ABSTRACT

Essential oil components are often found in the glands or intercellular spaces in plant tissue. They may exist in all parts of the plant but are often concentrated in the seeds or flowers. Many components of essential oils are steam-volatile and can be isolated by steam distillation. Other methods of isolating essential oils include solvent extraction and pressing (expression) methods. Esters (see the essay “Esters-Flavors and Fragrances”) are frequently responsible for the characteristic odors and flavors of fruits and flowers, but other types of substances may also be important components of odor or flavor principles. Besides the esters, the ingredients of essential oils may be complex mixtures of hydrocarbons, alcohols, and carbonyl compounds. These other components usually belong to one of the two groups of natural products called terpenes or phenylpropanoids.

Anyone who has walked through a pine or cedar forest, or anyone who loves flowers and spices, knows that many plants and trees have distinctively pleasant odors. The essences or aromas of
plants are due to volatile or essential oils, many of which have been valued since antiquity for their characteristic odors (frankincense and myrrh, for example). A list of the commercially important essential oils would run to more than 200 entries. Allspice, almond, anise, basil, bayberry, car-away, cinnamon, clove, cumin, dill, eucalyptus, garlic, jasmine, juniper, orange, peppermint, rose, sandalwood, sassafras, spearmint, thyme, violet, and wintergreen are some of the familiar examples of such valuable essential oils. Essential oils are used for their pleasant odors in perfumes and incense. They are also used for their taste appeal as spices and flavoring agents in foods. A few are valued for antibacterial and antifungal action. Some are used medicinally (camphor and eucalyptus) and others as insect repellents (citronella). Chaulmoogra oil is one of the few known curative agents for leprosy. Turpentine is used as a solvent for many paint products.

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*Terpenes*

Chemical investigations of essential oils in the 19th century found that many of the compounds responsible for the pleasant odors contained exactly 10 carbon atoms. These 10-carbon
compounds came to be known as terpenes if they were hydrocarbons and as terpenoids if they contained oxygen and were alcohols, ketones, or aldehydes.

Eventually, it was found that there are also minor and less volatile plant constituents containing 15, 20, 30, and 40 carbon atoms. Because compounds of 10 carbons were originally called terpenes, they came to be called monoterpenes. The other terpenes were classified in the following way.

<table>
<thead>
<tr>
<th>Class</th>
<th>No. of Carbon</th>
<th>Class</th>
<th>No. of Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemiterpene</td>
<td>5</td>
<td>Diterpenes</td>
<td>20</td>
</tr>
<tr>
<td>Monoterpene</td>
<td>10</td>
<td>Triterpenes</td>
<td>30</td>
</tr>
<tr>
<td>Sesquiterpenes</td>
<td>15</td>
<td>Tetraterpenes</td>
<td>40</td>
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</tbody>
</table>

Further chemical investigations of the terpenes, all of which contain multiples of five carbons, showed them to have a repeating structural unit based on a five-carbon pattern. This structural pattern corresponds to the arrangement of atoms in the simple five-carbon compound isoprene. Isoprene was first obtained by the thermal “cracking” of natural rubber.

As a result of this structural similarity, a diagnostic rule for terpenes, called the isoprene rule, was formulated. This rule states that a terpene should be divisible, at least formally, into isoprene units. The structures of a number of terpenes, along with a diagrammatic division of their
structures into isoprene units, is shown in the figure on the next page that accompanies this essay. Many of these compounds represent odors or flavors that should be familiar to you.

Modern research has shown that terpenes do not arise from isoprene; it has never been detected as a natural product. Instead, the terpenes arise from an important biochemical precursor compound called mevalonic acid (see above). This compound arises from acetyl coenzyme A, a product of the biological degradation of glucose (glycolysis), and is converted to a compound called isopentenyl pyrophosphate. Isopentenyl pyrophosphate and its isomer 3,3-dimethylallyl pyrophosphate (double bond moved to the second position) are the five-carbon building blocks used by nature to construct all the terpene compounds.
Phenylpropanoids

Aromatic compounds, those containing a benzene ring, are also a major type of compound found in essential oils. Some of these compounds, like p-cymene, are actually cyclic terpenes that have been aromatized (had their ring converted to a benzene ring), but most are of a different origin.
Many of these aromatic compounds are phenylpropanoids, compounds based on a phenylpropane skeleton. Phenylpropanoids are related in structure to the common amino acids phenylalanine and tyrosine, and many are derived from a biochemical pathway called the shikimic acid pathway.

It is also common to find compounds of phenylpropanoid origin that have had the three-carbon side chain cleaved. As a result, phenylmethane derivatives, such as vanillin, are also common in plants.
Essay: Terpenes and Phenylpropanoids

Sources


