TERPENOIDS

There are many different classes of naturally occurring compounds . Terpenoids also form a group of naturally occurring compounds majority of which occur in plants, a few of them have also been obtained from other sources. Terpenoids are volatile substances which give plants and flowers their fragrance. They occur widely in the leaves and fruits of higher plants, conifers, citrus and eucalyptus.

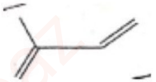
The term terpene' was given to the compounds isolated from terpentine, a volatile liquid isolated from pine trees. The simpler mono and sesqui terpenes are chief constituent of the essential oils obtained from sap and tissues of certain plants and trees. The di and tri terpenoids are not steam volatile. They are obtained from plant and tree gums and resins. Tetraterpenoids form a separate group of compounds called Carotenoids.

The term 'terpene was originally employed to describe a mixture of isomeric hydrocarbons of the molecular formula $C_{10}H_{16}$ occurring in the essential oils obtained from sap and tissue of plants, and-trees. But there is a tendency to use more general term terpenoids which include hydrocarbons and their Oxygenated derivatives. However the term terpene is being used these days by some authors to represent terpenoids.

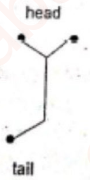
By the modern definition: "Terperioids are the hydrocarbons of plant origin of the general formula $(C_5H_8)_n$ as well as their oxygenated, hydrogenated and dehydrogenated derivatives".

Isoprene rule: Thermal decomposition of terpenoids give isoprene as one of the product. Otto Wallach pointed out that terpenoids can be built up of isoprene unit.

Isoprene rule stats that the terpenoid molecules are constructed from two or more isoprene unit.

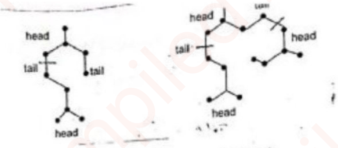


Further Ingold suggested that isoprene units are joined in the terpenoid via 'head to tail' fashion. Special isoprene rule states that the terpenoid molecule are constructed of two or more isoprene units joined in a 'head to tail' fashion.

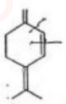


But this rule can only be used as guiding principle and not as a fixed rule. For example carotenoids are joined.tail to tail at their central and there are also some terpenoids whose carbon content is not a multiple of five.

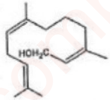
In applying isoprene rule we look only for the skeletal unit of carbon. The carbon skeletons of open chain mono terpenoids an sesqui terpenoids are,



Examples.

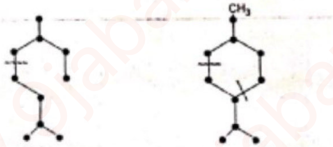


Myrcene (monoterpene)



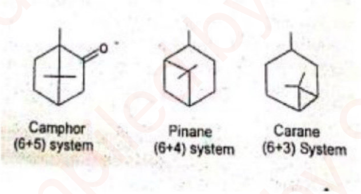
Farnesol (Sesquiterpene)

Ingold (1921) pointed that a gem alkyl group affects the stability of terpenoids. He summarized these results in the form of a rule called `gem dialkyl rule' which may be stated as "Gem dialkyl group tends to render the cyclohexane ring unstable where as it stabilizes the three, four and five member rings."
This rule limits the number of possible structure in closing the open chain to ring structure. Thus the monoterpenoid open chain give rise to only one possibility for a monocyclic monoterpenoid i.e the p-cymene structure.



P-cymene structure

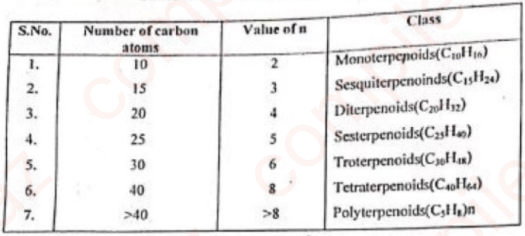
Bicyclic monoterpenodis contain a six member and a three member ring. Thus closure of the ten carbon open chain monoterpenoid gives three possible bicyclic structures.



Classification of Terpinoids

Most natural terpenoids hydrocarbon have the general formula $(C_5H_8)_n$. They can be classified on the basis of value of n or number of carbon atoms present in the structure.

Table-1: Classification of Terpenoids



S.No.	Number of carbon atoms	Value of n	Class
1.	10	2	Monoterpepoids($C_{10}H_{16}$)
2.	15	3	Sesquiterpenoinds($C_{15}H_{24}$)
3.	20	4	Diterpenoids($C_{20}H_{32}$)
4.	25	5	Sesterpenoids($C_{25}H_{40}$)
5.	30	6	Troterpenoids($C_{30}H_{48}$)
6.	40	8	Tetraterpenoids($C_{40}H_{64}$)
7.	>40	>8	Polyterpenoids(C_5H_8)n

Each class can be further subdivided into subclass according to the number of rings present in the structure.

i)**Acyclic Terpenoids**: They contain open structure.

ii)**Monocyclic Terpenoids**: They contain one ring in the structure

iii)**Bicyclic Terpenoids**: They contain two rings in the structure.

iv)**Tricyclic Terpenoids**: They contain three rings in the structure.

v)**Tetracyclic Terpenoids:** They contain four rings in the structure.

Some examples of mono, sesqui and di Terpenoids:

A) Mono terpenoids

Atuple nt Verah

4th April, 2024

Classification of Tapenoids

Most natural tapenoids hydrocarbon have the general formula $(C_5H_8)_n$.

They can be classified on the basis on the value of n or the number of carbon atoms, present in the structure.

Isoprene unit	No. of carbon atoms	Class of terpenoid	Remark.
1	~~C_5H_8~~ 5	Isoprene (C_5H_8)	—
2	~~$C_{10}H$~~ 10	monoterpenes $(C_{10}H_{16})$	They are usually volatile oils and they are used in perfumery
3.	15	Sesquiterpenes $(C_{15}H_{24})$	
4	20	Diterpenes $(C_{20}H_{32})$	Non volatile solids obtained from plants gums and resins
5	25	Sestertepenes $(C_{25}H_{40})$	
6	30	Triterpenes $(C_{30}H_{48})$	
8	40	tetraterpenes $(C_{40}H_{64})$	Carotenoids

Terpene unit	n		
	>40	polyterpenoids $(C_5H_8)_n$	rubber

Class of oils

Food oils	Vegetable

Each class can be further subdivided into sub classes according to the number of rings present in the structure.

(i) Acyclic Terpenoids: These are terpenoids that contain open structure. An example is monoterpenes (→ no ring)

(ii) Monocyclic Terpenoids: These are terpenoids that contains one ring in the structure

(iii) Bicyclic Terpenoids: They are terpenoids that contain two rings in the structure

(iv) Tricyclic Terpenoids: Contains three rings in the structure

(v) Tetracyclic Terpenoids: Contains four rings in the structure

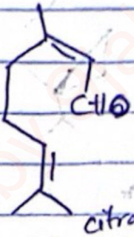
Ⓐ Monoterpenoids: we have;

(i) Acyclicmonoterpenoids: e.g

(i)

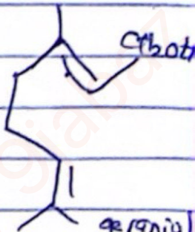
myrcene

(ii)



citral

(iii)



geraniol

(2) Monocyclic monoterpenoids: Examples are;

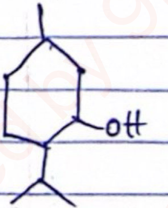
(i)

limonene

(ii)

α- terponeol

(iii)



menthol

(3) Bicyclic monoterpenoids: These are further divided into three classes

ⓐ Contains (6 + 3 membered rings)

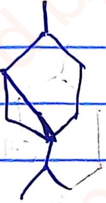
ⓑ Contains (6 + 4 membered rings)

ⓒ Contains (6 + 5 membered rings)

08-04-2025

Examples of Bicyclic monoterpenoids

(a) (i)



Thujane

(ii)

(6+3 membered ring)

Carane

(b) (i)

Pinane

(6+4 membered ring)

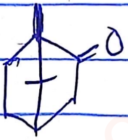
(ii)

pinene

(c) (i)

Bornane

(ii)



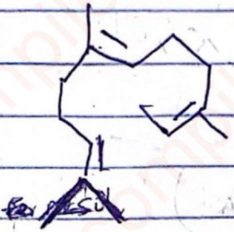
Camphor

~~(B) Sesquiterpenoids~~

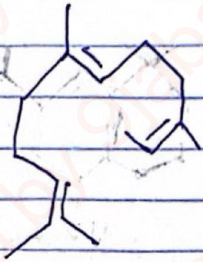
~~(i) Acyclic Sesquiterpenoids~~

B Sesquiterpenoids

(i) Acyclic Sesquiterpenoids



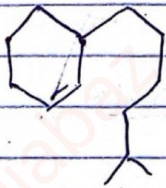
fernesol



farnesene

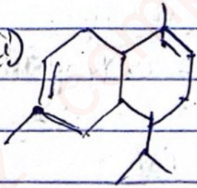
(ii) Monocyclic Sesquiterpenoids

(i)



zinziberene

(ii)



cardinene

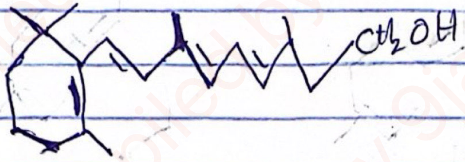
B Diterpenoids

1. Acyclic diterpenoid

(i)

phytol

(2) Monocyclic diterpenoids



Vitamin A (retinol)

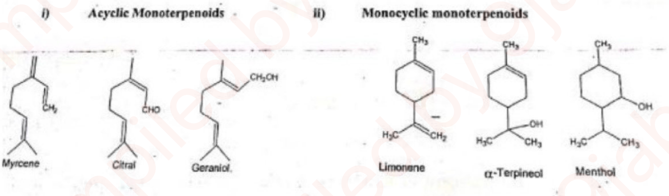
15-04-2025

(i) Isolation of essential oil: comes out as mixture of different essential oils.

Methods of extractions of oils
(a) Expression method: eg peel of orange
(b) Steam distillation
(c) extraction by means of volatile solvent
(d) adsorption in purified fats

(ii) Separation of Terpenoids from essential oils: Terpenes comes up first (more volatile)

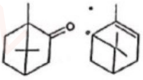
* Isoprene 2-methyl butan-1-3-diene



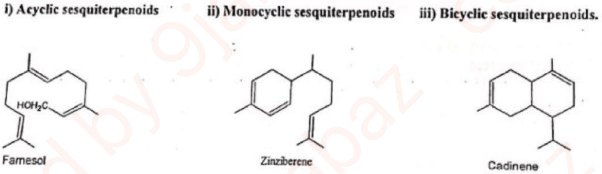
iii) **Bicyclic monoterpenoids**: These are further divided into three classes.
a)Containing -6+3-membered rings
b)Containing -6+4- membered rings.
c)Contining -6+5-membered rings

Containing -6+3-membered rings -6+4-membered rings -6+5-membered rings

Some bicyclic monoterpenes are:

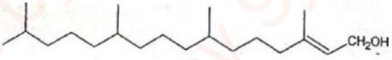


B) Sesquiterpenoids:



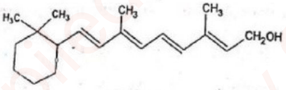
C) **Diterpenoids:**

i) **Acyclic diterpenoids**



Phytol

ii) **Mono cyclic diterpenoids:**



Vitamin A

Isolation of mono and sesquiterpenoids

Both mono and sesquiterpenoids have common source i.e essential oils. Their isolation is carried out in two steps:

i)Isolation of essential oils from plant parts
ii)Separation of Terpenoids from essential oils

i) **Isolation of essential oils from plant parts**: The plants having essential oils generally have the highest concentration at some particular time. Therefore better yield of essential oil plant material have to be collected at this particular time. e.g. From jasmine at sunset.there are four methods of extractions of oils.

a) Expression method
b) Steam distillation method
c) Extraction by means of volatile solvents
d) Adsorption in purified fats

Steam distillation is most widely used method. In this method macerated plant material is steam distilled to get essential oils into the distillate form these are extracted by using pure organic volatile solvents. If compound decomposes during steam distillation, it may be extracted with petrol at 50°C. After extraction solvent is removed under reduced pressure.

ii) **Separation of Terpenoids from essential oil**: A number of terpenoids are present in essential oil obtained from the extraction. Definite physical and chemical methods can be used for the separation of terpenoids. They are separated by fractional distillation. The terpenoid hydrocarbons distill over first followed by the oxygenated derivatives.

More recently different chromatographic techniques have been used both for isolation and separation of terpenoids.

General properties of Terpenoids

1.Most of the terpenoids are colourless, fragrant liquids which are lighter than water and volatile with steam. A few of them are solids e.g. camphor. All are soluble in organic solvent and usually insoluble in water. Most of them are optically active.

2.They are open chain or cyclic unsaturated compounds having one or more double bonds. Consequently they undergo addition reaction with hydrogen, halogen, acids, etc. A number of *addition* products *have* antiseptic properties.

3. They undergo polymerization and dehydrogenation.

4.They are easily oxidized nearly by all the oxidizing agents. On thermal decomposition, most of the terpenoids yields isoprene as one of the product.

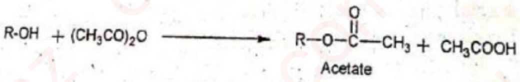
General Methods of structure elucidation

Terpenoids

1) Molecular formula: molecular formula is determined by usual quantitative analysis and mol.wt determination methods and by means of mass spectrometry. If terpenoid is optically active, its specific rotation can be measured.

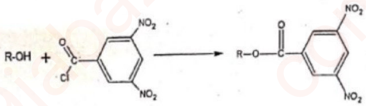
2)Nature of oxygen atom present: If oxygen is present in terpenoids its functional nature is generally as alcohol aldehyde, ketone or carboxylic groups.

a) **Presence of oxygen atom present:** presence of —OH group can be determined by the formation of acetates with acetic anhydride and benzoyate with 3.5-dinitirobenzoyl chloride.



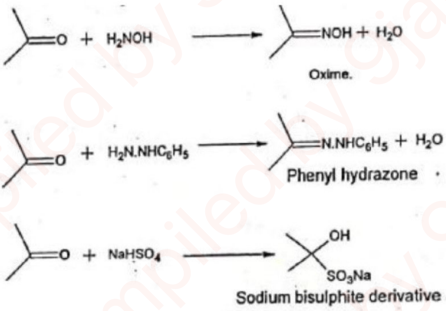
$$R\text{-}OH + (CH_3CO)_2O \longrightarrow R-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH$$

Acetate



Primary alcoholic group undergo esterification more readily than secondary and tertiary alcohols.

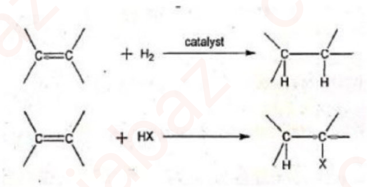
b) **Presence of >C=0 group**: Terpenoids containing carbonyl function form crystalline addition products like oxime, phenyl hydrazone and bisulphite etc.



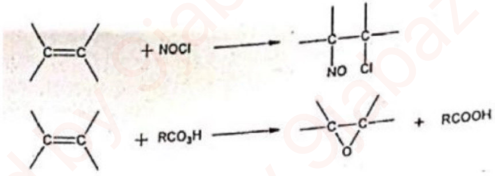
if carbonyl function is in the form of aldehyde it gives carboxylic acid on oxidation without loss of any carbon atom whereas the ketone on oxidation yields a mixture of lesser number of carbon atoms.

iii)**Unsaturation**: The presence of olefinic double bond is confirmed by means of bromine, and number of double bond determination by analysis of the bromide or by quantitative hydrogenation or by titration with monoperpthalic acid.

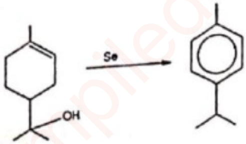
Presence of double bond also confirmed by means of catalytic hydrogenation or addition of halogen acids. Number of moles of HX absorbed by one molecule is equal to number of double bonds present.



Addition of nitrosyl chloride(NOC1) **(Tilden's reagent)** and epoxide formation with peracid also gives idea about double bonds present in terpenoid molecule.



iv)Dehydrogenation: On dehydrogenation with sulphur, selenium, polonium or palladium terponoids converted to aromatic compounds. Examination of these products the skelton structure and position of side chain in the original terpenoids can be determined.
For example α-terpenol on Se-dehydrogenation_yields *p*-cymene.



Thus the carbon Skelton of terpenol is as follows.

v)Oxidative degradation: Oxidative degradation has been the parallel tool for elucidating the structure of terpenoids. Reagents for degradative oxidation are ozone, acid, neutral or alkaline potassium permanganate, chromic acid, sodium hypobromide, osmium tetroxide, nitric acid, lead tetra acetate and peroxy acids. Since oxidizing agents are selective, depending on a particular group to be oxidized, the oxidizing agent is chosen with the help of stfucture of degradation product.

vi)Number of the rings present: With the help of general formula of corresponding parent saturated hydrocarbon, number of rings present in that molecule can be determined.

vii)Relation between general formula of compound and type of compounds: Table 2

Table-2: Relation between general formula of compound and type of compounds

General formula of parent saturated Hydrocarbon	Type of structure
C_nH_{2n+2}	Acyclic
C_nH_{2n}	Monocyclic
C_nH_{2n-2}	Bicyclic
C_nH_{2n-4}	Tricyclic
C_nH_{2n-6}	Tetrayclic

For example limonene (mol. formula. $C_{10}H_{16}$)absorbs 2 moles of hydrogen to give tetrahydro limonene (mol. Formula $C_{10}H_{20}$) corresponding to the general formula. C_nH_{2n}. It means limonoene has monocyclic structure.

viii) **Spectroscopic studies:** All the spectroscopic methods are very helpful for the confirmation of structure of natural terpenoids and also structure of degradation products. The various methods for elucidating the structure of terpenoids are:

a)**UV Spectroscopy**: In terpenes containing conjugated dienes or α,β–unsaturated ketones, UV spectroscopy is very useful tool. The values of λ_{max} for various types of terpenoids have been calculated by applying Woodward's empirical rules. There is generally good agreement between calculation and observed values. Isolated double bonds, α,β-unsaturated esters , acids, lactones also have characteristic maxima.

b)**IR Spectroscopy**: IR spectroscopy is useful in detecting group such as hydroxyl group (-3400cm^{-1}) or an oxo group (saturated 1750-1700cm^{-1}). Isopropyl group, cis and trans also have characteristic absorption peaks in IR region.

c)**NMR Spectroscopy**: This technique is useful to detect and identify double bonds, to determine the nature of end group and also the number of rings present, and also to reveal the orientation of methyl group in the relative position of double bonds.

d)**Mass Spectroscopy**: It is now being widely used as a means of elucidating structure of terpenoids. Used for determining mol. Wt., Mol. Formula, nature of functional groups present and relative positions of double bonds.

ix**) X-ray analysis**: This is very helpful technique for elucidating structure and stereochemistry of terpenoids.

x)**Synthesis**: Proposed structure is finally confirmed by synthesis. In terpenoid chemistry,many of the synthesis are ambiguous and in such cases analytical evidences are used in conjunction with the synthesis.

MYRCENE

Myrcene has molecular formula $C_{10}H_{16}$. It occurs in verbena and bay oils. It is a liquid with b. pts of 166 – 168˚C.

- Catalytic hydrogenation of myrcene in the presence of Pt converts it to decane, $C_{10}H_{22}$.

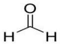
$$C_{10}H_{16} \xrightarrow[\text{[H]}]{\text{Pt}} C_{10}H_{22}$$

Thus, myrcene contains 3 double bonds (dbs) and it is an open chain (structure) compound. Since myrcene forms an adduct with maleic anhydride, therefore, 2 of the dbs are conjugated. This conjugation is supported by the fact that myrcene shows optical exaltation (i.e. increase in the refractive index).

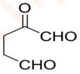
- Ozonolysis of myrcene produce acetone, formaldehyde and ketodialdehyde;

(i)

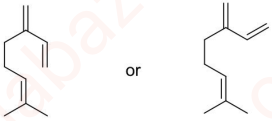
(ii)



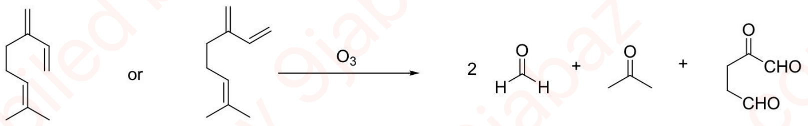
(iii)



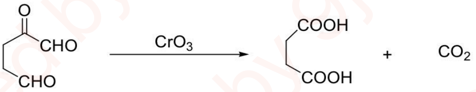
The suggested structure based on the above chemical analysis is;



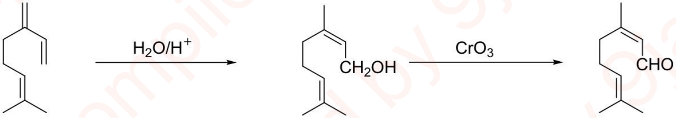
Which implies that;



- The ketodialdehyde on oxidation with chromic acid gave succinic acid and CO_2



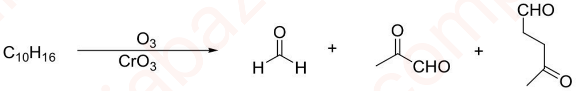
- Hydration of myrcene in acidic medium gave an alcohol known as geraniol, $C_{10}H_{18}O$, which on further oxidation gave citral

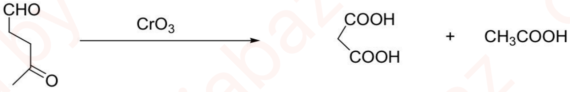


OCIMENE

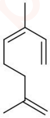
Ocimene has molecular formula $C_{10}H_{16}$. It occurs in the leaves of a plant called *Ocimium basilicum.* It has a boiling point of 81˚C/30 mm Hg.

- Catalytic hydrogenation resulted in addition of 3 moles of H_2 to form decane, this implies that ocimene is an acyclic compound with 3 dbs.
- It also forms an adduct with maleic anhydride, therefore, 2 of the dbs are conjugated.
- Ozonolysis of Ocimene produce formaldehyde, methylglyoxal, laevulaldehyde, acetic & malonic acids & acetone.

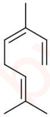




Proposed Structures:



or

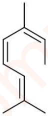


I

II

From relative amount of aldehyde z& ketone, it is believed that structure (II) is the major constituent of the mixture.

Ocimene is unstable and is yet to be obtained in the pure form. When heated, it readily isomerizes to Allo-ocimene in which all the 3 dbs are conjugated.



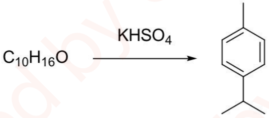
Allo-ocimene

CITRAL

Citral is the most important of the acyclic monoterpenoids because the structures of most other compounds in this group are based on that of citral. It has a molecular formula $C_{10}H_{16}O$. It has a boiling point of -77˚C. It is widely distributed. About 60-80% is obtained in lemon grass oil. It is liquid with lemon odour.

- It contains an oxo-group (carbonyl functional group), hence, it forms an oxime (This reaction was used to determine the structure of citral).

- On heating with $KHSO_4$, it forms p-cymene



- It can be reduced by Na/Hg to form an alcohol, called geraniol.

$$C_{10}H_{16}O \xrightarrow[NaHg]{2[H]} C_{10}H_{18}O$$

- It can be oxidized by Ag_2O to geranic acid $C_{10}H_{16}O_2$

$$C_{10}H_{16}O \xrightarrow[Ag_2O]{[O]} C_{10}H_{16}O_2$$

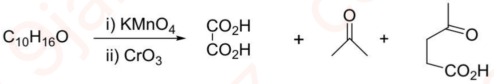
Both the above 2 last reactions show that oxo group in citral is therefore an aldehydic group. Citral also reduces Fehling's solution, further confirming the presence of aldehydic group.

Also, since there is no loss of C on oxidation to the acid, the oxo group in citral is, therefore an RCHO group.

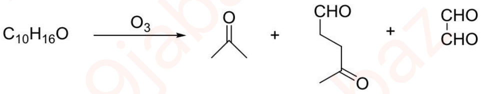
- It adds on 2 molecules of Br_2, shows the presence of 2 dbs.

$$C_{10}H_{16}O \xrightarrow{4[Br]} C_{10}H_{16}Br_4O$$

- Oxidation of citral with alkaline $KMnO_4$ followed by CrO_3 gives acetone, oxalic acid and laevulic acid.



- Ozonolysis of citral also yields acetone, laevulaldehyde and glyoxal



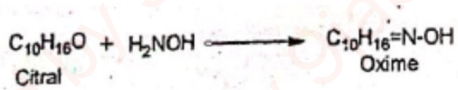
Citral

Citral is an acyclic monoterpenoid. It is a.major constituent of lemon grass oil in which it occurs to an extent of 60-80%. It is pale yellow liquid having strong lemon like odour and can be obtained by fractional distillation under reduced pressure from Lemongrass oil.

Constitution:

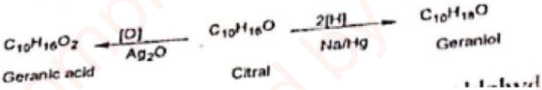
i) Mol. formula $C_{10}H_{16}O$, b.p-77°C

ii)Nature of Oxygen atom: Formation of oxime of citral indicates the presence of an oxo group in citral molecule.



$$\underset{\text{Citral}}{C_{10}H_{16}O} + H_2NOH \longrightarrow \underset{\text{Oxime}}{C_{10}H_{16}{=}N\text{-}OH}$$

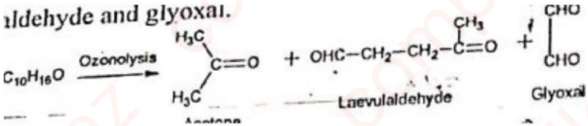
On reduction with Na/Hg it gives an alcohol called geraniol and on oxidation with silver oxide it give a monocarboxylic acid called Geranic acid without loss of any carbon atom.



$$\underset{\text{Geranic acid}}{C_{10}H_{16}O_2} \xleftarrow[Ag_2O]{[O]} \underset{\text{Citral}}{C_{10}H_{16}O} \xrightarrow[Na/Hg]{2[H]} \underset{\text{Geraniol}}{C_{10}H_{18}O}$$

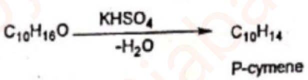
Both these reaction reveal that oxo group in citral is therefore an aldehyde group. Citral reduces Fehling's solution. further confirming the presence of aldehydic group.

iii)It adds on two molecule of Br_2 shows the presence of two double bonds. On ozonlysis, it gives acetone, laevulaldehyde and glyoxal.



Formation of above products shows that citral is an acyclic compound containing two double bonds. Corresponding saturated hydrocarbon of citral (mol. Formula $C_{10}H_{22}$) corresponds to the general formula C_nH_{2n+2} for acyclic compounds, indicating that citral must be an acyclic compound.

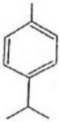
iv) Formation of *p*-cymcne and product obtained from the ozonolysis reveals that citral is formed by the joining of two isoprene units in the head to tail fashion



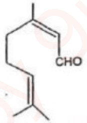
$$C_{10}H_{16}O \xrightarrow[-H_2O]{KHSO_4} \underset{\text{P-cymene}}{C_{10}H_{14}}$$

v) On the basis of above facts following structure was proposed for citral.

Carbon skelton of citral

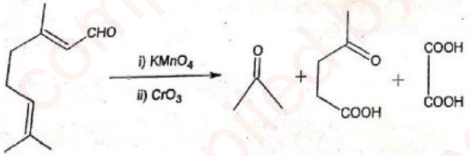


p-cymene

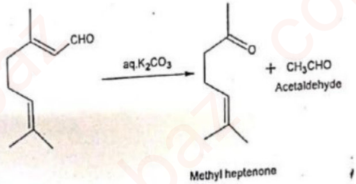


Citral

vi) Above structure was further supported by the degradation of citral on treatment with alkaline $KMnO_4$ followed by chromic acid.



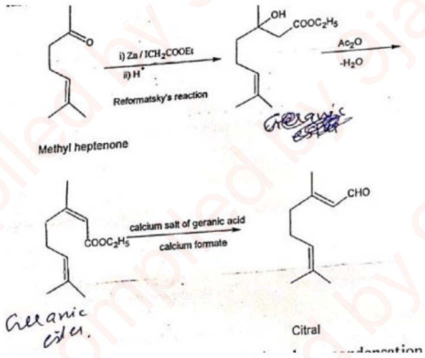
Verley found that citral on boiling with aqueous potassium carbonate yielded 6-methyl hept-5- ene-2-one and acetaldehyde. The formation of these can only be explained on the basis of proposed structure.



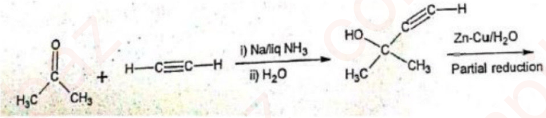
It Appears that citral is product of aldol condensation of these two.

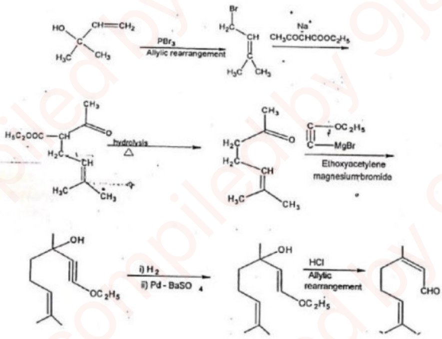
Synthesis: Finally the structure of citral was confirmed by its synthesis.

a) **Barbier-Bouveault-Tiemann's synthesis**: In this synthesis methyl heptenone is converted to geranic ester by using Reformatsky's reaction. Geranic ester is then converted to citral by distilling a mixture of calcium salts of geranic and formic acids.

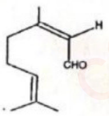


b)**Arens-Van Drop's Synthesis**: This synthesis involves condensation of acetone with acetylene in the presence of liquid ammonia. Condensation product is then reduced and treated with PBr$_3$, allylic rearrangement takes place. The rearranged product so obtained is treated with sodium salt of acetoacetic ester and then hydrolysed to yield methyl heptenone. The latter compound on condensation with ethoxy acetylene magnesium bromide, followed by the partial reduction and acidification yields citral by allylic rearrangement.

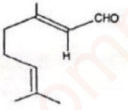




Isomerism of citral: two geometrical isomers occur in nature.



Cis-citral; citral-b:
neral; Z-form

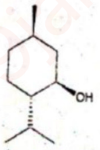


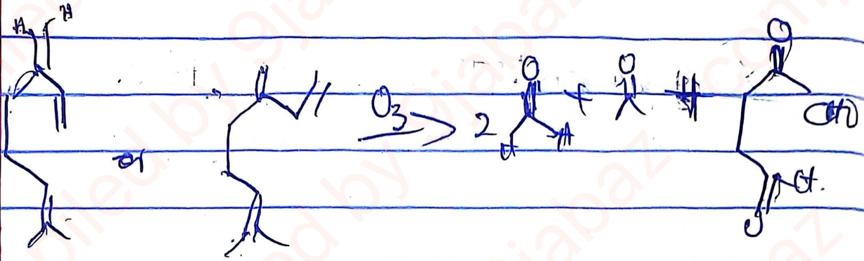
Trans-citral; Citral-a;
geranial; E-form

The existence of the two isomeric Citrals in natural citral has been confirmed chemically by the formation of two different semicarbazones and formation of geraniol and nerol on reduction.

Menthol

Menthol is the major constituent of Mentha Piperi. It is used as an antiseptic and anesthetic. Menthol (also called peppermint camphor or mint camphor) is the major constituent of peppermint oil and is responsible for its odour and taste and the cooling sensation when applied to the skin. It is ingredient in cold balms. Menthol is optically active compound with mol. formula $C_{10}H_{20}O$.





hydrolysed
A Myrcene in water will produce myrcenol

CITRAL

Formula: $C_{10}H_{16}O$, boiling point = 77°C, it is found in large quantity in Lemon grass. it has the largest concentration of citral.

$C_{10}H_{16}O \xrightarrow[\Delta]{KHSO_4}$

p-cymene

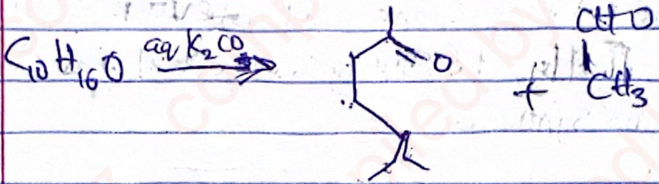
Reduction of citral (Na(Hg)) → Geraniol
Oxidation of citral (Ag_2O) → Geranic acid

$C_{10}H_{16}O \xrightarrow[Na/Hg]{2[H]} C_{10}H_{18}O$
Geraniol

$C_{10}H_{16}O \xrightarrow[Ag_2O]{[O]} C_{10}H_{16}O_2$
Geranic acid

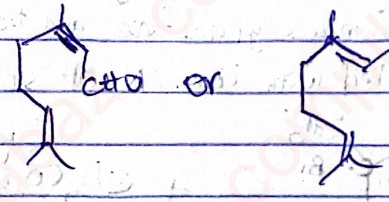
$K_2CO_{3(aq)}$ +

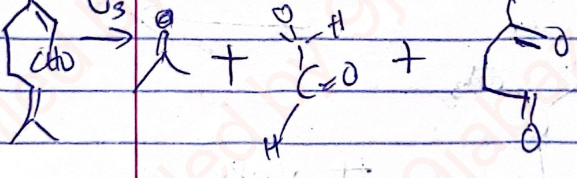
Aqueous K_2CO_3 converted citral into ~~6-methyl~~ 6-methyl hept-5-en-2-one



This last reaction implies that citral undergoes cleavages at the α-β unsaturation

On the basis of the above chemical analysis, citral is therefore





Synthesis of Citral

Synthesis of Citral

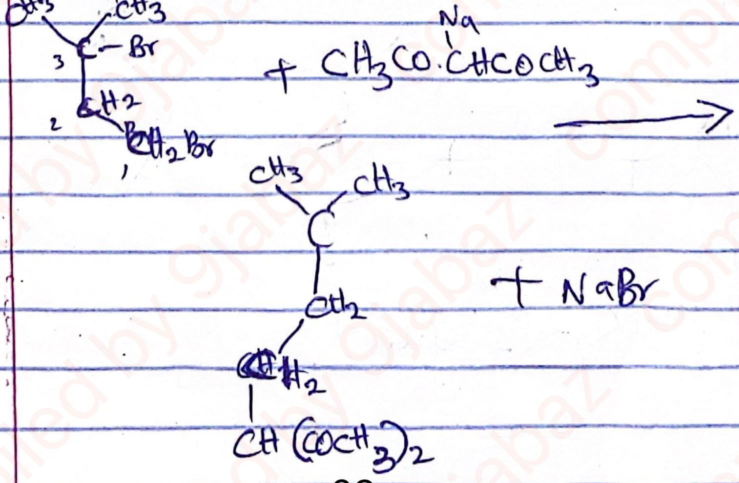
Synthesis of 6-methylhept-5-en-2-one

This cleavage by alkali reagent is a general reaction by α-β unsaturated carbonyl compounds. The methyl heptenone itself is oxidized to acetone and laevulic acid

Finally, the structure of citral was confirmed by its synthesis

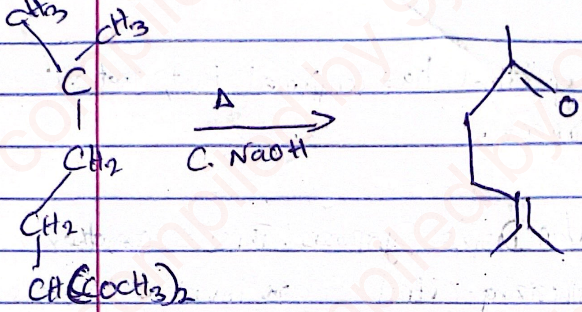
Synthesis of 6-methylhept-5-en-2-one

1,3 dibromo-3-methyl butane is condensed with sodium acetylacetone and the resulting compound is heated with conc. NaOH solution



Reformatsky rxn Condenses aldehyde and ketones to halo ester

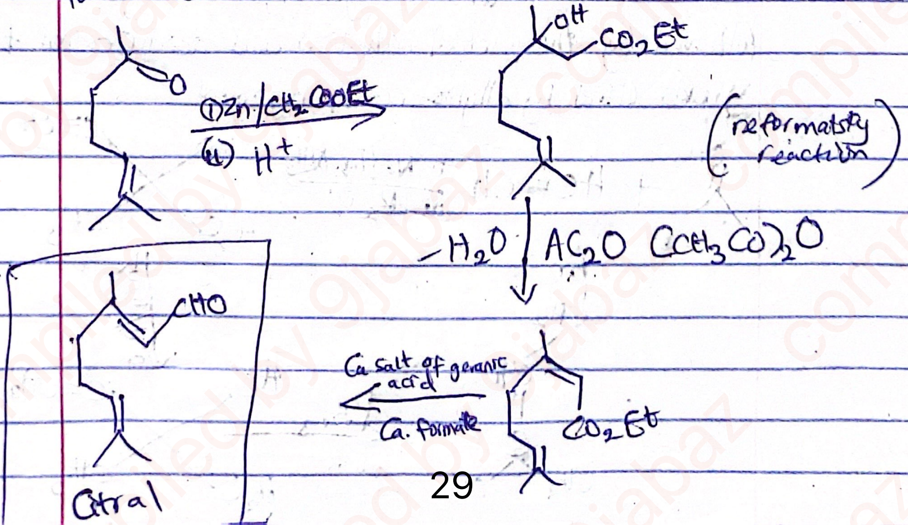
AC (CH_3CO)



Conversion of 6-methyl hept-5-en-2-one to Citral

① Using Barbier - Boureault - Tiemann's Synthesis:

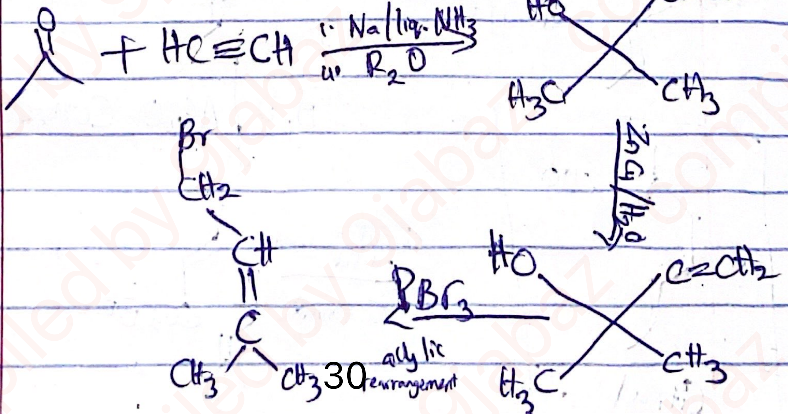
This reaction convert 6-methyl hept-5-en~~e~~-2-one ~~conver~~ to geranic ester by using Reformatsky reaction
Geranic ester is then converted to citral by distilling a mixture of calcium salts of geranic acid and formic acid.

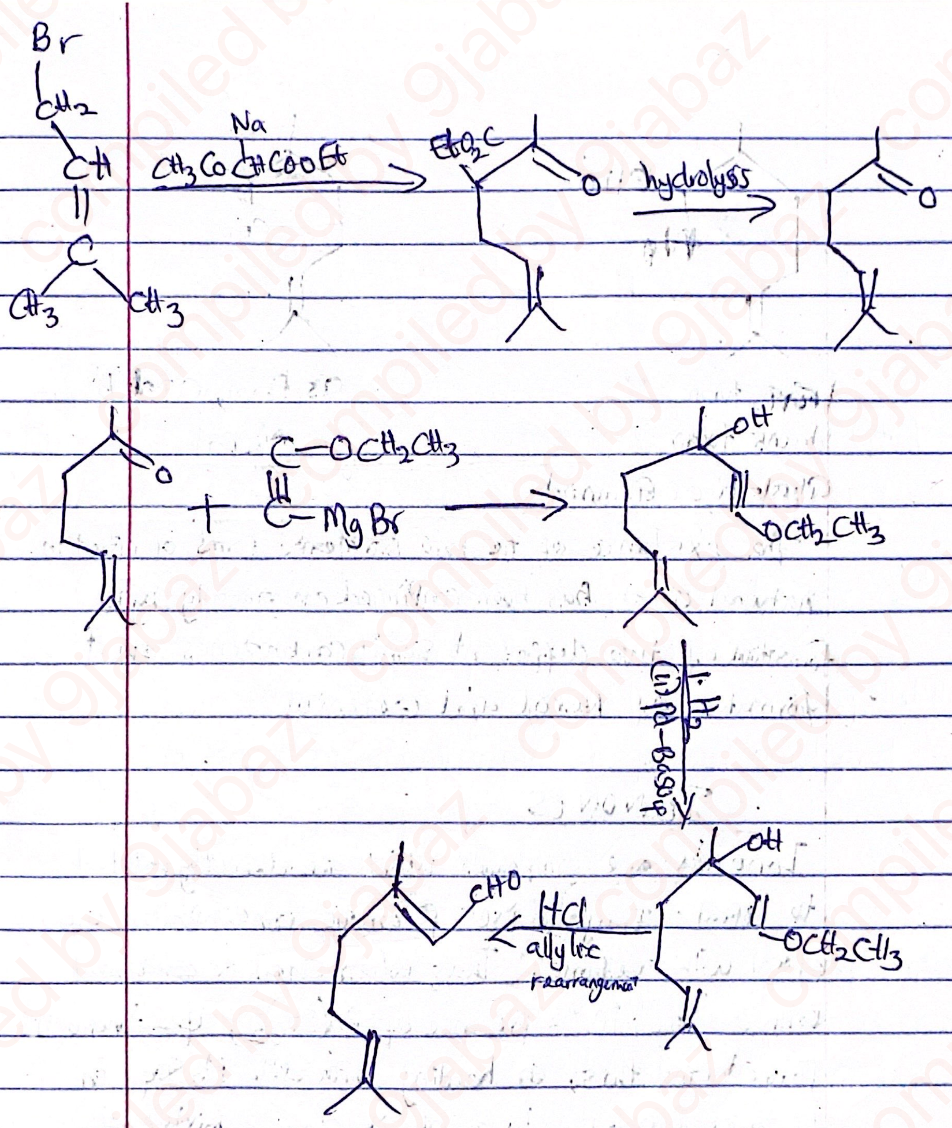


The synthesis of citral has confirmed that, that structure of citral is correct.

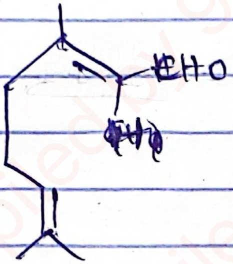
② Using Arens-Van Drop's Synthesis: This is another method of synthesizing citral and involves condensation of acetone with acetylene in the presence of liquid ammonia. The condensation product is then reduced and treated with phosphorus tri bromide (PBr_3) in which there is an allylic rearrangement.

The rearranged product so obtained is treated with sodium salt of acetoacetic ester and then hydrolyzed to yield methyl heptenone and the compounds obtained on condensation with ethoxyacetylene magnesium bromide followed by the partial reduction and acidification that yields citral by allylic rearrangement

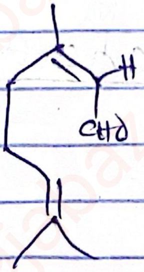




Citral exists in two isomeric forms, i.e cis and trans forms;



~~trans form~~
trans form
Citral-'a' or Geranial

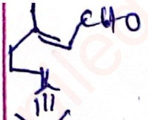


cis form, ~~citral~~ citral 'b'
or Neral

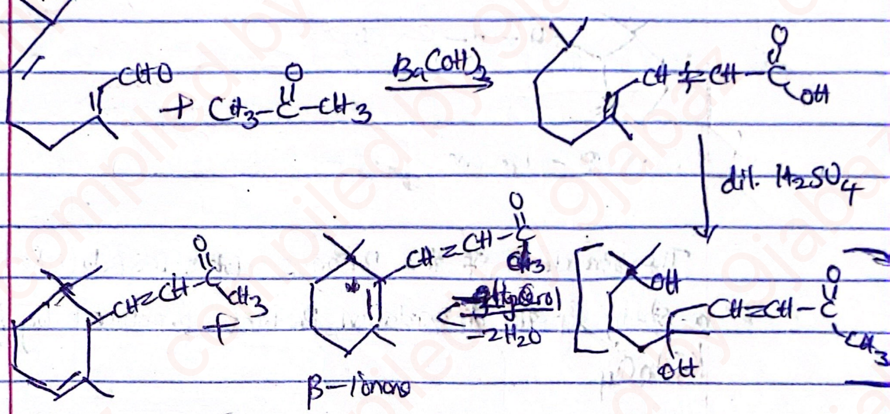
The existence of the two isomeric forms of citral in natural citral has been confirmed chemically by the formation of two different semi-carbazones and formation of Nerol and Geraniol

IONONES

Ionones are compounds which are directly related to citral. They arise from the condensation of citral with acetone. Thus, when citral is condensed with acetone, in the presence of $Ba(OH)_2$, ψ-ionone is formed and this, on heating with dil. H_2SO_4 in the presence of glycerol, it forms a mixture of α-ionone and β-ionone



24th April, 2024



β-Ionone
Main product

α-ionone

- Glycerol is acting as cyclising agent.

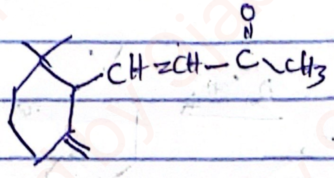
The proportion of α & β ionone varies with the nature of the cyclizing agent used

H_3PO_4 (o-phosphoric acid)

With H_2SO_4, β-ionone is the main product, but with H_3PO_4 α-ionone is the main product.

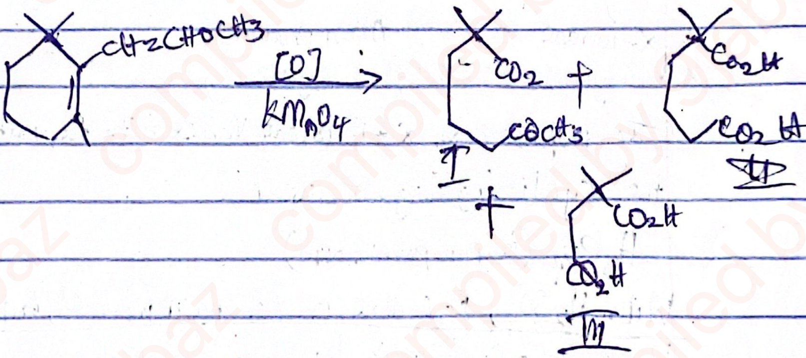
Both ionones can be obtained from natural sources, the β-ionone / β-isomer is optically inactive. i.e, (does not have chiral carbon), while α-ionone is optically active (contains chiral carbon). It can exist in optically active forms since it contains 1 assymetric carbon

We also have the γ-ionone which is synthetic.

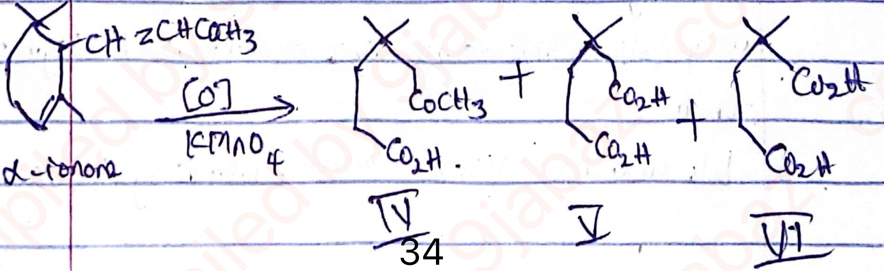


γ- Ionone.

The structure of the ionones were established by a study of the oxidation product produced by ~~KMnO4~~ KMnO$_4$



Ⓘ
β-ionone gives Geronic acid from geronic acid,
(II) α,α-dimethyl adipic acid
(III) α,α-dimethyl succinic acid



On the other hand, α-ionone gives a mixture of

(IV) Isogeronic acid

(V) β, β-dimethyl adipic acid

(VI) α, α-dimethylglutaric acid

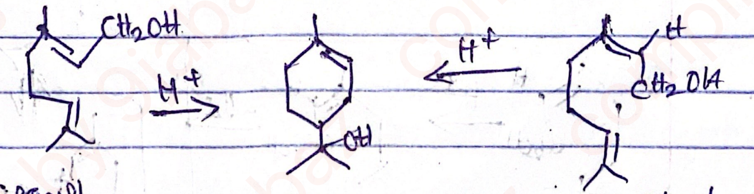
Geraniol, $C_{10}H_{18}O$

Boiling point range (229–230°C) / 757 mmHg

It is found in many essential oils, especially rose oil

It is a primary alcohol, on oxidation form RCHO. It forms a tetrabromide with two molecule of bromide. It has 2-double bonds

Reduction of citral produces geraniol & nerol (cis form)

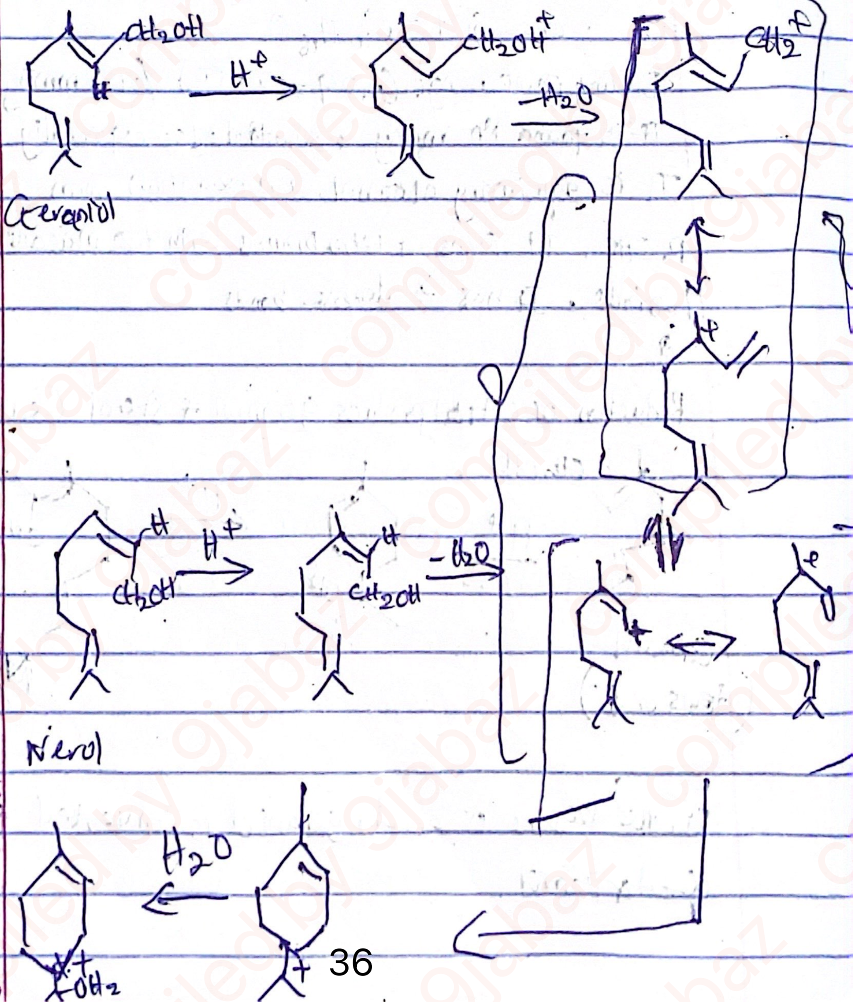


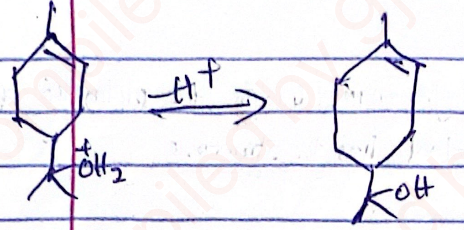
Geraniol (trans or E⁻)

Nerol (cis or Z⁻)

In the presence of acid, geraniol is converted to α-terpeniol most acyclic monoterpenoid under cyclization to form 6-membered rings, usually in paramethane derivative (4-isopropyl ~~1-~~methyl cyclohexane).

Cyclization of Geraniol and Nerol





α - terpineol

Nerol occurs naturally in various essential oils e.g oil of Neroli, oil of bergamots etc.

The boiling point of Nerol is 225°C - 226°C

LINALOOL ($C_{10}H_{18}O$)

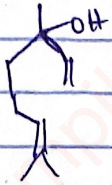
Boiling point range is 198 - 199°C

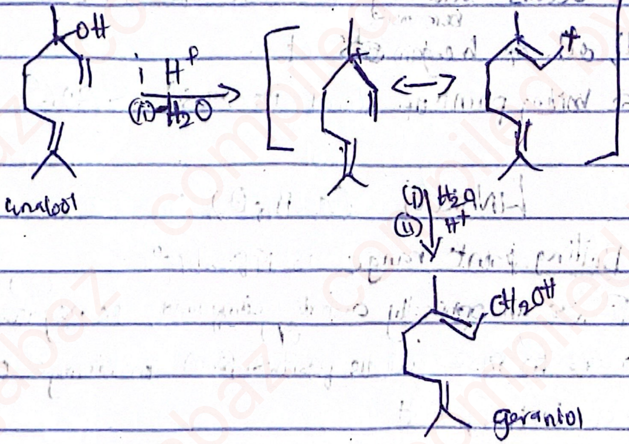
It is an optically active compound, the negative (−) form occurs in rose and the positive (+) form in orange oil. It is a tertiary ROH

- * It is tertiary ROH
- * It has two moles of hydrogen on catalytic hydrogenation Therefore, Linalool must contain two double bonds.
- * When heated with acetic anhydride ($(CH_3CO)_2O$), linalool is converted to geranylacetate, which can be converted back to linalool by heating with steam at 200°C under presu

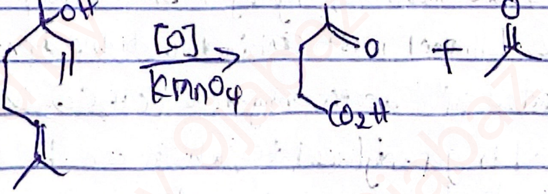
$$C_{10}H_8O \xrightarrow[\Delta]{(CH_3CO)_2O} \text{Geranylacetate}$$

** Linalool isomerises to geraniol under the influence of acids. Therefore, linalool has the structure



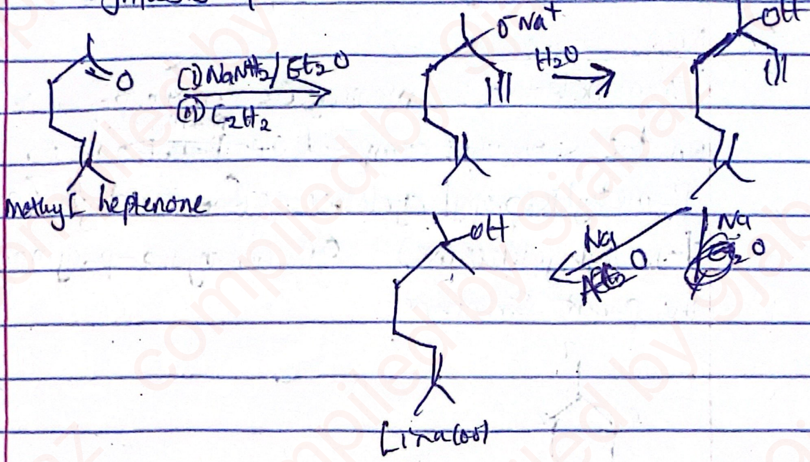


Oxidation of linalool gives laevulic acid and acetone

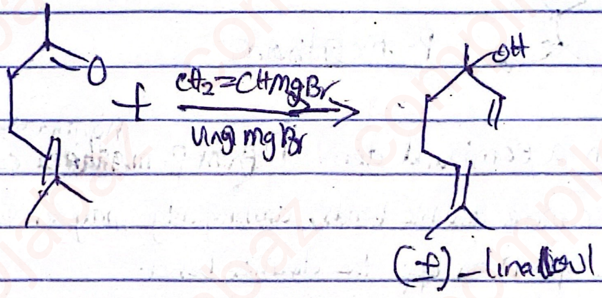


Syntesis of Linalool

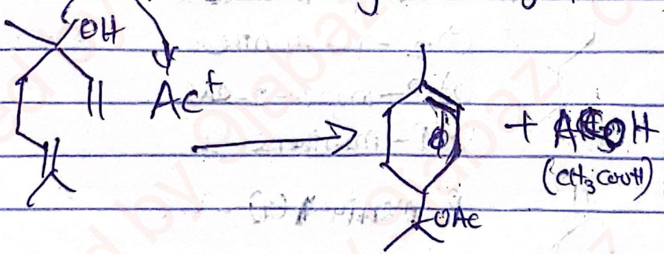
(1)



(ii)



Stereoselective Ring Closure By Aceticanhydrid



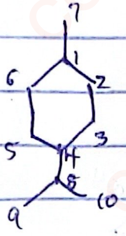
α-terpineol acetate
or
α-terpinyl acetate

p-methane →

Monocyclic Monoterpenoid

Nomenclature

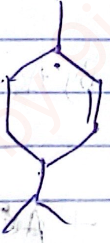
Nomenclature of monocyclic monoterpenoid is based on the saturated compound of ~~p-methane~~ p-menthane or ~~p~~ p-methylisopropyl cyclohexane (~~or 4-methyl~~ (or 4-isopropyl-1-methylcyclohexane) or hexahydro-p-cymane as the parent structure.



P- menthane

When a compound derived from p-~~methane~~ menthane contains one or more double bonds, ambuguity may arise as to the position off the double bond.

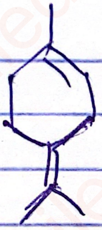
①



(i) Δ^2-p-menthene
(ii) 2-P- menthane
(iii) P-menth-2-ene
(iv) P- menthene-2

②

P- mentha-1(7)-ene

③  p-menth-1(2), 4(8)-diene

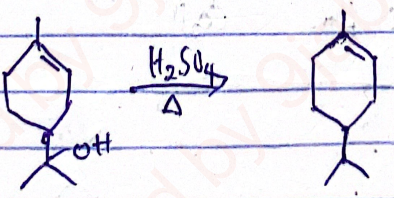
29/04/2025

α - Terpeneol $C_{10}H_{18}O$, mp 35 °c (solid)

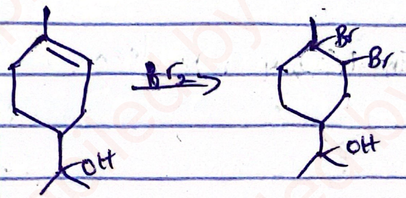
It is a solid, liquid or Vapour especialy for the racemic medication

- ✱ It is opticaly active and occur naturally in the (+) and (−) forms and also (±) - forms can also be found in nature.
- ✱ The oxygen atom is present as a tertiary -ROH group
- ✱ It adds on 2 Br atoms, therefore it contains one double bond
- ✱ The saturated α- terpeneol will therefore have $C_{10}H_{20}O$, indicating 1 DBE that it is a monocyclic.

When heated with H_2SO_4, it forms paracymene, implies that it contains p-cymane skeleton/structure. Thus the structure of α - terpeneol



α- terpeneol p- cymene

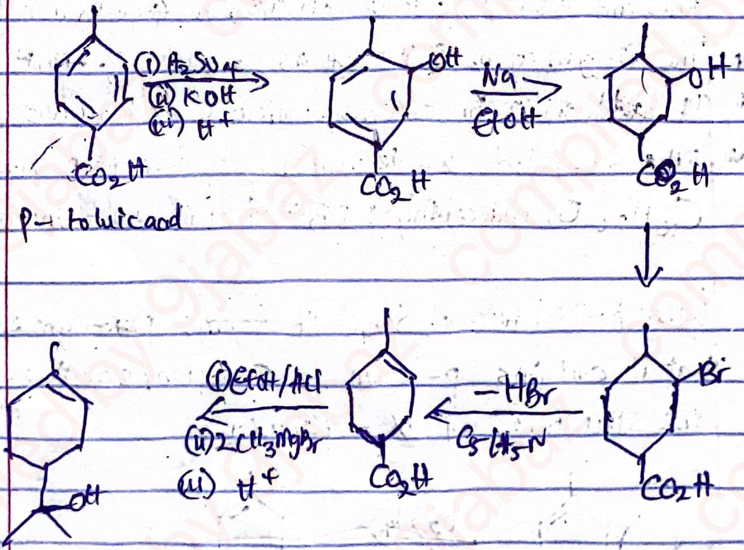


Possible Synthetic Routes of α- Terpineol

~~How can we sy~~

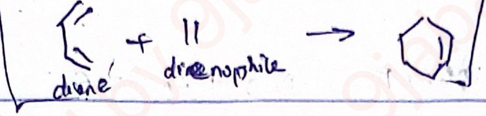
α- terpeneol can be synthesized in the lab through;

(i) Starting with p- toluidine acid



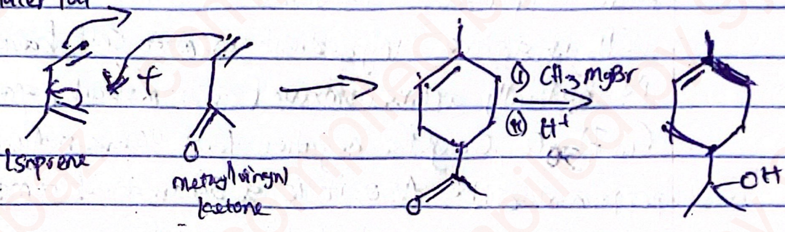
p- toluic acid

cf. Dreld — alder's reaction

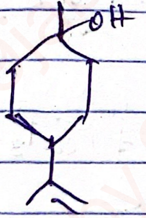


* read diels-alder's reaction

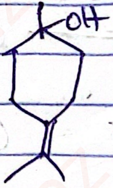
(27) A much simpler method of synthesizing α-terpeneol was carried out ~~As by carrying out~~ by Alder and Vogt, in 1949 through the use of Diels-Alder's reaction, using isoprene and methyl vinyl ketone as the starting material



Other Terpeneols



β-terpeneol
Mp. 32–33°C



γ-terpeneol
Mp 68–70

MENTHOL AND MENTHONE

Mentol is the major constituent of Mentha piperita. It is known as (peppermint camphor or mint camphor) is the major constituent of peppermint oil, and it is responsible for its odour and taste and the cooling sensation when it is applied on the skin.

It is active ingredient in most cold balms. Mentol is optically active compound with molecular formular $C_{10}H_{20}O$, Only the negative form occurs naturally in peppermint oil. Also, it is a saturated compound, and the oxygen is an alcoholic group.

* Oxidation of mentol gives mentone i.e a ketone. This implies that the OH group in menthol is 3°-ROH

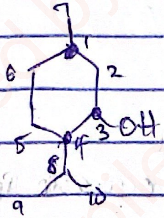
$$C_{10}H_{20}O \xrightarrow{[O]} \underset{\text{mentone}}{C_{10}H_{18}O}$$

* $C_{10}H_{20}O \xrightarrow{PCl_5} C_{10}H_{19}Cl + POCl_3 + HCl$

* On dehydration followed by dehydrogenation, it gives P-cymene

$$C_{10}H_{20}O \xrightarrow[\text{(ii) Dehydrogenation}]{\text{(i) Dehydration}}$$

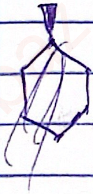
Therefofe, the structure of mentol is

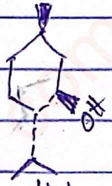


It has three chiral carbon on Position 1, 3, 4

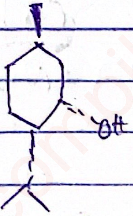
Optically active $= 2^3 = 8$

Racemic mixture $= 4$

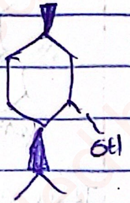




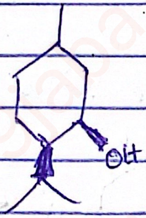
menthol



neomenthol



Isomenthol



Neo isomenthol

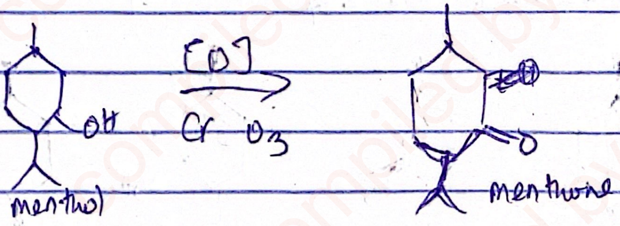
MENTHONE

molecular formular $C_{10}H_{18}O$

bp: 204°C / 750mmHg

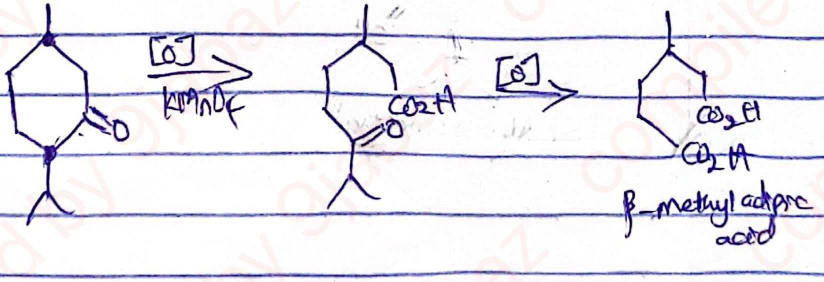
~~([illegible]) form~~

(-)- form of menthone occurs in peppermint oil and can also be prepared from (-)- form methone by using chromic acid for oxidation.



It is also a saturated compound with characteristic properties of ketone

* Oxidation of menthone leads to a ketoacid



Optical isomers = $2^2 = 4$

CARVONE

Carvone is $C_{10}H_{14}O$ and has a bp 230°C/750mmHg.

It occurs in various essential oils, e.g in spearmint and caraway oils in optically active forms.

* And as racemic modifications, it behaves as a ketone and adds on four atoms of bromine, i.e it has two double bonds

$$C_{10}H_{14}O \xrightarrow{4[Br]} C_{10}H_{14}OBr_2.$$

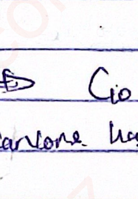
* It is converted to carvacrol when heated with Phosphoric acid

$$C_{10}H_{14} \xrightarrow[\Delta]{H_3PO_4} C_{10}H_{14}O$$

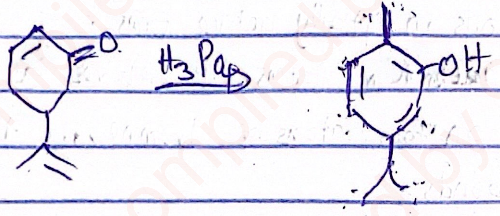
This implies that carvone has the p-cymene skeleton

* Carvone can be prepared from α-terpeneol

Structure of carvone;



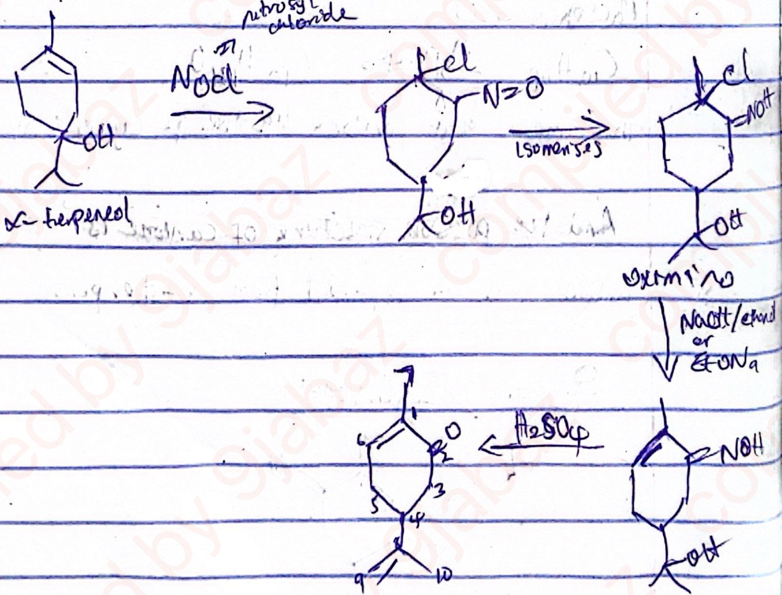
When Carvone is heated H_3PO_4, we are left with Carvacrol



Carvacrol

$C_{10}H_{14}O$

Preparation from α-Terpeneol



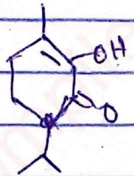
α-terpeneol

oximino

p-ment-6,8-dien-2-one

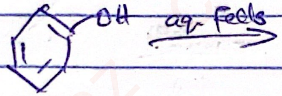
DIOSPHENOL

molecular formular $C_{10}H_{16}O_2$, mp is 83°C
It is found is leaves of buchu plants



λmax = 274nm

The enolic structure accounts for its acidic properties (soluble in alkaline solution) and gives intense green colour with ferric chloride



intense blue black colouration

It is optically active ~~but~~ only as racemate because of the number of negative and positive forms ((−)- and (+)- forms)

The molecule contains a chiral center, but diosphenol has been obtained only as a racemate, this could also be due to either or both of the following mechanism.