VOLATILE OILS

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INTRODUCTION

- Volatile oils may be defined as oily liquids which are entirely, or almost entirely, volatile without decomposition.
- The odorous, volatile principles of plants and animal sources
- As they evaporate when exposed to air at ordinary temperatures- Ethereal oils
- They represent essence or active constituent of plant---Essential oil
- Chemically they are derived from terpenes and their oxygenated compounds
- Made up of isoprene unit (C_5H_8)

PROPERTIES OF VOLATILE OILS

- Almost **entirely volatile without decomposition.**
- Density: Most are **less than 1g/ml**.
  - 2 are heavier – Oil of Cinnamon and Clove oil.
- **Soluble** in **ether, chloroform** & **alcohol**.
- **Slightly soluble in water:** give it a **characteristic odour & taste.**
- Leaves a **temporary translucent stain** on paper which disappears as the oil volatilizes.
- Most are **colourless**. **Oxidize on exposure to air** and resinify → colour becomes **darker** (**odour changes** slightly).
- All are **characteristic odours**.
- Most are **optically active**.

- They are secreted in special structures such as
  - Oil ducts of umbelliferous fruits,
  - Oil cells or oil glands occurring in the sub-epidermal tissue of the lemon and orange,
  - Mesophyll of eucalyptus leaves,
  - Schizogenous or lysigenous glands,
  - Trichomes etc.

- Commonly found in the species of Labiatae, Rutaceae, Piperaceae, Zingiberaceae, Umbelliferae, Myrtaceae and Lauraceae--Present in entire plant or in any part of plant

- Terpene—only the hydrocarbons $(C_5H_8)_n$
- Terpenoids—the hydrocarbons as well as the oxygenated derivatives like alcohol, aldehydes and ketones
- Among the chief constituents of the essential oils are the terpenoids having carbon atoms up to C_{15} and their oxygenated derivatives such as alcohols, aldehydes and ketones.
- In most cases, the volatile oil pre-exists in the plant, in few cases the volatile oil does not pre-exist, but is formed by the decomposition of a glycoside.
- e.g. whole black mustard seed is odourless, but upon crushing the seeds and adding water to it a strong odour is evolved due to decomposition of a glycoside, sinigrin, by an enzyme, myrosin.

USES OF VOLATILE OILS

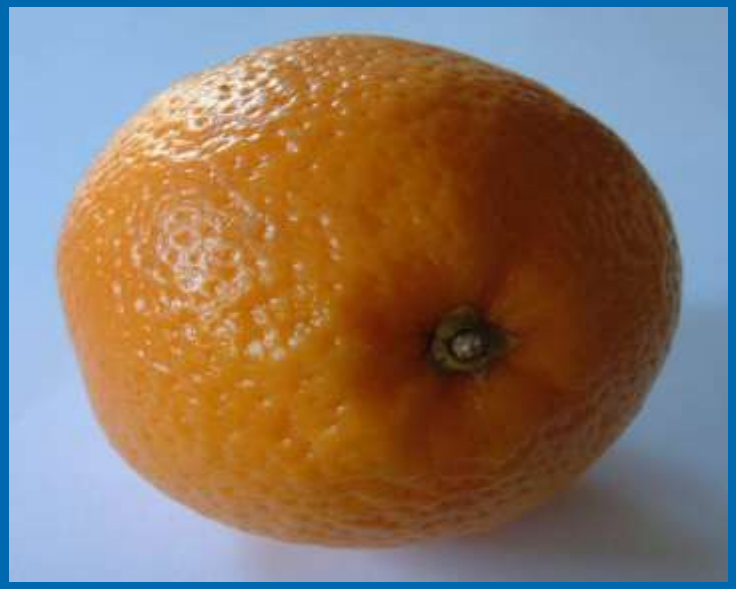
- **Therapeutically** (Oil of Eucalyptus)
- **Flavouring** (Oil of Lemon)
- **Carminatives** (Oil of Clove),
- **Perfumery** (Oil of Rose)
- **Starting materials** to synthesize other compounds (Oil of Turpentine)
- **Anti-septic** – due to high phenols (Oil of Thyme).
- **Preservative** (oils interfere with bacterial respiration)
- **Anti-spasmodic** (Ginger, Lemon balm, Rosemary, Peppermint, Chamomile, Fennel, Caraway)
- **Aromatherapy**

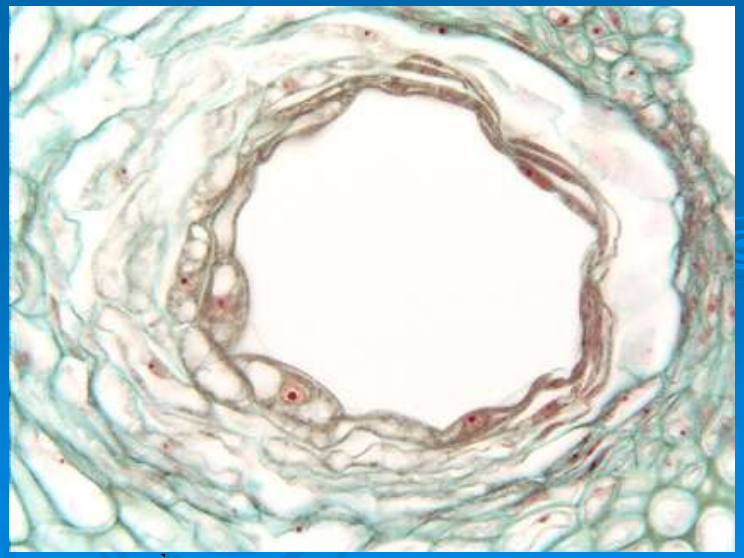
Volatile oils are administered as

- **Inhalation** (eucalyptus oil),
- **Orally** (peppermint oil),
- As gargles and mouth washes (thymol)
- **Transdermally** (lavender, rosemary)
- Oral use is minimized due to the **irritation** which they produce to the mucous membrane

Important V.O. with their main terpenoid constituents

Essential oil	Terpenoids
Turpentine	Pinene
Caraway	Carvone, α-limonene
Citronella	Geraniol, citronellal
Coriander	Linalool, pinene
Eucalyptus	Cineole
Geranium	Geraniol
Jasmine	linalool
Lavendar	Linalool
Lemon	D-limonene
Rose	Geraniol, citronellal
Cardamom	Terpineol
Sandalwood	Santalol
Camphor	Camphor
Ginger	Zinziberene





CLASSIFICATION OF VOLATILE OILS

Based on the chemical groups they contain

1. Oils containing mainly Terpenes and Sesquiterpenes
   e.g. Cedar wood oil, Ginger, Orange, Turpentine etc.
2. Oils containing mainly Alcohols and their esters:
   1. Aliphatic saturated alcohols- Heracleum oil
   2. Aliphatic unsaturated alcohols– Coriander, Lavender, Lime, Rose
   3. Monocyclic and dicyclic alcohols– Peppermint, Pine, Rosemery
   4. Aromatic alcohols and esters– Jasmine oil
3. Oils containing Aldehydes :
   1. Aliphatic unsaturated aldehydes: Citronella, Lemon, Lemon grass
   2. Aromatic aldehydes: Bitter Almond oil, Cinnamon, Cassia
4. Oil containing Ketones :

Monocyclic and dicyclic ketones:

Artemisia oil, Camphor, Caraway, Dill, Peppermint, Spearmint

5. Oil containing Esters:

a. Aliphatic acids: Calamus, Cardamom, Chamomile

b. Aromatic acid esters: Gaultheria

c. Undetermined acids: Celery oil

6. Oils containing Phenols and Phenol Ethers:

a. Monoatomic phenols & their ethers: Ajowan, Anise, Fennel

b. Diatomic phenols and their ethers: Camphor, Cinnamon leaf

c. Triatomic phenols and their ethers: Asarum oil

d. Tetraatomic phenols and their ethers: Parsley oil

7. Oils containing Sulphur: Garlic, Mustard, Onion

8. Oils containing Neutral bodies: Eucalyptus, Laurel leaves etc.

Types of volatile oils

i. Concretes

ii. Pomades

iii. Resinoids

iv. Absolutes

Isolation of volatile oils

Because of wide occurrence, there is no general method for their isolation
Essential oils may be produced

i. By Distillation
   - Simple steam distillation
   - Saturated steam distillation
   - Hydrodiffusion

i. By scarification/expression
   - Sponge process
   - Ecuelle process

ii. By Non-volatile Solvent
   - Enfleurage
   - Maceration
   - Spraying

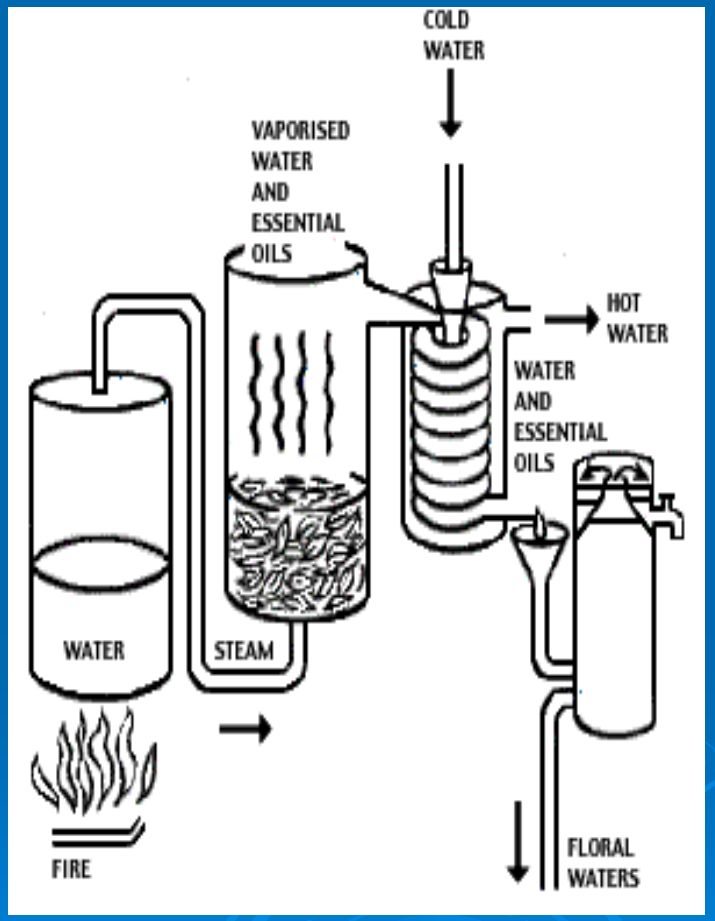
iii. By solvent extraction

iv. By extraction by supercritical gasses

DISTILLATION

SIMPLE STEAM DISTILLATION

- Widely used method
- Carried out either by water or steam
- Better to use fresh material
- Plant material is immersed directly in a still filled with water. This is then brought to a boil.
- Heterogeneous vapours are condensed on a cold surface.
- Essential oil separates based on difference in density and immiscibility.



SATURATED STEAM

- Plant does not come into contact with the water → steam is injected through the plant material placed on perforated trays.
- It is possible to operate under moderate pressure.

- **Advantages:** Limits the alteration of the constituents of the oil
- It shortens the duration of the treatment
- It conserves energy
- It can also be conducted on on-line in automated set ups.

HYDRODIFFUSION

- Pulses of steam is sent through the plant material at very low pressure from (top to bottom).

- **ADVANTAGE:** Normally produces a product of high quality.
- Saves time and energy.

ii. EXPRESSION /SCARIFICATION

Used for the preparation of oil of Lemon, oil of Orange etc.

This oils are found in large oil-glands just below the surface in the peel of the fruit

1. Sponge process
2. Ecuelle process
3. Rasping process
4. Mechanical process

1.SPONGE PROCESS:

- Contents of fruit are removed after making longitudinal or transverse cut
- The peel has been immersed in water for short period of time.
- Then it is ready for expression.
- The softener peel pressed against the sponge,
- oil glands burst open and the sponge absorb the exuded oil, which is transferred to a collecting vessels. The turbid liquid consisting of oil and water.
- The essential oil separated from the aqueous phase by centrifugation.
- Process carried out in cool darkened rooms to minimize the harmful effects of heat and light on the oil

2. ECUELLE PROCESS

- In this process, the rinds are ruptured mechanically using numerous pointed projections with a rotary movement and oil is collected
- Machines break the cavities by depression, and collect the essential oil directly
- Prevents the degradation linked to the action of water.

3. RASPING PROCESS

- In this process, the outer surface of the peel of citrus fruits containing the oil gland is skillfully removed by a grater.
- The rasping are now placed in horsehair bags and pressed strongly so as to ooze out the oil stored in the oil glands.
- Initially, the liquid has a turbid appearance but on allowing it to stand the oil separates out which may be decanted and filtered subsequently.

4. Mechanical Process

- A substantial quantum of volatile oil across the globe is now prepared by various mechanical means solely based on the above principles.
- However, the use of heavy duty centrifugal devices may also be incorporated so as to ease the separation of oil/water emulsions invariably formed.
- It is pertinent to mention here that with the advent of modern mechanical devices the oil out put has increased appreciably and the older methods have only remained for the sake of history.

By Non-volatile Solvent

- A non volatile solvent is used in this process. E.g. Fine quality of either lard or olive oil
- After the saturation with floral oil the lard or olive oil is sometimes used as a flavouring base 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 dissolves the odorous substances.
- The mixed alcoholic solutions so obtained constitute the “triple extract” of commerce.
- Three chief methods
- - Enfleurage
- - Maceration
- - Spraying

ENFLEURAGE

A glass plate is covered with a thin coating of especially prepared and odourless fat (called a chassis).

The freshly cut flowers are individually laid on to the fat which in time becomes saturated with their essential oils. The flowers are renewed with fresh material.

Eventually the fragrance-saturated fat, known as pomade, may be treated with alcohol to extract the oil from the fat.

When oil is used- oil soaked cloth supported by a metal grid, oil is expressed from the cloths, used as perfumed oil, or prepared triple extract with alcohol

Maceration

Used to extract the vol. matters of flowers

Lard/oil-heated over a water bath- a charge of flowers added & the mixture stirred continuously.

Exhausted flowers are removed, pressed, the expressed fluid returned to the hot fat

Fresh flowers added & process continued until defined wt of flowers and solvent have been used

Again a triple extract is prepared by extracting the perfumed lard or oil with alcohol

Spraying

- 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

SOLVENT EXTRACTION

- Flowers are extracted by using solvent like light petroleum
- Solvent is distilled off at a low temp., leaving behind V.O.
- Extraction is generally preceded by a process of: bruising the fresh, wilted or semi-desiccated organs, chopping herbaceous drugs, pounding roots & rhizomes or turning wood into chips or shavings.
- The procedure is conducted in specialized facilities e.g. Soxhlet-type extractor.

SOLVENT EXTRACTION

The **solvent selection** is influenced by technical & economical factors

- **Selectivity** (being a good solvent for the specific constituents).
- **Stability** (chemical inertness)
- **Boiling point** should not be so high that the solvent can be completely eliminated; nor too low, to limit losses & control cost
- Handling **safety**

Solvents most used are aliphatic HC's – **petroleum ether, hexane, propane & liquid butane.**

Although **benzene** is a good solvent, its toxicity increasingly limits is use.

SOLVENT EXTRACTION

Main disadvantages of solvent extraction

- Lack of selectivity, many lipophilic substances may end up in the concretes & render further purification necessary.
- The toxicity of solvents → leads to the restrictive regulations regarding their use
- Residues in the final product.

EXTRACTION BY SUPERCRITICAL GASSES

Beyond its critical point, a fluid can have the density of a liquid & the viscosity of a gas → therefore diffuses well through solids, resulting in a good solvent.

CO_2 is the main gas used

Advantages of CO_2

- It is a natural product
- chemically inert, non-flammable
- non-toxic
- easy to completely eliminate
- selective, - readily available, - Inexpensive

DISADVANTAGE: Technical constraints

- High cost of initial investment

ADVANTAGES:

- obtain extracts which are very close in composition to the natural product.
- It is possible to adjust the selectivity & viscosity, etc by fine tuning the temperature & pressure
- All result in the increase of popularity of this type of method

USES

Initially developed to decaffeinate coffees, prepare hops extracts or to remove nicotine from tobacco, the method is now used to

- Prepare spice extracts (ginger, paprika, celery)
- Specific flavours (black tea, oak wood smoke)
- Plant oils
- To produce specified types of a certain product, e.g. thujoneless wormwood oil.

OTHER METHOD

- Steam distillation by microwaves under vacuum. In this procedure, the plant is heated selectively by microwave radiation in a chamber inside which the pressure is reduced sequentially.
- fresh plants require no added water.

- **ADVANTAGE:** This method is fast, consumes little energy and yields a product which is most often of a higher quality than the traditional steam distillation product.

Factors affecting Essential oil content

- Time of day when plant is picked
- Stage of growth when plant is picked
- Part(s) of the plant are distilled
- Length of distillation
- Method of distillation
- Plant is distilled immediately or whether it is dried first
- Storage conditions

Affect the constituents of essential oils, their quality and medicinal effects

Evaluation of V.O.

Product from different mfgers varies considerable

Environmental conditions can create substantial variability in essential oil quality e.g. sunlight, rainfall, mfging process

- Preliminary examination like odour, taste, colour
- Physical measurement-optical rotation, relative density, refractive index
- Chromatographic tech.-used to determine the proportions of individual components of certain oils
- Ketone and aldehyde content- reaction with Hydroxylamine HCl (oxime formation) & titration of liberated acid
- Oil passes the above examination, having good quality and therapeutic value

CONCRETES

Prepared from raw materials of vegetable origin (bark, flowers, leafs, roots etc.)

Extracted by HC type solvents, rather than distillation or expression – Becomes **necessary when the essential oil is adversely affected by hot water or steam** (e.g. jasmine).

Produces a more **true-to-nature fragrance.**

CONCRETES

Concretes contain about **50 % wax and 50 % essential oil** (jasmine).

Ylang ylang (concrete volatile) contains 80 % essential oil and 20 % wax.

Advantages of concretes: they are **more stable and concentrated** than pure essential oils.

POMADES

True pomades are (volatile oil) products of a process known as enfleurage (hot or cold).

Enfleurage is used for obtaining aromatic materials from flowers containing volatile oils to produce perfume long after they were cut.

RESINOIDS

Prepared from natural resinous material (dried material) by extraction with a non-aqueous solvent, e.g. Petroleum ether or hexane.

E.g. Balsams – Peru balsam or benzoin;

resins (**amber** or mastic);

Oleoresin (copaiba balsam and **turpentine**);

Oleogum resins (**myrrh**)

RESINOIDS

Can be viscous liquids, semi-solid or solid.

Usually homogeneous mass of non-crystalline character.

Uses: in perfumery as fixatives to prolong the effect of a fragrance.

ABSOLUTES

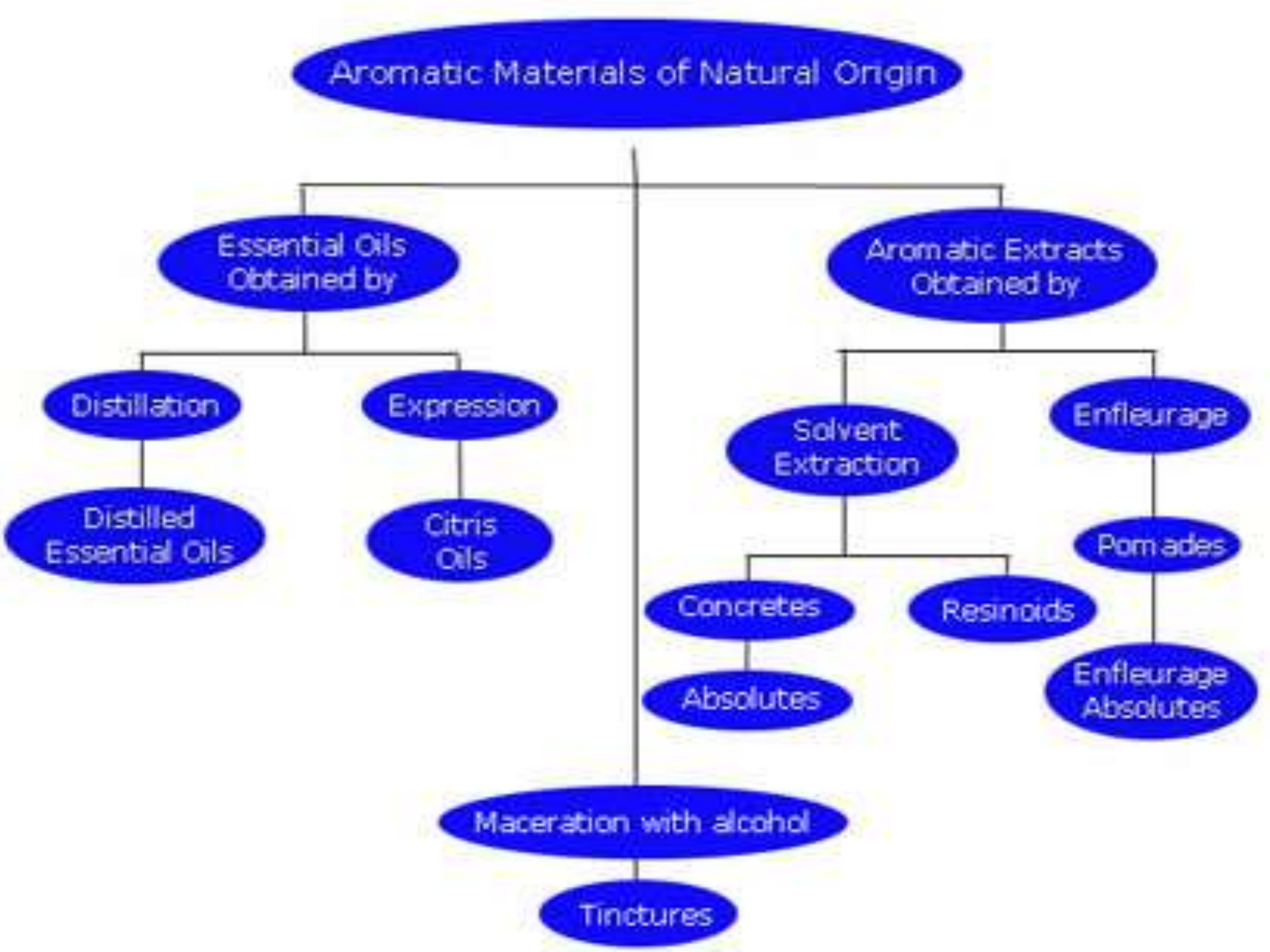
Obtained from a concrete, pomade, or a resinoid by alcoholic extraction.

The extraction process may be repeated.

The ethanol solution is cooled & filtered to eliminate waxes.

The ethanol is then removed by distillation.

They are usually highly concentrated viscous liquids.


Aromatic Materials of Natural Origin
Essential Oils Obtained by
Distillation
Distilled Essential Oils
Expression
Citris Oils
Aromatic Extracts Obtained by
Solvent Extraction
Concretes
Absolutes
Resinoids
Enfleurage
Pomades
Enfleurage Absolutes
Maceration with alcohol
Tinctures

Fx OF VOLATILE OILS

In most cases, the biological function of the terpenoids of essential oils remains obscure – it is thought that they play an ecological role – protection from predators & attraction of pollinators.

VOLATILE OIL COMPOSITION

- Mixtures of HC's and oxygenated compounds derived from these HC's.
  - Oil of turpentine – mainly HC's
  - Oil of Clove – mainly oxygenated compounds
- EXCEPTION: Oils derived from glycosides (e.g. bitter almond oil & mustard oil).
- Oxygenated compounds – responsible for the odour/smell of the oil. They are slightly water soluble – Rose water & Orange Water; more alcohol soluble.
- Most volatile oils are terpenoid. Some are aromatic (benzene) derivatives mixed with terpenes.
- Some compounds are aromatic, but terpenoid in origin (e.g. Thymol – Thyme)

CHEMICAL COMPOSITION

Volatile oils are divided into 2 main classes based on their biosynthetic origin

i. Terpene derivatives (formed via the acetate mevalonic acid pathway)

ii. Aromatic compounds (formed via the shikimic acid-phenylpropanoid route)

iii. Miscellaneous Origin

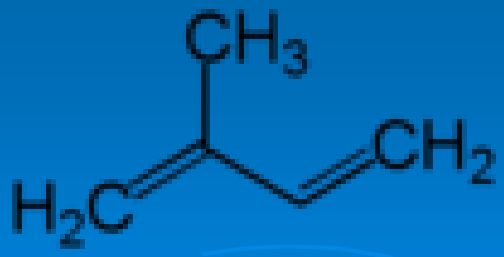
A. TERPENES

Terpenes, or terpenoids, are the largest group of secondary products (metabolites).

They are all formed from acetyl CoA or glycolytic intermediates.

Terpenoids are the secondary metabolites synthesized by plants, marine organisms and fungi by head to tail joining of **isoprene units**. They are also found to occur in rocks, fossils and animal kingdom.

The **terpenoids**, sometimes referred to as **isoprenoids**, are a large and diverse class of naturally-occurring organic chemicals similar to terpenes, derived from five-carbon isoprene units assembled and modified in thousands of ways.



Isoprene

- Material with molecular structure containing carbon backbones made up of Isoprene units (C_5H_8)
- Terpenes- hydrocarbons resulting form combination of several isoprene units
- Terpenoids- hydrocarbon and their oxygenated derivatives aldehydes, ketones, alcohols
- Terpenoids-modified terpenes, where CH_3 group is removed or moved, or oxygen atoms added
- Produced by plants, animals and micro organism
- The role of terpenoids in living organisms
  - **a) Functional b) Defense c) Communication**

FUNCTIONAL :

- Play a key part in metabolic processes of the organism in which they are present
- Vit A- precursor of pigments in eyes- detect light
- Chlorophyll-green pigment in leaves-photosynthesis

DEFENSIVE:

- Plants use to protect themselves
- 2 methods

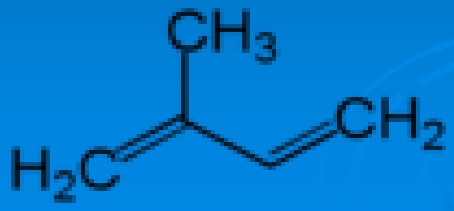
1. Production of resins which damaged & the production of mate. Which will render a plant or animal unattractive to predatives- resin seals the wound & prevent m.o. entry
2. Unpalatable to insects and animals, which would otherwise eat their foliage

COMMUNICATION:

- Communicate the messages to different part of plants or to the environment
- e.g. Giberellic acid- hormone –used by plants as a chemical messenger to control their growth rate
- Male moths can detect their females from miles away by the sex pheromones secreted in the females

Isoprene rule

- Terpenes are derived biosynthetically from units of isoprene, which has the molecular formula C_5H_8.
- The basic molecular formulas of terpenes are multiples of it, $(C_5H_8)_n$ where n is the no of linked isoprene units.
- This is called isoprene rule or the C5 rule.
- We could consider the molecule to resemble a nanoscalar tadpole with a head at the branched end of the molecule, the other end therefore constituting the tail.
- Thus the isoprene units may be linked together "Head to tail" to form linear chains or they may can be arranged to form rings. Occasionally, a tail to tail coupling occurs



Isoprene

CLASSIFICATION OF TERPENES

TYPE OF TERPENOIDS	NUMBER OF CARBON ATOMS	ISOPRENE UNITS
hemiterpene	C_5	one
monoterpenoid	C_{10}	two
sesquiterpenoid	C_{15}	three
diterpenoid	C_{20}	four
sesterterpenoid	C_{25}	five
triterpenoid	C_{30}	six
tetraterpenoid	C_{40}	eight

NOTE :

hemi = half
sesqui = one and a half

di = two
tri = three
tetra = four

TERPENOIDS

Terpenoids contain only the most volatile terpenes (i.e. molecular weight is not too high) → mono and Sesquiterpenes

May occur as oxygenated derivatives, e.g. alcohols, aldehydes, ketones, phenols, oxides & esters.

Uses of Terpenoids

- Antiseptic
- Anticancer
- Anti rheumatic
- Analgesic
- Anthelmintic
- Diuretic
- Stimulant carminative
- Counter irritant
- Insecticides and pesticides
- Due to flavour-used in perfumery, soaps, cosmetics and food and beverage industries

DRUGS CONTAINING TERPENES

i. Coriander
ii. Cinnamon bark
iii. Cassia bark
iv. Lemon peel
v. Lemon grass
vi. Dill
vii. Caraway
viii. Clove
ix. Fennel
x. Nutmeg
xi. Eucalyptus
xii. Chenopodium
xiii. Cardamom
xiv. Valerian
xv. Sandal wood
xvi. Mentha/ Pudina/ peppermint

THANK YOU