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Subject: Pharmamacognosy & Phytochemistry

Unit: Fourth

Topic: Introduction to secondary metabolites (**Volatile oils)**

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INTRODUCTION

Volatile oils are odorous volatile principles of plant and animal source, 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 secretary tissues, for example, thenoil 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 odorless, 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 aglycoside, sinigrin, by an enzyme, myrosin. Glycoside andenzyme 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 spoton filter paper nor saponified with alkalis.

CLASSIFICATION OF VOLATILE OILS

Volatile oils are classified on the basis of functional groups present as given in Table 1.

Table 1. Classification of volatile oil

Hydrocarbons	Turpentine oil
Alcohols	Peppermint oil, Pudina, Sandalwood oil, etc.
Aldehydes	Cymbopogon sp., Lemongrass oil, Cinnamon Cassia, and Saffron
Ketones	Camphor, Caraway and Dill, Jatamansi, Fennel, etc
Phenols	Clove, Ajowan, Tulsi, etc

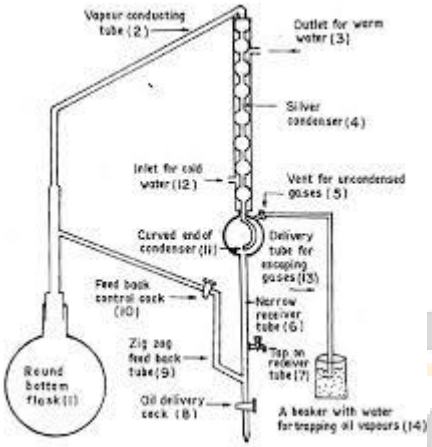
Phenolic ethers	Nutmeg, Calamus, etc
Oxides	Eucalyptus ,Cardamom, and Chenopodium oil
Esters	Valerian, Rosemary oil, Garlic, Gaultheria oil, etc

EXTRACTION OF VOLATILE OILS

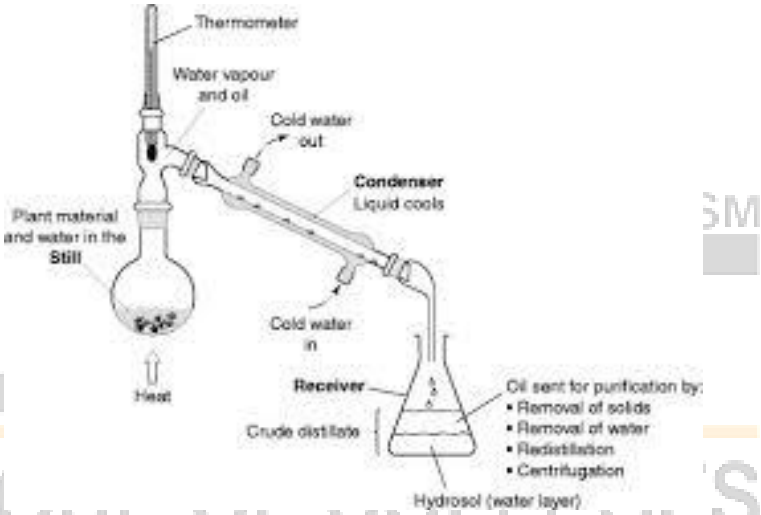
Volatile oils are prepared by means of several techniques and those techniques are discussed below:

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.



Clavenger apparatus



Hydro distillation apparatus

Extraction by Scarification

This method is used for the preparation of oil of lemon,
oil of orange, and oil of bergamot. These oils are foun 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.

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 flavoring 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 lardand 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 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.

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.

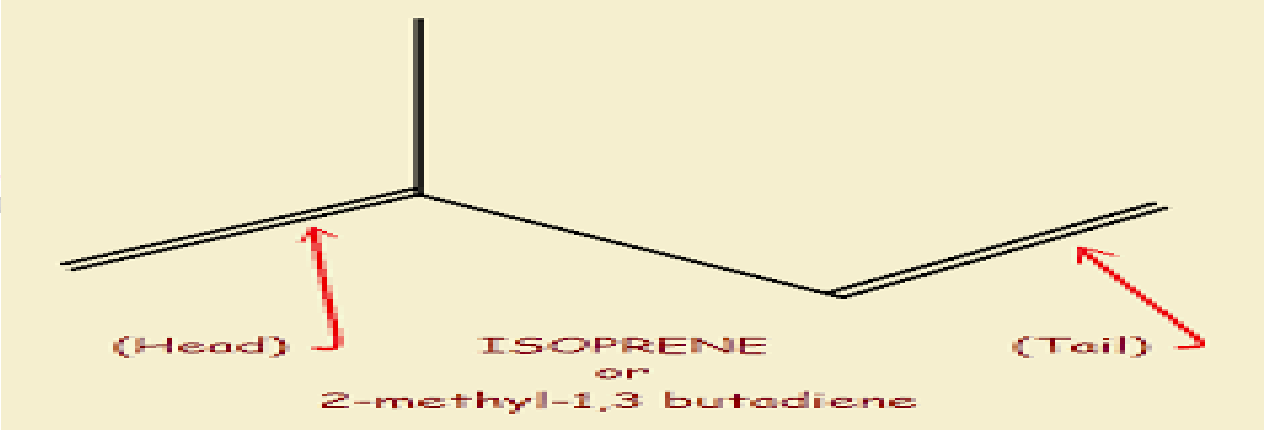
TERPENOIDS

There are many different classes of naturally occurring compounds. Terpenoids also form a group of naturally occurring compounds majority of which occur in plants,

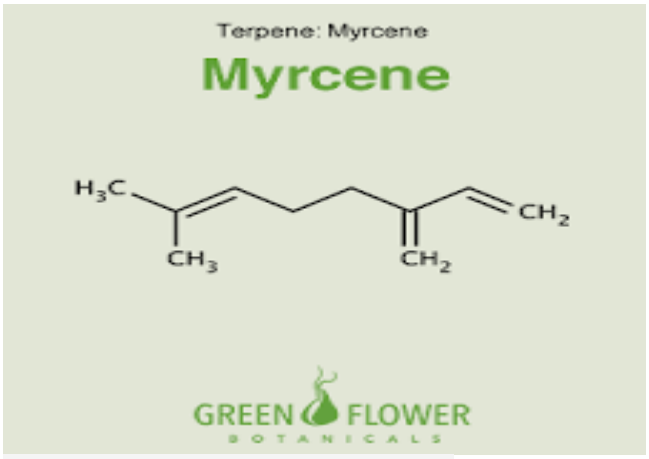
a few of them have also been obtained from other sources.Terpenoids are volatile substances which give plants and flowers their fragrance. They occur widely in the leaves and fruits of higher plants, conifers, citrus and eucalyptus.

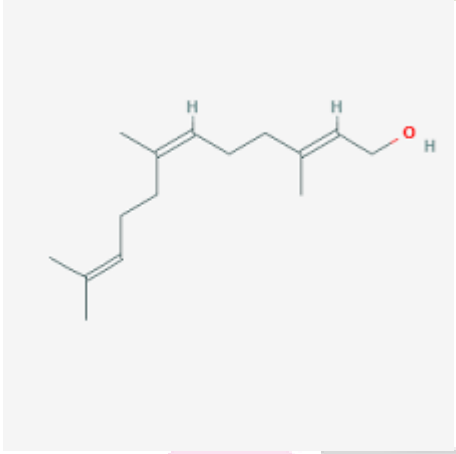
The term ‘terpene’ was given to the compounds isolatednfrom turpentine, a volatile liquid isolated from pine trees. The simpler mono and sesquiterpenes is the chief constituent of the essential oils obtained from sap and tissues of certain plant and trees. The di- and triterpenoids arenot steam volatile. 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 describea mixture of isomeric hydrocarbons of the molecular formula C10H16 occurring in the essential oils obtained fromsap 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 (C5H8)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. Head isoprene unit tail



Special Isoprene Rule





Farnesol

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

CLASSIFICATION OF TERPENOIDS

Most natural terpenoid hydrocarbons have the general formula $(C_5H_8)_n$. They can be classified on the basis of number of carbon atoms present in the structure.

Table 2 Classification of Terpenoids

S.NO	NO of carbon atom	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 (C40H64	
7.	>40	>8	Polyterpenoids (C5H8)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

EVALUATION OF VOLATILE OILS

Product from different manufacturers varies considerably, since it is inherently difficult to control all the factors thataffect 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 essentialnoils. 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.

CHEMICAL TESTS

Natural drugs containing volatile oils can be tested by following chemical tests:

1. Thin section of drug on treatment with alcoholic solution of Sudan III develops red colour in the presence of volatile oils.
2. Thin section of drug is treated with tincture of alkana, which produces red colour that indicates the presence of volatile oils in natural drugs.

STORAGE OF VOLATILE OILS

Volatile oils are liable to oxidation on storage in presencennof 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.

PHARMACEUTICAL APPLICATIONS

Volatile oils are used as flavouring agent, perfuming agent in pharmaceutical formulations, foods, beverages, and in cosmetic industries. These are also used as important medicinal agent for therapeutic purposes like:

1. Carminative (e.g. Umbilliferous fruits)

2. Anthelminitic (e.g. Chenopodium oil)
3. Diuretics (e.g. Juniper)
4. Antiseptic (e.g. Eucalyptus)
5. Counter irritant (e.g. Oil of winter green)
6. Local anesthetic (e.g. Clove)
7. Sedative (e.g. Jatamansi)
8. Local irritant (e.g. Turpentine)
9. Insect repellent (e.g. Citronella)
10. Source of vitamin A (e.g. Lemongrass)

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