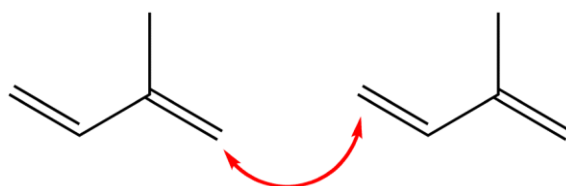


Volatile oils

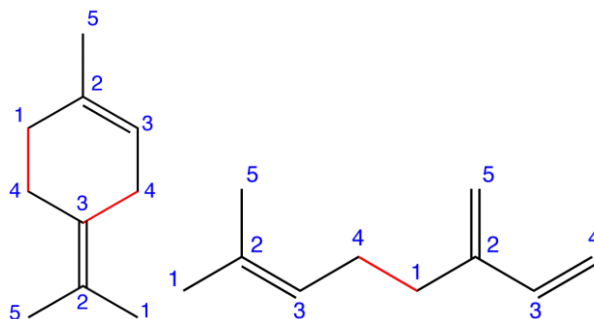
Together with the phenylpropenes, the monoterpenes are major constituents of the volatile oils that are common in plants and which contribute to their aroma.

Biosynthesis of volatile oils

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

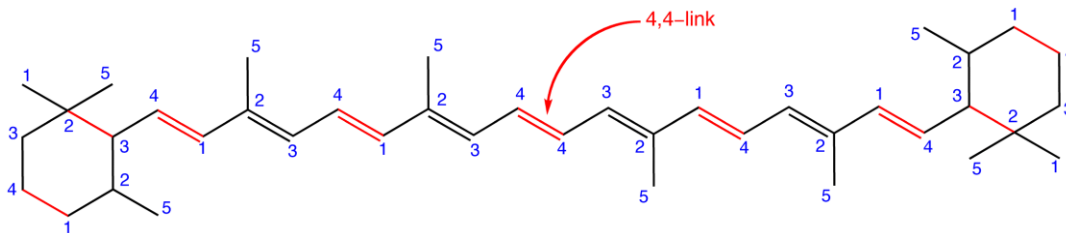


This link is called a head-to-tail or 1-4 link.

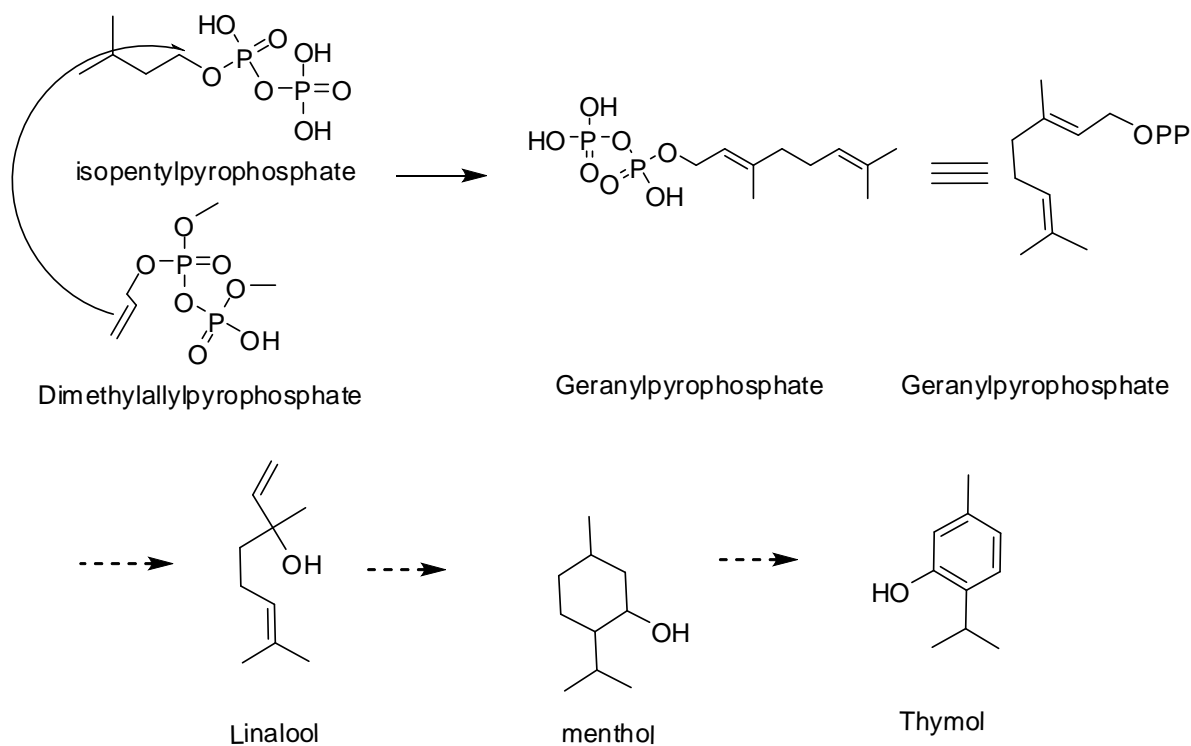


The monoterpenes (10 carbon atom) are produced by the reaction between DMAPP and IPP in the presence of the enzyme prenyltransferase

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 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 (Fig 1).



Biosynthesis of volatile oil

Figure 1

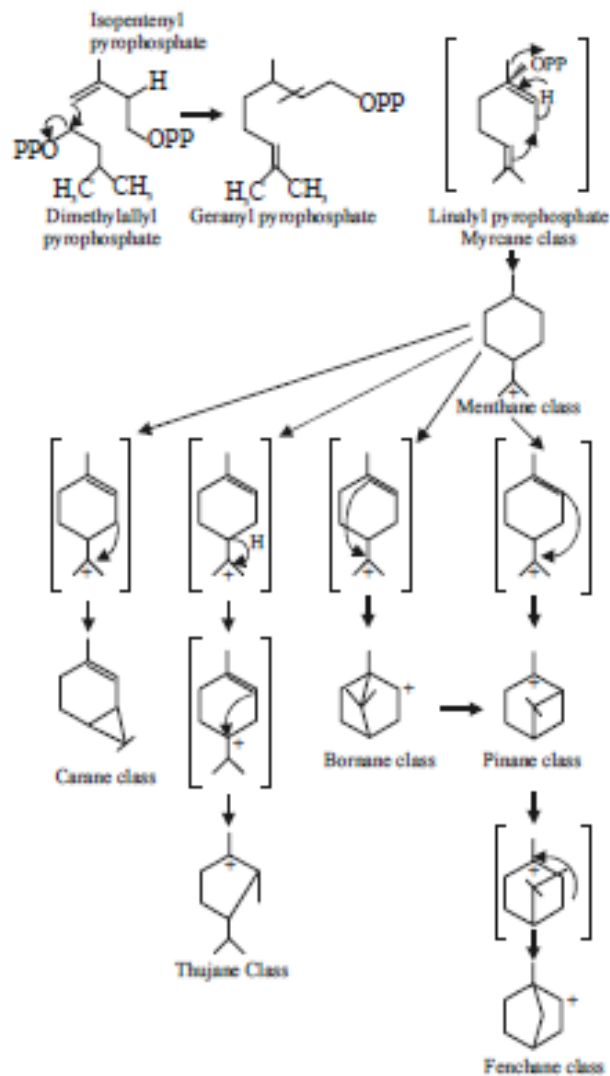


Fig. 5.4 Probable Mechanism for Biosynthesis of Various Monoterpenoids.
 (Adapted from 'Pharmacognosy and Pharmacobiotechnology' by Robbers J.E. *et al.*, 1996)

Geranyl pyrophosphate can also undergo many reactions to generate the variety of monoterpenes observed, such as simple modification to give the acyclic monoterpene β -citronellol, which is a component of rose oil. Geranyl pyrophosphate can be cyclized to give cyclic monoterpenes, which may be fully saturated, partially unsaturated or fully aromatic products of which menthol, piperitone and carvacrol are examples, respectively

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.

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 solvent.

Chemically they are two class depend on biosynthetic sub units

-terpenoids biosynthesized from acetate mevalonate path way

- aromatic formed via shikimate pathway

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

Chemistry of volatile oils

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

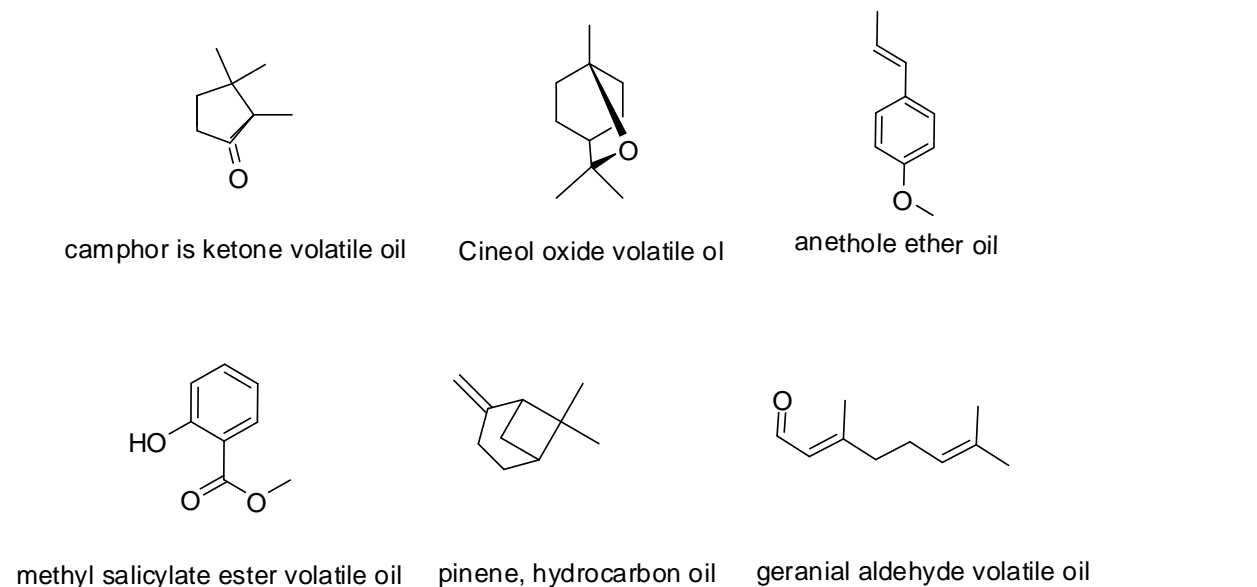


Figure 2: Types of structure found in volatile oil

Trivial Name

Geraniol

Limonene

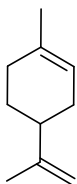
Myrcene

IUPAC Name

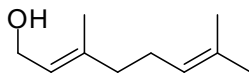
3, 7- Dimethyl-2, 6-octadien-1-ol;

1-Methyl-4-(1-methylethynyl)-cyclohexene;

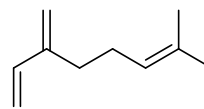
7-Methyl-3-methylene-1, 6-octadiene



Limonene



Geraniol



myrcene

Method of preparation from plants

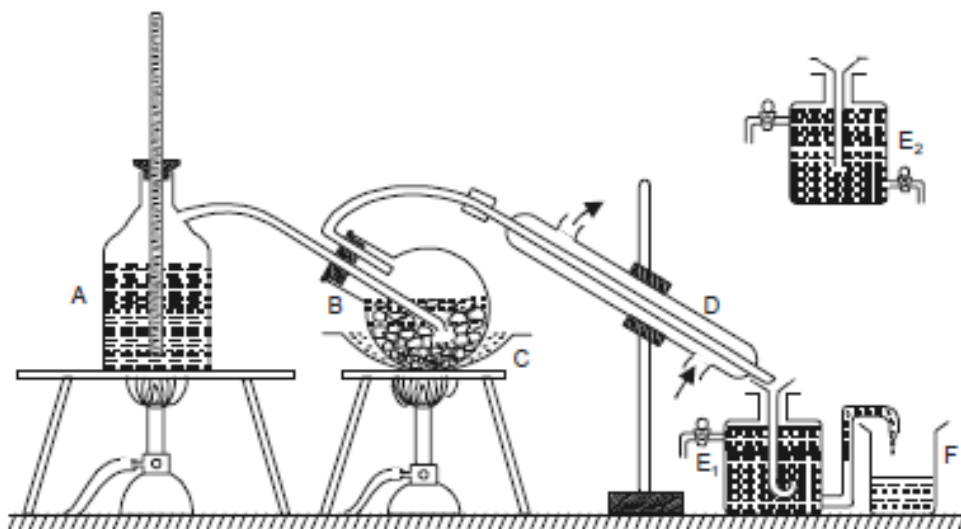


Fig. 5.1 Assembly for Preparation of Volatile Oils by Steam Distillation

Stereochemistry of volatile oils

Natural oil is stereochemically pure compound while synthetic oil is not. The odour of the oil is also determined by its stereochemistry (-) carvone smell like caraway oil while (+) carvone smell like spearmint, this because the receptor in nose is chiral.

Determination of volatile oils

The volatile oil content is determined by distillation and measurement of the volume of distilled oil.

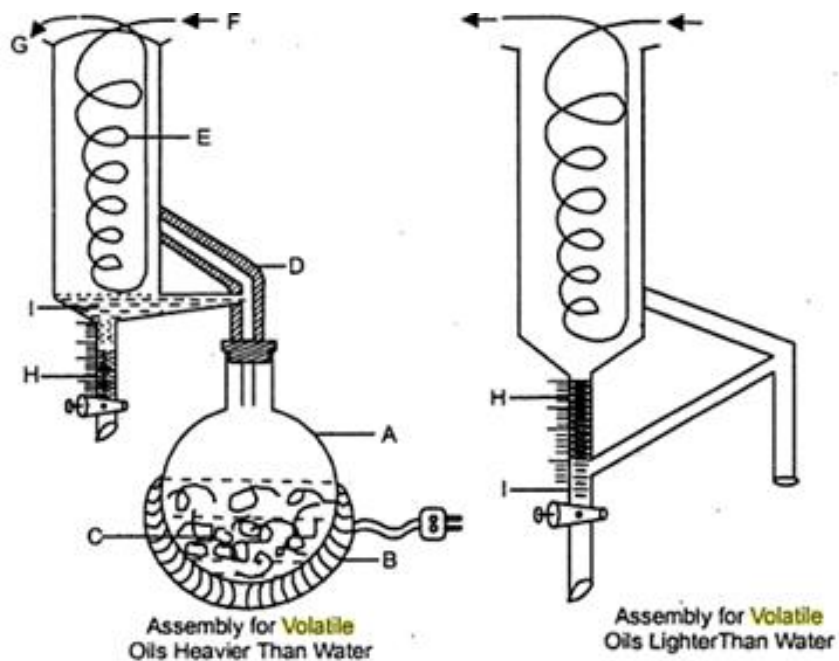


Fig 5.3 Apparatus for Quantitative Estimation of Volatile Oils

H = Volatile oil collected in a graduated stem

I = Excess water reintroduced in round bottomed flask

Trap in right hand side is used for oil lighter than water for example orange oil and rosemary oil, while the left hand side is used for oil heavier than water like clove oil.