VOLATILE OILS

Definition
Volatile oils are “odorous principles found in various plant parts and they evaporate when exposed to air at ordinary temperature so they are called volatile oils or ethereal oils”. They are also called essential oils because they produce essence (smell).

Physical Properties
- They are colorless when fresh but darken in color after prolong standing due to oxidation
- They have high refractive index
- They are optically active
- They are immiscible with water but soluble in organic solvent

Occurance
Volatile oils occur in special secretary cells. These cells are
- Glandular hairs in Piperaceae family
- Special tubes in pericarp of fruit of Umbelliferae family
- Lysigenous and schizogenous cavities in stem of Pinaceae family
  ✓ Lysigenous
  These cavities are formed in the center due to lysis of cells and volatile oil is present in these cavities.
  ✓ Schizogenous
  These cavities are formed due to large spaces between the cells and volatile oil goes from cells into these spaces and develop cavities.
In individual plants, they may occur in all tissues e.g. petals of rose flower, bark of cinnamon, fruit of coriander, leaves of peppermint

SIGNIFICANCE OF VOLATILE OILS
Volatile oils have great significance for both plants and human.

- Significance in Plants
  - Insect repellant
    Because of specific odour they prevent destruction of flowers by insect.
  - Insect attractant
    They also help in cross fertilization in plants by insects due to their fragrance.

- Significance for Human
  - They are used as flavoring agent to mask the unpleasant flavor/taste of bitter drugs.
  - They are used therapeutically.
  - They are used in perfumes and cosmetic industry.

Therapeutic Applications (Aromatherapy)
Aromatherapy is a form of Alternative Medicine that uses volatile liquid plant materials, known as Essential Oils, and other aromatic compounds from plants for the purpose of affecting a person's health. The pure essence of a plant, have been found to provide both psychological and physical benefits when used correctly and safely.

Purpose of Aromatherapy
Aromatherapy offers diverse physical and psychological benefits, depending upon the nature of essential oil or oil combination and method of application used. Essential oils are used to treat a wide range of symptoms and conditions, including, gastrointestinal discomfort, skin conditions, stress-related conditions, mood disorders, circulatory problems, respiratory infections, and wounds.

Pharmacological Effects Attributed to Essential Oils
- **Anti-inflammatory**: They are used as counter irritant in inflammation and rheumatism when applied to skin e.g. winter green oil (methyl salicylate + menthol)-Wintogeno Balm
- **Carminative**: They act as carminative (help in digestion) e.g. volatile oil from fennel, coriander and cardamom.
- **Expectorant**: Eucalyptus oil is an excellent expectorant.
- **Local Anesthetics**: They act as local anesthetics in toothache e.g. clove oil
- **Antibacterial**: In vitro testing has confirmed antibacterial effects in certain oils including rosemary, clove, lemon, cinnamon, thyme
- **Antiviral**: Volatile oil from peppermint, ginger and thyme are reported to be effective for in vitro testing against Herpes virus.
- **Anxiolytic**: Lemon oil, lavender oil and rose oil relieve anxiety when applied to tempels.
- **Antispasmodic**: Lavender oil, fennel oil and cardamom oil have sapamolytic effect.
- **Anthelmentics**: Some are employed as anthelmentics (vermifuge) e.g. Chenopodium oil.
- **Nasal Decongestants**: They are used as nasal decongestant e.g. menthol and camphor.
METHODS FOR OBTAINING VOLATILE OILS
Volatile oils are obtained by following different methods.

1. Distillation
2. Expression
3. Enfleurage
4. Enzymatic hydrolysis
5. Solvent extraction

1. Distillation
Following types of distillation are used for obtaining volatile oils.

- **Water Distillation**
  This method is applied to those plants which are not injured by boiling i.e. at 100°C e.g. turpentine oil is obtained by this method.

  **Procedure**
  The crude turpentine is introduced into distillation chamber along with water and subjected to heat until oil is condensed in condensing chamber.

- **Steam Distillation**
  This method is applied for those substances which are usually injured by direct heat e.g. clove, cinnamon, peppermint and spearmint. In this method, no water is used. Fresh drug containing sufficient moisture is placed on a grid i.e. a wire basket or similar material. Steam is forced through fresh plant material which takes away volatile oil into condensing chamber.
Destructive Distillation
Distillation without air is called destructive distillation. Usually members of Pinaceae family are used in this method. This is an efficient process.
Procedure
Broken pieces of wood (stem) are placed in chamber and heated with water without air. Decomposition of wood takes place and numbers of volatile oil compounds are obtained.

2. Expression (Ecuelle Method)
Some volatile oils are decomposed when subjected to heat so they may be obtained by expression e.g. lemon oil and citrus oil.
Procedure
Lemon peel is placed over the receiver having holes on it. Then a roller having small projections is rolled over it. The peel is injured and oil comes out and is collected below in receiver as oil globular drops.

3. Enzymatic Hydrolysis
Glycosidic volatile oil like mustard oil and bitter almond oil are obtained by this method. Specific enzymes subject the glycosides into hydrolysis and give rise to volatile oil. e.g. in case of black mustard seeds, glycoside Sinigrin is hydrolyzed by enzyme “Myrosin” and gives rise to volatile oil having composition allyl isothiocyanate.

4. Enfleurage
When a portion of drug which contains volatile oil in very small amounts e.g. Rose petals; it becomes very difficult to extract volatile oil commercially so they are obtained by enfleurage.
Procedure
A layer of fat is spread over glass plate and flower petals like rose petals are placed over fat layer which absorb oil and volatile oil is removed by solvent extraction.

5. Solvent Extraction
This is very costly method and is used in perfume industries.
Procedure
The plant parts containing volatile oil are extracted directly by one of the organic solvent and they are then separated.
CHEMISTRY OF VOLATILE OILS
Volatile oils are mixture of hydrocarbons and oxygenated compounds derived from these hydrocarbons.

**Hydrocarbons + Oxygenated Hydrocarbons = Volatile oils**

Hydrocarbon part is a liquid portion of volatile oils which consists of terpenes and formed by Acetate Mevalonic acid pathway and are also called **Eleoptenes**. Oxygenated Hydrocarbon part is a solid portion of volatile oils which consists of oxygenated terpenes and formed by Shikimic acid pathway and are also called **Stearoptenes**.

So, volatile oils are mixture of eleoptenes and stearoptenes.

The odor, taste and therapeutic activity of volatile oil is mainly due to stearoptenes which are water soluble.

ELEOPTENES
Eleoptenes are mixtures of terpenes. Terpenes are hydrocarbons having formula C\textsubscript{10}H\textsubscript{16}. The structure of a terpene is formed by two isoprene (isoprenoid) units which are formed by Acetate Mevalonic acid pathway. Isoprenes are 5 carbon units containing 2 unsaturated bonds having formula C\textsubscript{5}H\textsubscript{8}. In volatile oils, isoprene units are joined in head to tail fashion.

Chemical Classification of Terpenes
- **Monoterpenes** \((C\textsubscript{5}H\textsubscript{8})\textsubscript{2} = C\textsubscript{10}H\textsubscript{16}\)
  These consist of 2 isoprene units or they contain 1 terpene (1 terpene = 2 isoprenes).
- **Sesquiterpenes** \((C\textsubscript{5}H\textsubscript{8})\textsubscript{3} = C\textsubscript{15}H\textsubscript{24}\)
  These consist of 3 isoprene units
- **Diterpenes** \((C\textsubscript{5}H\textsubscript{8})\textsubscript{4} = C\textsubscript{20}H\textsubscript{32}\)
  These consist of 2 terpenes or 4 isoprenoid units
- **Triterpenes** \((C\textsubscript{5}H\textsubscript{8})\textsubscript{6} = C\textsubscript{30}H\textsubscript{48}\)
  These consist of 3 terpene or 6 isoprenoid units
• Tetraterpenes \((C_5H_8)_8 = C_{40}H_{64}\)
  These consist of 4 terpenes or 8 isoprenoid units

• Polytetrapenes \((C_5H_8)_n\)
  They contain many terpenes/or many isoprene units

A. MONOTERPENES \((C_{10}H_{16})\)

1. Acyclic (aliphatic/having no ring)
   e.g. Coriandrol & Geraniol

2. Monocyclic
   e.g. Menthol & Limonene

3. Dicyclic
   e.g. Thujone & Camphor

4. Tricyclic
   e.g. Tera santalol
B. SESQUITERPENES (C_{15}H_{24})

1. Acyclic
e.g. Farnesol

2. Monocyclic
e.g. Zingiberene

3. Dicyclic
e.g. β-cadinene

C. DITERPENES (C_{20}H_{32})

1. Acyclic
e.g. Phytol

2. Monocyclic
e.g. Vitamin A

3. Dicyclic
e.g. Agathic acid
4. **Tricyclic**
   e.g. Abeitic acid

**D. TRITERPENES (C_{30}H_{48})**

1. **Acyclic**
   e.g. Squalene

2. **Tetracyclic**
   e.g. Stigmasterol

3. **Pentacyclic**
   e.g. Glycyrrhetic acid

**E. TETRA-TERPENES (C_{40}H_{64})**

These are carotenoid pigments. Important pigments are orange, red and yellow.

1. **Acyclic**
   e.g. Lycopene (Present in Tomato)

2. **Monocyclic**
   e.g. α-carotene
   (Present in Carrot)
3. Dicyclic
   e.g. β-carotene
   (Present in Carrot)

F. Polyterpenes
   These are components of many isoprene units e.g. Ruffer rubber (natural) is a
   polyterpenoid of *Hevea brasiliensis*. This ruffer is a polymer containing 3000-6000
   isoprene units.

STEAROPTENES
   They are also called “phenyl propanoids”. These are oxygenated hydrocarbons which contain
   6-carbon phenyl ring (benzene ring) with attached 3-carbon propane.

Classification of Stearoptenes
   They are classified as under:
   1. Alcoholic Stearoptenes
      e.g. Menthol, terpineol, coriandrol (Linalool), borneol, gingerol

   2. Aldehydic Stearoptenes
      e.g. vanillin, cinnamaldehyde, geranial (Citral), citronellal
3. Ketonic Stearoptenes
   e.g. camphor, thujone, carvone, fenchone.

   Camphor

   Carvone

   Thujone

   Fenchone

4. Ester Stearoptenes
   e.g. Wintergreen (methyl salicylate), bornyl acetate.

   Methyl Salicylate

   Bornyl acetate

5. Oxide Stearoptenes
   e.g. Eucalyptol (Cineol)

   Cineol

6. Phenolic Stearoptenes
   e.g. Thymol, eugenol.

   Thymol

   Eugenol

7. Phenolic ether Stearoptenes
   e.g. Anethol, safrole.

   Anethol

   Safrol