Oils were used abundantly in daily life in ancient times. In this early Egyptian painting from the tomb of Senejem, a son presents a libation of fragrant oil to Senejem and his wife.

**ESSENTIAL OILS**

by A. J. Haagen-Smit

More than a million different species of plants and animals have already been described by taxonomists, and new species are discovered every day. Even in densely populated areas it is still possible to discover some new species, as George MacGinitie, Caltech's emeritus professor of biology, proved in our time by digging up a nearly-one-foot-long animal, the *urechis caupo*, on a California beach.

What has the chemist done with this wealth of material? In handbooks on chemistry we find listings of fat, carbohydrate, and protein content of many organisms, and in addition some 10,000 miscellaneous compounds which are found in individual species. When we realize that only a small fraction of all known organisms (less than half of one percent) have received little more attention than a label from taxonomists, it is clear that much work still has to be done. Nevertheless, the study of natural products has played an important role in the development of organic chemistry, and has given us products of great commercial and medical importance.

The present revival of interest in these compounds from natural products continues to give evidence of the astounding synthetic abilities of living organisms. Through a revolution in analytical methods, as well as progress made in biochemistry, new research avenues have been opened for such classical problems as those of alkaloids and pigments. These compounds no
The study of essential oils has had an exciting past. Now, with improved analytical techniques, it has an equally exciting future.

longer stand by themselves as freaks of nature, but have become expressions of general metabolic processes.

The same is true of another group of natural products known as essential oils. This name is a very old one and refers to the alchemists' idea of the most sublime extractive, the Quinta Essentia. This material was, in general, the active ingredient of pharmacologically important drugs. Later the name was applied to volatile materials responsible for the fragrance of plants. The manifold aspects of these materials have been studied by chemists, plant physiologists, and pharmacologists as well as historians.

One could write a world history on the basis of essential oils. These highly valued products have played a very important role in the economy of many countries—especially in classical times.

In the ancient countries of the Orient, in Greece, and in Rome the essence of flowers and roots was extracted by placing them in fatty oils. The glass bottles containing these mixtures were warmed in the sun, and finally the odoriferous oils were separated from the solid materials. Sometimes the flowers or plants were macerated with wine, and the product obtained by digestion was then filtered and boiled to a syrup.

These fatty oils and syrups containing the fragrance of flowers and leaves and the oleoresin of trees—such as labdanum, myrrh, and incense—were some of the most valuable products of commerce in ancient history.

Relics of the Egyptian period, several thousand years ago, show evidence of the use of these products. Even the one-room exhibit of Egyptian art in the L.A. County Museum contains many items relating to the abundant use of odoriferous oils and ointments in daily life, and in religious ceremonies. The empty mummy case in the corner of the Egyptian room has in the bottom of the case a life-size painting of the deceased which shows an oil jar at his right containing odoriferous oil. The mummy itself was preserved with cedar oil and other resins such as myrrh and cinnamon.

In the Bible (Exodus 30:63 and 64) we find some detailed recipes for the preparation of an ointment with which the altar, its vessels, candlesticks, and even the priest, should be anointed. The exact composition is also given for a perfume (a name used in the old original sense, meaning that which is produced by burning). In many places it mentions the use of spices and odoriferous oleoresins such as myrrh, cinnamon, and labdanum.

Caravans from India and China brought many of these products to Egypt. As the Bible tells us in Genesis 37:25, after Joseph was cast into a pit by his brothers:

"... they sat down to eat bread: and they lifted up their eyes and looked, and behold, a company of Ishmaelites came from Gilead with their camels bearing spicery and balm and myrrh, going to carry it down to Egypt."

Often the fragrant oils were endowed with mysterious properties and it is said that Helen of Troy possessed a secret perfume, revealed to her by Venus, which was responsible for her fabulous beauty. While the secret of such magic perfumes has been lost, later generations tried to make up for this in quantity. Laws were even passed in England during the reign of King George III, in 1774, which forbade women to "seduce and betray into matrimony any of His Majesty's subjects by the use of scents, cosmetics and other artificial means." Penalties were the same as those used against witchcraft and upon conviction the marriage would be null and void.

Our present Federal Food and Drug Administration may not go quite so far. It has stated repeatedly that it does not believe in the cure-all properties of fragrant oils, nor in the radio and television claims of irresistible effects of perfumes and ointments on males and females. Everyone can readily agree, however, that the fragrance of flower oils is pleasant, and the industry is hardly to blame if it has supplied us with an abundance of the volatile odoriferous products. Today, as thousands of years ago, natural as well as artificial scents accompany us from early morning to late at night.

These odors take many forms. The eucalyptus trees in the center of the Caltech campus give off the odor of a well-known brand of cough drops. On the other hand, the eucalyptus at the entrance to the Athenaenum smells quite different and resembles lemon; in fact it has been called E. citriodora, in distinction to
Distillation in the 16th century: “In fire the juice of all bodies, by means of art, becomes a vigorous liquid.”

the more common *E. globulus*.

Each plant has its peculiar odor, and this odor is most frequently the property of the oils secreted in special cells, or in intercellular spaces in the plant. These oil-filled spaces can readily be observed in an orange peel. By bending the peel, the cell walls of the container are torn and the droplets of orange oil form a spray, which can be seen by the light of a candle. The simple process of release of the oil by pressing is the basis of a large industry producing orange and lemon oil in the nearby towns of Ontario and Corona.

The old way of producing this oil was to press by hand and collect the oil in a sponge. When the sponge was saturated, the oil was squeezed out. This process is still used in Italy and Spain. An operator can collect from one to two pounds of oil per day from 200 pounds of fruit.

Our California lemon and orange byproducts industry solves this problem by mechanically reproducing the work of the individual hand presser. In this way the orange byproducts plant in Ontario supplies 400,000 pounds of orange oil per year. The lemon industry in Corona produces 650,000 pounds of lemon oil per year.

The oils so obtained are practically insoluble in water, just like fatty oils; however, unlike these, they are volatile. A drop of volatile oil on filter paper disappears after a time, while a fat gives a lasting spot. Turpentine can be used to remove the fat spot. This fat solubility has been recognized for a long time and forms the basis for a process called *enfleurage* still practiced chiefly in the south of France. Flowers are spread on glass plates covered with fat. These are held in a wooden frame and stacked one on top of the other so that the flowers are surrounded by fat. While the odors are given off by the flowers they dissolve in the fat and afterwards the fat is collected and extracted with alcohol. In this way the perfume industry obtains the highly valued and very expensive absolutes of *enfleurage*.

This process doesn’t fit too well into our present day economy and is gradually being replaced by solvent extraction with low-boiling petroleum fractions. The oils obtained by pressing oranges or lemons, or those obtained by fat extraction, are volatile by themselves, or they can be distilled over with steam.

In areas far from civilization these distillations are carried out in very much the same way that was described in the books on distillation printed in the 16th century.

In essential oil centers, on the other hand, we find the most modern stills, capable of handling large quantities of oil. American oil of turpentine is produced in this way in Georgia and Florida by steam distilling of the oleoresins from the pine trees. When the mixture of water vapor and the volatile material is condensed, two layers are formed. The top layer, above the water, is an oily liquid, which is the turpentine. What remains in the distilling flask is rosin. In this country 300,000 barrels of turpentine are processed every year (with 50 gallons in each barrel).

The same process is used in the preparation of oil of peppermint. In Michigan, Indiana, Oregon, and Washington, 1.5 million pounds a year are produced, largely for chewing gum flavoring. In addition, huge quantities are imported from Japan to satisfy the demands of the flavor industry for candy, dental

*May, 1961*
cream, ice cream, and numerous other products.

The public demand for these products has established an essential oil industry with a yearly turnover of an estimated $50,000,000. Far greater, however, is the turnover of the finished products that go to the consumer. Most of these finished goods, such as perfumes, require only a small amount of the oils, and this business runs into many billions per year.

The modern perfumer draws on thousands of odoriferous compounds to compose perfumes and flavors. The walls of his studio are lined with shelves filled with bottles of natural oils, individual fractions of the oils, and synthetics. None of the individual compounds would be satisfactory as a perfume, and it requires a great deal of skill and good taste to blend these so that they become acceptable.

Stimulated by the desire of the perfume and flavor industry to substitute synthetic odors for the natural ones, considerable work has been done on analysis of natural products, and the establishment of the correct chemical structure of the individual pure components. Only 200 years ago a PhD candidate at a university in Jena, Germany, could successfully defend the thesis that the ingredients of the distilled oils consisted of sulphur or phlogiston, earth, and salt. Now it is possible to indicate the exact structure of most of the molecular species of distilled oils, and synthetic methods allow the duplication in the laboratory of most of these molecules.

The terpenes — many and varied

The hundreds of pure chemical compounds isolated from oils form a heterogeneous lot from a chemical point of view, and we find among them hydrocarbons, alcohols, aldehydes, acids, esters, open-chain and cyclic compounds. Biochemically, however, most of them are associated in some way with fundamental life processes. Normal heptane from the turpentine of Pinus jeffreyi as well as decyl aldehyde from orange oil is linked to fat metabolism. The odoriferous indole produced during the evening by the night blooming jasmine is related to the amino acid metabolisms of all organisms.

By far the most frequent and diverse group of compounds from oils are the terpenes, named after their first isolation from turpentine. The odor from the eucalyptus leaf is due to a typical representative of this group. The cough-drop-smelling material is cineol, while the lemon type contains a large percentage of citronellall. Numerous members of this group are found in herb gardens and among many desert plants such as sage.

Interesting terpenes with strong pharmacological action are found in trees growing in southern California canyons. Anyone who has hiked through Monrovia Canyon, or climbed up to Sturtevant Falls, has rested in the shade of some large trees which spread a peculiar aromatic odor. This odor comes from the leaves of the California bay tree, *Umbellularia Californica.* In small amounts the odor is rather pleasant. Try, however, to inhale deeply the odors of a crumpled leaf and you will experience, for a second or so, a bursting headache, caused by the inhibitory action of one of the components of the volatile oil on the vagus of the heart, with a resulting temporary increase in blood pressure.

For the isolation of the compound the leaves are distilled with steam, and, after fractionation of the volatile oil, several pure compounds are obtained. Umbellulone, the blood-pressure-raising substance, is apparently the major component and is typical for this oil. The other components occurring in small quantities in this oil are major products in others. For example, safrole is the major flavor compound of the oil of sassafras, and consequently of root beer. (It has been coming in for some unfavorable publicity lately, since some attribute carcinogenic properties to this compound.) Eugenol is typical for oil of cloves, cineol is typical for eucalyptus oil, and pinene is the main ingredient of oil of turpentine.

Duplicating natural products

Perfume and flavor industries have for many years tried to make a complete analysis of essential oils with the intention of duplicating natural products. Only in recent years have the main difficulties towards this goal been overcome. Through the application of gas chromatography — aided by spectroscopic methods — tremendous progress has been made in the isolation and identification of oil compounds. This revolution is well illustrated by comparing present day analytical results with those obtained only a dozen years ago.

During the war years, an interest developed in the product of home grown rubber. One of the best sources was a desert shrub, *Parthenium argentatum,* commonly called guayule. This shrub is a most efficient rubber manufacturing plant and strains have been developed which contain up to 16 percent rubber. In addition, it contains $\frac{1}{2}$ percent of volatile products essentially similar to ordinary turpentine. The presence of alpha-pinene, beta-pinene, limonene, and a sesquiterpene alcohol, was established. This research took several months and a hundred pounds of leaves, which were carefully fractionated.

The new separation techniques are essentially based on difference in affinity. The gas mixture to be analyzed is pressed through a glass tube packed with a solid inert material coated with a solvent such as diethylene glycol. The high-boiling compounds with greater affinity to the solvent will move more slowly through the column than the more volatile components, and will separate in distinct fractions. With a sensitive detector, the organic materials which come through are measured and nicely separated peaks appear in the recorder of the gas chromatograph.
Chromatogram showing nine different pure compounds was produced in one day, with less than an ounce of leaves from the rubber-producing plant, guayule.

In a day’s work the chromatogram shown above was produced, showing nine distinct peaks, each indicating a different pure compound. Infrared spectra of these fractions showed that we were dealing with nine terpenes. This identification was accomplished by using less than an ounce of leaves, in a fraction of the time needed for the classical procedures. In addition to confirming the presence of the previously found terpenes, six new components were found and their identity established.

A look at the structures of the terpenes isolated from the guayule oil shows a common characteristic. They are all built of a chain of eight carbon atoms which has two methyl groups. This branched chain of carbon atoms is typical for the whole terpene group and can be constructed of two isopentane units, as shown at the right. All the other terpenes present in volatile oils can be constructed from this chain by connecting different carbon atoms and forming cyclic structures. For example, from plants and animals more complicated related structures containing many multiples of 5-carbon atoms have been isolated. Among these we find saponins, steroids, plant pigments, and rubber.

The recurrence of the isopentane unit in all these compounds has led in the past to much speculation about unit origin in plants or animals. Only in the last few years, through the work of many investigators in different countries, have we reached a better understanding of the biochemical processes in terpene formation. A key role in these syntheses is played by a 2-carbon unit – the acetate group. Through a coupling of three of these units with loss of one carbon atom the fundamental unit of 5-carbon atoms is formed. Two of these units in the form of their phosphate esters combine to form the terpenes present in the oils. When more of these units are coupled higher terpenes are formed, and this coupling culminates in the formation of rubber, which has several hundred of the isopentane building blocks.

Although, in the last few years, there has been tremendous progress in the knowledge of the nature of oil components, and in the biochemistry of their formation, much remains to be done. The improved analytical techniques allow us, for the first time, to make complete analyses of food flavors. This is of great importance to the food industry, which turns more and more to drastic processing of food, where often the desirable flavors are lost. An exact knowledge of these lost flavors becomes of decisive importance in the reconstitution of foods so that they regain most of the original quality.

Then there is the problem of what function these oils have in plants. Many theories have been proposed. All components of the oils are connected with major metabolic processes and it is possible that in many cases the oils could be byproducts in the numerous reactions carried out by the plant. Some of these products could serve a useful function and may, for example, serve as an attractant for insects, while others may act as repellants. We know that, especially among the higher terpenes, we find substances of great importance for the animal world as well as for the plant itself, such as hormones and vitamins. In general, however, we are completely in the dark about their function.

Finally we have to look into the genetic aspects and into the enzymatic reactions which lead to the formation of hundreds of different complicated organic structures. The study of essential oils has had a most exciting past and is bound to hold many surprises in the future.

CH3
\[\text{OCIMENE}\]

CH3
\[\text{LIMONENE}\]

The structures of ocimene and limonene, showing their formation from two isopentane units.