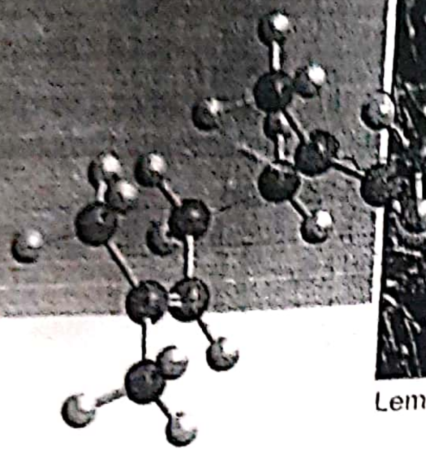
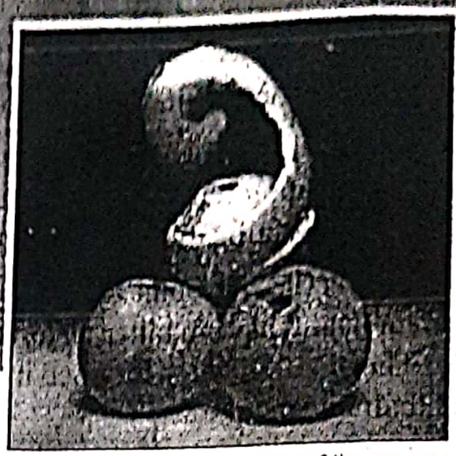
Terpenes



Lemongrass is a source of geraniol.



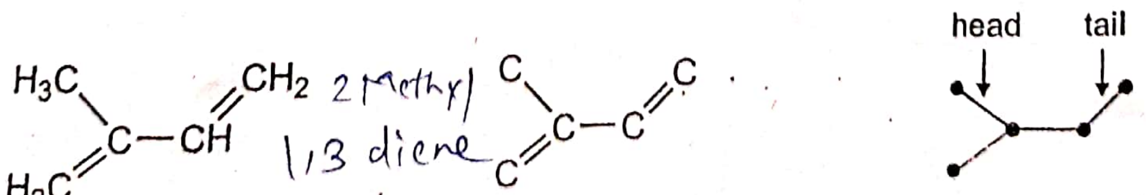
Orange peel is a source of limonene.

Terpenes are a class of compounds that give plants their odour, flavour, and in some cases colour. They occur widely in the leaves and fruits of higher plants as conifers, citrus, and eucalyptus. *When the plant source is distilled with steam, the oily materials so obtained are called* **Essential Oils** (essential parts of plants).

The essential oils are generally composed of mixture of either the hydrocarbons (*polyenes*) having general formula $(C_5H_8)_n$, or their oxygen derivatives (alcohols, aldehydes, ketones). This class of compounds are designated as **Terpenes** or **Terpenoids**.

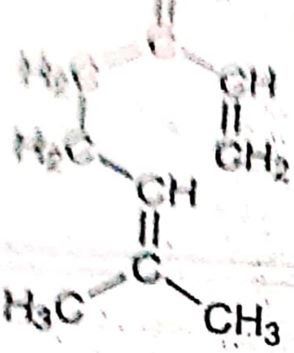
ISOPRENE RULE

From a study of the molecular structure of a large number of the then known terpenes, Otto Wallach (Noble Prize 1910) gave the so-called **Isoprene Rule**. It states that : **The molecules of all terpenes are constructed of two or more isoprene (iso-C_5) units, usually joined in a head-to-tail fashion.** Isoprene is 2-methyl-1,3-butadiene and may be represented as :

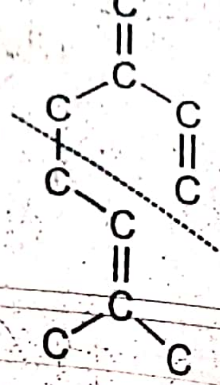


Isoprene   Condensed formula   Isoprene skeleton

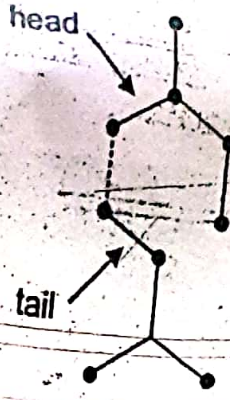
In applying Isoprene rule, we look only for the skeletal unit iso-C_5, neglecting the number and sition of double bonds. Thus the terpene known as *myrcene* could be dissected by the dashed line o two isoprene units that are joined 'head-to-tail'.



Myrcene



Condensed formula

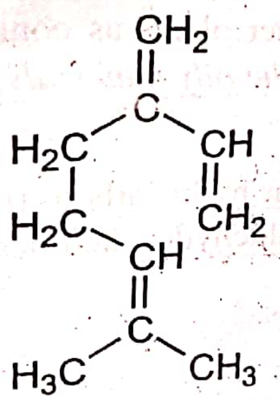


Carbon skeleton
(dotted bond shows
head-to-tail arrangement)

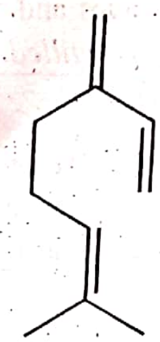
Isoprene rule although generally valid, is not universal. However, it has proved of great help i deriving the structure of terpenes.

LINE FORMULAS OF TERPENES

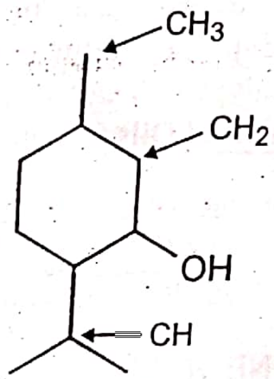
The structures are frequently written with line formulas. The carbon-carbon bonds are represente by lines. The carbon atoms with appropriate number of hydrogens are understood to be present a corners or junctions, and the ends of lines. Thus the line formulas of *myrcene* and *menthol* may be written as



Myrcene



Line formula



Menthol

CLASSIFICATION OF TERPENES

Terpenes are classified according to the number of isoprene units (C_5) in the molecule. The simplest terpenes have two isoprene units (ten carbons) and are called **Monoterpenes**. In fact, the designation **Terpenes** is by custom specifically reserved for the C_{10} compounds. Other classes are listed below :

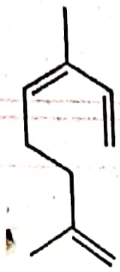
Monoterpenes	Two isoprene units	C_{10}
Sesquiterpenes	Three isoprene units	C_{15}
Diterpenes	Four isoprene units	C_{20}
Triterpenes	Six isoprene units	C_{30}
Tetraterpenes	Eight isoprene units	C_{40}

The above classes of terpenes are further subdivided according to the number of rings in the molecule :

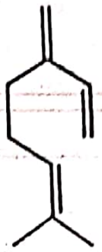
Acyclic	No rings (Straight chain)
Monocyclic	One ring
Bicyclic	Two rings
Tricyclic	Three rings, and so on.

Then terpenes are classified on the basis whether they are pure hydrocarbons or oxygen derivatives (aldehydes, ketones, alcohols or ethers). The classification of terpenes can be illustrated by the following examples:

Acyclic monoterpenes :

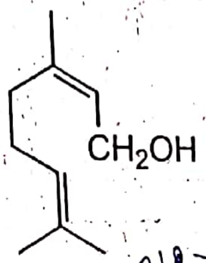


Ocimene
(basil oil)

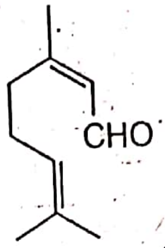


Myrcene
(bayberry oil)

Acyclic oxygenated monoterpenes :

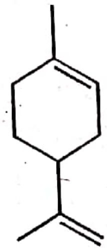


Geraniol
(rose oil)

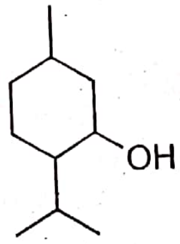


Citral
(lemon oil)

Monocyclic monoterpenes :

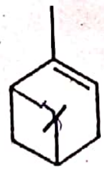


Limonene
(lemon and orange oil)

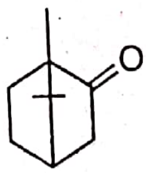


Menthol
(mint oil)

Bicyclic monoterpenes :



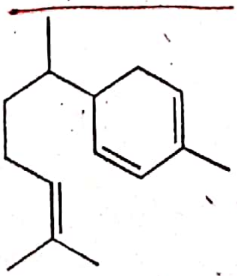
α-Pinene
(turpentine oil)



Camphor
(camphor oil)

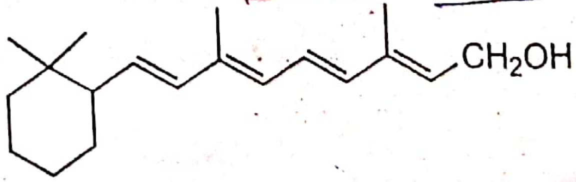
The discussion of *sesqui-*, *di-*, *tri-*, and *tetraterpenes* is beyond the scope of this book.

Sesquiterpenes C15



Zingiberene
(ginger oil)

Diterpene C20



Vitamin A

California laurel, *Umbellularia californica*, is a source of myrcene.

A camphor tree, *Cinnamomum camphora*.

ISOLATION OF TERPENES

Essential oils are first extracted from the plant source (leaves, flowers, stem or root) mainly by three methods :

(1) **Steam Distillation.** The mascerated plant material is steam distilled. The oil, if any, is collected separately. The aqueous steam distillate is saturated with salt and extracted with a purified solvent as light petroleum or benzene. The combined oil and the solvent extract are dried. The solvent is then removed by evaporation under reduced pressure to give the essential oil.

(2) **Direct Solvent Extraction.** If a particular terpene is decomposed under the conditions of steam distillation, the plant material is directly extracted with *light petroleum* or *ether* at room temperature. The extract is filtered and the solvent removed by evaporation under *vacuo* to recover the essential oil.

(3) **By Fat Adsorption (*Enfleurage Process*).** The flower petals are spread over a molten layer of fat (tallow and lard) for several days. The fat enriched with adsorbed essential oil from petals, is stirred with pure ethanol. The ethanol extract is then evaporated at 0°C in vacuum to give the essential oil.

The essential oils obtained as above are usually mixture of many terpenes. These are separated by fractional distillation or vapour-phase chromatography. Chemical methods are also used where possible.

GENERAL PROPERTIES OF TERPENES

(Physical). (1) Most terpenes are colourless, fragrant liquids having high refractive indices. A few of them e.g., camphor, are solids.

(2) They are lighter than water and readily volatile in steam.

(3) They are soluble in organic solvents (light petroleum, ether, benzene) but usually not in water.

(4) They are optically active and a number of them possess antiseptic properties.

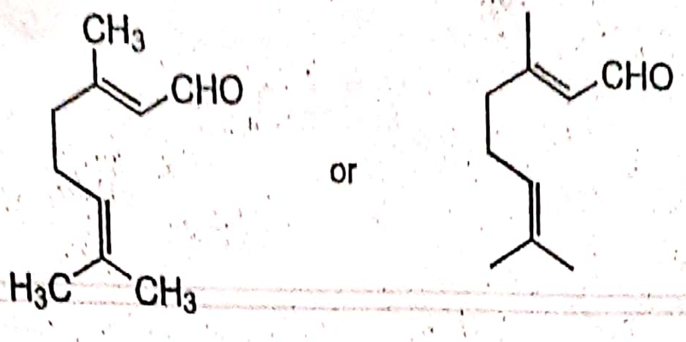
(Chemical). (1) They give the usual addition reactions of the carbon-carbon double bonds (*e.g.*, with HBr, Br_2, H_2, HOCl, O_3) and the aliphatic rings.

(2) They also show reactions characteristic of the functional groups such as –CHO, >CO, and –OH, when present in the molecule.

IMPORTANT TERPENES

CITRAL, $C_{10}H_{16}O$

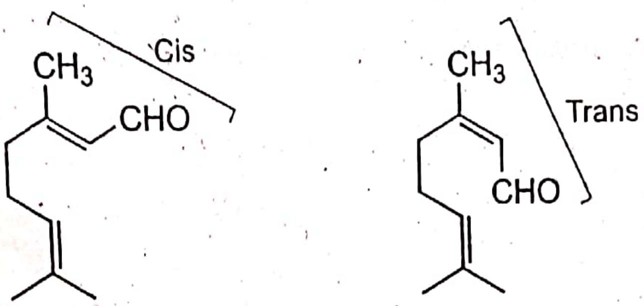
It is the most important acyclic (open chain) monoterpenoid and has the structural formula.



Citral occurs to the extent of 80 per cent in lemongrass oil. It is also present in the oil of citrus fruits (citron, orange, lemon).

Preparation. It is obtained from lemongrass oil by treatment with sodium bisulphite solution. Crystalline citral bisulphite derivative separates. This upon hydrolysis with sodium carbonate gives pure citral.

Properties. Citral is a colourless liquid, bp 224-228°C. It has a strong lemon-like odour. It exhibits geometrical isomerism about the double bonded carbons carrying CH_3 and CHO groups. The *cis*-isomer is known as Citral-*a* and the *trans*-isomer Citral-*b*. Ordinary citral obtained from lemongrass oil is, in fact, mixture of Citral-*a* (90%) and Citral-*b* (10%)



Citral-a Citral-*b*

Uses. Citral is used extensively in the perfume and flavour industry to stimulate lemon-like odour, and for the manufacture of vitamin A. Recently citral has become important as a drug for reducing blood pressure.

Structure. (1) Elemental analysis and molecular weight determinations show that the molecular formula of citral is $C_{10}H_{16}O$.

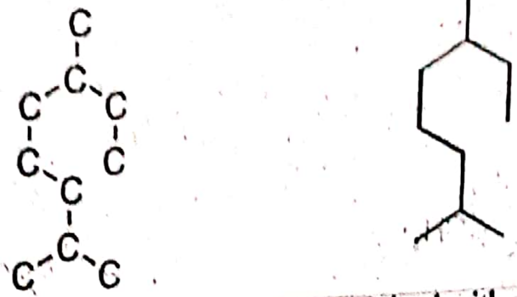
(2) **Presence of two C=C.** It adds two molecules of bromine to form a tetrabromide, indicating the presence of two carbon-carbon double bonds.

$$\underset{\text{Citral}}{C_{10}H_{16}O} + 2Br_2 \longrightarrow \underset{\text{Tetrabromide}}{C_{10}H_{16}OBr_4}$$

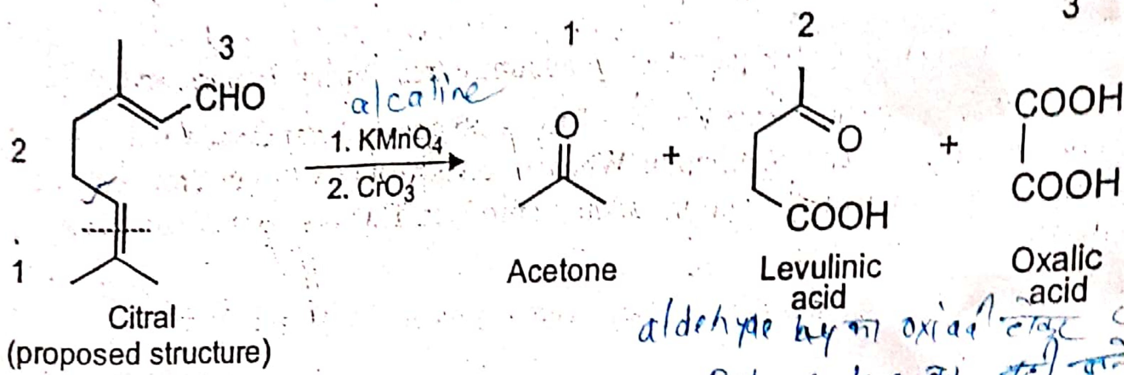
(3) **Presence of CHO.** It forms an oxime and on oxidation gives geranic acid without loss of any carbon atom.

$$\underset{\text{Citral}}{(C_9H_{15})-\overset{\overset{\displaystyle O}{\|}}{C}-H} + [O] \xrightarrow{Ag_2O} \underset{\text{Geranic acid}}{(C_9H_{15})-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

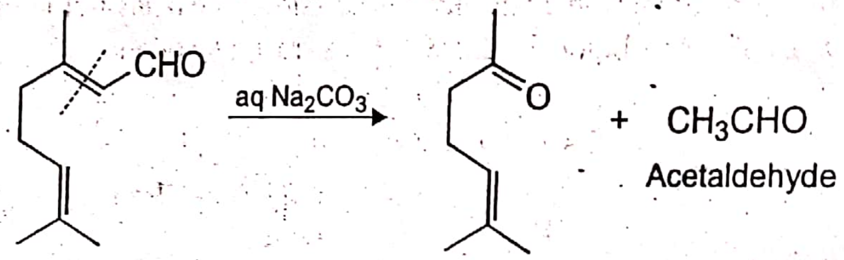
(4) **Carbon skeleton.** Simmler (1891) suggested that two isoprene units are joined head-to-tail in citral (*Isoprene rule*), and its carbon skeleton was



(5) **Position of C=C bonds indicated.** The oxidation of citral with alkaline permanganate, followed by chromic acid, gives acetone, levulinic acid, and oxalic acid. This is accountable only if the position of the double bonds is as shown in the formula below.

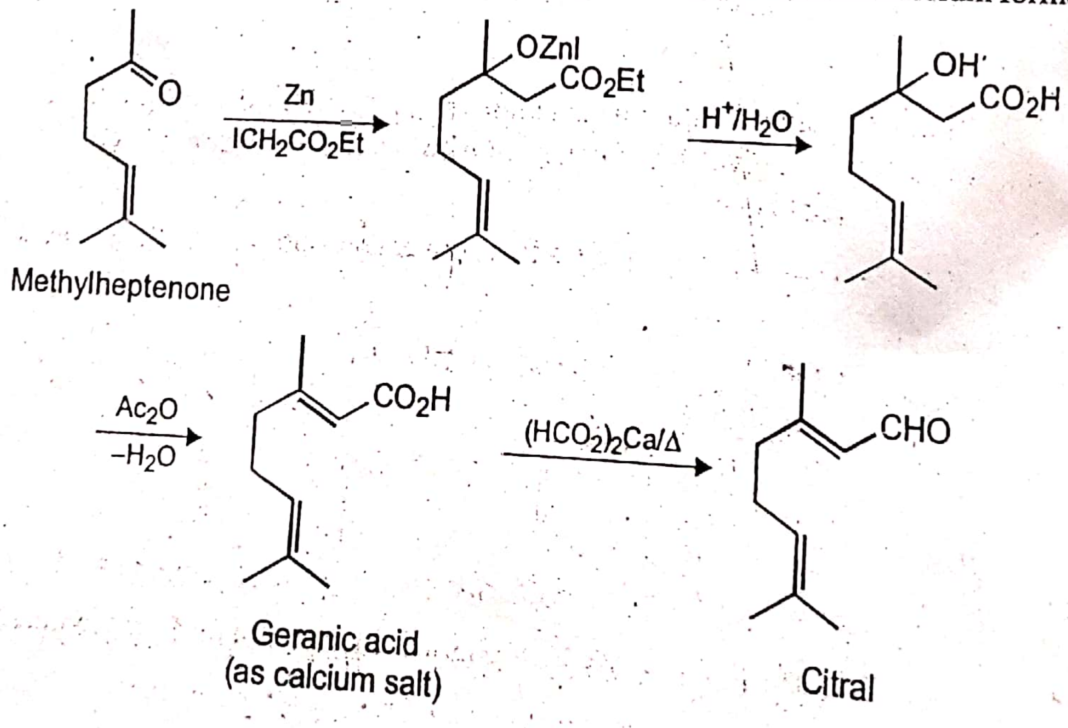


(6) **Position of double bonds confirmed.** The above structure of citral is supported by the decomposition of citral with aqueous Na_2CO_3 to give methylheptenone and acetaldehyde.



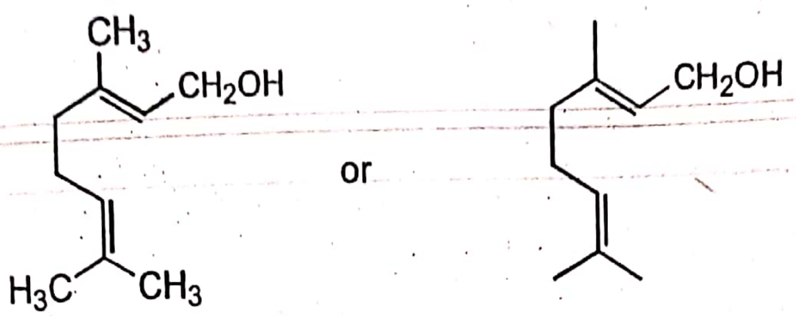
Citral Methylheptenone

(7) **Synthesis.** The structure of citral was confirmed by the following synthesis from nethylheptenone. The various steps are (*i*) Reformatsky reaction ; (*ii*) Hydrolysis with dilute acid; *iii*) Dehydration with acetic anhydride ; (*iv*) Distilling calcium geranate with calcium formate.



GERANIOL, $C_{10}H_{18}O$

It is an acyclic terpene alcohol and has the structure :



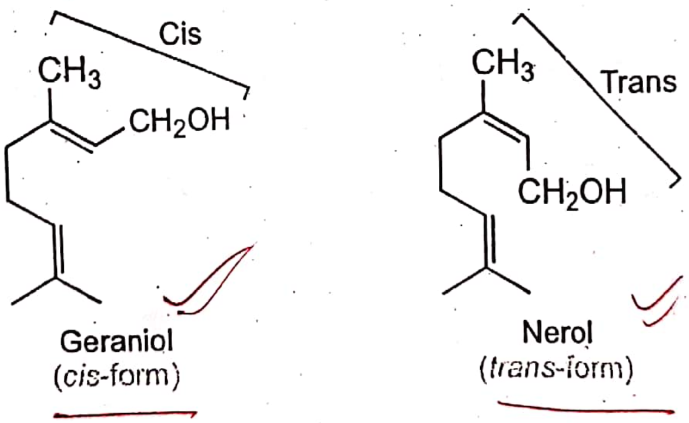
Geraniol occurs in oils of rose, palmrosa, geranium, citronella, lemongrass, and lavender.

Preparation. (1) From Palmrosa Oil. This is obtained cheap from a wild-growing grass, *Cymbopogon Martini*, by steam distillation. When the oil is treated with anhydrous calcium chloride, geraniol reacts with it to give a crystalline addition product. This is separated and decomposed with water to liberate geraniol.

(2) **From Citral-a.** Geraniol may also be prepared by reduction of Citral-*a* (geraniol) with aluminium amalgam.

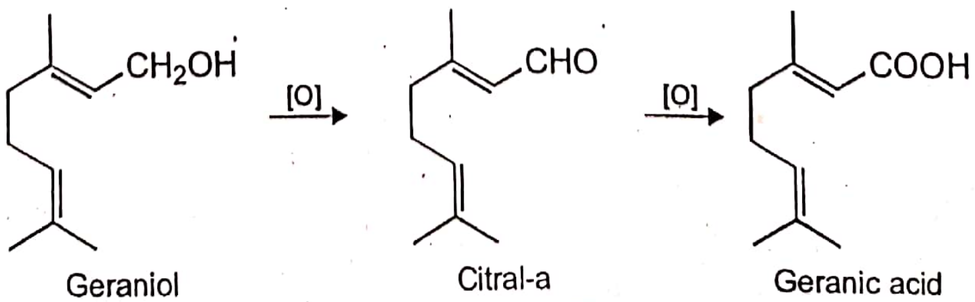
Properties. (*Physical*). Geraniol is a colourless liquid, bp 230°C, having pleasant rose-like odour. It is insoluble in water but dissolves in ethanol.

Geraniol exhibits geometrical isomerism and it is *cis*-form. The *trans*-isomer is another terpene **Nerol** (from *neroli oil*), colourless liquid, bp 225°C, having rose-like odour.

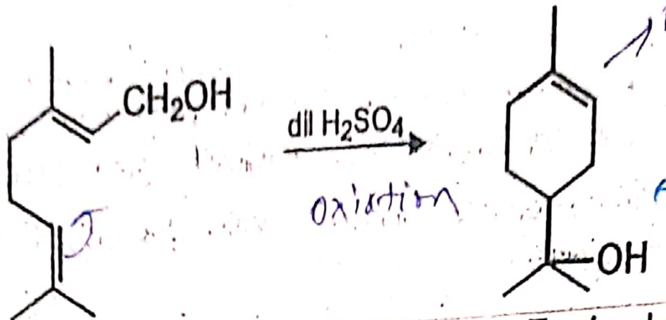


(*Chemical*). The structural formula of geraniol has two carbon-carbon double bonds and a primary alcohol group. Thus it gives the reactions of dienes as also of primary alcohols. Two of its important reactions are listed below.

(1) **Oxidation.** Upon oxidation, geraniol is first converted to citral-*a* and then to geranic acid.



(2) **Cyclization.** When treated with dilute sulphuric acid, geraniol forms α-terpineol.



Geraniol α-Terpineol

Uses. Geraniol and nerol are extensively used in perfumery to stimulate the odour of roses.

Structure. (1) Geraniol has the molecular formula $C_{10}H_{18}O$.

(2) **Presence of two C=C bonds.** It adds two molecules of bromine, and two molecules of hydrogen on catalytic hydrogenation, showing the presence of two carbon-carbon double bonds.

$$\underset{\text{Geraniol}}{C_{10}H_{18}O} + 2Br_2 \longrightarrow \underset{\text{Tetrabromide}}{C_{10}H_{18}OBr_4}$$

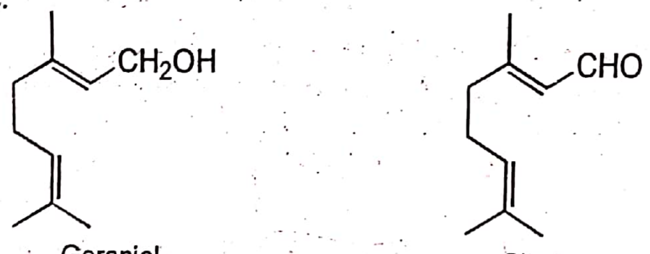
$$C_{10}H_{18}O + 2H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Saturated alcohol}}{C_{10}H_{22}O}$$

(3) **Presence of CH_2OH.** On oxidation it gives an aldehyde (citral-*a*) and then an acid (geranic acid) containing the same number of carbon atoms as geraniol.

$$\underset{\text{Geraniol}}{(C_9H_{15})CH_2OH} \xrightarrow{[O]} \underset{\text{Citral-}a}{(C_9H_{15})CHO} \xrightarrow{[O]} \underset{\text{Geranic acid}}{(C_9H_{15})COOH}$$

This proves that geraniol is a primary alcohol and the arrangement of C atoms as also the positions of the two double bonds are the same as in Citral-*a*.

(4) **Structure derived from that of citral.** Knowing the structural formula of citral-*a*, geraniol is assigned the structure.

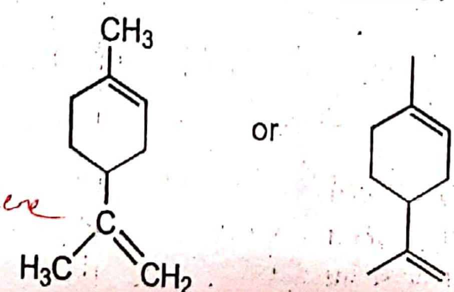


Geraniol Citral-a (*cis*-form)

Therefore, geraniol is also the *cis*-form which is confirmed by NMR studies.

LIMONENE, $C_{10}H_{16}$

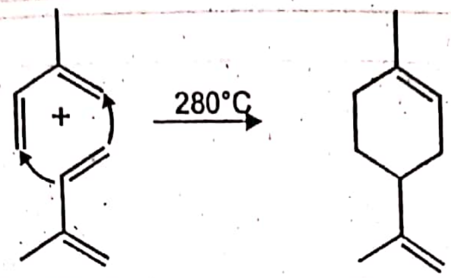
It is the most widely distributed terpene and has the structure :



(+)–Limonene occurs in orange and lemon peels, while (–)-limonene is found in pine needles. (±)-limonene known as **Dipentene** is present in turpentine.

Preparation. (1) From Essential Oils. Limonene and dipentene are separated from the relevant essential oils. The chemical method consists in formation of the tetrabromide by addition of Br_2, followed by debromination with zinc and acetic acid, when the product is dipentene.

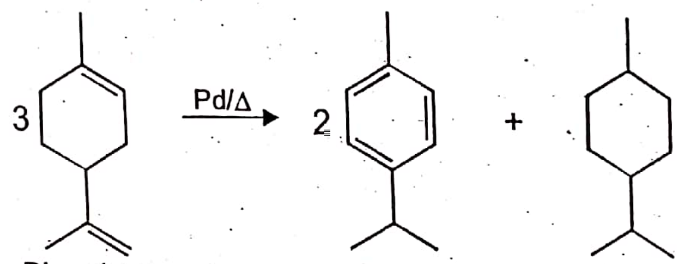
(2) **From Isoprene.** When isoprene is heated in a sealed tube at 280°C, Diels-Alder reaction with itself yields (±)-limonene or dipentene.



Isoprene (2 molecules) Dipentene

Properties. (*Physical*). Limonene is a liquid, bp 178°C. It has lemon-like odour. It is insoluble in water, but dissolves in ethanol and diethyl ether.

(*Chemical*). It gives the reactions of an alkadiene. On catalytic hydrogenation (S, Δ) it gives *p*-menthane, while with bromine it yields a tetrabromide. When heated in the presence of palladium (catalyst), it disproportionates to *p*-cymene and *p*-menthane.

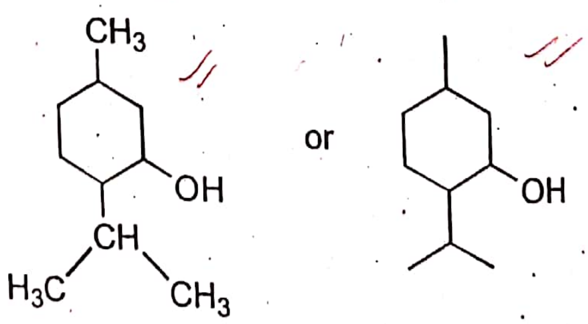


Dipentene *p*-Cymene *p*-Menthane

Uses. (1) Limonene is used as flavouring agent in foods, beverages, dental and shaving creams; (2) Dipentene is used in medicine and for the manufacture of *p*-cymene, *p*-menthane, and synthetic resins.

MENTHOL, $C_{10}H_{20}O$

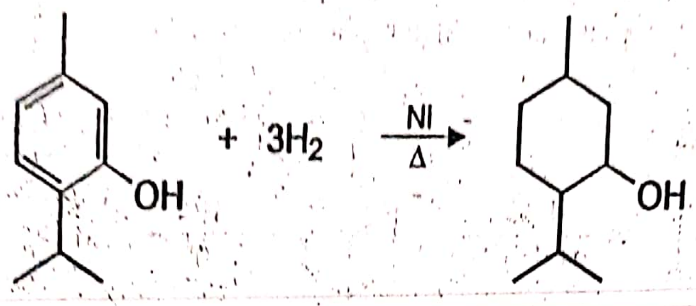
It is a monocyclic monoterpene secondary alcohol, having the structure :



Menthol occurs in peppermint oil and Japanese mint oil.

Preparation. (1) From Peppermint or Mint Oil. The oil is chilled when crystals of menthol separate. These are purified by recrystallisation.

(2) **From Thymol.** Menthol is also obtained by catalytic hydrogenation of thymol.

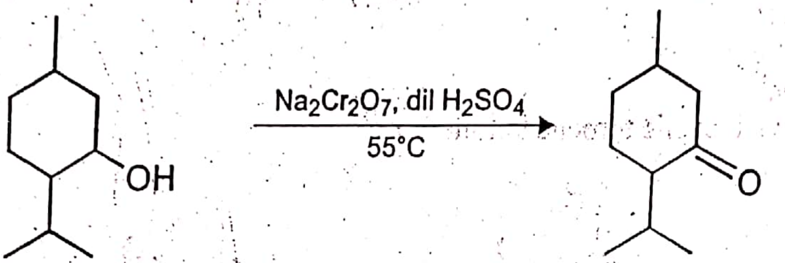


Thymol (±)-Menthol

Properties. (*Physical*). Menthol is a white crystalline solid with a strong minty odour and cooling taste. It melts at 42°C and boils at 216°C. Natural menthol is optically active, the (–)-form. It has anaesthetic and antiseptic action.

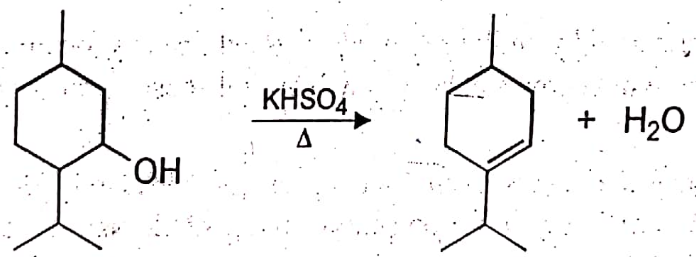
(*Chemical*). It gives the reactions of an alicyclic secondary alcohol.

(1) **Oxidation.** Upon oxidation with chromic acid, it gives the corresponding ketone, menthone.



Menthol Menthone

(2) **Dehydration.** When heated with potassium hydrogen sulphate, it gives menthene.

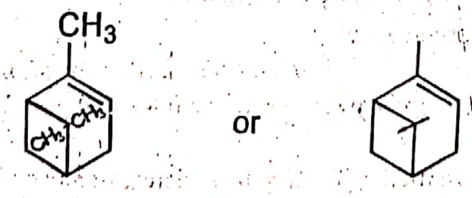


Menthol Menthene

Uses. Menthol, on account of its anaesthetic and antiseptic action, pleasant odour and cooling taste, is used : (1) in pharmaceuticals as local anaesthetic and for relief of headache ; (2) in mouth washes, nasal sprays and inhalers (**Vick's Inhaler**), cough drops, chewing-gums, and mentholated cigarettes ; (3) in cosmetics – toothpastes, shaving creams, shaving lotions, face creams and powders.

α-PINENE, $C_{10}H_{16}$

It is a *bicyclic monoterpene* and has the structure :

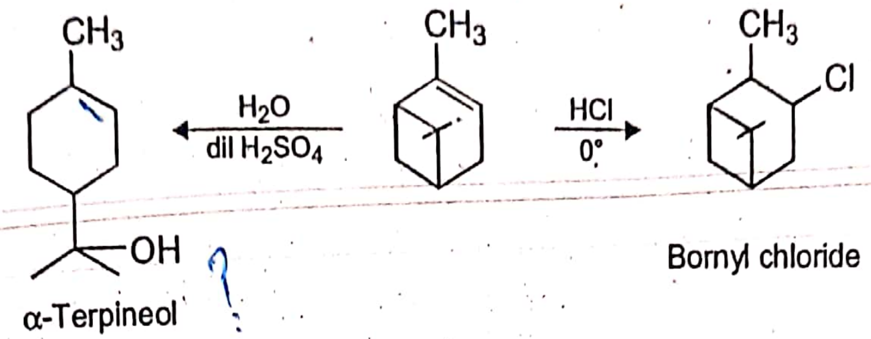


α-Pinene is the chief component of turpentine oil obtained from the pine tree.

Preparation. It is isolated from turpentine oil by steam distillation followed by fractional distillation. It is purified by conversion into nitrosyl chloride which upon treatment with aniline liberates α-pinene.

Properties. α-Pinene is a colourless liquid, bp 156°C. It has a characteristic odour and is optically active, $[\alpha]_D = 48.8°$.

(1) **Reaction with HCl.** It reacts with dry hydrogen chloride at 0°C to form bornyl chloride, mp 131°C, with a faint camphor odour ('artificial camphor').

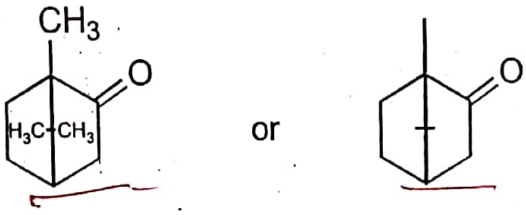


(2) **Reaction with H_2SO_4.** When treated with dilute H_2SO_4, the 4-carbon ring in terpene cleaves to form α-Terpineol.

Uses. Turpentine oil which is mainly α-pinene is used as a thinner for paints and for the commerical synthesis of camphor.

CAMPHOR, $C_{10}H_{16}O$

It is a well-known bicyclic terpene ketone



Preparation. It is prepared by chilling *Camphor oil* obtained by steam distillation of wood and leaves of the camphor tree which grows in Formosa. Now it is mostly produced by a synthetic method starting from α-pinene.

Properties. Camphor is a colourless crystalline solid, sp gr 0.999, mp 179°C, bp 209.1°C. It sublimes at room temperature and its vapour have a strong characteristic smell. Natural camphor is dextrorotatory, $[\alpha]_D = +44°$. Chemically it behaves as a ketone. It forms an oxime and on reduction forms a secondary alcohol, *Borneol.*

Uses. Camphor is used as : (*i*) a medicinal, incense ; (*ii*) plasticizer ; (*iii*) moth repeller ; and (*iv*) in embalming fluids.

EXAMINATION QUESTIONS

1. What are terpenes ? How are they classified ?
2. Write a note on : Isoprene Rule
   (Delhi BSc, 2002 ; Avadh BSc, 2003 ; Berhampur BSc, 2003)
3. What is Isoprene rule ? Indicate the isoprene units in the structure of citral and α-pinene.
   (Delhi BSc, 2005)
4. How are terpenes classified ? Discuss the structure of any one terpene, along with its synthesis.
   (Sambalpur BSc, 2004)
5. Discuss the constitution (structure) of citral.
6. Discuss the constitution of geraniol.
7. How will you show that citral is an α,β-unsaturated aldehyde ?
8. How can position of double bonds be established in citral ? *(Anna BSc, 2002)*
9. What are the structural formulas and uses of :
   (*a*) Menthol (*b*) α-Pinene (*c*) Camphor *(Kerala BSc, 2004)*