Volatile oils

TERPENOIDS

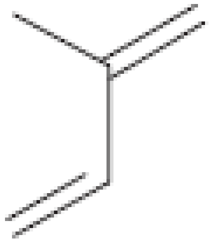
- There are many different classes of naturally occurring compounds. Terpenoids also form a group of naturally occurring compounds majority of which occur in plants, a few of them have also been obtained from other sources. Terpenoids are volatile substances which give plants and flowers their fragrance. They occur widely in the leaves and fruits of higher plants, conifers, citrus and eucalyptus.
- The term ‘terpene’ was given to the compounds isolated from terpentine, a volatile liquid isolated from pine trees. The simpler mono and sesquiterpenes is the chief constituent of the essential oils obtained from sap and tissues of certain plant and trees. The di- and triterpenoids are not steam volatile. They are obtained from plant and tree gums and resins. Tertraterpenoids form a separate group of compounds called ‘Carotenoids’.

The term ‘terpene’ was originally employed to describe a mixture of isomeric hydrocarbons of the molecular formula $C_{10}H_{16}$ occurring in the essential oils obtained from sap and tissue of plants and trees. But there is a tendency to use more general term ‘terpenoids’, which includes hydrocarbons and their oxygenated derivatives. However, the term terpene is being used these days by some authors to represent terpenoids.

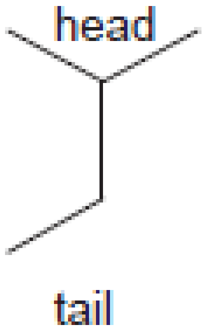
According to modern definition, ‘Terpenoids are the hydrocarbons of plant origin of the general formula $(C_5H_8)_n$ as well as their oxygenated, hydrogenated, and dehydrogenated derivatives.’

Isoprene Rule

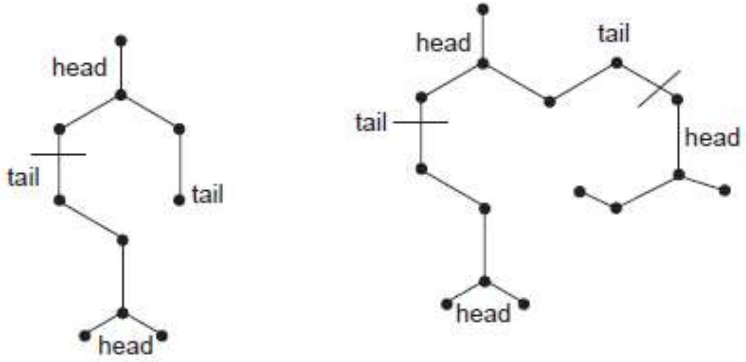
Thermal decomposition of terpenoids gives isoprene as one of the product. Otto Wallach pointed out that terpenoids can be built up of isoprene unit. Isoprene rule states that the terpenoid molecules are constructed from two or more isoprene unit.



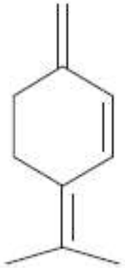
isoprene unit

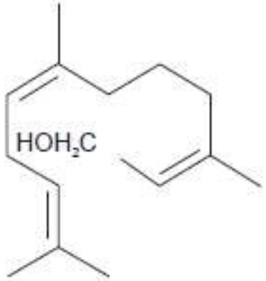


It states that the terpenoid molecules are constructed of two or more isoprene units joined in a ‘head to tail’ fashion.



Examples


Myrcene
(monoterpene)

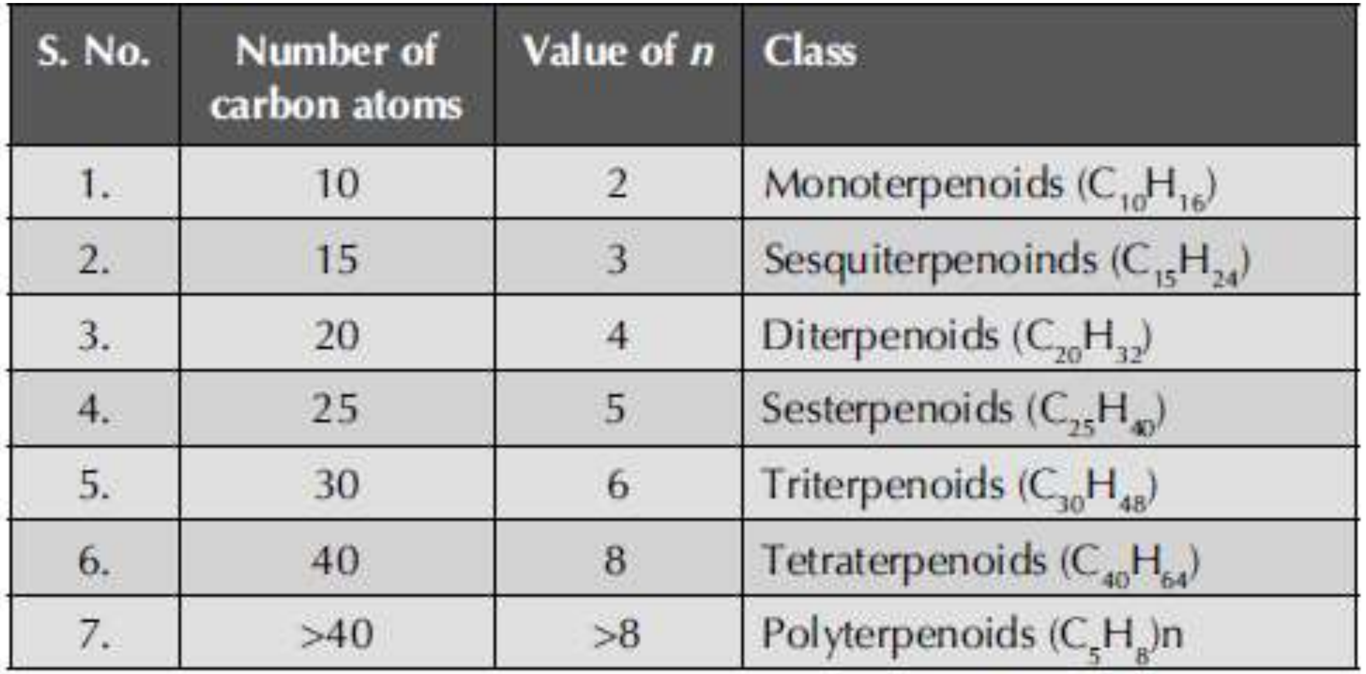


Farnesol
(sesquiterpene)

But this rule can only be used as guiding principle and not as a fixed rule. For example carotenoids are joined tail to tail at their central, and there are also some terpenoids whose carbon content is not a multiple of five.

CLASSIFICATION OF TERPENOIDS

Most natural terpenoid hydrocarbons have the general formula (C5H8)n. They can be classified on the basis of number of carbon atoms present in the structure.



S. No.	Number of carbon atoms	Value of *n*	Class
1.	10	2	Monoterpenoids ($C_{10}H_{16}$)
2.	15	3	Sesquiterpenoinds ($C_{15}H_{24}$)
3.	20	4	Diterpenoids ($C_{20}H_{32}$)
4.	25	5	Sesterpenoids ($C_{25}H_{40}$)
5.	30	6	Triterpenoids ($C_{30}H_{48}$)
6.	40	8	Tetraterpenoids ($C_{40}H_{64}$)
7.	>40	>8	Polyterpenoids $(C_5H_8)n$

Each class can be further subdivided into subclasses according to the number of rings present in the structure.

- 1. Acyclic Terpenoids: They contain open structure.
- 2. Monocyclic Terpenoids: They contain one ring in the structure.
- 3. Bicyclic Terpenoids: They contain two rings in the structure.
- 4. Tricyclic Terpenoids: They contain three rings in the structure.
- 5. Tetracyclic Terpenoids: They contain four rings in the structure.

Volatile oils are odorous volatile principles of plant, evaporate when exposed to air at ordinary temperature, and hence known as volatile or etheral oils.

These represent essence of active constituents of the plant and hence also known as essential oils. In most instances the volatile oil preexists in the plant and is usually contained in some special secretory tissues, for example, the oil ducts of umbelliferous fruits, the oil cells, or oil glands occurring in the sub-epidermal tissue of the lemon and orange, mesophyll of eucalyptus leaves, trichomes of several plants, etc.

- In few cases the volatile oil does not preexist, but is formed by the decomposition of a glycoside. For example, whole black mustard seeds are odourless, but upon crushing the seeds and adding water to it a strong odour is evolved. This is due to allyl isothiocyanate (the main constituent of essential oil of mustard) formed by decomposition of a glycoside, sinigrin, by an enzyme, myrosin. Glycoside and enzyme are contained in different cells of the seed tissue and are unable to react until the seeds are crushed with water present, so that the cell contents can intermingle.

- Volatile oils are freely soluble in ether and in chloroform and fairly soluble in alcohol; they are insoluble in water. The volatile oils dissolve many of the proximate principles of plant and animal tissues, such as the fixed oils and fats, resins, camphor, and many of the alkaloids when in the free state.
- These are chemically derived from terpenes (mainly mono and sesqui terpenes) and their oxygenated derivatives. These are soluble in alcohol and other organic solvents, practically insoluble in water, lighter than water (Clove oil heavier), possess characteristic odour, have high refraction index, and most of them are optically active. Volatile oils are

colourless liquids, but when exposed to air and

direct sunlight these become darker due to oxidation.

- Unlike fixed oils, volatile oils neither leave permanent

grease spot on filter paper nor saponified with alkalis.

CLASSIFICATION OF VOLATILE OILS

Essential oils could be divided into 3 groups. Essential oils, wich contain as the main component:

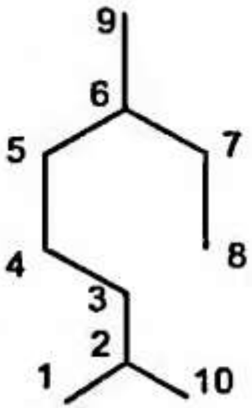
- Monoterpens.
- Sesquiterpens.
- Aromatic compounds.

Monoterpenoids are composed of 2 isoprene units and have the general molecular formula $C_{10}H_{16}$. They can occur in acyclic, monocyclic and bicyclic forms.

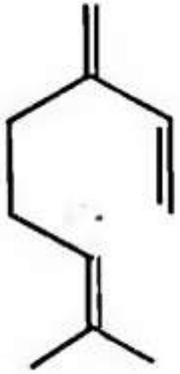
Sesquiterpenoids are composed of 3 isoprene units and have the general molecular formula $C_{15}H_{24}$. They can occur in acyclic, monocyclic, bicyclic and tricyclic forms.

All terpenes of volatile oils are hydrocarbons and their oxygenated derivatives such as alcohols, aldehydes, ketones, oxides and esters.

Acyclic monoterpenoids are derivatives of 2,6-dimethyloctan.

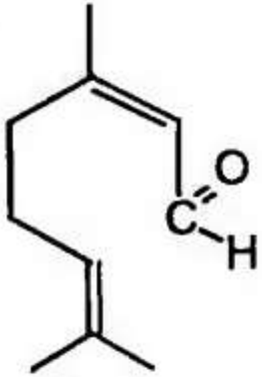


2,6-Dimethyloctan

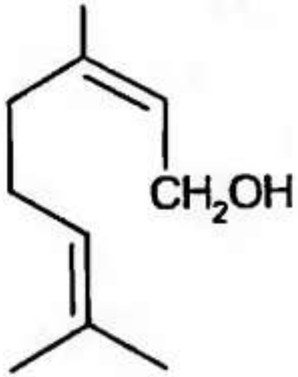


ß-Myrcene

Linalool



Citral

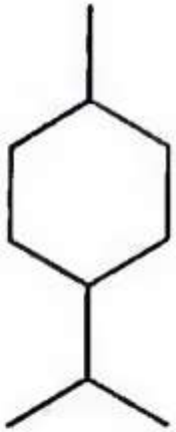


Geraniol

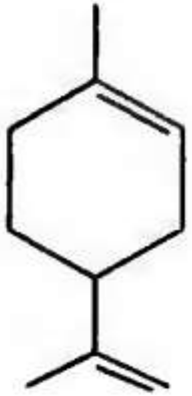
ß-Myrcene is contained in lemon oil, linalool — in coriander oil and orange flower oil. Geraniol is the main component of rose oil. Some lemon oils contain up to 13% of citral, but a range of 2 to 4%

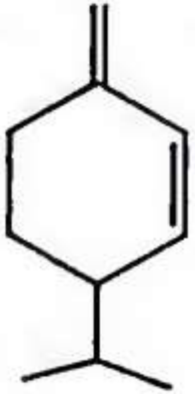
Monocyclic monoterpenoid derivatives belong to *p*-menthan type.

Hydrocarbon derivatives

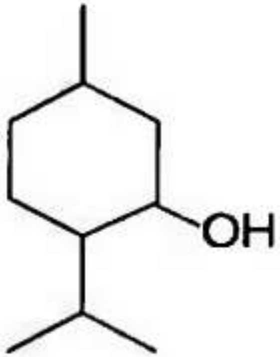

p-Menthan


α-Terpinene

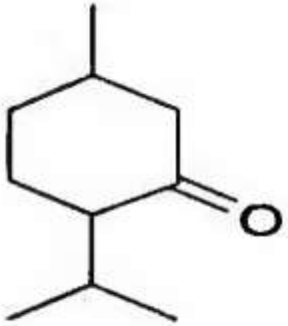

Limonene


β- Phellandrene

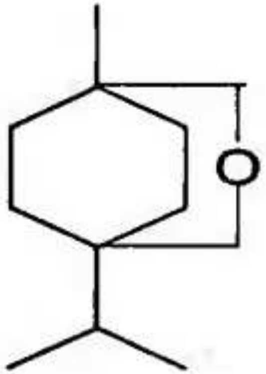
Oxygenated derivatives



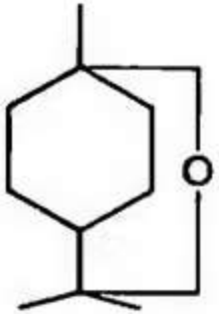
Menthol



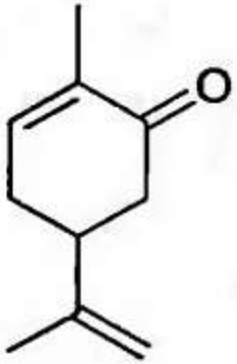
Menthone



1,4-Cineol



1,8- Cineol



Carvone

Limonene is probably the most widely distributed monocyclic hydrocarbon. It occurs in citrus, mint, caraway, thyme, cardamom, coriander and many other oils. Lemon oil contains about 70–80% of limonene.

Among the important oxygenated derivatives is menthol or menthan-3-ol. It is an alcohol obtained from diverse mint oils or prepared synthetically. Menthol may be levorotatory [(-)-menthol], from natural or synthetic sources, or racemic [(±)-menthol] produced synthetically. Menthol is usually prepared from peppermint oil by refrigeration (-22 °C), during which the menthol crystallises. Synthetic racemic menthol is produced by hydrogenation of thymol.

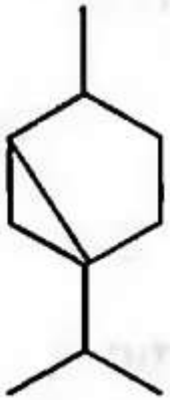
Menthol may also be prepared from pinene. Menthone is also contained in mint oil.

Cineol is found in *Eucalyptus* and *Salvia officinalis*.

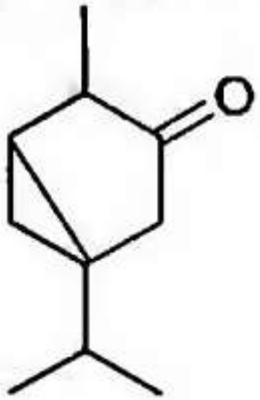
Menthol occurs as colourless, hexagonal crystals that are usually needle like, as fused masses, or as a crystalline powder. It has a pleasant, peppermint like odour.

Caraway oil contains about 50–85% of carvone.

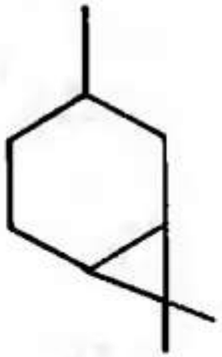
Bicyclic monoterpenes have two condensed rings. There are some types of these compounds: carane, pinane, camphane, fenchane types.



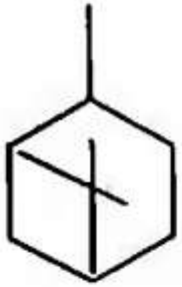
Thujane



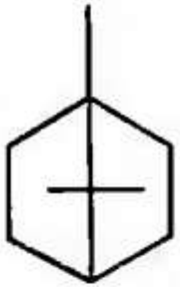
Thujone



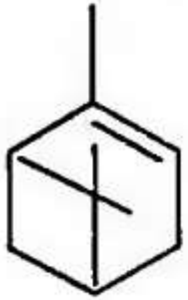
Carane



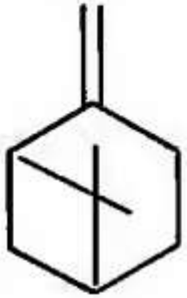
Pinane



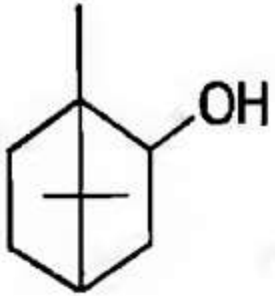
Camphane



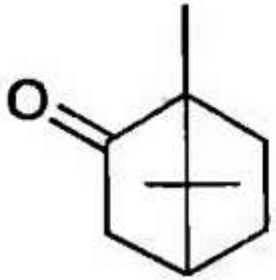
α-Pinene



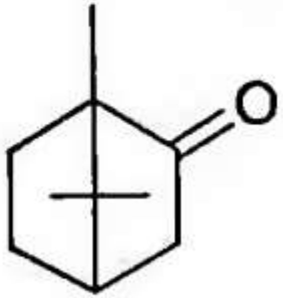
β-Pinene



Borneol



(+)-Camphor



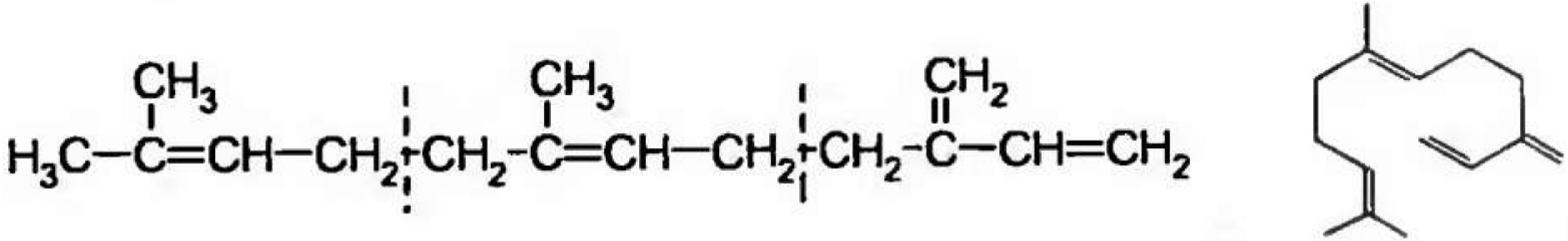
(-)-Camphor

Thujan derivatives are found in *Arthemisia absinthium* (wormwood oil), *Juniperus communis* (juniper oil). Pinane and bornane derivatives are found in pine oil, juniper oil, cinnamon oil. Cedar oil contains thujone, fenchone and pinene.

Camphor is a ketone obtained from *Cinnamomum camphora*, Fam. *Lauraceae*, (natural camphor) or produced synthetically (synthetic camphor). Natural camphor occurs as a crystalline product in clefts in the woody stems and roots and, to a greater extent, dissolved in the volatile oil. Synthetic camphor is made from pinene, the principal constituent of turpentine oil. The specific rotation of natural camphor is between +41° and +43°.

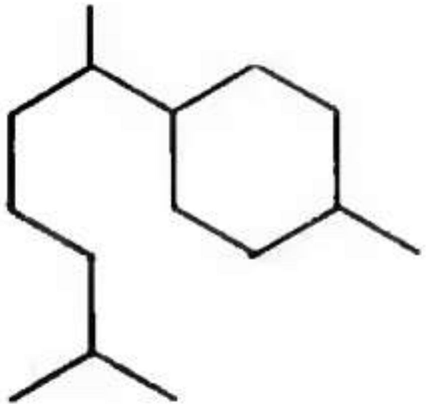
Synthetic camphor is the optically inactive racemic form.

Sesquiterpenoids ($C_{15}H_{24}$) biogenetically derived from farnesyl pyrophosphate and in their structure may be acyclic (linear), monocyclic, bicyclyc and tricyclic.

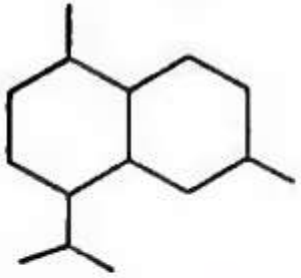


$$H_3C-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\vdots CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\vdots CH_2-\overset{CH_2}{\overset{\|}{C}}-CH=CH_2$$

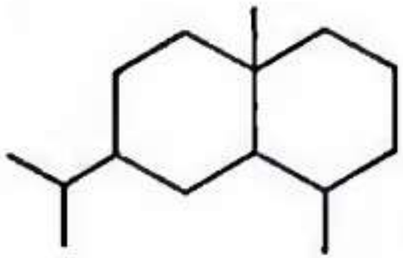
Two variants of the farnesene structure (acyclic)



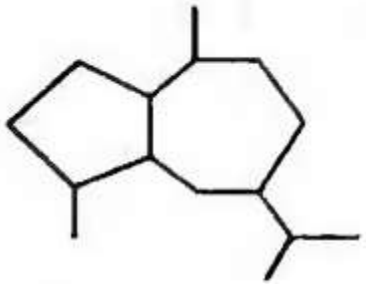
Bisabolane (monocyclic)



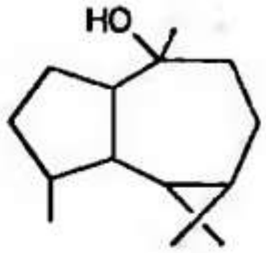
Cadinane



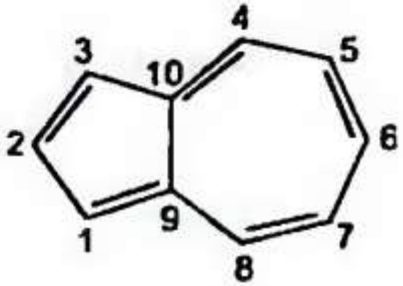
Eudesmane



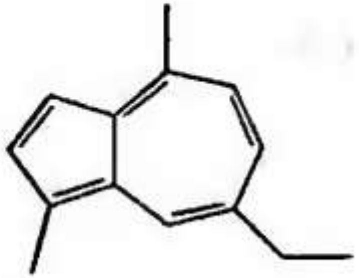
Guaiane



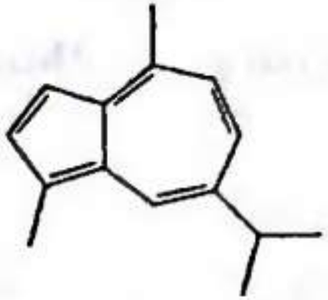
Ledol (tricyclic)



Azulene



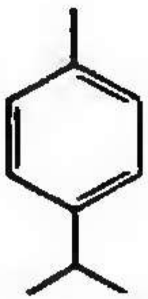
Chamazulene



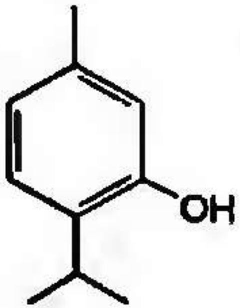
Guaiazulene

Aromatic compounds

p-Cymene type

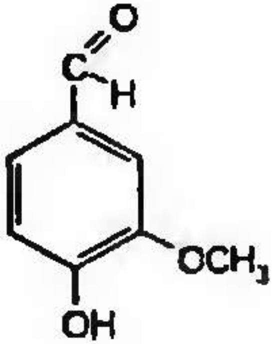


p-Cymene



Thymol

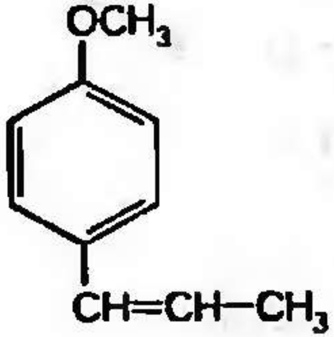
Benzene type



Vanillin

Phenylpropan type

Eugenol

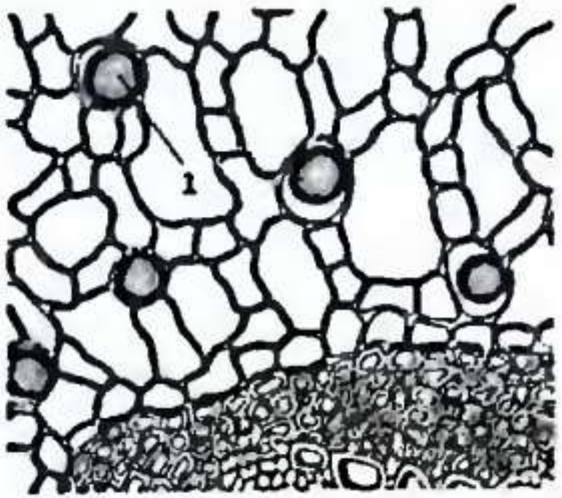


Anetole

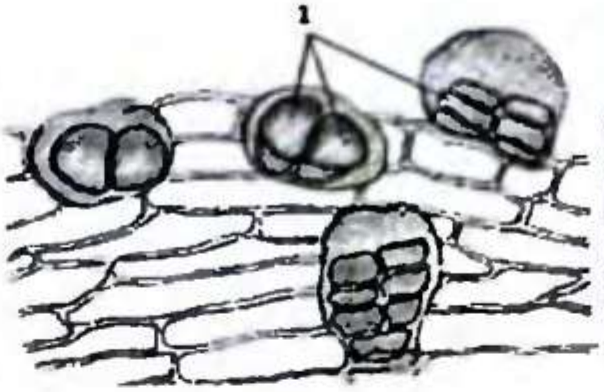
Distribution and occurrence

Some families are rich in species producing volatile oils (about 2,000 species representing about 87 families). The chief families are *Pinaceae, Lauraceae, Rutaceae, Myrtaceae, Apiaceae, Lamiaceae* and *Asteraceae.*

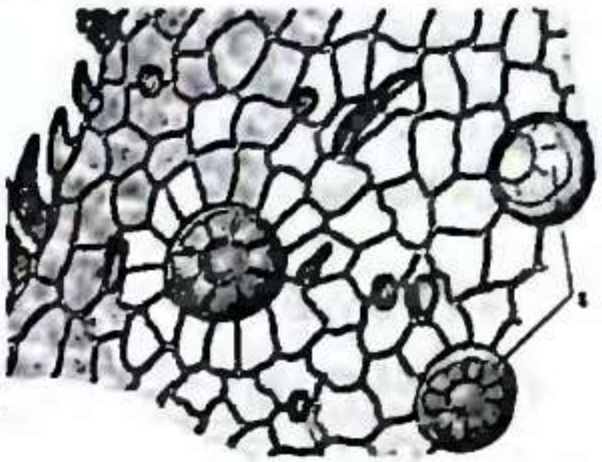
Depending on the plant family, volatile oils may occur in specialized secretory structures, such as glands (*Lamiaceae* and *Asteraceae*), modified parenchyma or oil cells (*Lauraceae* and *Piperaceae*), oil tubes or ducts (*Apiaceae*), as well as in internal lysigenous or schizogenous passages or glands (*Pinaceae* and *Rutaceae*).



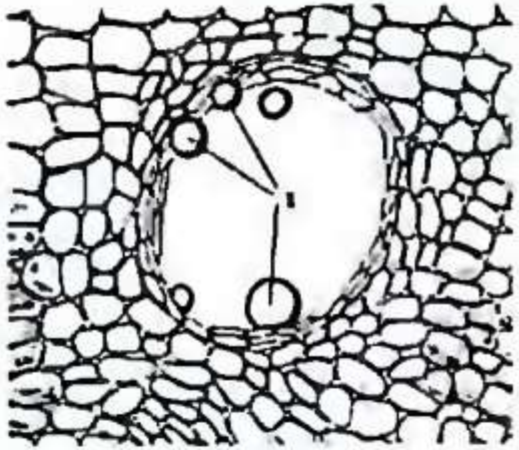
Essential oil cells



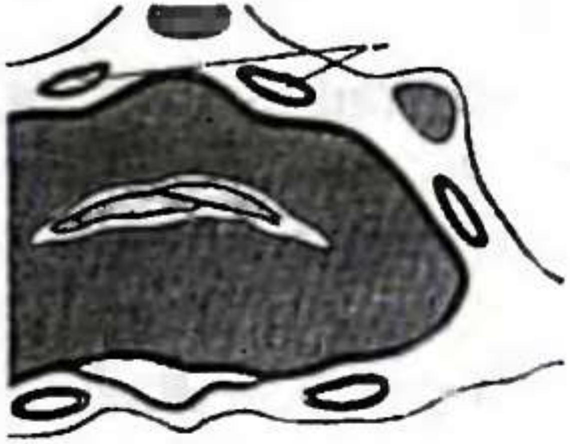
Glands (fam. *Asteraceae*)



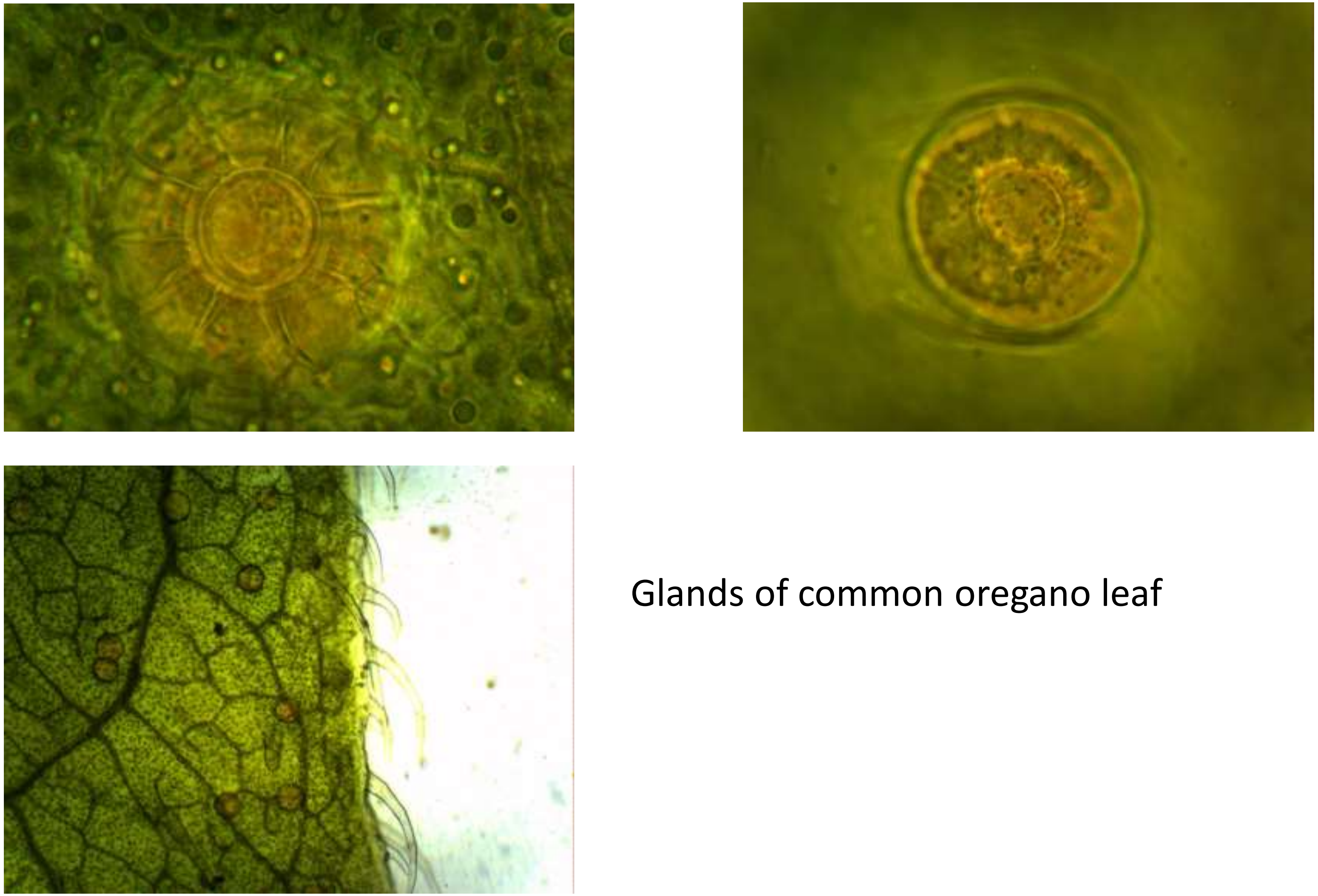
Glands (fam. *Lamiaceae*)



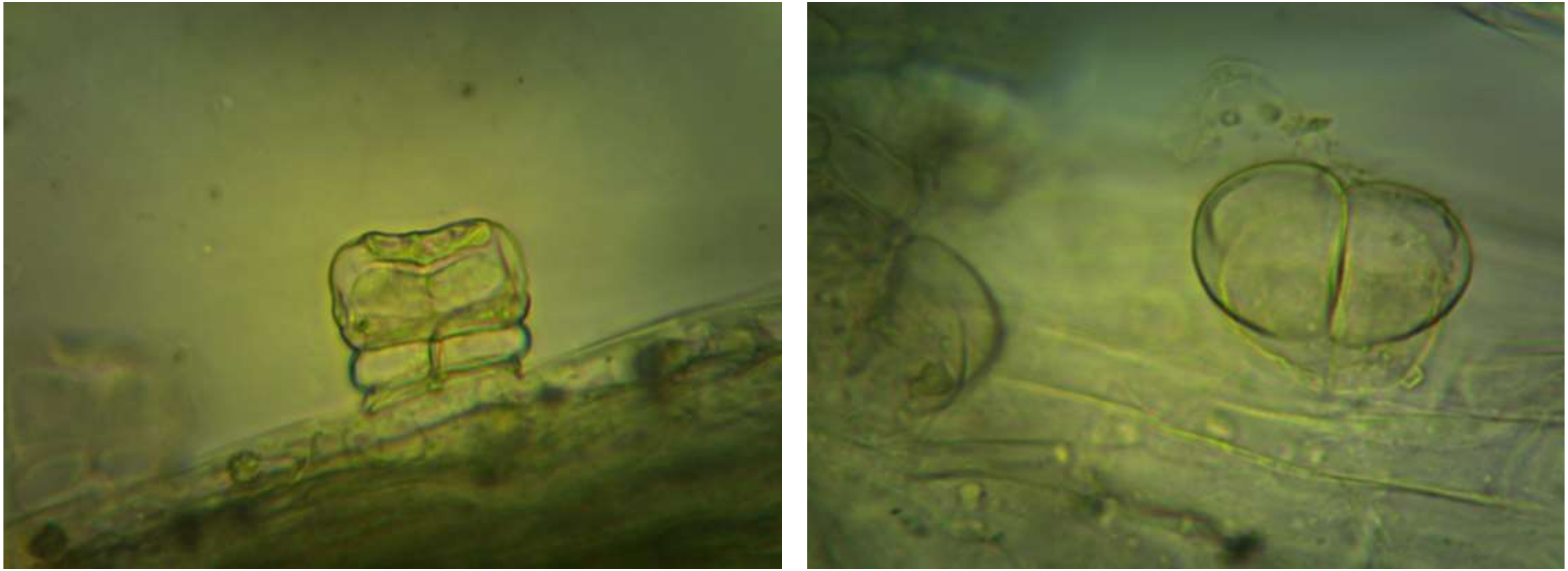
Essential oil reservoir



Essential oil tubes (ducts)

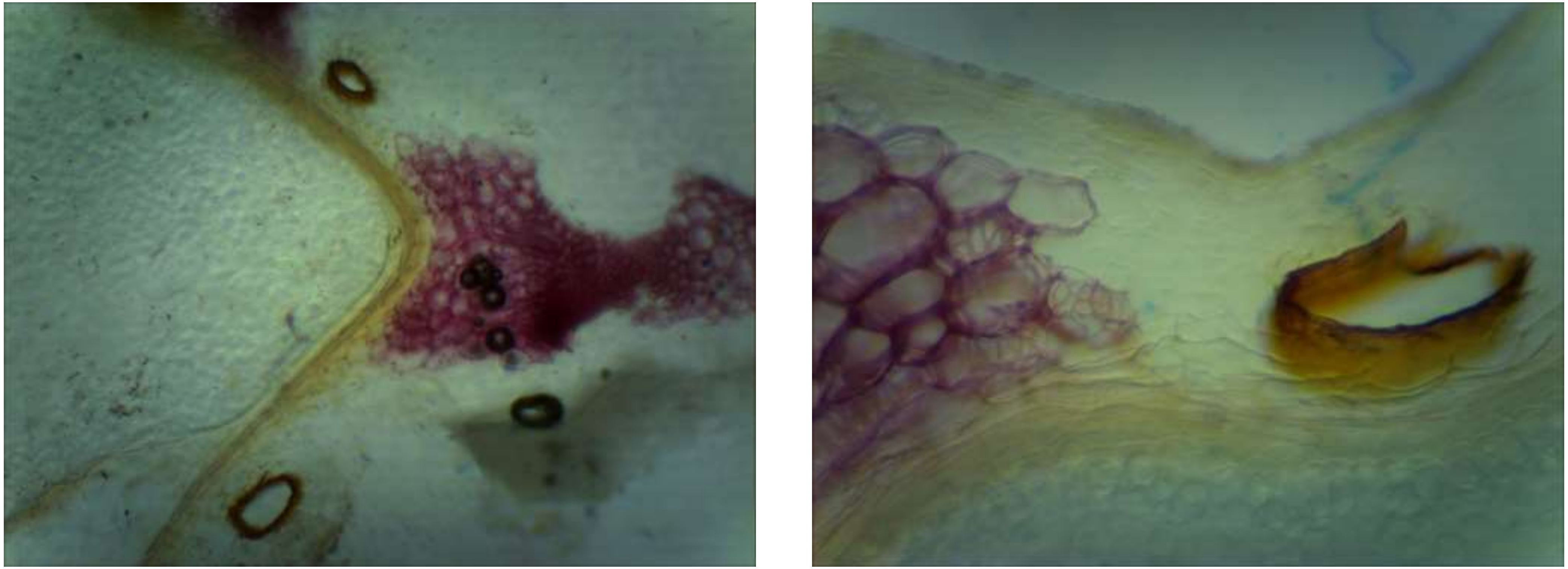


Glands of common oregano leaf



Chamomile flowers glands

essential oil reservoir of elecampane root



essential oil ducts of fennel fruit

Volatile oils may be formed directly by the protoplasm, by the decomposition of the resinogenous layer of the cell wall or by hydrolysis of certain glycosides.

In the conifers volatile oils may occur in the tissues; in the rose they appear in appreciable quantities only in the petals; in cinnamon only in the bark and in the leaves; in umbelliferous fruits only in the pericarp, in the mints in the glands of the stems and leaves, and in orange, one kind of oil in the flower petals and another kind in the rind of the fruit. Volatile oils are frequently found in the plant associated with other substances such as gums and resins and they, themselves, tend to resinify on exposure to air.

In most cases essential oils obtained from different organs of the same species, have similar compositions, but in few instances, essential oils obtained from different organs of the same plant possess different physical, chemical and odour characteristics. For instance, the essential oil of the bark of while, the essential oil prepared from the leaves of the plant contains eugenol as the main constituent. The volatile oil obtained from the root of the same plant, however, is rich in camphor.

EVALUATION OF VOLATILE OILS

Product from different manufacturers varies considerably, since it is inherently difficult to control all the factors that affect a plants chemical composition. Environmental conditions such as sunlight and rainfall, as well as manufacturing process can create substantial variability in essential oil quality. Various procedures are given for the evaluation of essential oils. Preliminary examinations like odour, taste, and colour.

Physical measurements, which includes optical rotation, relative density, and refractive index. Chromatographic techniques are used to determine the proportions of individual components of certain oils. The ketone and aldehyde content of oils are determined by reaction with hydroxylamine hydrochloride (oxime formation) and titration of the liberated acid. The oil, which passes the above examinations, would be having good quality and therapeutic value.

EXTRACTION OF VOLATILE OILS

Volatile oils are prepared by means of several techniques and those techniques are discussed below:

- **Extraction by Distillation**

The distillation is carried out either by water or steam. The volatile oils from fresh materials are separated by hydrodistillation, and volatile oils from air dried parts are separated by steam distillation. However it is better to use fresh materials in either case.

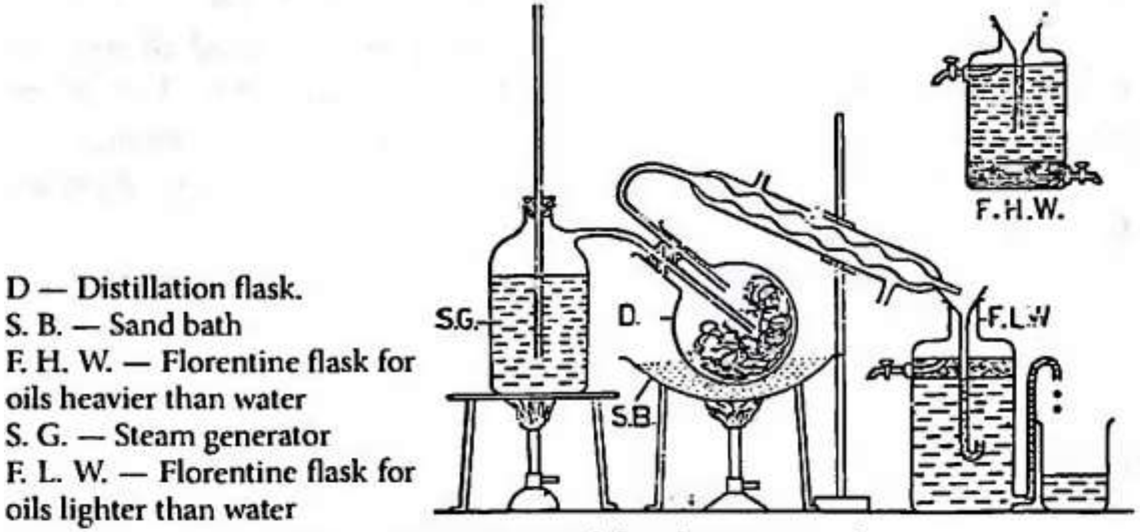


Fig. 9.1. **Apparatus used for the preparation of volatile oils by steam distillation**


connecting conduit
closing clip
Cooling water inlet
Material bottle
2000mL
Cooling water outlet
Liquid filling port
exhaust vent
Hydrosol export
stills
2000mL
Closed electric furnace
Export of essential oils

- **Extraction by Scarification**

This method is used for the preparation of oil of lemon, oil of orange, and oil of bergamot. These oils are found in large oil glands just below the surface in the peel of the fruit. The two principal methods of scarification are the sponge and the ecuelle method.

- *(a) Sponge Process:* In this process the contents of the fruit are removed after making longitudinal or transverse cut, and the peel is been immersed in water for a short period of time. Then it is ready for expression. The operator takes a sponge in one hand and with the other presses the softener peel against the sponge, so that the oil glands burst open and the sponge absorbs the exuded oil, which is transferred to a collecting vessel.

The turbid liquid consisting of oil and water is allowed to stand for a short time, whereupon the oil separates from water and is collected. The whole of the above process is carried out in cool, darkened rooms to minimize the harmful effects of heat and light on the oil.

- *(b) Ecuelle Process:* In this process, the rinds are ruptured mechanically using

numerous pointed projections with a rotary movement and the oil is collected.

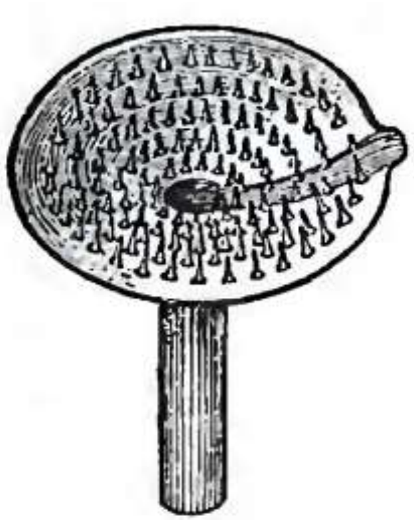


Fig. 9.2. **Machine Processes**

- **Extraction by Non-Volatile Solvent**

A nonvolatile solvent, for example, a fine quality of either lard or olive oil, is used in this process. After saturation with the floral oil the lard or olive oil is sometimes used as a flavouring base for the preparation of pomades, brilliantine, etc., or converted to a triple extract. In the latter instance the lard or oil is agitated with two or three successive portions of alcohol, which dissolve the odorous substances. The mixed alcoholic solutions so obtained constitute the ‘triple extract’ of commerce. There are three chief methods that come under this; they are enfleurage, maceration and a spraying process.

- *(a) Enfleurage:* In this a fatty layer is prepared using lard and the flower petals are spreaded over it, after the imbibitions is over the fatty layer is replaced with fresh petals. After the saturation of fatty layer the odorous principles are removed by treating with alcohol and a triple extract then prepared. When oil is used as a solvent the flowers are placed on an oil-soaked cloth supported by a metal grid enclosed in a frame. Fresh flowers are added as required, and finally the oil is expressed from the cloths. It may then be used as perfumed oil, or extracted with alcohol to produce a triple extract.
- *(b) Maceration:* This is also used to extract the volatile matters of flowers. The lard or oil is heated over a water bath, a charge of flowers added and the mixture stirred continuously for some time. The exhausted flowers are removed, pressed, the expressed fluid returned to the hot fat, fresh flowers, added and the process continued until defined weights of flowers and solvent have been used. Again, a triple extract is prepared by extracting the perfumed lard or oil with alcohol.
- *(c) Spraying:* In this process a current of warm air is sprayed through a column of the flowers. Then oil or melted fat is sprayed over this oil-laden air which absorbs and dissolves most of the perfume, the collected oil or fat is then extracted with alcohol as described above.

Enfleurage

- **Extraction by Volatile Solvent**

In this the flowers are extracted by using the solvent light petroleum and the latter is distilled off at a low temperature, leaving behind the volatile oil.

Determination of the percentage of a volatile oil in the plant material

A laboratory quantitative distillation of an essential oil from a plant material is often necessary to evaluate the raw material to be used on a large scale commercial distillation. The determination of die essential oil content is also important in evaluating the quality of spices and oleoresins. Such determinations may be conveniently carried out in a special apparatus devised by Clavenger (Fig. 9.3). This apparatus offers the following advantages: compactness, cohobation of distillation waters, and the accurate determination of the essential oil content using only small quantities of the plant material. Furthermore, this apparatus may be used to advantage for steam rectification of small amounts of essential oils. The chemical and physical properties of the oil separation may be determined and its odour and flavour may be studied.

Determination of Volatile Oil In Plant Materials. A known weight of the drug in the specified condition (entire or cut in small pieces or powdered) is introduced into the round bottom pyrex distillation flask (one litre capacity) together with a distillation liquid (which may be water or mixture of water and glycerin) usually as 3–6 times the weight of the plant material. Distillation is carried out for a certain period of time (usually 5–6 hours). The distillate is received in a specially constructed receiver (trap), which is graduated, being of 5 ml capacity and each ml mark is subdivided into ml.

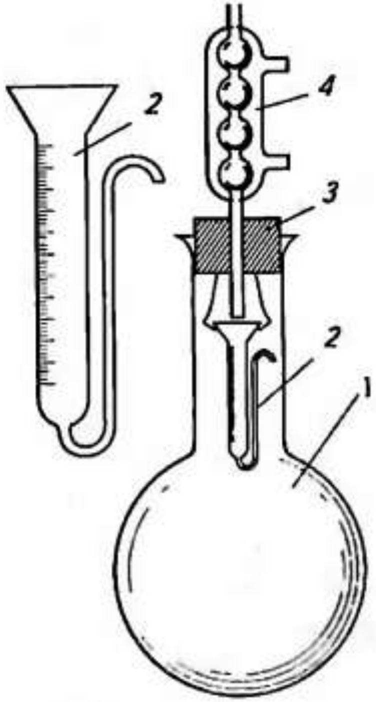


Fig. 9.3. **Clavenger apparatus:**

1. A round bottom pyrex distillation flask;
2. A receiver (trap);
3. A cork;
4. A condenser

There are two types of traps: one for oils lighter than water, and the other for oils heavier than water. These two types differ only in the mechanism of the return of the aqueous layer to the distillation flask, keeping the volatile oil layer in its position.

Distillation is continued until no further increase of the oil is observed, i.e., all the oil has distilled off. This is known by leaving to cool and reading the volume of the distilled oil, then distillation is again continued for one hour, leaving to cool and reading the volume of the oil to see whether it has increased or not. The percentage of the volatile oil is calculated and expressed v/w.

Physical Properties of Volatile oils

Although volatile oils differ greatly in their chemical composition, they have a number of physical properties in common. We can say that with few exceptions, volatile oils are colourless strongly refracting liquids, insoluble in water and readily soluble volatile in steam. They are characterized by a pleasant smell and many of them are optically active.

Odour: Volatile oils possess pleasant or characteristic odours, which vary considerably.

This is detected by dropping 1 or 2 drops of the volatile oil on a piece of filter paper and then smelling it. An expert can judge the quality of the oil and can differentiate between adulterated and genuine volatile by their odours.

Nature: They are generally mobile liquids at ordinary temperatures. Of the more important oils, only two volatile oils are solids at just below room temperature. These are the oil of anise, which solidifies at 15 °C and melts at 17 °C, and the oil of rose, which solidifies at 18 °C and melts at 19 °C.

Some volatile oils, however, deposit a solid substance on cooling and this substance is called 'Stearoptene'. For example, menthol deposits from the oil of peppermint, and thymol from the oil of thyme, leaving a liquid portion called 'Oleopteme'.

Volatility: Essential oils are nearly entirely volatile, with the exception of some oils as oil of lemon, which contains also a non-volatile substance of gummy nature. The volatile oils, as well as their pure constituents evaporate rapidly and completely when placed in the air. They are also readily volatile in steam. In this respect, they differ markedly from fixed oils, which are non-volatile. Volatile oils do not leave a stain when smeared on a piece of filter paper.

Colour: As a rule, volatile oils are colourless, particularly when they are freshly obtained, but on long standing they may oxidize and resinify, thus darkening in colour. This colour can be removed through redistillation. To prevent this, volatile oils should be stored in a cool, dry place in tightly stoppered, preferably in full (not half-emptied) amber glass containers.

Refractivity: Volatile oils are characterised by high refractive indices. The refractive index of volatile oils vary from 1.43–1.61 (the refractive index of pure water at 20° is 1.333). By referring to standard books the refractive index of the genuine oil is seen and compared by the specimen to see whether it is genuine or adulterated.

Optical activity: Most of them are optically active. The specific rotation is often a valuable diagnostic property. Most essential oils when placed in a beam of polarized light possess the property of rotating the plane of polarization to the right (+, dextrorotatory) or to the left (-, laevorotatory). This property is related to the chemical constitution of the oil or its constituents. The optical rotation and specific rotation give an indication whether the oil is genuine or adultrated. In some cases, it may give an indication to the variety of the oil (laevo or dextro), e.g. French oil of turpentine is laevo, while American turpentine is dextro. It may indicate also, whether the substance is natural or synthetic, e.g. natural menthol is laevo-rotatory while the synthetic one may be laevo or racemic. Also natural camphor is dextro, while synthetic camphor is laevo or racemic.

Specific Gravity: The specific gravity of essential oils varies from 0.8–1.17 and the majority of the official volatile oils are lighter than water (specific gravity less than 1). Those heavier than water are oil of cinnamon (specific gravity 1.04), oil of cloves (1.03–1.06) and oil of winter green (1.17). The specific gravity may give an indication to the constituent of the volatile oil; oil having a specific gravity less than 0.9 contains a higher percentage of terpenes and other aliphatic hydrocarbons, while an oil having a specific gravity more than 0.9 and less than 1.0 contains different components belonging to different classes of chemical composition. Those having a specific gravity more than 1.0 are mainly aromatic compounds.

Solubility: Volatile oils, as a rule, are immiscible with water, but they are sufficiently soluble (very sparingly) to impart their odour and taste to water and the official aromatic waters are dependent on this slight solubility. Volatile oils are freely soluble in most organic solvents, e.g. ether, chloroform, absolute alcohol, carbon bisulfide, hexane, ethyl acetate and acetone. They are also miscible with lipids and lipoid solvents, and are soluble in petroleum ether with the exception of cinnamic aldehyde and oils containing it. They are fairly soluble in dilute alcohol. The solubility in alcohol of different strengths offers a valuable means to detect adulteration of volatile oils.

The difference in the solubility of the volatile oil in alcohol of different strengths can be used to detect common adulterants of volatile oils. For example, fixed oil or petroleum ether, when added to the volatile oil lessens its solubility in alcohol.

To carry out this test, 1 ml of the oil is introduced into ml graduated measuring cylinder, then alcohol of known strengths (95, 90, 80, 70, 60, 50%), added, until the complete solution is obtained (at the known temperature). The behaviour of the solubility of the volatile oil in alcohol is best described by the following typical notation: soluble, opalescent, turbid, hazy, etc., e.g. 'clearly soluble in 3 volumes of 40% alcohol and up to 10 volumes'.

The acid value (the number of milligrams of potassium hydroxide required to neutralise the free acids in 1g of the oil) indicates the amount of free acids present in the oil. High acid values arise in rancid oils.

Ether value is the number of milligrams of potassium hydroxide required to saponify the esters in 1g of the volatile oil.

Ether value after acetylation is determined for volatile oils, the quality of which is characterised by the quantity of alcohols, such as linalool, geraniol, cytronellol.

STORAGE OF VOLATILE OILS

Volatile oils are liable to oxidation on storage in presence of air, moisture, and light. The oxidation is followed by the change in colour, increase in viscosity, and change in odour. Hence, volatile oils must be stored in well-closed completely filled containers and away from light in cool places.

Uses of volatile oil

Volatile oils play an important role in the economy. They may be used for their therapeutic action, e.g. local stimulants, carminatives, diuretics, mild antiseptics, local irritants, anthelmintics, parasaticides. They may be also used as spices and for flavouring of foods, confections, beverages, pharmaceuticals, cosmetics and tobacco. Undoubtedly, the presence of the antiseptic oils in the spices prevents excessive growth of bacteria, resulting in less food spoilage. In addition, they are most widely used in perfumery.

The preparation of volatile oils has developed in modern times into a large industry and the world production of essential oils is estimated at about 20 million kilograms annually.

Although large quantities of odoriferous substances are also produced by purely synthetic methods, yet the finest perfumes are derived from natural sources. The importance of auxiliary constituents of essential oils is great. For instance, artificial mixtures of menthol and menthyl acetate in the same proportion as in peppermint oil do not have the fine flavour of the natural oil, since small amounts of other natural constituents are lacking.