

PharmacognosyII

Lec. 7

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Volatile oils

The monoterpenes are major constituents of the volatile oils that are common in plants and which contribute to their aroma.

Biosynthesis of volatile oils:

The head of one isoprene molecule could link with the tail of another isoprene molecule (isoprene rule).

The monoterpenes (10 carbon atom) are produced by the reaction between DMAPP (dimethylallyl pyrophosphate) and IPP (isopentenyl pyrophosphate) in the presence of the enzyme prenyltransferase. A terpene that does not obey the isoprene rule is called irregular terpene (carotene). Geranyl pyrophosphate can then undergo many reactions to generate the variety of monoterpenes observed, such as simple modification to give the acyclic monoterpene linalool which is a component of coriander oil. Geranyl pyrophosphate can be cyclized to give cyclic monoterpenes, which may be fully saturated, partially unsaturated or fully aromatic products of which menthol and thymol from thymus plant.

Geranyl pyrophosphate can also undergo many reactions to generate the variety of monoterpenes observed, such as simple modification to give the acyclic monoterpene b-citronellol, which is a component of rose oil.

The perfume industry has a great interest in monoterpene mixtures and uses preparative GC to separate and isolate individual components, which a highly qualified perfumer then smells to find compounds with a distinctive, novel or

unusual aroma that can be blended with other volatiles to give a popular fragrance.

Fixed oil	Volatile oils
Glycerol ester	Terpene or phenylpropane
Can not be distilled, prepared mainly by expression	Can be distilled
Saponify with alkalies	Canot be saponify
Rancid when exposed to air and sunlight	Oxidize and resinify
Leave a permanent spot on filter paper	Do not leave a permanent spot on filter paper

Physical and chemical properties

- Evaporate when exposed to the air at ordinary temperatures, therefore they are called ethereal oil or essential oils (odour of the plants).
- High refractive indices.
- Optically active and their specific rotation is used as a diagnostic property.
- Immiscible with water.
- Soluble in ether and most organic solvents.

Chemically, they are two classes depend on biosynthetic sub units:

- Terpenoids biosynthesized from acetate mevalonate pathway.
- Aromatic formed via shikimate pathway.

Chemistry of volatile oils

Volatile oils are of highly complex chemical composition (hydrocarbon, oxide, ether, aldehyde, ketone, ester and others).

Extraction of oils used in perfume

Certain oils used in perfumery such as oil of rose are prepared by steam distillation but many flower perfumes require other treatment, they can be prepared by digestion in melted fat, in the enfleurage process glass plates are covered with a thin layer of fixed oil or fat upon which the fresh flowers are spread.

The volatile oil gradually passes into the fat and the exhausted flowers are removed and replaced by a fresh supply.

Thyme oil

Is obtained by steam distillation from the fresh flowering aerial parts of *thymus vulgaris*. The oil resembles that obtained from the official drug described above but reflects any changes that occur during drying and storage. The oil may vary in colour from yellow to dark reddish–brown. It has an aromatic spicy odour suggesting that of thymol.

Cumin oil

Biological source

Cumin consists of the dried ripe fruits of (*Cuminum cyminum*), it resembles caraway at first glance.

Geographical Source

Spain and Egypt are the major cumin oil producers.

Compositions

Cumin yields 2.5%-4% of volatile oil. This contains 25-35% of aldehyde (cuminic aldehyde), pinene and alpha-terpinole, some 16 monoterpenoid glycosides and new sesquiterpenoid glucoside, e.g. cuminoside A and B.

Use

- Cumin used in digestion problems, including diarrhea, colic and bowel spasms.
- It is also used to increase urine flow (as a diuretics), and give to start menstruation.
- Also used as a flavoring component.

Methods of extraction

1- Distillation by water

It is applied to plants which are not injured by boiling, terpentine oil is obtained by this method. Crude of terpentine is introduced into the distillation chamber along with water and subjected to heat below 40c, a mixture of water and oil is obtained as a distillate which is collected in a flask. The distillate is separated into two layers of oil being withdrawn through the upper outlet of the condenser and water from the lower outlet or vice versa in case of clove as clove oil is heavier than water.

2- Water and steam distillation

Use for substances that are usually injured by direct heat, for example, glove and cinnamon. Dried drug ground and covered with a layer of water, steam passes through the mixture, steam is generated by another chamber and piped into a container having drug, the vapour contain the vol oil is introduced in a condensing chamber cooled and collected.

3- Destructive distillation without air (vacuum)

Tough materials such as bark, seeds and roots may be comminuted to facilitate extraction. Broken pieces of wood are placed in a chamber and heated with

water without air in the vacuum. The decomposition of wood occurs and the volatile oil is generated and collected through the condenser.

4- Ecuelle method

It is used for the extraction of citrus oil where oil cells in rind are ruptured mechanically using pointed projection by twisting raw material over them in clockwise direction either mechanically or manually.

5- Enfleurage

Is used for extraction of delicate perfumes. In this method a layer of fat is spread over a glass plate and flower petals are placed over fat layer which absorbs v.o., the exhausted petals are replaced by fresh petals. This process continues till the fatty layer is saturated, volatile principles which are then extracted with lipid solvent.

6- Solvent extraction

It is used in perfume industry and is an expensive method, in this technique parts containing volatile oil are extracted directly by one of the organic solvent as they are crushed and mixed in the solvent and are separated by distillation, e.g. oil of rose.