

Chapter 9

VOLATILE OILS

It has been known for many centuries that different organs of certain plants contain **volatile** odoriferous substances that affect the olfactory sense and are responsible for the fragrance.

Volatile oils constitute the most important odorous principles found in various plant parts. Because they evaporate when exposed to air at ordinary temperatures, they are called **volatile oils, etherial oils** or **essential oils**. The last term is applied since volatile oils represent the essences or the active constituents of such plants.

Several points of differentiation exist between volatile oils and fixed oils and they differ entirely from each other in both chemical and physical properties. Volatile oils, being capable of volatilization, can be distilled from their natural sources. They do not consist of glycerol esters of fatty acids, and hence do not leave a permanent grease spot on paper, they cannot be saponified with alkalis. Volatile oils do not become rancid as fixed oils, but instead, on exposure to light and air, they will oxidize and resinify.

As odoriferous plants usually grow in one season of the year and hardly grow in others, drying was tried as a method of conservation of the plant or its organs and it was found that the odoriferous principles may be totally unaffected or partially affected.

The development of science and discovery of the distillation process together with the knowledge that odorous substances are volatile, lead to the preparation of volatile oils in a systematic manner by steam distillation. The distillate possessing the aroma and odour of the plant. When saturated, oil globules, separate.

It was also noticed that when fatty oil was left for sometime in contact with some organs containing the volatile oil, it acquired the odour and taste of these odoriferous principles and thus they began to prepare scented ointments and liquids.

Practically all volatile oils consist of chemical mixtures that are often quite complex; they vary widely in chemical composition. Almost any type of organic compound may be found in volatile oils (hydrocarbons, alcohols, ketones, aldehydes, ethers, oxides, esters, and others). ***“usually volatile oils are classified according to the type of organic compounds”***. It is not uncommon for a volatile oil to contain over 200 components, and often the trace constituents are essential to the odor and flavor. The absence of even one component may change the aroma. Chemical constituents of volatile oils may be divided into 2 broad classes, based on their

biosynthetic origin: terpene derivatives, formed via the acetate-mevalonic acid pathway; and aromatic compounds formed via the shikimic acid-phenylpropanoid route.

Essential oil could be divided on 3 group. Essential oil which contain as main component:

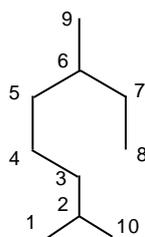
1. Monoterpenes;
2. Sesquiterpenes;
3. Aromatic compounds.

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.

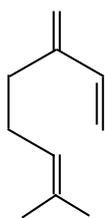
Sesquiterpenoids are composed of 3 isoprene units and have the general molecular formula $C_{15}H_{24}$. They can occur in acyclic, monocyclic, bicyclic and tricyclic forms.

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

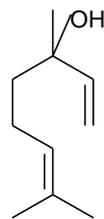
Acyclic monoterpenoids are derivatives of 2,6-dimethyloctan



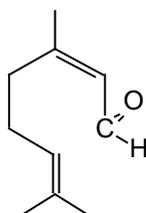
2,6-Dimethyloctan



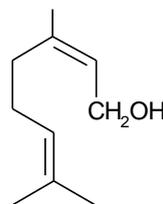
β -Myrcene



Linalool



Citral

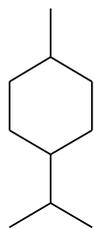


Geraniol

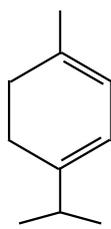
β -Myrcene is contained in lemon oil, linalool – in coriander oil and orange flower oil. Geraniol is main component of rose oil. Some lemon oils contain up to 13% of citral, but a range of 2 to 4 % is optimum for a high-quality oils. Citral is rather rare in plants and can be used from linalool.

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

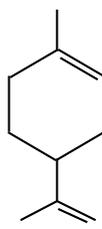
Hydrocarbon derivatives



p-Menthan



α-Terpinene

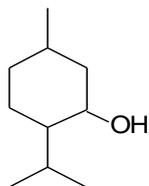


Limonene

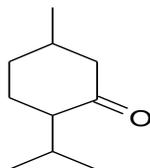


β- Phellandrene

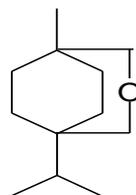
Oxygenated derivatives



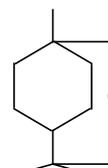
Menthol



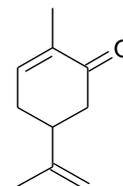
Menthone



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. Limon 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 crystallizes. 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*.

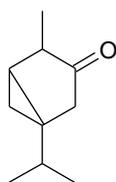
Menthol occurs as colorless, hexagonal crystals that are usually needlelike, as fused masses, or as a crystalline powder. It has a pleasant, peppermint like odor.

Caraway oil contains about 50-85 % of carvone.

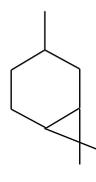
Bicyclic monoterpenes have two condensed rings. There are some types of these compounds: carane, pinane, camphane, fenchane types.



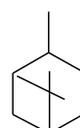
Thujane



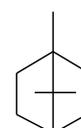
Thujone



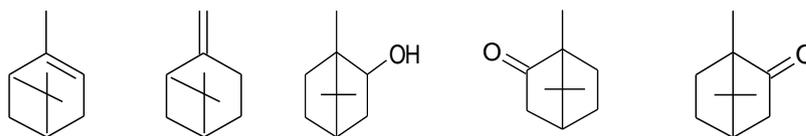
Carane



Pinane



Camphane



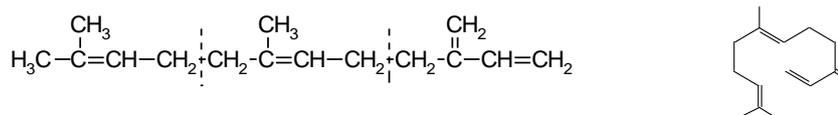
α -Pinene β -Pinene Borneol (+)-Camphor (-)-Camphor

Thujan derivatives are found in *Artemisia 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.

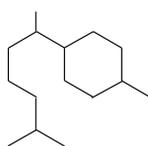
Camphor is a ketone obtained from *Cinnamomum camphora* (Linne) Nees et Ebermaier, Fam. *Lauraceae*, (natural camphor) or produced synthetically (synthetic camphor). Natural camphor occurs as a crystalline product in clefts in the woody stems and roots and, to a greater extent, dissolved in the volatile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

Synthetic camphor is the optically inactive racemic form.

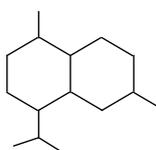
Sesquiterpenoids ($C_{15}H_{24}$) biogenetically derived from farnesyl pyrophosphate and in structure may be acyclic (linear), monocyclic, bicyclic and tricyclic.



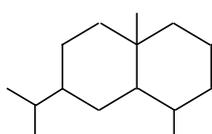
Two variants of the farnesene structure (acyclic)



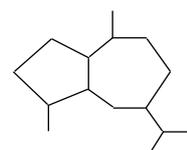
Bisabolane (monocyclic)



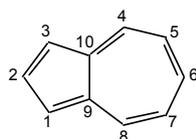
Cadinane



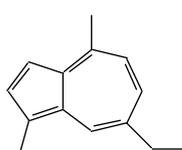
Eudesmane



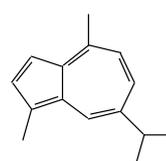
Guaiane



Azulene



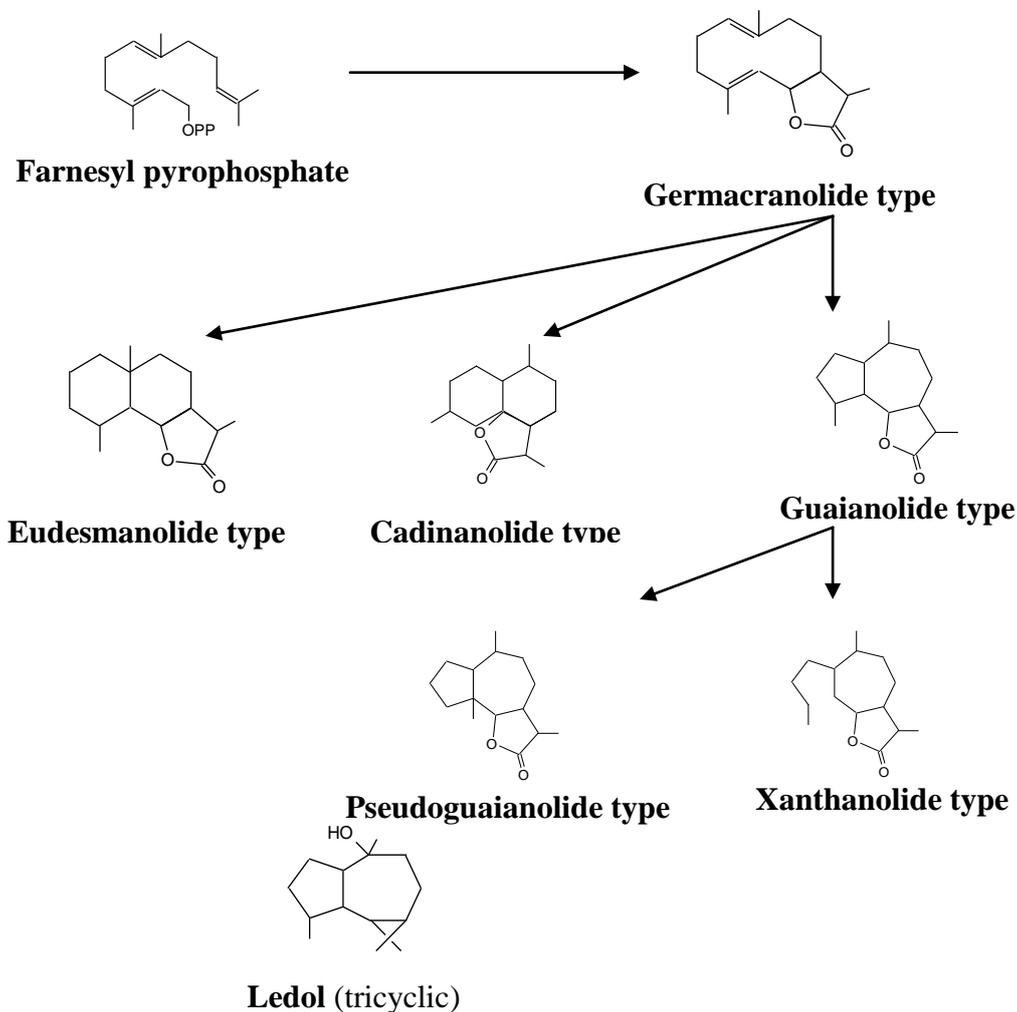
Chamazulene



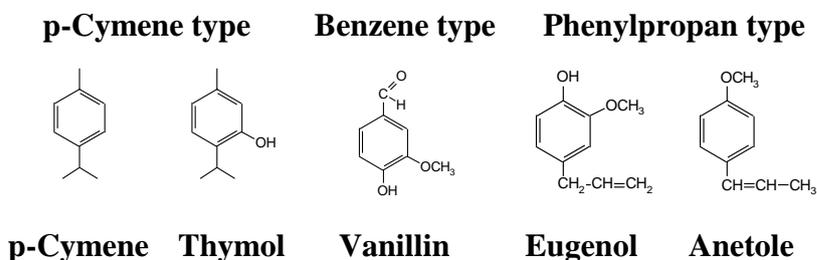
Guaiazulene

Sesquiterpene lactones

Over 6000 compounds of this group are known. They are particularly characteristic of the *Asteraceae* but also occur sporadically in other families. Chemically, the compounds can be classified according to their carbocyclic skeletons.



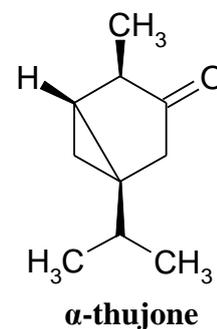
Aromatic compounds



Phenylpropanoids contain the C₆ phenyl ring with an attached C₃ propane side chain. Many of the phenylpropanoids found in volatile oils are phenols or phenol ethers. In some cases, the propane side chain has been abridged to give a C₆-C₁ structure, such as vanillin.

In addition to the molecular structure, the stereochemistry of the constituents of volatile oils markedly determines the type of olfactory response evoked by the compounds. Geometric isomers, whether *ortho/meta/para* or *cis/trans*, are in most cases readily distinguished both as to quality and strength of odor. An interesting stereo-chemical feature of many terpenes is the fact that both enantiomers (optically active isomers) exist in nature. In some cases, a plant species produces only one of the enantiomers, whereas a different species may produce both. Among the monoterpenes that occur as the (+) form in certain species and as the (-) enantiomeric form in others are limonene, α -terpineol, α -fenchol, borneol, menthone, carvone, and linalool. In addition, limonene, α -terpinol, α -fenchol, carvone, and camphor, as well as many others, can be found in plants as the racemic mixture.

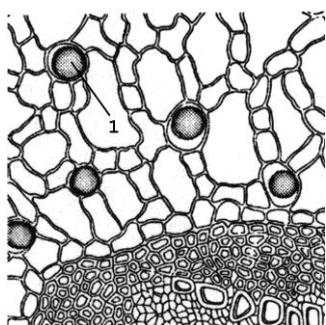
Thujone is best known for being a toxic chemical in absinthe, a product extract from *Artemisia absinthium*. Its psychedelic effects consecutive to absinthe consumption is disputed. Pharmacologically, thujone acts mainly on the GABA receptors in the brain and exhibits psychoactive response. In many countries the amount of thujone allowed in food or drink products is regulated (in Europe, the maximum level tolerated is 25 mg/l). Other plants containing thujone, such as the coniferous *Thuja occidentalis*, are used in herbal medicine, mainly for their immune-system stimulating effects.



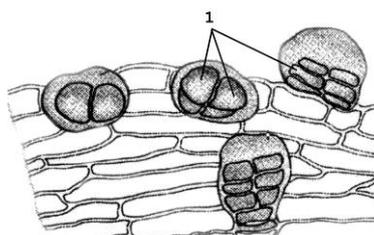
Distribution and occurrence

Some families are rich in species producing volatile oils (about 2000 species, representing about 87 families). The chief families *Pinaceae*, *Lauraceae*, *Rutaceae*, *Myrtaceae*, *Apiaceae*, *Lamiaceae* and *Asteraceae*.

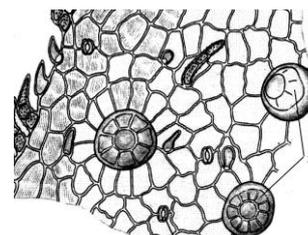
Depending on the plant family, volatile oils may occur in specialized secretory structures, such as glands (*Lamiaceae* and *Asteraceae*), modified parenchyma or oil cells (*Lauraceae* and *Piperaceae*), oil tubes or ducts (*Apiaceae*), as well as in internal lysigenous or schizogenous passages or glands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



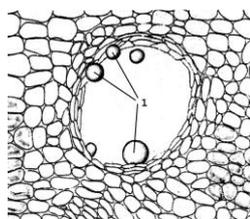
Essential oil cells



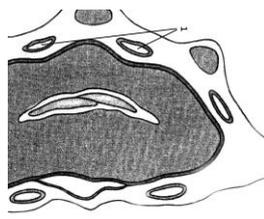
Glands (fam. Asteraceae)



Glands (fam. Lamiaceae)



Essential oil reservoir



Essential oil tubes (ducts)

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 main constituent. The volatile oil obtained from the root of the same plant, however, is rich in camphor.

It should also be noted that the chemical composition of an essential oil prepared from the same organ of one species, varies to some degree, according to the environmental conditions under which the plant has grown

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, parasiticides. 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.

Physiological significance

Some scientists consider volatile oils to be waste products and not substances formed to serve any biological function. It is possible that volatile oils serve the function of eliminating certain abnormal metabolic products of the plant and thus may be detoxification products.

However, several ecological theories attribute to them such tasks as attraction of insects, thus aiding in cross pollination of the flowers or may act as repellents to insects or animals (defense agents), thus preventing the destruction of the flowers and leaves. They may also serve as solvents for wound healing resins.

Methods of preparation of volatile oils

The development of science and discovery of the distillation process together with the knowledge that odorous substances are volatile, lead to the preparation of volatile oils in a systematic manner by steam distillation. The distillate possessing the aroma and odour of the plant.

The principal methods used in the preparation of volatile oils from plants depend on:

- I. Distillation in water or steam.
- II. Scarification and expression.
- III. Extraction with solvents (Extraction with volatile solvents and the enfleurage method).
- IV. Enzymatic hydrolysis.

I. Distillation method.

The distillation of volatile oils by means of water or steam has long been practiced. This distillation method is the most economical method of preparation of volatile oils. It is of wide application and is based on the fact that when water is mixed with another liquid which is immiscible with it and the two liquids are boiled, they will boil at a temperature lower than that of the high boiling point component and nearly equal or slightly lower than the boiling point of water; because at this temperature, the vapor pressure of the two components will be equal to the

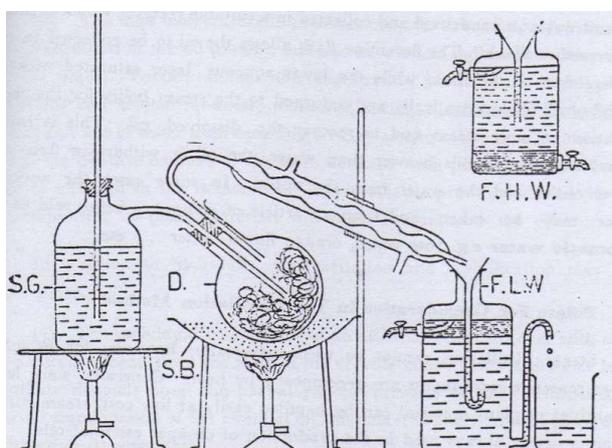
vapour pressure of the atmosphere. For example: turpentine oil which boils at 160 °C, when mixed with water, it will begin to boil at 95 °C. At this temperature, the vapour pressure of water is 64,7 cm mercury and the vapor pressure of turpentine is 11,3. The resultant vapour pressure of the two is 76 cm Hg, which is the atmospheric pressure and thus the liquid begins to boil. That is to say: the contribution to the total vapor pressure made by the volatile oil and water in the form of steam causes the oil to be carried over as vapor with the steam at a temperature far below the normal b.p. of the oil. This allows for the distillation of volatile oils at temperatures considerably below their decomposition points.

The method used in the preparation of volatile oil depends on the condition of the plant material. Three types of distillation are used by industrial firms:

1. water,
2. water and steam,
3. direct steam.

Water distillation is applied to plant material that is dried and not subject to injury by boiling. Turpentine oil is also obtained in this manner. The crude turpentine oleoresin is introduced with water into the distilling chamber and subjected to heat until all volatile matter (both turpentine oil and water) is condensed in the condensing chamber.

Water and steam distillation is employed for plant materials (either dried or fresh) that their volatile oils may be injured by boiling. In the case of dried materials (cinnamon, clove), the drug is ground and then covered with a layer of water, and steam is passed through the macerated mixture. Since the oil might be impaired by direct boiling, the steam is generated elsewhere and is piped into the container holding the drug. The oily upper layer, of the condensed distillate is separated from the aqueous lower layer, and the oil may be marketed with or without further processing.



D - Distillation flask.

S. B. - Sand Bath

F. H. W. - Florentine flask for oils heavier than water

S. G. = Steam Generator .

F. L. W. = Florentine flask for oils lighter than water .

Figure 9.1. Apparatus used for the preparation of volatile oils by steam

distillation

In case of direct steam distillation applicable to fresh drugs (peppermint, spearmint), the crop is cut and taken directly to the distilling chamber. Instead of being allowed to macerate, the drug is suspended in a wire basket or perforated trays or a similar container (grid). Since the plant material is still green and contains considerable natural moisture, no maceration is necessary. Steam is forced through the fresh herb carrying the oil droplets to the condensing chamber. These modern stills possess many advantages over the older stills, in which charring and undesirable decomposition of the oil often take place.

During steam distillation certain components of a volatile oil tend to hydrolyze whereas other constituents are decomposed by the high temperatures. Ideal distillation methods utilizing steam should provide for the penetration or diffusion rate of steam and water "hydro diffusion" through plant membranes to be as high as possible and should thus keep the hydrolysis and decomposition at a minimum. The distillate, which consists of a mixture of oil and water, is condensed and collected in a suitable receiver which is called "florentine flask". The florentine flask allows the oil to be collected in the upper layer in the flask, while the lower aqueous layer saturated with oil is siphoned off automatically and returned to the steam boiler for the regeneration of more steam and to recover the dissolved oil. This is called cohobation. For oils heavier than water, the oil is withdrawn from the lower outlet and the water from the upper. In some cases the aqueous layer may be taken and form an article of commerce being sold as an aromatic water e.g. rose water, orange flowers water etc.

II Expression methods

Some volatile oils cannot be distilled without decomposition and so should be prepared if possible by mechanical methods.

For oils occurring in the rind of the fruit, e.g. peel of orange, lemon, bergamot etc., the extrusion by the application of pressure (squeezing out) is satisfactory. These oils are obtained industrially by such methods, because the fragrance of the oils, when obtained from these sources by distillation, is inferior.

Expression can be carried out by means of any of the following processes:

The sponge method. The citrus fruit (orange, lemon, bergamot) is washed, cut into halves and the juicy part removed. The rind is turned inside out (squeezed), when secretion glands (sacs) rupture and the oil collected by means of the sponge, until the sponge becomes saturated with exuded water and oil. The sponge is then periodically squeezed in a vessel. The upper oily layer in the vessel is separated.

The Scarification (ecuelle a piquer) process. On the Revieras in France, an instrument known as "ecuelle a piquer" (literally a bowel for pricking) is used (Fig. 9.2). This consists of a funnel made of copper and tinned inside. The upper saucer-like part bears on its inner surface

numerous strong metal pins just long enough to penetrate the epidermis. The stem-like portion serves both as a handle and as a receiver for the oil. By repeatedly rotating the instrument after placing lemons in the bowl, the oil glands are punctured (scarified) and discharge their contents which collect in the handle. The liquid is poured off at intervals into a large vessel, where it is allowed to stand until the oil can be decanted and filtered.

Much oil is prepared by machines based on the above principles. A centrifuge may be used to separate the emulsion of oil and water. These machine methods have now almost completely replaced the old hand methods.

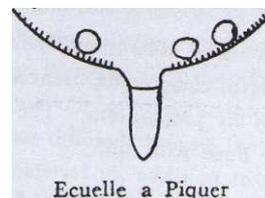


Figure 9.2. Machine Processes.

III Extraction methods

This method is used for the preparation of those oils which decompose by the action of steam, or are present in extremely small quantities in plant organs containing them, that the removal of oil is not commercially feasible by the above methods. The minute quantities of oil actually distilling over are lost in the large volume of distillation water from which the oil cannot be recovered. This is applied to flowers such as Jasmine, violet, tuberose, gardenia, acacia, narcissus, mimosa, hyacinth and few others. The method of extraction is carried out using volatile solvents of low boiling point, such as benzene, or hexane, etc. or non-volatile solvents such as lard, tallow, olive oil.

Extraction with volatile solvents. The material containing the volatile oil is extracted with the volatile solvent, with low boiling point, by percolation or by continuous extraction (Soxhlet). The volatile oil solution obtained is evaporated under reduced pressure, where the volatile solvent will evaporate, leaving the volatile oil behind although some of the volatile oil will be lost.

The chief advantage of extraction over distillation is that uniform temperatures (usually 50°C.) can be maintained during most of the process. As a result, extracted oils have a more natural odour unmatched by distilled oils (which may have undergone altered chemical constitution by the high temperatures. This feature is of considerable importance to the perfume industry. However, because of the high cost involved, the extraction process, probably are not very widely adopted by volatile oil production firms. The established distillation method is a low-cost operation compared to the extraction process.

Extraction with non-volatile solvents. This process is used for the preparation of the finest of perfume oils. It is used in the preparation of natural flower oils, where the volatile oil content of the fresh plant parts e.g. flower petals, is so small that oil removal is not commercially feasible by other methods. The most important centre for extraction of flower oils is Grasse in Southern France.

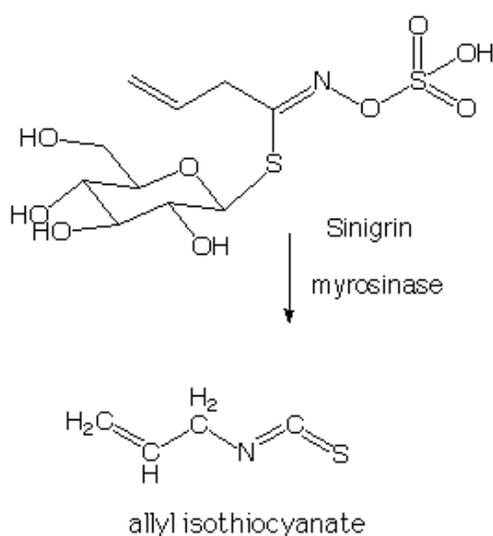
The enfleurage method. A mixture of melted beef tallow and lard is thickly smeared on both surfaces of each of the glass plates, which are enclosed in a wooden frame (the chassis). Each glass plate is sprinkled with flowers to cover its top. Under this condition each layer of the flowers will be enclosed between two layers of fat. Batteries of the plates are left for twenty four hours. The flowers are then removed and replaced by a fresh supply. This is repeated until after some weeks, the fat becomes saturated with essential oil of the flowers or until a certain concentration is reached. In case of jasmin flowers, the entire enfleurage process lasts seventy days.

The flowers are then removed (defleorage) and the fat is separated off and is stirred with absolute alcohol which will take the volatile oil and leave the fat, being insoluble in alcohol. The alcoholic extract is carefully cooled and filtered to remove any traces of fat which might remain in solution or suspension. Three successive extractions with alcohol are used to obtain the volatile. If the volatile oil is wanted, either fractional distillation or evaporation in vacuum at 0°C is used, or the alcoholic extract is diluted with water and saturated with sodium chloride, where the oil will separate having retained the odour of the fresh flowers.

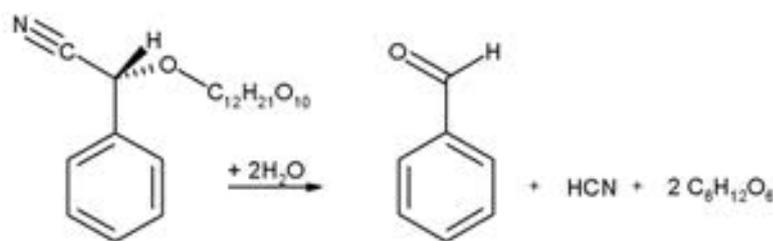
IV. Preparation of volatile oil after enzymatic hydrolysis

Occasionally, the volatile oil is found in the plant in a glycosidal combination. The odoriferous substance is set free only by hydrolysis of certain odourless glycosides present in the plant. The following are examples of such oils.

The volatile oil of black mustard (*Brassica nigra*, Fam. *Brassicaceae*) is present in glycosidal combination in the form of the glycoside sinigrin. Sinigrin on hydrolysis with the enzyme myrosin, gives allylisothiocyanate, potassium acid sulfate and glucose.



The volatile oil of bitter almond (benzaldehyde) is present in the kernels of bitter almond in the form of the glycoside amygdalin.



Amygdalin

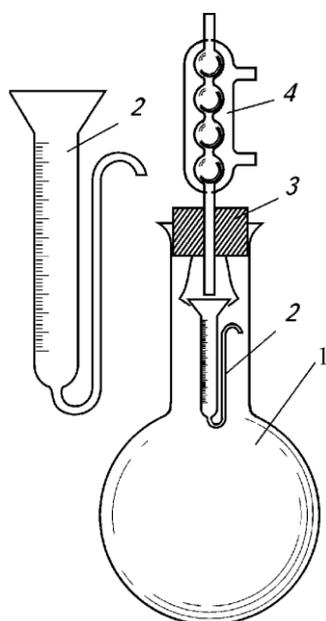
Benzaldehyde of the volatile oil of bitter almond

The seeds of bitter almond are crushed and exposed to pressure to free from fixed oil. The residual cake is again recrushed and treated with water in a closed vessel, then left for sometime at a temperature of about 40°C, so that the enzyme may act and hydrolyse the glycoside. On distillation with steam, benzaldehyde and hydrocyanic acid being volatile will come over, with the steam. The distillate will contain benzaldehyde and about 2—4% HCN, partly in the free form and partly combined as benzaldehyde cyanohydrate. The presence of HCN renders the volatile oil of bitter almond poisonous.

To remove HCN, the oil obtained in the distillate is treated with calcium hydroxide solution where calcium cyanide is formed. On addition of ferrous sulfate, calcium ferrocyanide $\text{CaFe}(\text{CN})_6$ is produced as well as calcium saliate, and these being non-volatile will remain in the still.

Determination of the percentage of a volatile oil in a 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 appraising-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 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.

Figure 9.3. Clavenger apparatus.

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

Determination 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 liter 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.

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 constitution, they have a number of physical properties in common. We can say that with few exceptions, volatile oils are colorless strongly refracting liquids, insoluble in water and readily 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 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 oil of anise which solidifies at 15°C and melts at 17 °C and 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 oil of peppermint, and thymol from 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 and evaporate rapidly and completely when placed in 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 characterized 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 (+, dextro-rotatory) 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 adulterated. In some cases, it may give an indication to the variety of the oil (levo or dextro) e.g. French oil of turpentine is levo, while American turpentine is dextro. It may indicate also, whether the substance is natural or synthetic, e.g. natural menthol is levo-rotatory while the synthetic may be levo or racemic. Also natural camphor is dextro, while synthetic camphor is levo 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 lipid 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 complete solution is effected (at a known temperature). The behavior 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 neutralize 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, quality of which is characterized by the quantity of alcohols, such as linalool, geraniol, citronellol.