Essential Oils (Volatile Oils)

Prof. Dr. Ali H. Meriçli

Essential oils (essences, volatile oils) are products, generally of rather complex composition, comprising the volatile principles contained in plants, and more or less modified during the preparation process. To extract these volatile principles, there are various procedures. Of these, only two may be used to prepare official oils : steam distillation of oil-containing plants or of selected plant parts (mostly with Clevenger apparatus) and expression. The second way is recommended for obtaining the *Citrus* fruit oils.

The definition by procedure is restricitive : it excludes the products obtained by solvent **extraction**, as well as those obtained by any other process (pressurized gas, enfleurage, and others). Therefore it is useful to first define the terms most commonly used in this field.

- concrete : extract of characteristic odor, obtained from a fresh starting material of vegetable origin, by extraction with a non-aqueous solvent

- resinoid : extract of characteristic odor, obtained from a dried starting material of natural origin, by extraction with a non-aqueous solvent. Here starting material of natural origin means “of vegetal, animal, or microbiological origin, including products derived from these starting materials by enzimatic routes.

- pomade : perfumed fat obtained from flowers either by “cold enflorage” or by “hot enflorage”. **Enfleurage** is a process that uses odorless fats that are solid at room temperature to capture the fragrant compounds exuded by plants.

- absolute : product of characteristic odor, obtained from a concrete, a pomade, or a resinoid, by ethanol extraction at room temparature. The resulting ethanol solution is generally cooled and filtered in order to eliminate waxes; the ethanol is than removed by distillation.

- spices : natural plant products or their mixtures, free of foreign matter, that are used to impart flavor and aroma, and to the season food; the term applies both to the entire product and to the powder.

- aroma : the concept of aroma is at the same time different from, and broader than, that of essential oil, since it applies to any fragrant principle emanating from natural substances or which is generated by a physical,chemical, or enzymatic process (examples include roasted coffee, grilled meat, fish, cheese).

DISTRIBUTION, LOCALIZATION, AND FUNCTION

Distribution : Essential oils occur virtually only in higher plants : according to Lawrence, there are 17.500 aromatic species. The genera capable of elaborating the compounds that constitute essential oils are distributed in a limited number of families, for example Lamiaceae, Myrtaceae, Rutaceae, Asteraceae, Apiaceae, Cupressaceae, Poaceae, Zingiberaceae, and Piperaceae.

Essential oils accumulate in all of the types of vegetable organs: flowers of course (bergamot tree, rose, tuberose), but also leaves (citronella, eucalyptus, laurel), barks (cinnamon), woods (rosewood, sandalwood), roots (vetiver), rhizomes (turmeric, ginger), fruits (anise, star anise), and seeds (nutmeg).

All the organs of a given species may contain an essential oil, but the composition of this oil may vary with the localization. Thus, in the case of the bitter orange tree (*Citrus aurantium* ssp. *aurantium,* Rutaceae) the zest, that is the fresh pericarp of the fruit, is used to produce bitter orange oil or “essence de Bigarade”, the flower is used to produce “neroli, neroli oil, or orange flower essential oil”, and steam distillation of the leaves, twigs, and small fruits produces “petitgrain oil”. This three essential oils have different compositions.

Localization : The synthesis and accumulation of essential oils are generally associated with the presence of specialized histological structures, often located on or near the surface of the plant : oil cells of the Lauraceae or Zingiberaceae, glandular trichomes of the family Lamiaceae, secretory cavities of the Myrtaceae or Rutaceae, and secretory canals of the Apiaceae or Asteraceae.

Function : In most cases, the biological function of the terpenoids of essential oils remains obscure. Some theories are: particularly germination inhibitors, protection against predators like insects and fungi and attraction of pollinating species.

PHYSICAL PROPERTIES

Essential oils are liquids at ambient temperature, but they are also volatile, which is what differentiates from the “fixed oils”. They are only very rarely colored. Their density is generally lower than that of water (the essential oils of sasafras, clove, and cinnamon are the exceptions). They have a high refractive index. They are soluble in common organic solvents. They are sparingly soluble in water; they are water-soluble enough, however, to impart a distinct fragrance to water.

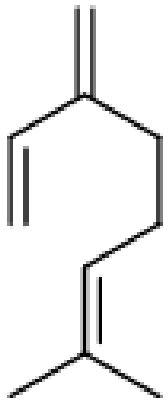
CHEMICAL COMPOSITION

Essential oils are complex and highly variable mixtures of constituents which belong virtually exclusively, to two groups characterized by distinct biogenetic origins: the group of terpenoids, and the group, far less common, of aromatic compounds derived from phenylpropane. Some essential oils contain degradation products of non-volatile constituents.

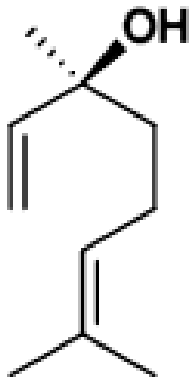
TERPENOIDS

Essential oils contain only the most volatile terpenes, in other words whose molecular weight is not too high: mono- and sesquiterpenes

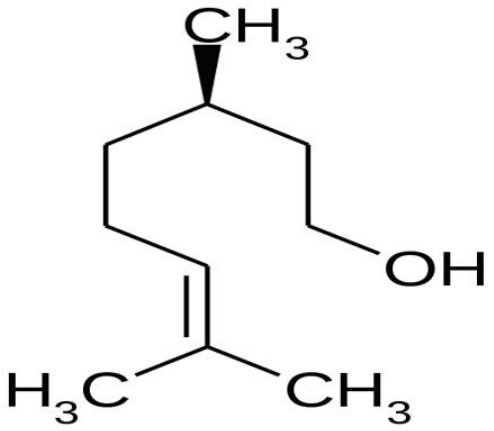
Monoterpenes : The hydrocarbons are always present. They may be acyclic (myrcene, ocimene), monocyclic (α- and γ-terpinene, p-cymene) or bicyclic (pinenes, δ-carene, camphene, sabinene). Sometimes, they constitute over 90% of the essential oil, for example in the *Citrus* oils.



Myrcene

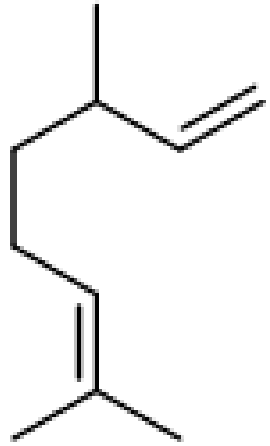


Linalool

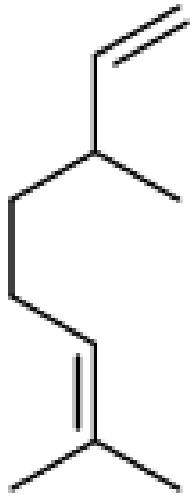


Citronellol

3,7-Dimethyloct-6-en-1-ol

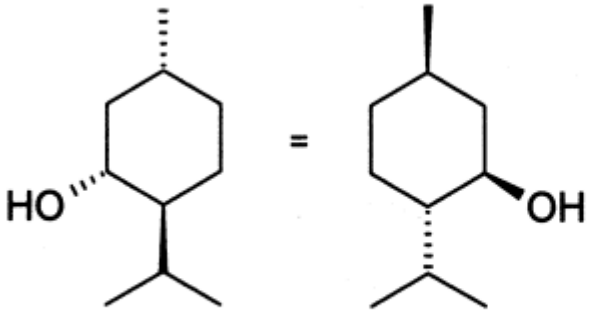


cis-Ocimene

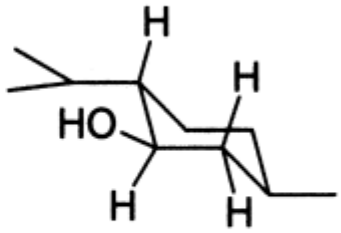


trans-Ocimene

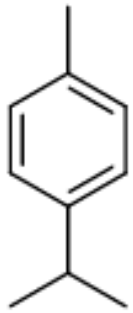
Some acyclic monoterpenes



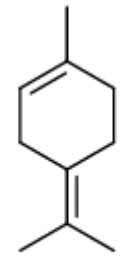
(-)-Menthol



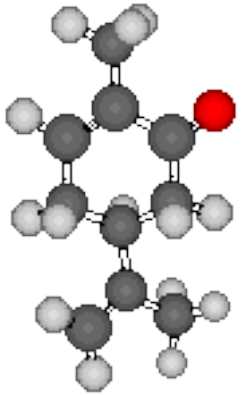
Chair form of
(-)-Menthol

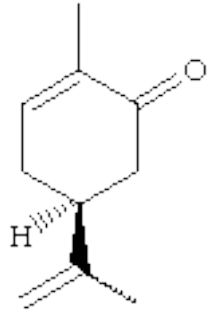


p-Cymene

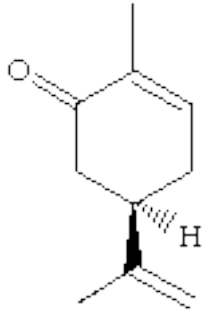


δ-Terpinene

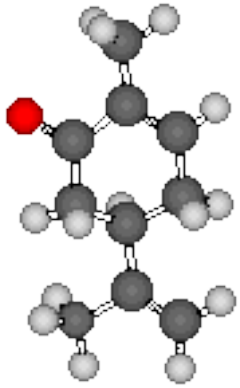




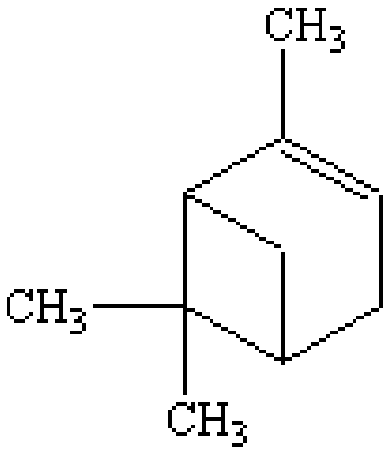
(*S*)-(+)-carvone



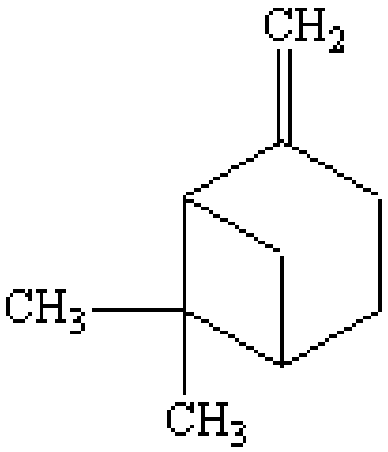
(*R*)-(–)-carvone



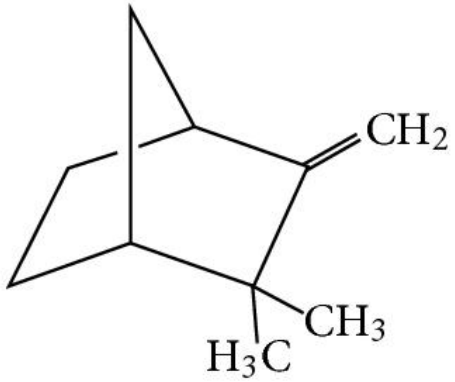
Some monocyclic monoterpenes



α- *Pinene*

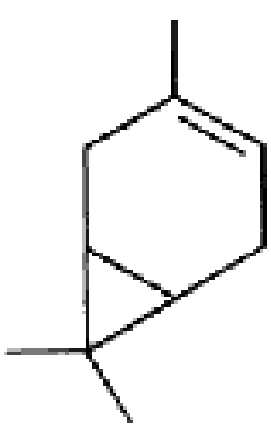


β- *Pinene*

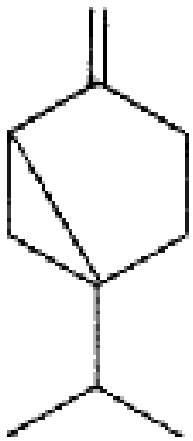


(+)-Camphene

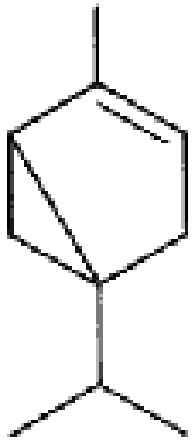
Some bicyclic monoterpenes



car-3-ene



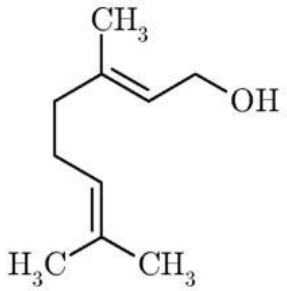
sabinene



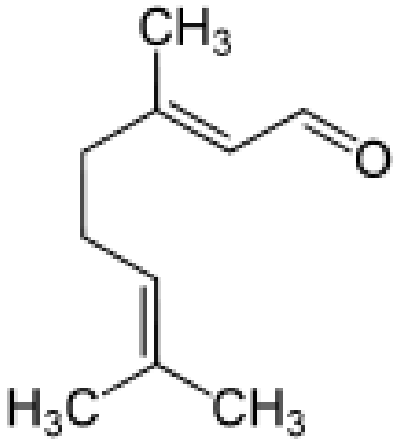
α-thujene

Other definitions

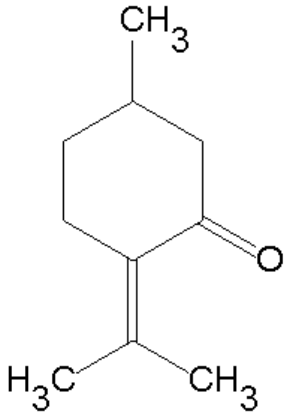
- alcohols : geraniol



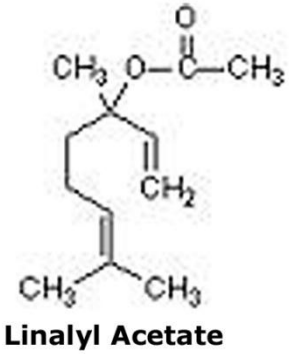
- aldehydes : geranial



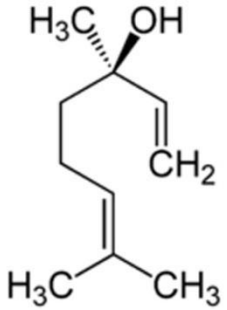
- ketones : pulegone



- esters : linalyl acetate

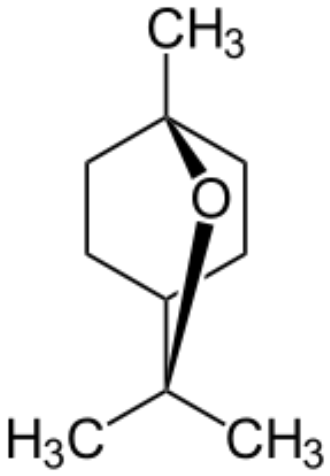


Linalyl Acetate

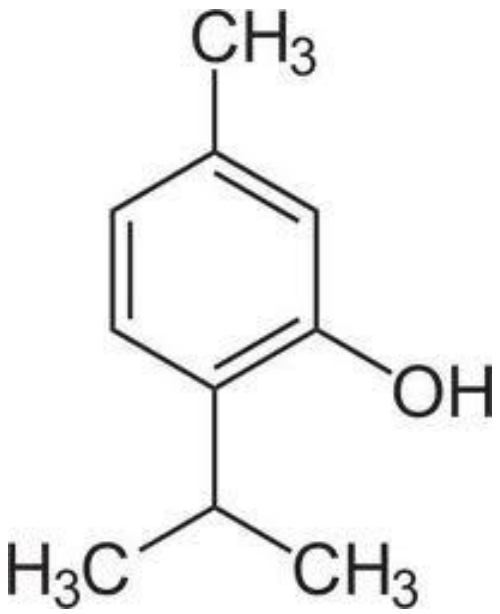


Linalool

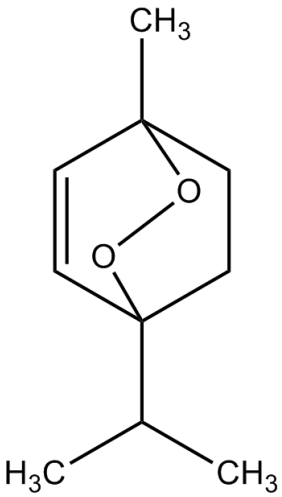
- ethers : 1,8-cineole



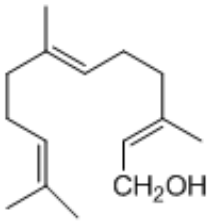
- phenols : thymol



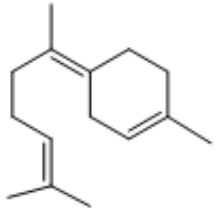
- peroxides : ascaridol



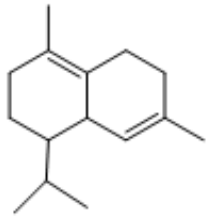
Sesquiterpenes : Structural variations in this series are of the same nature as in the monoterpenes, with hydrocarbons, alcohols, and ketones being the most common. Examples of sesquiterpenes characteristic of essential oils are: mono- or polycyclic hydrocarbons (β-bisabolene, β-caryophyllene,), alcohols (farnesol, β-santalol), ketones (nootcatone, β-vitivone), aldehydes (sinensals) and esters (cedryl acetate).



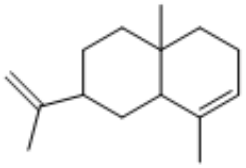
farnesol



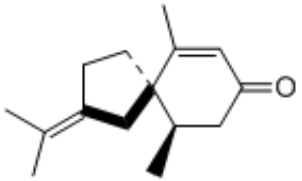
bisabolene



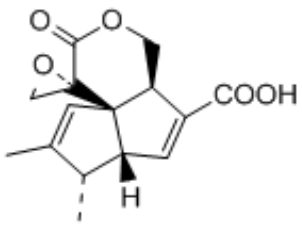
cadinene



selinene

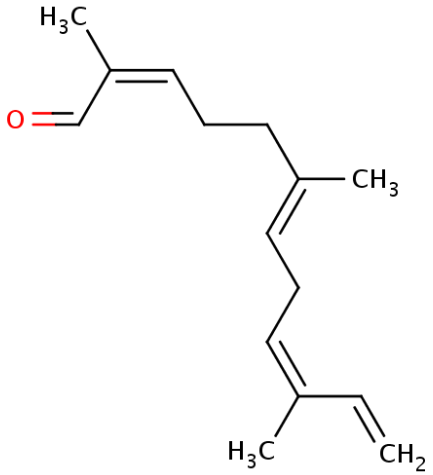


vetivone

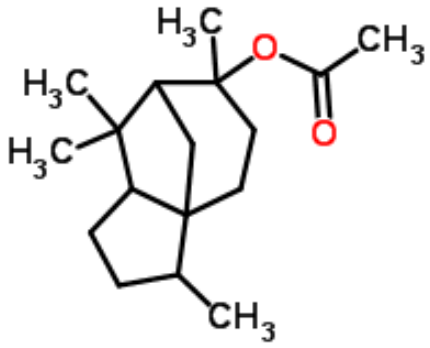


pentalenolactone

Some sesquiterpenes in the volatile oils

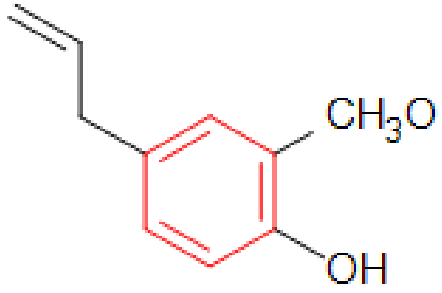


α-sinensal



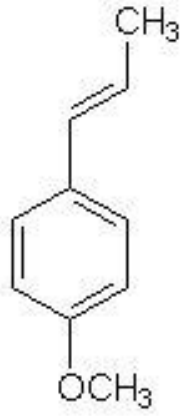
cedryl acetate

Aromatic compounds : Phenylpropanoids (C_6-C_3) are far less common than terpenoids . Very often, they are allyl- and propenylphenols, and sometimes, they are aldehydes characteristic of certain Apiaceae oils (anise, fennel, parsley: anethole, anisaldehyde, apiole), but also of those of clove, nutmeg, calamus, cinnamons and more (eugenol, safrole, asarones, cinnamaldehyde). Also found in essential oils are C_6-C_1 compounds such as vanillin or methyl anthranilate.

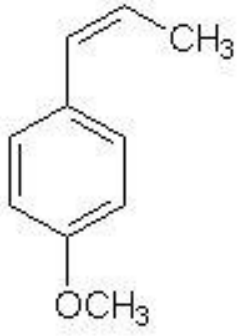


Eugenol

Aromatic compound extracted from clove essential oils

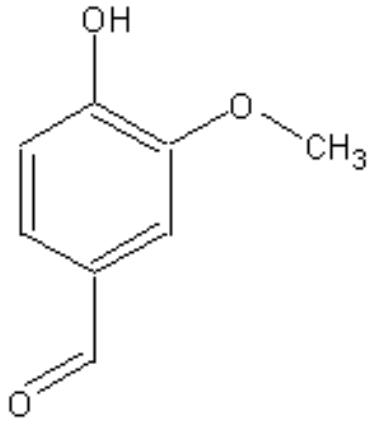


trans-



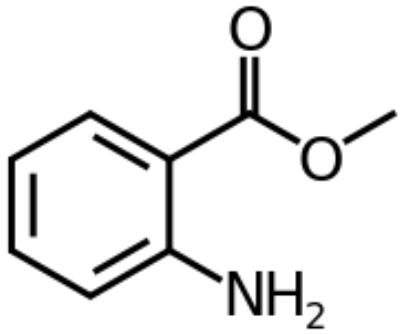
cis-

Anethol



4-hydroxy-3-methoxybenzaldehyde

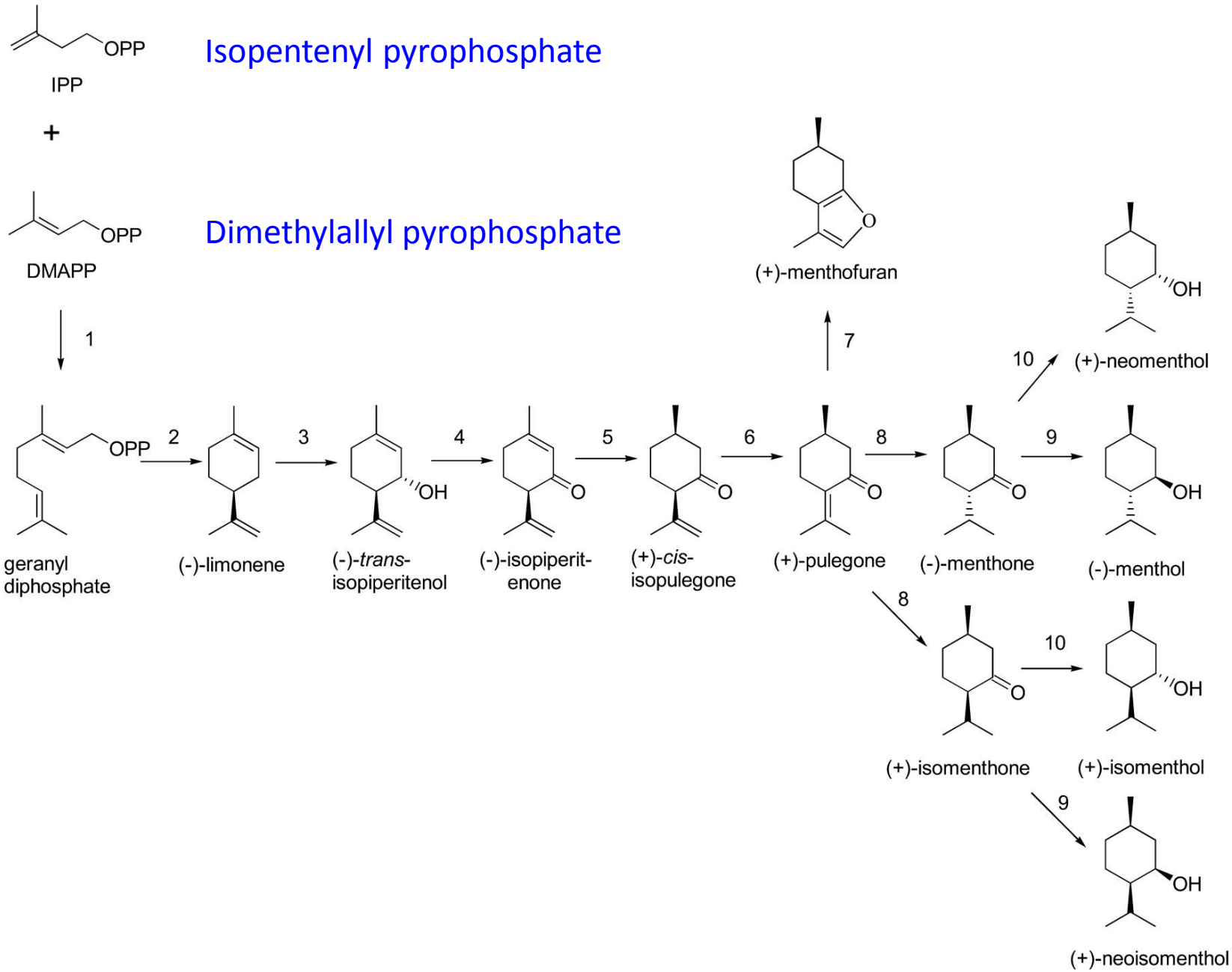
Vanillin



Methyl anthranilate

Some aromatic compounds in the volatile oils

BIOSYNTHESIS PATHWAY OF TERPENOIDS



METHODS OF PRODUCTION

A. Of Essential oils

By Steam Distillation

Simple steam distillation consists in immersing the plant material to be treated directly in a still filled with water, which is then brought to a boil. This is the most used method.

In saturated steam distillation the plant does not come in contact with the water : the steam is injected through the plant material placed on perforated trays.

Saturated steam distillation can also be conducted on-line, in automated set-ups. For the production of some essential oils (lavender, mint), mobile stills are used, which are truck-size containers designed to be filled with the harvested plant material, then fitted between the steam generator and the condenser tank at the destillation facility.

Hydrodiffussion consists of sending pulses of steam under very low pressure (0.02-0.15 bar) through the plant material, from top up bottom. The composition of the resulting products is qualitative markedly different from that of the products obtained by classic methods. The procedure saves time and energy.

By Expression of *Citrus* Pericarps

The principle of this method is quite simple : the rind is lacerated, and the contents of the ruptured secretory cavities are recovered by a physical process. The classic process consists in applying an abrasive action on the surface of the fruit in a flow of water. After eliminating the solid waste, the essential oil is separated from the aqueous phase by centrifugation. Other machines break the cavities by depression, and collect the essential oil directly.

B. Of Concretes and Resinoids

Solvent Extraction

The solvents most often used are aliphatic hydrocarbons : petroleum ether, hexane, but also propane, or liquid butane. Although benzene is a good solvent, its toxicity limits its use more and more. Halogenated solvents are also used, as well as ethanol, which is mostly used to obtain absolutes and washed resinoids. After extraction, the solvent is distilled. At the end of the procedure, the solvent contained in the plant material is recovered by steam injection.

Methods Using Oils and Fats

These procedures take advantage of the liposolubility of the fragrant components of plants in fats. In the technique referred to as “enfleurage”, the plant material is placed contact with the surface of the fat, and the extraction is achieved by cold diffussion into the fat, whereas the “digestion” technique is carried out with heat, by immersing the plant parts in the melted fat. The resulting product is a floral pomade.

Exraction by Supercritical Gases

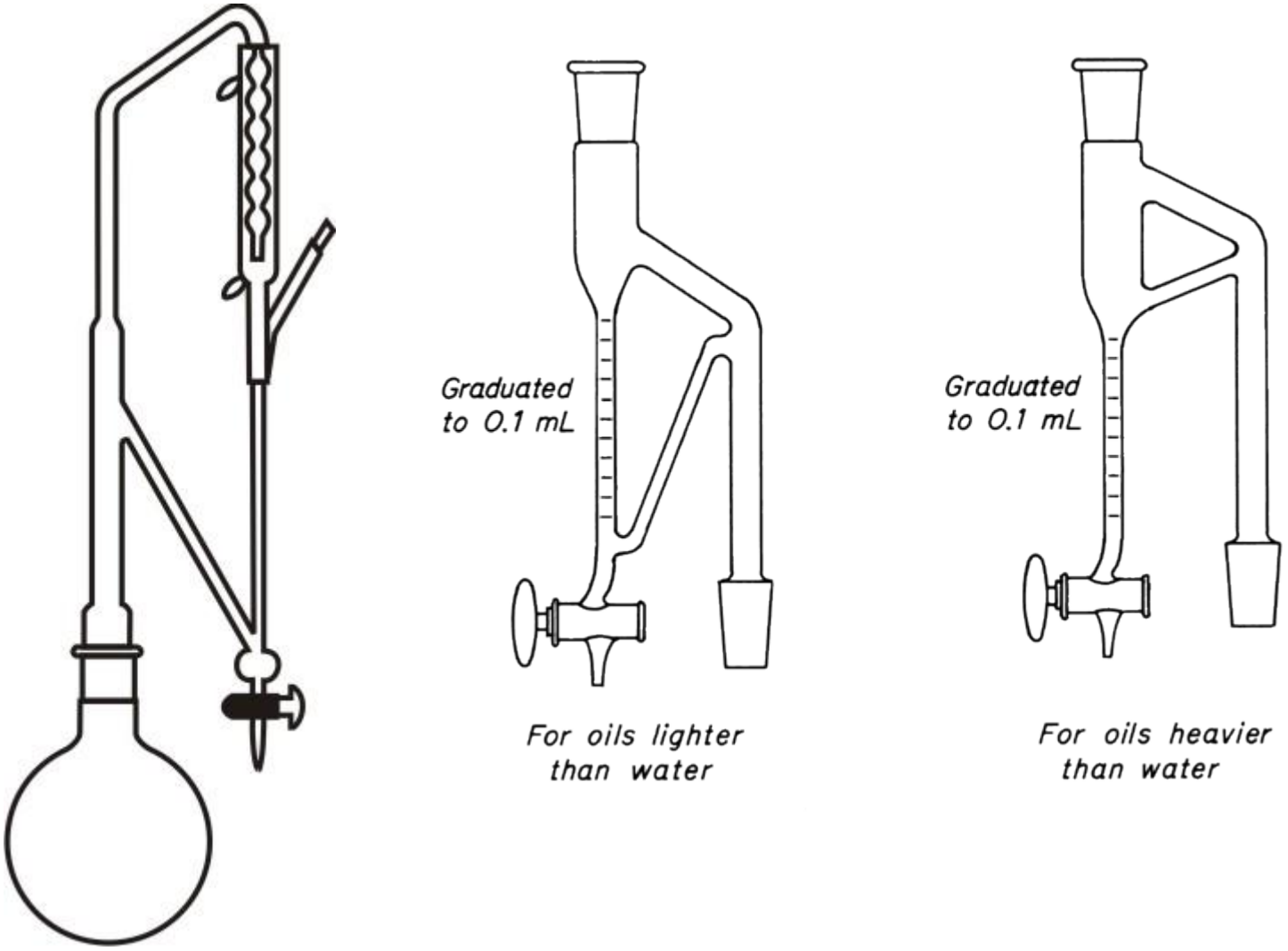
Beyond its critical point, a fluid can have the density of a liquid and the viscosity of a gas, therefore it diffuses well through solids, and it is a good solvent. Although in theory, several gases can be used, the focus is exclusively on carbon dioxide, and the reason for this becomes clear when considering its advantages : it is a natural product, chemically inert, non-flammable, perfectly non-toxic, easy to eliminate completely, selective, readily aveilable, chemically unreactive and inexpensive.

This method is currently spreading desipite the high cost of the initial investment because of its advantages : the ability to obtain extracts of composition very close to that of natural products.

QUALITY CONTROL FOR DRUGS CONTAINING ESSENTIAL OILS AND QUALITY CONTROL FOR ESSENTIAL OILS

Quantitation of the Essential Oil : This quantitation is carried out by steam distillation in a special apparatus. The procedural steps are as follows : distillation of the drug in aqueous suspension, recovery of the distillate in the graduated tube, which already contains a known amount of xylene.

The role of xylene is to retain the essential oil, phase separation by decanting , reading of the total volume of the organic phase, and calculation of the volume of the essential oil by subtracting the known volume of xylene.



Apparatus for the quantitation of essential oils in plant drugs (Clevenger apparatus)

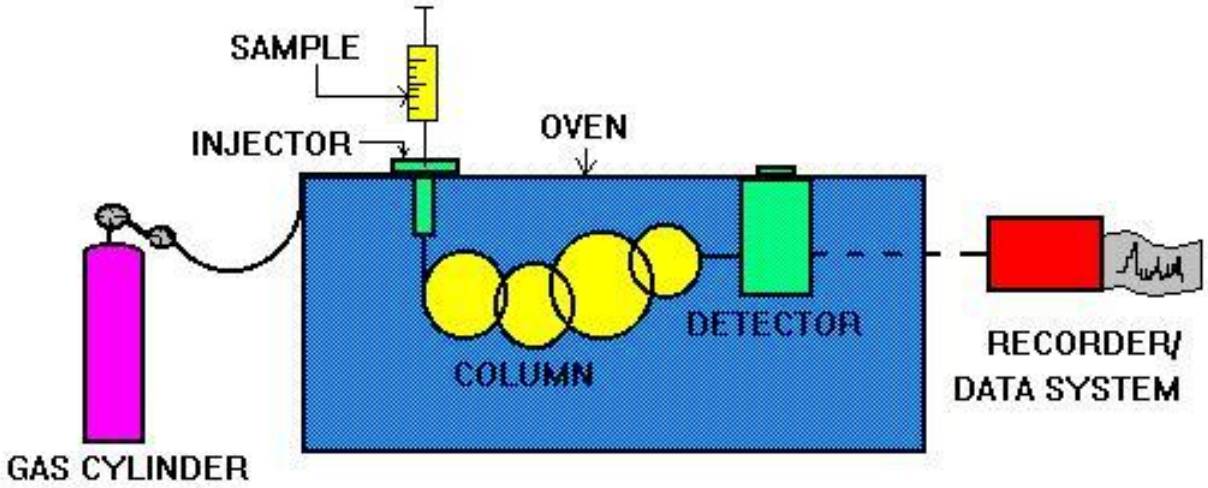
Quality Control of Essential Oils :

Pharmacopoeias require different tests : evaluation of the miscibility with ethanol, physical measurements (refractive index, optical rotation, relative density, sometimes solidification temperature), determination of various indexes (acid, ester, carbonyl), and in some cases verification of the absence of fixed (fatty) oil, and resinified essential oils, residue on evaporation, and so on. They also require an analysis of the essential oil by a chromatographic technique.

Although less powerful than GC, TLC of essential oils can be used routinely for quality control purposes (silica gel plates, solvent systems based on toluene or benzene, and chloroform, ethyl acetate, or both; detection by UV and by spraying various reagents : sulfuric acid followed by vanillin and heat, antimony chloride, and more).

Gas Chromatography : Given the volatility of the constituents, most suitable analytical method is GC.

GAS CHROMATOGRAPHY



High Pressure Liquid Chromatography :

Of the little interest for volatile fractions, HPLC is an efficient way to check the authenticity of *Citrus* oils by analysing their non-volatile constituents, or to quantitate herniarin (a coumarin) in lavender or terragon oil. HPLC is a very good method for studying the non-volatile constituents of concretes and absolutes. Like GC, it can be coupled with mass spectrometry (LC-MS, HPLC-MS).

B. PHARMACOLOGICAL PROPERTIES OF ESSENTIAL OILS

First of all, the activity of an essential oil is sometimes confused with that of the plant which it came. In reality, such an assumption is rarely justified : for example, the rosemary oil is an antibacterial agent, whereas the plant infusion is traditionally used to treat miscellaneous digestive symptoms, based on antispasmodic and chloretic properties, which are probably linked to the presence of phenolics.

Secondarily, although it is possible to study and describe the biological or pharmacological effects of a pure monoterpene, sesquiterpene, or alkylbenzene, it is difficult, if not impossible , to discuss the pharmacology, pharmacokinetics, or the metabolism of an essential oil , because it is a mixture.

In spite of this, a few fundamental properties stand out :

- Antiseptic Activity : This antiseptic activity is against various pathogenic bacteria, that are usually resistant to antibiotics. Some essential oils are also active against fungi responsible for mycoses, and against yeasts (*Candida*). The doses required for activity are generally low, and all the more so to the use as a preservative. Savory, cinnamon, thyme, clove, lavender, and eucalyptus are among the most antiseptic essential oils. Compounds such as citral, geraniol, linalool, or thymol are 5.2, 7.1, 5 and 20 times more antiseptic than phenol respectively.

- Spasmolytic and Sedative Properties : A large number of essential oil drugs (mint, vervain) are thought to be efficacious in decreasing or suppressing gastrointestinal spasms. Frequently, they stimulate gastric secretion, hence the adjectives “digestive” and “stomachic”, and may play a role in all the possible consequences of this “eupepsia”.

In vitro, many essential oils (angelica, sweet basil, chamomile, clove, mint, thyme, balm) have marked spasmolitic activity on the isolated guinea pig ileum.

- Irritating Properties : When used externally, products such as turpentine cause an increase in capillary blood flow, substantial rubefaction, a sensation of heat, and in some cases, a slight local anestesic activity. Even today, there are many ointments, creams, or gels based on essential oils, are designed to relieve sprains, soreness, strains, or other joint of muscular pains.

When administered internally, essential oils are thought to trigger “irritation” processes at different levels. Thus, the oils of eucalyptus, pine, or niaouli are thought to stimulate mucus cells, and to increase the motility of the ciliated epithelium in the bronchia; other oils are thought to enhance the renal excretion of water by a direct local effect (juniper). Other activities are attributed to essential oils (choleretic, healing, nervous sedative, and more).

TOXICITY OF ESSENTIAL OILS

Acute toxicity : As a general rule, the acute toxicity of essential oils by the oral route is low or very low : many of the oils currently used have an LD_{50} between 2 and 5 g/kg (anise, eucalyptus, clove) and for most of them, it is greater than 5 g/kg (chamomille, cirtonella, lavender, marjoram, vetiver).

Known is the neurotoxicity of thujone-containing essential oils (thuja, wormwood, tansy, official sage)or those containing pinocamphone (hyssop).

Skin toxicity : Since essential oils are widely used in perfumery and in the cosmetics industry, extensive research has been conducted on their potential toxicity by topical aplication, and on their irritating (mustard, thyme), sensitising (cinnanaldehyde), or phototoxic potential (angelica, bergamot). The results have led international organizations to emit recommendations on their use and that of their constituents.

Carcinogenicity : Several allyl- and prophenylphenols are capable of inducing cancer in rodents : in rats, safrole (sassafras) induces the formation of hepatic tumors, β-asarone (sweet flag) that of tumors of the small intestine, and in mice estragole (sweet basil, tarragon) causes liver cancer. These phenylpropanic derivatives are hydroxylated at C-1’ on the allylic residue (1’-hydroxysafrole, 1’-hydroxyestragole) by microsomal enzymes in the rodents’ liver. In the current stage of knowledge, apiole, dill-apiole, eugenol, and myristicin are considered non-carcinogenic.

USES OF DRUGS CONTAINING ESSENTIAL OILS

Pharmacy : The vast majority of drugs are used crude, especially for the preparation of infusions, especially herbal teas (mint, balm, thyme), and under the form of simple galenicals.

Essential oils are also underpinning of a specific therapy : “aromatherapy”.

Essential oils must be kept of the reach of children and it would be best if they could be packaged properly and labeled correctly.

Perfumery : Perfumery is the main outlet for essential oils, concretes, absolutes, and other resinoids obtained from the drugs.

Essential oils also can be used in balneotherapy, in bath products (“soothing” and “relaxing” baths).

Food technology : Some drugs are used raw (herbs and spices), others are used as essential oils, resinoids, or oleoresins, dispersed, encapsulated or complexed.

STORAGE

Evidently, the relative instability of the constituents of essential oils make their storage a challenge. The decomposition possibilities are numerous, easy to measure through indexes (peroxide, refraction), the determination of physical characteristics (viscosity, miscibility with alcohol, optical activity), and GC analysis. There are multiple risks : photoisomerization, photocyclization, decomposition to ketones and alcohols, termoisomerization etc.

Since degradation can be alter properties or jeopardize product safety, it must be avoided by using small vials made of aluminum, stainless steel, or tinted glass, nearly completely filled, tightly closed, sealed under a nitrogen or to other inert atmosphere, and protected from heat and light. It is always possible to add antioxidants.

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