TERPENOIDS

⇒ Originally, the term terpene was applied to a mixture of isomeric hydrocarbons of the molecular formula $C_{10}H_{16}$ occuring in terpentine and many other essential oils. The oxygenated derivatives, like alcohols, aldehydes, ketones etc, at that time were called camphors. But as the discovery of the related compounds increased with time, the definition changed and empirical formula is given C_5H_8 which will cover all the compounds under the name of terpenoids; ie. The terpenes and camphors of the earlier time are thus now called as the terpenoids.

⇒ The term terpene represents only hydrocarbons $(C_5H_8)_n$ while the term terpenoids represent the hydrocarbon as well as the oxygenated derivatives, ie all the compounds having $(C_5)_n$, so all the terpenes are terpenoids but not vice-versa.

Occurance :- In our daily practice we see that the fruits, flowers, leaves, stems, barks and roots of nearly all the plants have some pleasant smell. It has been observed that this pleasent smell of the fruits is actually due to the presence of certain steam volatile oils known as essential oils. The essential oils are complex mixtures of hydrocarbons and their oxygenated derivatives, though some, such as oil of bitter almond and oil of wintergreen consists mainly of one constituent, viz. C_6H_5CHO and methyl salicylate, respectively.

Among the chief constituents of the essential oils are the terpenoids having carbon atoms upto C_{15} (ie. mono and sesqui-terpenoids) and their oxygenated derivatives such as alcohols, aldehydes and ketones, as well as some closely related open chain alcohols, aldehydes and ketones.

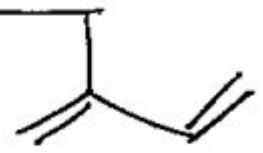
Due to their pleasent smelling nature the mono and sesqui terpenoid are of considerable commercial importance particularly in perfumery industry. Moreover various terpenoids show biological activity, viz. insecticidal, anthelmintic, or antiseptic action and thus also useful in pharmacy.

As far as the occurrence of higher terpenoids is concerned the di- and tri-terpenoids are thus found in plants gums and resins.

Classification :- As we shall see, a common feature of terpenes is that the carbon skeletons of their molecules are built of isoprene (C_5)

units. They are, therfore, classified into different categories - depending on the number of isoprene units present in them. The various categories are:

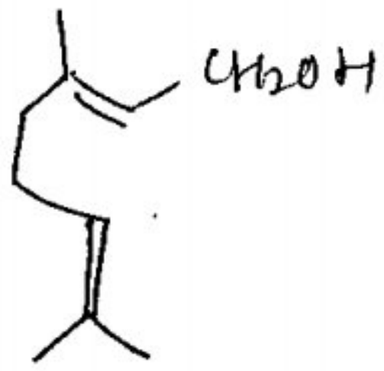
(i) Hemiterpenes : are the compounds having one isoprene unit, the simplest compound is isoprene itself (C_5H_8).



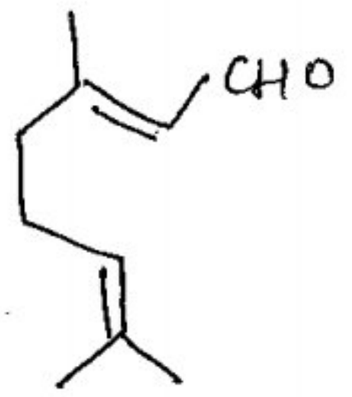
(ii) Monoterpenes :- are the compounds having two isoprene units (10 carbons) depending upon the nature of carbon skeleton, they are further sub-divided into @ acyclic, ⓑ mono cyclic, and ©bicyclic monoterpenes.

@ Acyclic monoterpenes

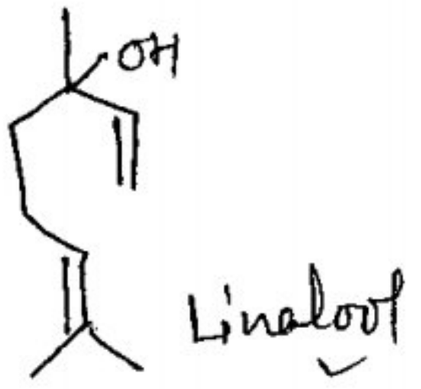
β-Myrcene



Geraniol

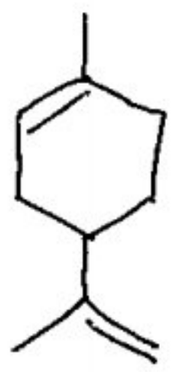


citral

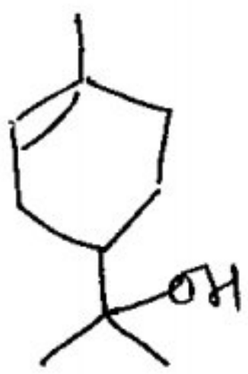


Linalool

ⓑ monocyclic monoterpenes:

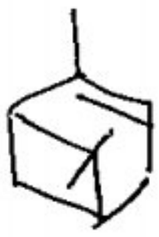


Limonene



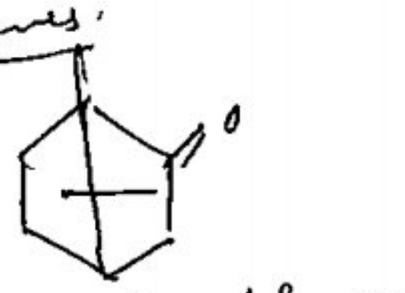
α-terpeniol

©Bicyclic monoterpenes:



α-Pinene

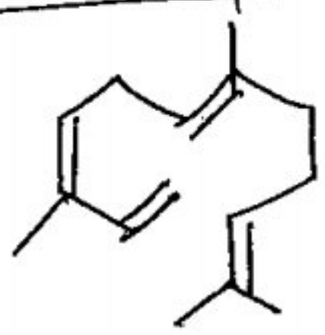
β-pinene



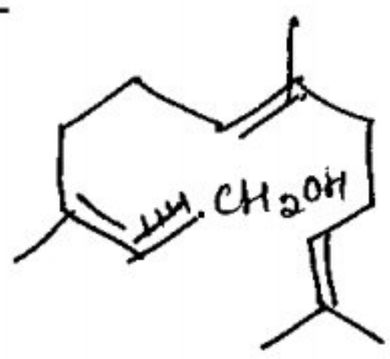
Camphor

(iii) Sesquiterpenes :- are the compounds having three isoprene units (C15) They form higher boiling fractions of essential oils and like mono-terpenes, they are also divided into various sub groups.

@ Acyclic sesquiterpenes!

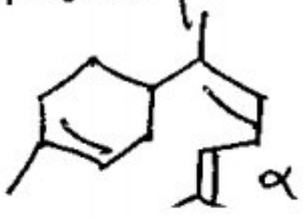


α - Farnesene



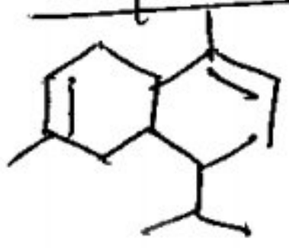
Farnesol

ⓑ monocyclic sesquiterpenes.



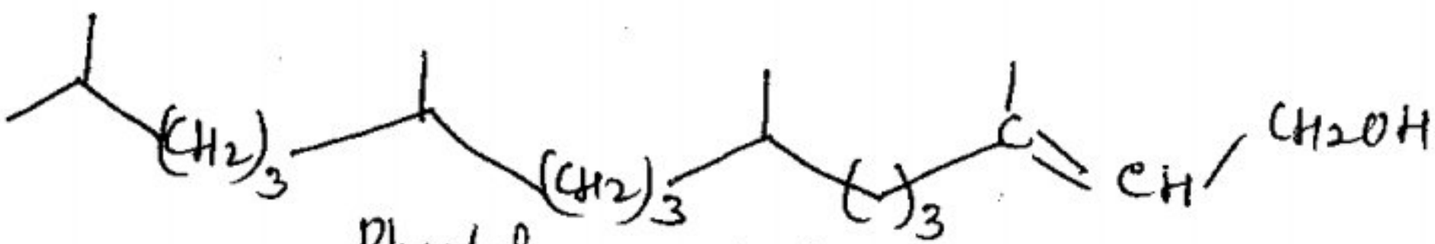
α - Bisabolene

© Bicyclic sesquiterpenes.

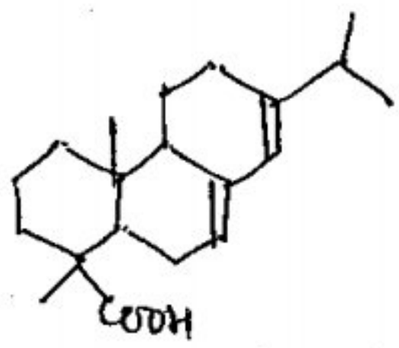


α-cadinene

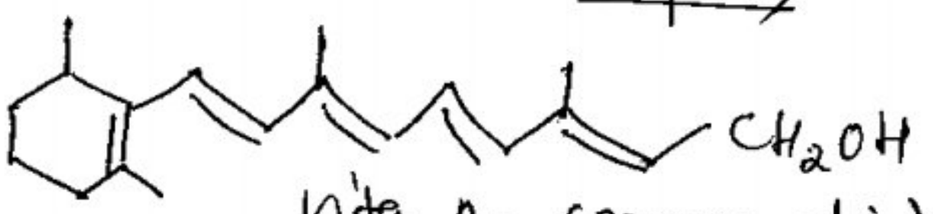
(iv) Diterpenes:- are the compounds having four isoprene units (20 carbons)



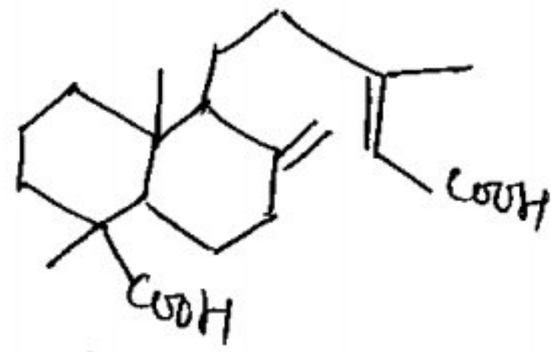
Phytol (Acyclic)



Abietic Acid (Tricyclic, a resin acid)

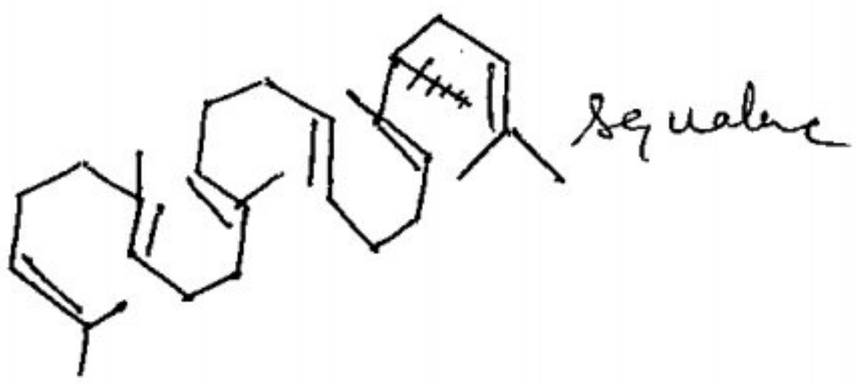


Vita A. (Monocyclic)



Agathic acid (a resin Acid) (Bicyclic)

(v) Triterpenoids: are the compounds having six isoprene units (C30). ~~Carotenoids the colouring principles of carrots belong to this class.~~ Squalene, an important constituent of shark liver oil.



Squalene

(vi) Tetraterpenes: May be regarded as composed of eight isoprene unit (C40) Carotenoids, the colouring principles of carrots, bilong to this class.

(vii) Polyterpenes:- have more than 40 carbon atoms. Rubber, $(C_5H_8)_n$ is an example of this class.

Isolation:- Essential oils are extracted from plants by several methods,

(i) Steam distillation: The powdred plant material is steam distilled when the constituents of the essential oil go into the distillate from which they are extracted by low-boiling solvents such as ether or light petroleum. This method has a disadvantage that some of the constituents of essential oils, such as esters, are hydrolysed to non or less-fragrant products during the course of steam distillation.

(ii) Solvent Extraction:- The essential oil which are sensitive to heat are extracted from the plant material with low boiling solvents such as light petroleum or ether at room temperature. Distillation of the solvent from the filtered extract under reduced pressure leaves the essential oil.

(iii) Adsorption method: the petals of the flowers are left in contact with a fat preparation (a mixture of lard and tallow) for several days at about 50°C until the fat is saturated with the essential oil. The saturated fat is then

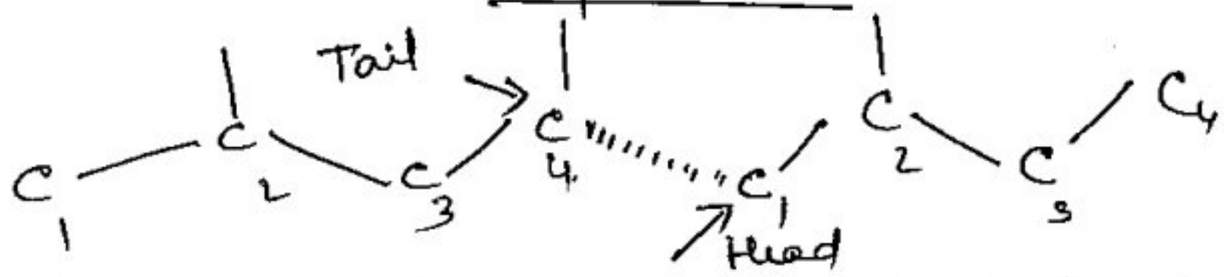
extracted with ethanol and the solvent (ethanol) removed under reduced pressure at 0°C. Recently activated charcol has been used instead of fat. After isolation of essential oils; which are mixtures of a number of compounds the constituents are separated by a variety of methods depending upon their physical and chemical properties.

(a) Physical Methods: The most commonly used physical methods are fractional distillation and chromatography. Of these two methods, chromatography is now more in use. The essential oil is adsorbed on a column of a suitable adsorbent such as alumina or silica gel and subsequently eluted using solvents of increasing polarity. Each eluate representing a class of terpenes is then further chromatographed to separate its constituents.

(b) Chemical Methods:- The actual method to be adopted depends upon the chemical nature of the constituents. For instance, an unsaturated terpene hydrocarbon such as myrcene may be separated through its crystalline adducts with hydrogen halides or nitrosyl chlorides. An alcohol, for instance, geraniol may be separated through its ester with phthalic anhydride or through phenylurethane obtained by treatment with phenylisocynate. The aldehydic or ketonic terpenes may be separated by reaction with carbonyl reagents such as sod. bisulphite, semicarbazide 2,4-dinitrophenyl hydrazine, etc. The terpene is then regenerated by hydrolysis of the products.

Isoprene Rule:- OR Structural features:

The observation that almost all terpene hydrocarbons on pyrolysis give isoprene (2-methyl-1,3 butadiene; C_5H_8) as one of the products led to the generalization that the carbon skeletons of terpenes are divisible into isoprene units which are generally joined in a head to tail fashion, i.e. the C_4 position of one unit is linked to the C_1 position of another. This is known as special isoprene rule and that is why terpenoids are also called or known as isoprenoids:



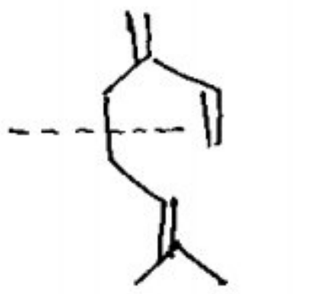
(Head to tail union of two isoprene unit)

⇒ The isoprene rule has received support from the observation that isoprene can be dimerized in the laboratory to give a widely occuring terpene, ie dipentene [(±)-limonene].

$$2\ C_5H_8 \longrightarrow C_{10}H_{16}$$

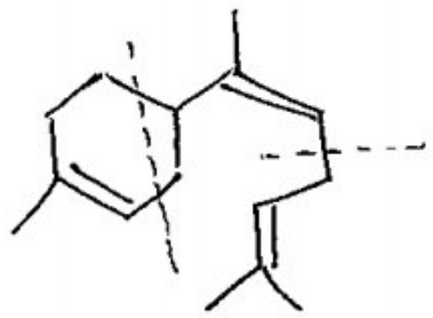
Dipentene.

Structures of some terpenes given below showing (by broken lines) the head to tail union of two or more isoprene units, C_5H_8 with or without concomitant cyclisation.

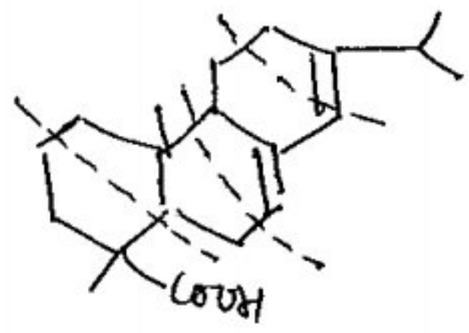


Myrcene
$2 \times C_5H_8$

Limonene
$2 \times C_5H_8$

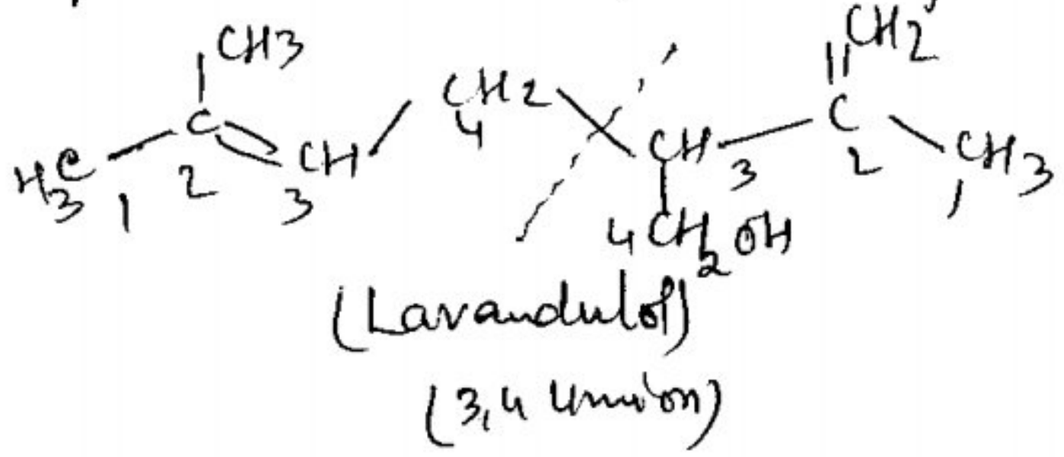


Bisabolene
$3 \times C_5H_8$

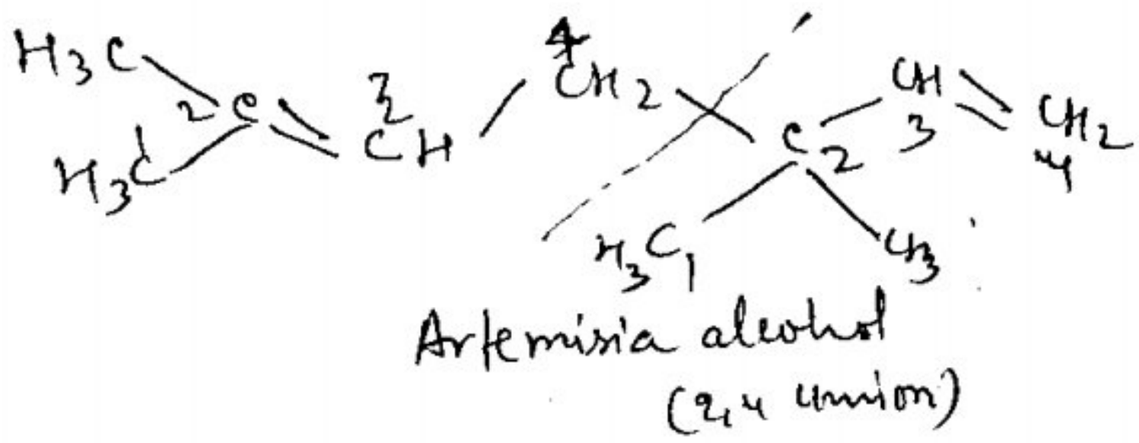


Abetic Acid
$(4 \times C_5H_8)$

⇒ On the other hand, there are some examples of terpenoids where carbon skeletons are divisible into isoprene units but they are not linked ~~head to~~ head to tail. Lavandulol and artemisia alcohol provide good examples. The relationship of such compounds with isoprene forms the basis of the General Isoprene rule which embraces all structures that are divisible into isoprene units irrespective of the positions of their linkage.

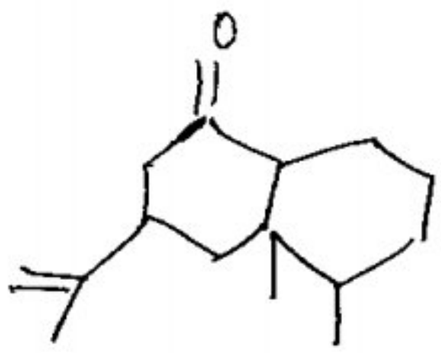


(Lavandulol)
(3,4 Union)

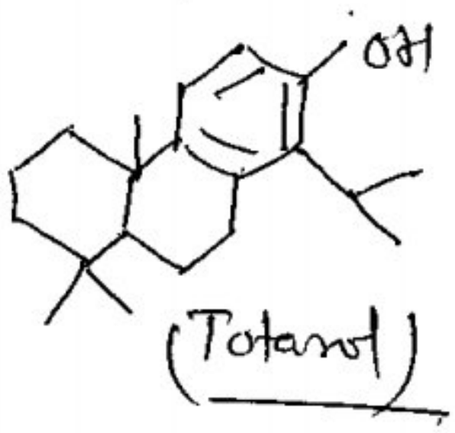


Artemisia alcohol
(2,4 Union)

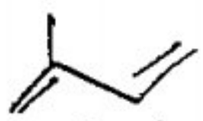
But isoprene rule is valid in most of the cases, but there are a few exceptions which violate the rule, for instance, eremophilone and totarol structures cannot be divided into isoprene units.



Eremophilone



(Totarol)



isoprene
(2-methyl-1,3-butadiene)