private communication of Mr. A. E. Slessman, Fremont, Ohio.

TABLE 2.19

Property	I	II	III	IV	V	VI	VII	VIII	IX
Specific Gravity at 15°	0.896 to 0.960	0.8964	0.9040	0.884 to 0.910	0.941	0.932	0.938	0.924	0.901
Optical Rotation	+0° 4′ to −0° 56′	Inactive	−0° 10′	+0° 15′ to +3° 40′	−2° 48′	−4° 24′	−3° 19′	−3° 0′	±0°
Refractive Index at 20°	...	...	1.49307	1.4869 to 1.4955	1.5044	1.5010	1.5032	1.4941	1.4935
Saponification Number	...	5.6	...	...	...	...	...	...	...
Phenol Content (Carvacrol)	30.0 to 42.0%	31.25%	40.0%	23.8 to 42.0%	55.0%	39.0%	47.1%	31.5%	34.0%
Solubility	Soluble in 2 vol., occasionally in 10 vol. of 80% alcohol	...	Soluble in 9 vol. and more of 80% alcohol	Soluble in 0.5 vol. and more of 90% alcohol; clear to turbid with more	Soluble in 3 to 3.5 vol. and more of 70% alcohol	Soluble in 1 to 1.5 vol. and more of 80% alcohol	Soluble in 1.5 vol. and more of 80% alcohol	Soluble in 1 vol. of 80% alcohol; opalescent with more	Turbid to hazy in 80% alcohol, up to 10 vol.

According to Bauer and Pohloudek,[2] the essential oil content of this herb is highest during full flowering; the same authors found its fluctuation from bud formation to the end of flowering to be small.

Physicochemical Properties.—The principal constituents of the oil are phenols, consisting mainly of carvacrol. The higher the phenol content of the oil, the higher is its specific gravity and the lower its optical rotation. The limits of these properties can be judged from Table 2.19.

I. Limits as suggested by Gildemeister and Hoffmann.[3]

II. An oil distilled by Albricci [4] from plants cultivated in Calabria.

III. An oil distilled by the Bulgarian Experiment Station in Kazanlik, and analyzed in the laboratories of Schimmel & Co.[5]

IV. Oils distilled in Fremont, Ohio, and analyzed in the laboratories of Fritzsche Brothers, Inc., New York.

V. to VII. Three oils distilled in Dalmatia, and analyzed by Fritzsche Brothers, Inc., New York.

VIII. An oil distilled by the author in Seillans (Var), France.

IX. Oil distilled in Palestine and analyzed by Fritzsche Brothers, Inc., New York.

Chemical Composition.—The chemistry of oil of *Satureia hortensis* was investigated by Jahns [6] who found that it contained the following compounds:

p-Cymene. About one-third of the hydrocarbons boiled between 173°–175° at 760 mm. and consisted of *p*-cymene.

Another Terpene(?). About two-thirds of the hydrocarbons boiled between 178°–180° at 760 mm., d_{15} 0.855, α_D −0° 12′, and contained a terpene which was not identified.

Carvacrol and Another Phenol(?). The phenols consisted mainly of carvacrol, the principal constituent of the oil, also traces of another phenol not further investigated.

[2] *Pharm. Zentralhalle* **83** (1942), 277. *Chem. Abstracts* **38** (1944), 2166.
[3] "Die Ätherischen Öle," 3d Ed., Vol. III, 722.
[4] *Rivista ital. essenze profumi* **7** (1925), 16. *Ber. Schimmel & Co.* (1926), 9.
[5] *Ber. Schimmel & Co.* (1932), 7.
[6] *Ber.* **15** (1882), 816.

OIL OF *SATUREIA MONTANA* L.

Description, Habitat, and Range.—*Satureia montana* L., our "winter savory" or, as the French call it, "poivre d'âne," grows wild on sunny and calcareous arid hillsides of Southern France, especially in the Alpes-Maritimes. It is a hardy, shrub-like perennial attaining a height of 8 to 14 in., with small, yellowish or slightly purple flowers growing alone on top of the branches. The leaves are tough, linear, the stalks woody at the base, and the seeds brown and finely shagreened. The plant seeds itself.

The herb is collected during the flowering season and, for the herbalist trade, dried in sheds. For distilling it is preferable to use the fresh or, still better, the clover-dried material. *Satureia montana* is seldom cultivated, mostly wild growing herb being gathered. Plantings may be started from seed or root divisions.

Distillation.—The herb is distilled like *Satureia hortensis*, the yield from fresh flowering *Satureia montana* ranging from 0.15 to 0.23 per cent.

Physicochemical Properties and Chemical Composition.—Gildemeister and Hoffmann [1] indicated these properties for oil of *Satureia montana:*

Specific Gravity at 15°/15°	0.908 to 0.939
Optical Rotation	−1° 42′ to −4° 48′
Phenol Content	27.0 to 65.0%
Solubility	Soluble in 1.5 parts of 80% alcohol

According to Paulet,[2] distillation of mountain savory yields 0.1–0.2 per cent of oil. The same author reported the following properties:

Specific Gravity at 15°	0.924
Optical Rotation	−2° 48′
Refractive Index at 20°	1.4918
Ester Content, Calculated as Bornyl Acetate	2.9%
Carvacrol Content	32%
Solubility	Soluble in 2.1 vol. of 80% alcohol

The chemistry of *Satureia montana* oil is similar to that of *Satureia hortensis* oil. Haller,[3] and later Leone and Angelescu [4] identified the following compounds in oil of *Satureia montana:*

[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 723.
[2] *Parfumerie moderne* **19** (1926), 311. *Chem. Abstracts* **21** (1927), 985.
[3] *Compt. rend.* **94** (1882), 132.
[4] *Gazz. chim. ital.* **51**, II (1921), 386.

Dipentene. Amounting to about 14 per cent of the oil. Identified as nitrolbenzylamine derivative m. 108°.

p-Cymene. Amounting to about 27 per cent of the oil. Oxidation yields hydroxyisopropylbenzoic acid m. 156°–157°.

Carvacrol. The main constituent of the oil which contains 28 to 65 per cent of phenols. Identified as nitro derivative m. 77°–78°.

An Alcohol(?). Ten per cent of the oil freed from phenols consists of this alcohol, the nature of which was not elucidated. (Ester number after acetylation 54.3.)

Igolen and Sontag,[5] distilled *Satureia montana* L. and obtained the following:

	Per Cent
Volatile Oil from Fresh Herb in Full Bloom	0.333
Volatile Oil from Dried Herb	0.1477
Volatile Oil from 1,000 Kg. of Herb	0.100

The oils had these physicochemical properties, respectively:

	I	*II*	*III*
Specific Gravity at 15°	0.938	0.914	0.920
Optical Rotation	−1° 50′	−2° 10′	−3° 40′
Refractive Index at 20°	1.5065	1.4963	1.4983
Phenol Content	56.0%	25.0%	33.0%
Ester Number of the Nonphenolic Fraction	...	...	11.22
Ester Number after Acetylation of the Nonphenolic Fraction	...	...	72.95
Ester Number after Cold Formulation of the Nonphenolic Fraction	...	...	84.17

The oil obtained from the 1,000 kg. of herb material had the following composition:

	Per Cent
Phenols (Carvacrol, Thymol and an Unidentified Phenol Giving a Dinitrobenzoate m. 93°)	30.40
Acids (Acetic Acid and an Unidentified Solid Acid m. 56°)	0.43
Ketones (*l*-Carvone, *l*-Menthone)	0.30
Alcohols (*l*-Linaloöl, *l*-Terpineol, *d*-Borneol, Dihydrocuminyl Alcohol)	25.00
Terpenes (*p*-Cymene)	33.70

Adulteration.—The chemical composition of savory oil resembles that of origanum oil (*Coridothymus capitatus* Rchb. f.), which is produced in large quantities from plants growing wild on the sunny hillsides of Southern Spain and Morocco.

[5] *Rev. Marques Parfums France* **17** (1939), 109, 143.

Therefore, adulteration of savory oil with this much lower priced oil is tempting, especially in view of the fact that it can hardly be detected by chemical analysis, the constants of savory and origanum oils being similar. However, an expert familiar with the delicate and characteristic odor and flavor of genuine savory oil will have little difficulty recognizing sophistication with origanum oil which possesses a coarse, phenol-like character. This is true also if the savory oil has been adulterated with synthetic carvacrol.

Occasionally thyme oil (*Thymus vulgaris* L.) is used for the adulteration of savory oil, both oils possessing similar properties. However, thyme oil contains as main constituent thymol, a crystallizable phenol which can be separated by congealing; whereas savory oil contains as main constituent carvacrol, a noncrystallizable phenol.

Use of Oil of Savory

Oil of savory is a most useful and valuable ingredient in the flavoring of soups, sausages, and canned meats. It forms an important constituent in spicy table sauces.

According to Schultzik,[6] the oil is an efficient antidiarrheic due to the presence of phenols, principally carvacrol.

OIL OF THYME

Essence de Thym *Aceite Esencial de Tomillo* *Thymianöl*
Oleum Thymi

Introduction.—The botany of the plants from which thyme oils are distilled is somewhat confused, since in Spain alone—the main producing country of this oil—there exist numerous species and varieties of wild growing *Thymus*, some of them bearing vernacular names. The same is true of Morocco and other countries bordering the Mediterranean.

In commerce, the designation thyme oil is occasionally applied indiscriminately, and erroneously, to oils distilled from plants belonging to species other than *Thymus vulgaris* L. or *T. zygis* L.

[6] *Münch. med. Wochschr.* (1933), 1824. *Ber. Schimmel & Co.* (1934), 121.

Some years ago, the author [1] suggested that for practical purposes thyme oils be classified according to their chemical composition as follows:

I. Thyme Oil—Thymol Type.—The oil contains 42 to 60 per cent of phenols which consist mainly of thymol (crystallizable phenol).

II. Origanum Oil—Carvacrol Type.—This oil contains 63 to 74 per cent of phenols which consist mainly of carvacrol (noncrystallizable phenol).

III. Lemon Thyme Oils.—These oils contain citral, which accounts for their somewhat lemon-like odor. Commercially, this group has remained unimportant.

Spanish Thyme Oil
(Thymol Type)

Botany.—According to literature, Spanish thyme oil is distilled from the flowering subshrubs *Thymus vulgaris* L. and *Thymus zygis* L., both of which grow wild on vast heaths, the so-called "Tomillares," in the southeastern part of Spain. The botanical nomenclature of the plants from which Spanish thyme oil is distilled has been a matter of much controversy and is characterized by considerable confusion. There seem to exist in Spain from 30 to 40 *Thymus* species and varieties, some of which are difficult to distinguish one from the other. Several of them are known locally by the same popular name; others bear several names, thus adding to the confusion. The reader interested in details will find further information—although quite contradictory—in the publications of Willkomm,[2] Hartwich,[3] Blas Lázaro é Iviza,[4] Dorronsoro,[5] Rubeck and Holmes,[6] and Blaque.[7] However, the observations of these botanists are of little help in determining the taxonomy of the plants from which Spanish thyme oil is distilled at present, because their work dates back prior to 1914, in which year commercial production of Spanish essential oils was started.

According to Flores and Bordas,[8] Spanish thyme oil is derived today

[1] "Spanish Essential Oils," *Am. Perfumer* **24** (1929), 291. Cf. Albers, "The Occurrence of Thymol and Carvacrol in the Plant Kingdom and Their Significance in Botanical Systematics," *Pharm. Arch.*, May (1942), 39.

[2] "Grundzüge der Pflanzenverbreitung auf der iberischen Halbinsel." Leipzig (1896).

[3] *Apoth. Ztg.* **21** (1906), 842.

[4] "Compendio de la Flora Española" (1907).

[5] "Estudio quimico de esencias naturales españolas" Madrid (1919), 134.

[6] *Perfumery Essential Oil Record* **11** (1920), 339.

[7] *Ibid.* **14** (1923), 239.

[8] Private communication of Mr. Ramon Bordas, Sevilla, Spain, an experienced and large-scale producer of Spanish essential oils, who in 1948, in collaboration with Dr. Rivas Goday, Facultad de Farmacia de la Universidad Central, Madrid, undertook a botanical study of the plants which actually serve for distillation of Spanish thyme oil.

almost exclusively from *Thymus zygis* L. var. *gracilis* Bois. The flowers of this variety are white and grow at some distance from the branches, by which features the variety can readily be distinguished from the other species of *Thymus*, which are usually in a more advanced flowering stage. The plant material carried by the gatherers to the field stills is thus of uniform appearance.

In the Lorca section of the Province of Murcia, there exists another variety, viz., *Thymus zygis* L. var. *floribundus* Bois., which to a very small extent is also used for the distillation of thyme oil. In appearance it resembles the var. *gracilis*, except that it bears heavier flowering branches. The essential oil derived from var. *floribundus* is of excellent quality, as it contains from 44 to 60 per cent of phenols.

Inferior qualities of Spanish thyme oil find their way into the market because of insufficient care exercised in the selection and collection of the plant material, or sometimes because of adulteration with thyme oils derived from plants other than those indicated above. Commercial qualities of oils with a lower thymol content may be obtained by adding the non-phenolic fractions (thymene) obtained in the production of natural thymol, of which one of the principal present sources is Spanish thyme oil.

For the sake of completeness another species of *Thymus* should be briefly mentioned here, viz., the so-called "tomillo negro" which has been classified as *Thymus vulgaris* L. var. *capitatus* W.K. This species, together with still another, viz., "tomillo de las olivas" or "aceitunero" (which seems to be *Thymus loscossi* W.K., the "tomillo sanjuanero" of B. Lázaro), is collected for the purpose of exportation of the leaves to England and France where they are used as condiment. The two last named species exhibit a much softer odor than *T. zygis* var. *gracilis* and *floribundus* as their essential oils contain only a low percentage of thymol.

"Tomillo negro" has white and reddish-violet flowers, forming a tight spike in the form of a terminal ball. The essential oil derived from this plant is dextrorotatory (α_D about $+16°$), contains about 3 per cent of phenols, about 12 per cent of cineole, and seems to contain citral also (whence its delicate lemon-like odor).

"Tomillo de las olivas" has whitish-red or purple flowers. The essential oil derived from it exhibits laevorotation (α_D $-12°$ to $-38°$), contains 2–3.5 per cent of phenols, and about 35 per cent of cineole. It possesses an odor reminiscent of marjoram and laurel.

For the flavoring of olive oil the leaves of only those species and varieties of *Thymus* are employed which contain a very low percentage of

phenols ("negro," "de las olivas"), except in the western part of Andalusia (Huelva, Sevilla, Cadiz, and Cordova) where origanum, also called "tomillo carrasqueño" or "tomillo andaluz" (*Coridothymus capitatus*) is also used for this purpose.

The oils of "tomillo negro" and "tomillo de las olivas" are not produced on a commercial scale, except perhaps in small quantities here and there by a few distillers who use these oils for the adulteration of normal thyme oils derived from *Thymus zygis* var. *gracilis*, and var. *floribundus*.

To conclude, genuine and high-quality commercial Spanish thyme oils are distilled chiefly from *Thymus zygis* L. var. *gracilis* Bois., and to a very small extent from *Thymus zygis* L. var. *floribundus* Bois.

The flowers, leaves, and other herbaceous parts of *Thymus zygis* L. and *Thymus vulgaris* L. contain an essential oil of pungent, aromatic odor and flavor, for which reason dried thyme and the essential oil derived from the overground parts of the plant are widely employed for the seasoning of food products.

Origin, Habitat, and Range.—Thyme, a native of Mediterranean countries, grows abundantly over wide areas on arid mountain slopes in the south of France, in the southeastern provinces of Spain, in Algeria, and in Morocco. For culinary purposes *Thymus vulgaris* is grown in gardens of Europe and the United States, but for distillation only the wild plant is employed. Originally thyme oil was distilled in France (Alpes-Maritimes), but for the last thirty years the lower priced Spanish oils have replaced the French oils.

The Spanish producing regions, where at present the bulk of thyme oil originates, are located in the provinces of Murcia and Almeria, entirely separated from the producing sections of Spanish origanum oil.

Collection of Plant Material.—Gathering of thyme in Spain takes place during the blooming period of this low growing shrub, from July to August; it is a task even more tedious than the collection of spike or rosemary.

The foreman in charge of a field distillation post who, from experience, selects the most advantageous location for the placement of his stills, refuses to accept plant material if he suspects that all the thyme growing in the plains ("ramblas") at the foot of the hills has been harvested, and that the gatherers are bringing him plant material collected from the slopes of the hills; such plants yield oil inferior in yield and quality. When distilling in the highlands, these difficulties are not encountered, and the placement of the stills offers no problem.

Distillation.—Movable field stills, as described in the monograph on "Spanish Oil of Spike Lavender," are employed also for the distillation of thyme oil.

The plant material is packed into the stills, and water is added up to about 15 cm. above the perforated grid (about 500 liters of water for 30 arrobas of plants). A charge consists of 30 to 40 arrobas (345 to 460 kg.) of plant material, the distillation lasting from 5 to 8 hr., according to the capacity of the still and the condition of the material. Operation is completed when about 140 to 180 liters of water have distilled over. The yield of oil ranges from 0.69 to 0.74 per cent. Experience has shown that after the third charge there is an increase in the yield of oil, moreover that the quality of the oil improves, probably due to an accumulation of salts in the water within the still, which affects the conditions of distillation.

On the average, the yield of thyme oil in the Spanish field stills ranges around 1 kg. per 12 arrobas of plant material (1 arroba = 11.5 kg. or about 25 lb.), i.e., about 0.73 per cent of oil. The condition of the plant material and the rather primitive method of distillation (in part a water distillation with resulting excessive wetting of the plant charge) are probably the causes of the relatively low oil yield obtained in the Spanish field stills. (For details see the monograph on "Spanish Oil of Spike Lavender.")

Youngken and Feldman [9] found *Thymus vulgaris* to contain on the average 2.00 per cent of volatile oil; the stems contain 1.02 per cent.

According to Rosenthal,[10] the content of volatile oil in *Thymus vulgaris* varies considerably among single plants. The maximum was found to be 2.60 per cent, as calculated upon the dried herb. The second cutting yields more oil than the first one. In the course of a day, the maximum yield was obtained during the early afternoon.

Schratz [11] found that the first cut of cultivated thyme yielded on the average 1.58 per cent of volatile oil, whereas the second cut in October gave 1.9 per cent oil. Wintered and largely frost resistant plants yielded from 0.5 to 1.7 per cent, on the average 1.1 per cent of oil.

(About fertilization experiments on cultivated American *Thymus vulgaris* see Bulletin No. 4, The Herb Society of America, Boston, Mass., March 1944.)

Physicochemical Properties.—Genuine oils distilled under the author's supervision in Spain had the following properties:

[9] *Bull. Natl. Formulary Comm.* **9** (1940), 70.
[10] *Pharm. Ind.* **10** (1943), 22. *Chem. Abstracts* **38** (1944), 4756.
[11] *Deut. Heilpflanze* **8** (1942), 120. *Ber. Schimmel & Co.* (1942–1943), 34.

Place of Origin	*Specific Gravity at 25°/25°*	*Phenol Content (%)*	*Solubility at 25°*
Almeria	0.931	60.0	Soluble in 1.5 vol. of 80% alcohol, cloudy with more
Almeria	0.923	50.0	Slightly opalescent in 1.5 to 2 vol. of 80% alcohol
Almeria	0.923	51.0	Slightly opalescent in 1.5 to 2 vol. of 80% alcohol
Almeria	0.924	50.0	Slightly opalescent in 1.5 to 2 vol. of 80% alcohol
Almeria	0.922	51.0	Slightly opalescent in 1.5 to 2 vol. of 80% alcohol
Mula (Murcia)	0.930	55.0	Soluble in 1.5 vol. of 80% alcohol, cloudy with more

The oils produced in the provinces of Almeria (particularly near Lorca) and Murcia contain a high percentage of phenols (up to 60 per cent). Because of the favorable climate a high phenol content is more easily obtained in Murcia than in Almeria. The plant material used in these provinces consists principally of *Thymus zygis* var. *gracilis*, with some of the var. *floribundus* admixed.

The phenols in thyme oil are crystallizable; this is the most important feature in the analysis of thyme oil, distinguishing it from origanum oil. A high specific gravity is associated with a high phenol content. The phenol content is determined by volume, as described in the chapter on "Examination and Analysis of Essential Oils, Synthetics, and Isolates," Vol. I of this work, p. 291.

Genuine red thyme oils [12] imported from Spain in the course of years and analyzed in the laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°/25°	0.916 to 0.934
Optical Rotation at 25°	−0° 16′ to −1° 52′
Refractive Index at 20°	1.4971 to 1.5040
Phenol Content (by Volume)	42.5 to 59.0%
Solubility	Soluble in 2.5 to 3.5 vol. and more of 70% alcohol, on rare occasions with slight turbidity. Soluble in 3 vol. and more of 80% alcohol
Color	Yellow-reddish

[12] The commercial designation "Red Thyme Oil" implies that the oil has not been rectified. (See "White Thyme Oil," below.)

The isolated phenols on standing at room temperature should crystallize. In a very few and most exceptional cases, however, the author observed that the isolated phenols of supposedly pure oils on standing and even on cooling did not crystallize. The author can think of only one explanation, viz., that these exceptional oils were not distilled from *Thymus vulgaris* or *Thymus zygis* but from a closely allied species or variety about which there is still considerable confusion.

The laboratories of Fritzsche Brothers, Inc., New York,[18] made the following observations:

If the phenols separated from Spanish thyme oil crystallize at room temperature (20° C.) after seeding, the phenols of the original oil consist of more than 40 per cent thymol; these oils cannot be of the carvacrol type. Such behavior is indicative that the oil is primarily of the thymol type, official in the N.F. VIII.

Furthermore, if the separated phenols crystallize within 5 min. when cooled to 0° and seeded, the phenols of the original oil contain more than 20 per cent thymol.

Adulteration of Spanish Thyme Oil.—Thyme oil is occasionally adulterated by adding terpenes or the commercial product called "thymene," which is a by-product in the manufacture of thymol from ajowan oil and consists mainly of *p*-cymene, some camphene, and γ-terpinene. Since these terpenes are also natural constituents of thyme oil, the analyst has difficulty in proving that they have been added; however, the phenol content of the oil will be decreased correspondingly. In order to reconstitute the phenol content, the adulterator usually adds synthetic carvacrol (a noncrystallizable phenol). Therefore, the presence of substantial amounts of noncrystallizable phenol in a thyme oil indicates addition of synthetic carvacrol. This is usually confirmed by a slight creosote-like "by-odor," especially toward the end of evaporation on testing paper. When ordering thyme oil, the buyer would do well to specify a certain percentage of crystallizable phenols (thymol) rather than phenols in general.

Total Production of Spanish Thyme Oil.—Prior to World War II the total yearly production of thyme oil in Spain varied from about 12,000 kg. in 1932 to almost 15,000 kg. in 1935; it averaged 10,000 kg. in normal years. With the outbreak of the Spanish Civil War in 1936, production of thyme oil fell off considerably but since 1939 has again increased. World War II caused a heavy demand for Spanish thyme oil on the part of Central Europe, especially Germany. The production in 1946 was 24,000 kg., but only 5,000 kg. in 1947. In 1948, about 25,000 kg. of oil were produced in

[18] *J. Am. Pharm. Assocn.* **38** (1949), 261.

Spain. As in prewar days, the most important buyers again were the United States and the United Kingdom.

White Thyme Oil.—Natural thyme oil distilled in Spain or Morocco possesses usually a yellowish red, sometimes deep red, color, caused by the action of phenols upon iron condensers in the field stills.

An almost colorless oil can be obtained by redistilling (rectifying) the red oil. The process is accompanied by some loss of oil, and by a corresponding increase in the phenol content of the rectified or white thyme oil. Thus, the phenol content of genuine white thyme oils is usually slightly higher than that of red oils.

Upon prolonged storing, white thyme oil has a tendency to redden again, especially when stored in metal containers.

In past years (occasionally even today) white thyme oils were offered on the market with a phenol content as low as 20 per cent. This situation was brought about by the specifications of earlier editions of the U.S.P. which permitted a phenol content of 20 per cent as lower limit. Such oils, however, do not represent natural products; they are made by adding oil of turpentine, steam distilled pine oil, camphor oil fractions, or *p*-cymene to genuine white thyme oils which possess a natural high phenol content.

Moroccan Thyme Oil

As the author reported [14] after a visit to the interior of Morocco in '37, that country had started to produce a number of essential oils, especially those which Spain could no longer supply during the Spanish Civil War (1936 to 1939).

The climate of Morocco resembles that of Southern Spain, and the flora of the two countries are similar. Aromatic plants like rosemary, thyme, origanum, pennyroyal, rue, myrtle, labdanum, etc., grow abundantly on the arid, sunny slopes of the Atlas and Riff mountains. Morocco is also favored by an ample supply of low-priced and good labor. With the conclusion of the Riff Wars in the early 1920's, France had succeeded in subduing the ever warring Berber tribes, once fierce desert marauders. It was another and more difficult task to settle the vanquished and to convert their nomadic habits into useful occupations, lest they create a serious problem of unemployment. The idea of producing essential oils through these tribes was welcomed by the French authorities as a step toward relief. A highly intelligent, proud and honest race, the Berbers are incredibly sturdy and used to a primitive life in the deserts and barren mountains of Morocco's interior. Raising sheep and goats is still their main occupation, but

[14] "Moroccan Essential Oils," *Drug & Cosmetic Ind.* **42** (1938), 307.

the distilling of aromatic plants in movable stills appeals to their independent, nomadic spirit. Even the art of distilling was not difficult for them to learn, as distillation was originally introduced to Europe (Spain) by the conquering Moors hundreds of years ago. To march thirty miles in the burning sun with a handful of dates for sustenance and to sleep in the freezing nights under a primitive tent made of old goatskins means no hardship to the Berber, so long as he remains free to move about the wide open spaces.

The pioneer work and actual development of this new industry was accomplished by the late Mr. E. Chalureau,[15] a former Commander in the French Foreign Legion, whose experience with the Berbers and high reputation among their chiefs proved of great value in this novel task. First he trained a few foremen at his headquarters in Meknès, teaching them to set up and operate stills. These men then returned to their tribes and organized crews of distillers who, accompanied by their families, went into the mountains where plant supply was most abundant. It is usually no problem for a Berber to find water and dig wells. Under an old army tent pitched near the still, they feel at home and happy. While the men attend the stills, the women and ragged children go to the mountains, pull the flowering tops by hand, and carry the sacks of plant material many miles back to the stills—all for a few cents as daily income. The plant material is then weighed near the stills and paid for in cash by the foreman.

From this picture it appears evident that Morocco's essential oil industry offers considerable possibilities for the future, having suffered a setback during the years of World War II.

Habitat and Range.—Thyme grows wild and abundantly on sunny mountain slopes throughout the Medium Atlas at altitudes ranging from about 1,000 to 2,000 m.

Collection of Plant Material.—Beginning in April with plants (flowering tops) growing at 1,000 m. altitude, the harvest ends in August with plants growing up to 2,000 m.

Distillation.—The portable stills employed in Morocco were copied from models constructed in Grasse (France) and are, therefore, of somewhat more advanced design than those used in Spain. The stills, usually of 600 liter capacity, are provided with a grid above which the plant material is packed. The water beneath the grid is brought to a boil by direct fire under the still. Since the plant gatherers in Morocco usually do not cut the plants, but strip leaves and flowers from the stalks by hand, only the essential oil-containing parts of the plant are distilled, not the whole overground plant as in Spain and elsewhere. This feature undoubtedly explains

[15] Killed in action during World War II.



Courtesy of Fritzsche Brothers, Inc., New York.

Field distillation of thyme in Morocco.



Courtesy of Fritzsche Brothers, Inc., New York.

A condenser and oil separator of a thyme still in Morocco.

the higher yield of oil obtained in Morocco per charge of plant material. Tougher plants which must be cut with sickles are first dried in the sun, and the leaves and flowering tops subsequently removed by hand. Thus the charge of aromatic plant material per still is larger, and one still can produce greater quantities of oil daily. This method has the further advantage of yielding oils of better odor. It also somewhat affects the properties of the Moroccan oils, as compared with those distilled in Spain.

One hundred to 120 kg. of leaves and flowering tops are charged into a still and distilled from 2 to 4 hr. Depending upon seasonal and weather conditions, and the altitude at which the plants grow, the yield of oil varies from 0.5 to 1.2 per cent.

If, on the other hand, the entire overground part of the plant is cut and distilled as such, only 60 kg. can be packed into a still, the yield of oil then varying from 0.4 to 0.7 per cent.

Physicochemical Properties.—The fact that Moroccan producers distill a charge of plants only for 2 to 4 hr. is doubtless responsible for the relatively low thymol content of Moroccan thyme oil. Distilling up to 8 hr., the Spanish producers obtain oils with a phenol content varying from about 50, up to 60 per cent. By prolonging distillation, the phenol content of the Moroccan oils could most likely be increased.

There is, however, a possibility that other factors (such as different botanical varieties, altitude, etc.) may be responsible for the relatively low phenol content of the Moroccan thyme oils. As was pointed out above, plant material growing up to an altitude of 2,000 m. is used in distillation, whereas in Spain, plants growing in the plains are preferred.

Two genuine red thyme oils procured by the author in Morocco had these properties:

(a) Oil of Thyme distilled June 5, 1937, in the Medium Atlas, from the entire plants, fresh and blooming; length of distillation 2 hr.

Specific Gravity at 25°/25°	0.891
Optical Rotation at 20°	−3° 12′
Refractive Index at 20°	1.4909
Phenol Content	28.0%
Solubility at 25°	Soluble in 7 vol. and more of 80% alcohol

(b) Oil of thyme distilled in the Medium Atlas, July 16, 1937, exclusively from flowers and dried leaves; length of distillation 2½ hr.

Specific Gravity at 25°/25°	0.909
Optical Rotation at 20°	−3° 12′
Refractive Index at 20°	1.4969
Phenol Content	37.0%
Solubility at 25°	Soluble in 1.5 vol. and more of 80% alcohol

An imported genuine lot of Moroccan red thyme oil, analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 25°/25°	0.910
Optical Rotation at 20°	−2° 20′
Refractive Index at 20°	1.4947
Phenol Content	35.0%
Solubility at 25°	Soluble in 1 to 1.5 vol. and more of 80% alcohol

Chemical Composition and Use of Thyme Oil

Chemical Composition.—The first investigation of the chemistry of thyme oil dates back to 1853 when Lallemand [16] identified thymol as the main constituent of thyme oil. The results of later work, however, have remained somewhat confused, for the reason that no clear distinction was made between thyme oil (*Thymus vulgaris* L. or *T. zygis* L.) and origanum oil (*Coridothymus capitatus* Rchb. f.—*Thymus capitatus* Hoffmg. et Link) and even other species, either oil being designated simply as "thyme oil." The most thorough investigation was undertaken by Schimmel & Co. [17] who examined a Spanish thyme oil.

The presence of the following compounds has been established:

Amyl Alcohol. Identified by the Schimmel chemists in the lowest boiling fractions b. 130°–132°, as naphthylurethane m. 51°–52°.

β,γ-Hexenol. When benzoylated in pyridine solution, the small fraction b. 145°–150° gave a benzoate which, upon saponification, yielded an alcohol possessing the characteristic odor of β,γ-hexenol b. 156°. Characterized as naphthylurethane m. 58°–60° (not sharp).

Walbaum [18] had previously identified $\beta\gamma$-hexenol as phenylacetic acid ester, in the last runs of Japanese mint oil.

A Terpene(?). This terpene possesses a carrot-like odor; its structure remains unknown.

(1) B. 155°, d_{15} 0.8533, α_D +4° 50′, n_D^{20} 1.46201.
(2) B. 155°–156°, d_{15} 0.8537, α_D +4° 35′, n_D^{20} 1.46231.

l-α-Pinene(?). The *l*-rotatory terpene $C_{10}H_{16}$, b. 160°–165° originally named thymene by Lallemand,[19] was shown to be actually *l*-α-pinene by the Schimmel chemists.[20] Its presence in thyme oil, however, is still doubtful; it seems to occur

[16] *Compt. rend.* **37** (1853), 498. *Liebigs Ann.* **101** (1857), 119. *Ann. chim. phys.* [3], **49** (1857), 148. *Liebigs Ann.* **102** (1857), 119.
[17] *Ber. Schimmel & Co.* (1922), 71.
[18] *J. prakt. Chem.* [2], **96** (1917), 245.
[19] *Compt. rend.* **37** (1853), 498. *Liebigs Ann.* **101** (1857), 119. *Ann. chim. phys.* [3], **49** (1857), 148. *Liebigs Ann.* **102** (1857), 119.
[20] *Ber. Schimmel & Co.*, October (1894), 57.

in the oil in such small quantities that considerable amounts of oil must be fractionated before the terpene can be identified.

β-Pinene. Identified by the preparation of nopinic acid m. 126°–127°. Only a small quantity is present in thyme oil.

Adida and Demigneux [21] reported that a French thyme oil (*Thymus vulgaris* L.) contained 7.5 per cent of *l*-rotatory pinene.

Camphene. Conversion to isoborneol m. 208°–210°, according to Schimmel & Co.[22]

p-Cymene. Very small quantities occur in the fraction b. 175°–179°. Oxidation to hydroxyisopropylbenzoic acid m. 153°–154°.

γ-Terpinene. The main constituent of the nonphenolic portions. Present in the fraction b. 176°–183°. Identified as dihydrochloride m. 51°–52°. Oxidation with potassium permanganate and potassium hydroxide gave the erythritol m. 236°–237°.

α-Terpinene, according to the Schimmel chemists,[23] is not present in thyme oil. These workers also established the presence of the following alcohols:

Linaloöl. Characterized by the preparation of the phenylurethane m. 65°.

l-Borneol. M. 204°. Oxidation to camphor.

Terpinen-4-ol. In the fraction b_{6-7} 86.5°–91.5°; identified as terpinene dihydrochloride m. 51°–52°.

Efforts to prove the presence of α-terpineol in thyme oil were unsuccessful.

Geraniol. Small quantities occur in the fraction b_7 91.5°–102°; characterized as diphenylurethane m. 82°; oxidation to citral.

Thymol. Thyme oil contains about 50 per cent of phenols, which consist mainly of thymol. In old oils thymol occasionally separates in the form of crystals. The phenols can be isolated by treating the oil with aqueous potassium hydroxide or sodium hydroxide solutions; by acidifying, the phenols are regenerated.

Carvacrol and a Phenol(?). The bulk of the phenols, thus isolated, crystallize as thymol. A small quantity remains liquid, and consists of carvacrol and, probably another phenol which, so far, has not been identified.

(A method of separating thymol and carvacrol has been patented by Chem. Fabrik Von Heyden A. G.[24])

Caryophyllene. Caryophyllene is present, according to the Schimmel chemists, in the high boiling fractions b_7 102°–106° of thyme oil. Characterized by conversion into caryophyllene alcohol m. 94°–95°.

A Sesquiterpene(?) and a Sesquiterpene Alcohol(?). Caryophyllene seems to be accompanied by another sesquiterpene and by small quantities of a sesquiterpene alcohol.

[21] *Bull. sci. pharmacol.* **33** (1926), 65.
[22] *Ber. Schimmel & Co.* (1922), 72.
[23] *Ibid.*
[24] German Patent No. 462150, January 24, 1926.

Adida and Demigneux [25] applied the term "thymene" to that fraction of thyme oil which distills between 160° and 185°. The same term is also used commercially and loosely comprises the terpenes which remain after the isolation of thymol by fractional distillation of thyme oil.

Use.—Oil of thyme, a powerful germicide, finds wide application as a disinfectant and antiseptic of rather pleasant odor. It is used as such in many pharmaceuticals and oral preparations—gargles and mouth washes, for example.

The oil is said to cause mental excitement; it serves as a diffusible stimulant in collapse.

Oil of thyme is used also for the scenting of soaps.

On an increasing scale, oil of thyme serves for the flavoring of all kinds of food products, meats, sausages, sauces, and canned foods, in which it replaces the botanical as condiment.

Suggested Additional Literature

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F. La Face, "Calabrian Oils of Thyme," *Boll. ufficiale staz. Reggio Calabria,* June (1926). *Parfums France* **4** (1926), 366.

B. N. Rutovski and I. V. Vinogradova, "Essential Oils of Caucasian and Crimean *Thymus*," *Trans. Sci. Chem. Pharm. Inst. Moscow* (1927), No. 17, 98. *Chem. Abstracts* **23** (1929), 3049.

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[25] *Bull. sci. pharmacol.* **33** (1926), 65.

H. G. Mäckel, "Spanish Thyme from *Thymus zygis* L.," *Z. Lebensm.-Untersuch. u. -Forsch.* **87** (1944), 83. *Chem. Abstracts* **41** (1947), 7575.

A. Fernandes Costa and J. Cardosa do Vale, "Some Essential Oils of the Genus *Thymus*," *Bol. escola farm. univ. Coimbra Portugal* **5** (1945), 1. *Chem. Abstracts* **42** (1948), 3908.

OIL OF *THYMUS HIEMALIS* LANGE

("Thyme Lemon Oil"—"Spanish Verbena Oil")

Essence de Verveine d'Espagne *Aceite Esencial de Verbena de España*
Spanisches Verbenaöl

There still seems to exist some confusion regarding the nomenclature of the plant from which verbena oil is distilled, although more than twenty years ago Umney [1] and Holmes [2] studied the plants morphologically.

True verbena oil is distilled from *Lippia citriodora* (Lam.) Knuth, fam. *Verbenaceae*, whereas the so-called Spanish verbena or thyme lemon oil is said to be derived from *Thymus hiemalis* Lange.[3] The oils are similar, both containing citral as main constituent. The true verbena oil, however, is laevorotatory, Spanish verbena oil dextrorotatory. The latter oil, in turn, closely resembles "tomillo limonero" (*Thymus hirtus* Willd.); see section on "Spanish Thyme Oil." Oil of *Thymus hiemalis* has not attained any commercial importance.

Physicochemical Properties.—The properties of oil of *Thymus hiemalis* have been determined by several investigators [4] who reported the following limits:

Specific Gravity at 15°	0.901 to 0.926
Optical Rotation	+2° 45′ to +18° 30′
Refractive Index at 20° (of only a few oils)	1.48024 to 1.48267
Aldehyde Content (Citral)	13.0 to 34.0%

[1] *Perfumery Essential Oil Record* **3** (1912), 212.

[2] *Ibid.* **11** (1920), 339.

[3] Index Kewensis does not list *Thymus hiemalis* Lange, but it describes *Salvia hiemalis* Brot. which is identical with *Salvia verbenaea* L., growing in Mediterranean and Atlantic Europe. Spanish verbena has also been classified as *Verbena triphylla*, L.

[4] Kerschbaum, *Ber.* **33** (1900), 887. Parry and Bennett, *Chemist Druggist* **69** (1906), 481. *Ber. Schimmel & Co.*, April (1907), 107. Chiris, *Parfums France* **3** (1925), 18.

Two of these oils had, in addition, these properties:

	I	*II*
Saponification Number	7.45	15.44
Ester Number after Cold Formylation	66.82	92.55
Free Alcohol Content, Calculated as $C_{10}H_{18}O$	16.89%	22.26%
Total Alcohol Content	19.06%	26.50%
Ester Content, Calculated as $C_{12}H_{20}O_2$	2.76%	5.40%

Chemical Composition.—Our knowledge of the chemistry of this commercially unimportant oil is rather incomplete. The presence of the following compounds has been reported:

Citral. The oil contains from 13–34 per cent of aldehydes, mainly citral, according to Parry and Bennett.[5] The occurrence of citral in *a*- and *b*- form has been suggested by Kerschbaum.[6]

Verbenone. The same author also reported the presence in thyme lemon oil of a new ketone $C_{10}H_{16}O$ which he named verbenone, b_{16} 103°–104°, d_{17} 0.974, α_D +66° 0′, n_D 1.49951; semicarbazone m. 208°–209°; oxime m. 119°–120°.

Terpenes(?) and Alcohols(?). According to Kerschbaum, the oil contains about 86 per cent of terpenes and alcohols which, however, have not been identified.

OIL OF *THYMUS HIRTUS* WILLD.

An oil closely allied to *Thymus hiemalis* Lange is that of *Thymus hirtus* Willd., known in Spain as "tomillo limonero." *Thymus hirtus* grows wild on calcareous hills in the province of Granada. Commercially the oil has not attained any importance.

Physicochemical Properties.—An oil investigated by Dorronsoro [1] had a lemon-like odor and the following properties:

Specific Gravity at 15°	0.909
Optical Rotation at 15°	+13° 20′
Refractive Index at 15°	1.4825
Acid Number	4.2

[5] *Chemist Druggist* **69** (1906), 481.
[6] *Ber.* **33** (1900), 887.
[1] "Estudio Quimico de Esencias naturales españoles," *Mem. acad. cienc. exactas Madrid* **29** (1919). *Ber. Schimmel & Co.* (1921), 87.

Ester Number	18.34
Ester Number after Acetylation	95.35
Ester Content, Calculated as Acetate of Alcohol $C_{10}H_{18}O$	6.42%
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	28.35%
Free Alcohol Content	22.52%
Citral Content	
(Bisulfite Method)	6.60%
(Hydroxylamine Method)	12.54%
Boiling Range	
155°–173°	9.05%
173°–180°	9.80%
180°–190°	18.00%
190°–200°	19.11%
200°–210°	23.25%
210°–220°	8.92%
220°–225°	6.05%
Residue	5.82%

Chemical Composition.—According to Dorronsoro,[2] the oil contains the following compounds:

d-Limonene(?). Twenty to 25 per cent of the oil consists probably of *d*-limonene b. 175°–176°, d_{15} 0.850.

Linaloöl(?). Probably present in the fraction b. 190°–220°.

d-Fenchone. Identified as semicarbazone m. 176°–178°.

Dorronsoro concluded that the oil is composed as follows:

	Per Cent
Terpenes (Limonene)	20.00 to 25.00
Citral	12.54
Esters, Calculated as Acetate of Alcohol $C_{10}H_{18}O$	6.50
Free Alcohols, Calculated as $C_{10}H_{18}O$	22.60
Fenchone, Resins, etc.	33.36

SUGGESTED ADDITIONAL LITERATURE

E. J. Parry, "Essential Oil Production in British East Africa," *Perfumery Essential Oil Record* **8** (1917), 263.

[2] *Ibid.*

OIL OF *THYMUS SERPYLLUM* L.

("OIL OF WILD THYME")

Essence de Serpolet *Aceite Esencial de Tomillo Silvestre* *Quendelöl*
Oleum Serpylli

Thymus serpyllum L. grows wild in many parts of Southern Europe, Central Asia, and North America. The yield of oil is small, distillation of the fresh herb giving 0.27 per cent and that of the dried herb up to 0.60 per cent of oil.

The oil has not attained any commercial importance, except perhaps in Russia, which country, according to Zander,[1] at one time produced several thousand kilograms. This information, however, may be incorrect, the plant having possibly been confused with some other *Thymus* species.

Physicochemical Properties.—Gildemeister and Hoffmann [2] give the following properties for oil of *Thymus serpyllum* L.:

Specific Gravity at 15°/15°	0.873 to 0.920
Optical Rotation	−1° 44′ to −21° 0′

Flowering fresh herb grown on the Crimea peninsula and distilled by Rutovski, Vinogradova, and Kondratski [3] yielded 0.27 per cent of an oil possessing these properties:

	Oil from Wild Herb	*Oil from Planted Herb*
Specific Gravity at 20°/4°	0.9131	0.8734
Optical Rotation	−8° 48′	−1° 26′
Refractive Index at 20°	1.4941	1.4865
Acid Number	3.6	1.09
Ester Number	21.72	15.25
Ester Number after Acetylation	14.03	59.44
Solubility	Soluble in 0.4 vol. of 90% alcohol	Soluble in 0.5 vol. of 90% alcohol

The properties of these Russian oils are somewhat different from those of oils of Mediterranean origin.

Cancer [4] recorded the following properties of an oil of *Thymus serpyllum* distilled in Calabria from wild growing herb (yield 0.22 per cent):

[1] *Chem. Ind.* **51** (1928), 116.
[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 772.
[3] *Repts. Sci. Chem. Pharm. Inst. Moscow* **11** (1925), 83. *Ber. Schimmel & Co.* (1926), 169.
[4] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **17** (1939), 156.

Specific Gravity at 20°	0.8895
Optical Rotation	−3° 40′
Refractive Index at 21°	1.4880
Acid Number	0.73
Ester Number	2.85
Saponification Number	3.68
Ester Content, Calculated as Linalyl Acetate	0.99%
Total Alcohol Content	28.19%
Phenol Content	24.0%
Solubility	Soluble in 1 vol. of 85% alcohol

An oil of very similar composition and physicochemical properties had been described some years earlier by La Face.[5]

More recently, Salgues[6] studied different types of oil of *Thymus serpyllum* L. distilled in Provence (France) from plants growing in the mountains, and in the fields, and at different stages of plant development. These oils contained approximately 50 to 55 per cent of carvacrol, 2–4 per cent of thymol, and 1.5 to 3 per cent of borneol.

In the light of these later data, earlier investigations of the chemical composition of oil of *Thymus serpyllum* L. reported below must be viewed with suspicion.

Oil of *Thymus serpyllum* L. has an agreeable odor, slightly reminiscent of *Thymus vulgaris* L.

Voss[7] studied the odor of *Thymus serpyllum* plants ("Feldthymian") growing wild in the *Riesengebirge* (Germany) and observed that plants of the same botanical species seemed to contain essential oils of entirely different composition.

Chemical Composition.—The chemistry of this commercially unimportant oil is not well defined. The presence of the following compounds has been reported:

p-Cymene. The bulk of the oil boils between 175°–180° at 760 mm. and consists of *p*-cymene, according to Febve.[8]

A Hydrocarbon(?) $C_{10}H_{16}$. Only traces of this dextrorotatory hydrocarbon are present.

Carvacrol, Thymol and a Phenol(?). Jahns[9] reported that the oil contains about 1 per cent phenols, consisting of carvacrol, thymol, and another still unidentified phenol.

[5] *Ibid.*
[6] *Rev. gen. sci.* **52** (1942), 35. *Chem. Abstracts* **39** (1945), 5398.
[7] *Seifensieder-Ztg.* **70** (1943), 60.
[8] *Compt. rend.* **92** (1881), 1290.
[9] *Arch. Pharm.* **216** (1880), 277. *Ber.* **15** (1882), 819.

Sesquiterpenes(?). According to the same author, sesquiterpenes are probably present in the fractions b. 200°–250°.

Adida and Demigneux [10] claimed to have identified *l*-pinene in the fraction b. 155°–160° of commercial oil of *Thymus serpyllum* (oxidation to pinonic acid and preparation of the semicarbazone m. 201°–203°). However, it is quite possible that the oil investigated by these authors, like most commercial so-called wild thyme oils was adulterated (e.g., with an oil that contained *l*-pinene).

Distilling *Thymus serpyllum* L. growing wild in Punjab and Kashmir, Singh and Rao [11] obtained 0.5 per cent of an oil with these properties:

Specific Gravity at 30°/30°	0.9269
Specific Optical Rotation at 30°	−4° 48′
Refractive Index at 30°	1.4968
Phenol Content (Mainly Carvacrol)	52.7%

Singh and Rao reported the presence of:

	Per Cent
p-Cymene	About 17.0
Terpenes (γ-Terpinene and Others)	About 8.0
Terpene Alcohols	About 5.0
Sesquiterpenes (Zingiberene and Others)	About 4.0
Phenols (Mainly Carvacrol and Another Phenol Not Identified)	About 53.0

Suggested Additional Literature

T. Kaku and I. Yamagami, "*Thymus serpyllum* var. *Prezewalski* Komarov. Chemical studies," *Japan. J. Med. Sci.* [IV] *Pharmacol.* **11**, No. 2/3, *Proc. Japan Pharmacol. Soc.* **12** (1938), 116. *Chem. Abstracts* **34** (1940), 7534.

[10] *Bull. sci. pharmacol.* **33** (1926), 65.
[11] *J. Indian Inst. Sci.* **15A** (1932), 78. *Ber. Schimmel & Co.* (1934), 61.

INDEX

Numbers in *italics* indicate main entries; in the case of a plant species, they indicate references to monographs (or sections of monographs) dealing with the *oil* of the species.

Wherever possible, synonymous names for chemical compounds have been brought together under one main heading, such heading being in each case that employed in Vol. II of this series. Cross references are made from the several synonyms. Thus: *Umbelliferone methyl ether* may be called *Herniarin, Methylumbelliferone,* or *7-Methoxycoumarin.* In this index, the last three names are cross-referred to *Umbelliferone methyl ether.* The researcher interested in tracing the occurrence of any specific chemical compound in the various oils treated here should find this system helpful.

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