

# \* Terpenoids \*

## \* Introduction

⇒ The terpenoids form a group of compounds the main group of which occur in the plant kingdom; a few terpenoids have been obtained from other sources. The dimethylmercapto- and sesquiterpenoids are the chief constituents of the essential oils.

⇒ Most natural terpenoid hydrocarbons have the molecular formula  $(C_5H_8)_n$  and their molecular formula is used as a basis for classification.

No. of carbon atoms	Class
(i) 10	Monoterpenoids ( $C_{10}H_{16}$ )
(ii) 15	Sesquiterpenoids ( $C_{15}H_{24}$ )
(iii) 20	Diterpenoids ( $C_{20}H_{32}$ )
(iv) 25	Sesterterpenoids ( $C_{25}H_{40}$ )
(v) 30	Triterpenoids ( $C_{30}H_{48}$ )
(vi) 40	Tetra terpenoids ( $C_{40}H_{64}$ )
(vii) 740	Polyterpenoids ( $(C_5H_8)_n$ )

# \* Isoprene rule \*

2-propanone  
1,3-butadiene

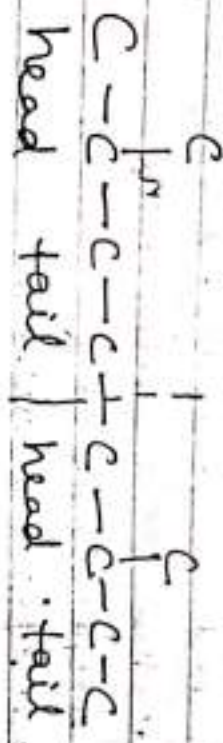
⇒ It was first pointed out by Wullich (1857).

⇒ Ingold (1925) pointed out that the isoprene units in natural terpenoids were joined "head to tail" (the head being the branched end of isoprene).

⇒ The divisibility into isoprene units, and their head to tail joining may conveniently be tested to as the special isoprene rule.  
↳ Exception ⇒ lavender and eucalyptene.

⇒ The carotenoids are joined tail to tail at their C<sub>10</sub> terpenoids → tail to tail centers. There are also some terpenoids such as carbon centers. Is not multiple of five and their carbon carbon centers is a multiple of five but cannot be divided into isoprene units.

⇒ The Carbon skeletons of open-chain monoterpeneoids (\*) and sesquiterpeneoids are.



(\*) Isolation of monoterpeneoids and sesquiterpeneoids (\*)

⇒ Plants containing essential oils usually have the greatest concentration at some particular time, eg. Termination of sunset. In general, the best method of extraction of the terpeneoids.

- (i) Extraction
- (ii) Steam distillation
- (iii) Extraction by means of volatile solvents.
- (iv) Adsorption in purified jets. Method (ii) is the one most widely used.

## ⊗ General methods of determining structure.

(i) A pure specimen is obtained, and the molecular formula is ascertained by the usual methods, and also by means of mass spectrometry. If the compound is optically active, its specific rotation is measured. Optical activity may be used as a means of distinguishing structures.

(ii) If oxygen is present in the molecule, its functional nature is ascertained, i.e. whether it is present as hydroxy, aldehyde, ketone, etc.

(iii) The presence of Olefinic bonds is ascertained by means of bromine, and the number of double bond is determined by analysis of the bromide, or by quantitative hydrogenation or by titration with manganopentoxide acid. These facts lead to the molecular formula of the parent hydrocarbon, from which the number of rings present in the structure may be deduced.

(iv) The preparation of methyl selenonitride and a study of their behavior.

v) Dehydrogenation of terpenoids, with sulphur, selenium, platinum, or palladium, and a re-examination of the products thereby obtained.

(vi) Measurement of the refractive index leads to a value for the molecular refraction. From this may be deduced the nature of the carbon skeleton. Also, optical exaltation indicates the presence of double bonds in conjugation.

(vii) ⇒ Degradative oxidation. The usual reagents used for this purpose are  $O_3$ ,  $O_2$  gas, acid, neutral  $KMnO_4$ , permanganate, chromic acid and sodium hypochlorite.

⇒ Other reagents are osmium tetroxide, nitric acid, lead tetra-acetate, peroxy-acids and  $N$ -bromosuccinimide for allylic bromination.



Q The absorption maximum of a diene system is affected by substituents and wavelength (1942) found that the position of the absorption maximum depends on the number and type of substituents,

## Polymers

Homocyclic dienes (Basic Value)	253 nm
Heterocyclic (and acyclic) dienes (Basic Value)	214 nm
Increment for each C-substituent	5 nm
" " " " " " " " " " " "	5 nm
" " " " " " " " " " " "	5 nm
" " " " " " " " " " " "	30 nm
Extensive conjugation	
$\lambda_{max}$ (of compound)	To find

For g)



(Methyls)

$\lambda_{max}$ : Observed, 224 nm

Calculated  $\lambda_{max}$  for an acyclic diene with one C-substituent

$$214 + 5 = 219 \text{ nm}$$

## (IX) Infrared Spectroscopy

⇒ IR is very valuable for detecting the presence of a hydroxyl group ( $3400 \text{ cm}^{-1}$ ) or an amine group (saturated:  $1750-1700 \text{ cm}^{-1}$ ,  $\alpha, \beta$ -unsaturated:  $1700-1660 \text{ cm}^{-1}$ ) etc.

## (X) NMR Spectroscopy

⇒ IR is used to detect and identify double bonds, to determine the nature of end groups and also the number of rings present, and to ascertain the orientation of methyl group in the molecule.

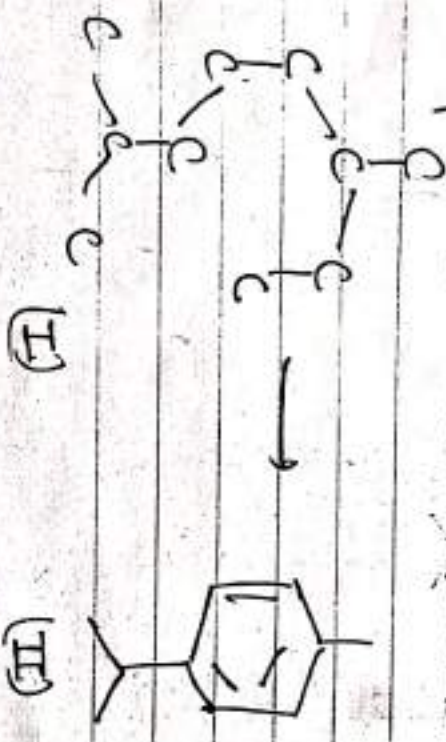
## (XI) Mass Spectrometry

IR is used as a means of elucidating the structure of terpenoids. If it is possible to determine molecular weights, molecular formula, the nature of various functional groups, and the relative position of double bonds.



# Citral, $C_{10}H_{16}O$

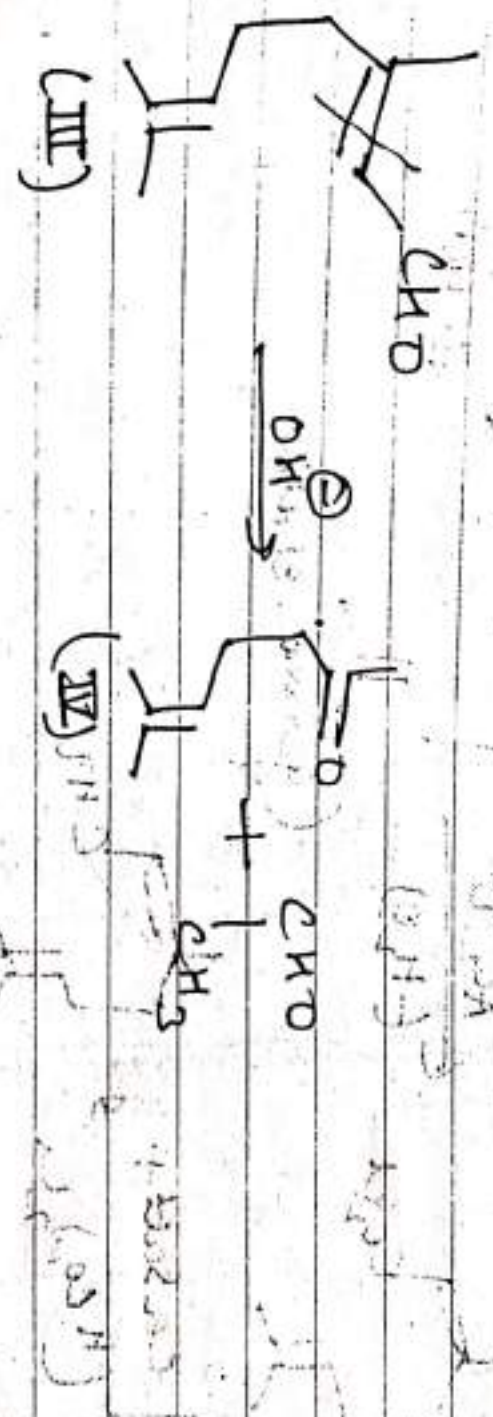
- ⇒ This is the most important member of the  $\alpha,\beta$ -unsaturated monoterpenoids, since the structures of almost all other compounds in this group are based on that of citral.
- ⇒ Citral is widely distributed and occurs to an extent of 60-80% in lemon grass oil. Citral is a liquid which has the smell of lemons.
- ⇒ Citral also shows + Coseim an  $\alpha$  group, e.g. it forms an osim, etc. On heating to with potassium hydroxide, it forms Citral forms p-cymene (II). (Semmler, 1891). This reaction was used by Semmler to determine the positions of the methyl and isopropyl groups in citral; Semmler applied it to citral molecule uses cyclic, and gave it the skeleton structure (Z) (two isoprene units joined head to tail).





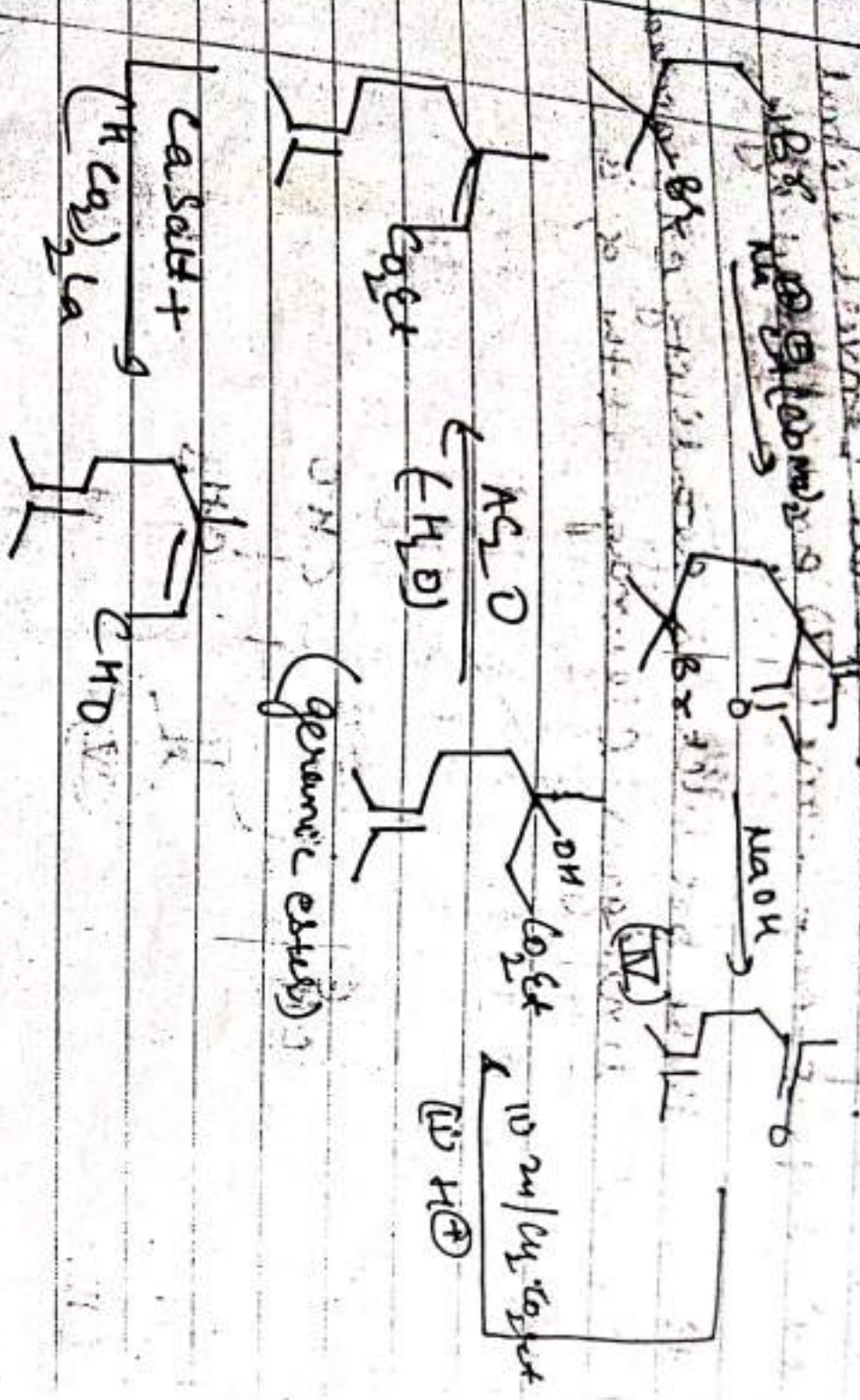
This structure is supported by the work of Vesely (1947), who found that aqueous potassium carbonate converted citral into 6-methylhept-5-en-2-one (IV) and acetaldehyde.

⇒ The formation of these products is readily explained by assuming (III) undergoes cleavage at the  $\alpha, \beta$ -double bond.



⇒ This cleavage by alkaline reagents is a general reaction of  $\alpha, \beta$ -unsaturated cyclic compounds.

Reimer-Tiemann's 1898 synthesis

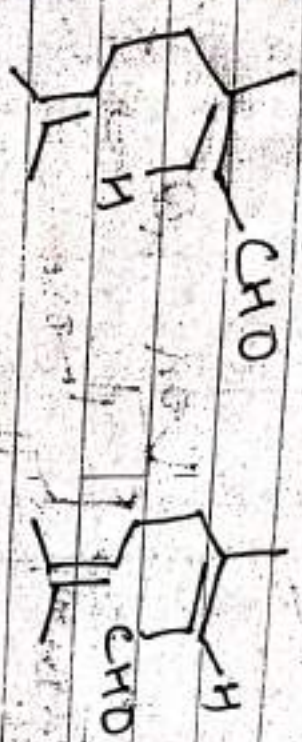


The structure of citral was confirmed by the synthesis of methyl heptanoate (IV), the conversion of this into geranic ester, which was then converted into citral by heating a mixture of the calcium salts of geranic and formic acids.



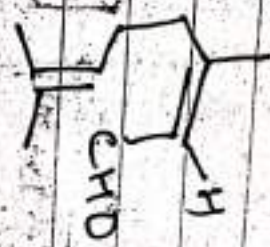
itself have also been obtained. Also known as geraniol has a b.p. 117-118°C/20 mm. Citral-a and Citral-b (also known as nerol) has a b.p. 118-119°C/20 mm.

The configuration of this form has been determined from a consideration of the lobes of the corresponding orbitals.

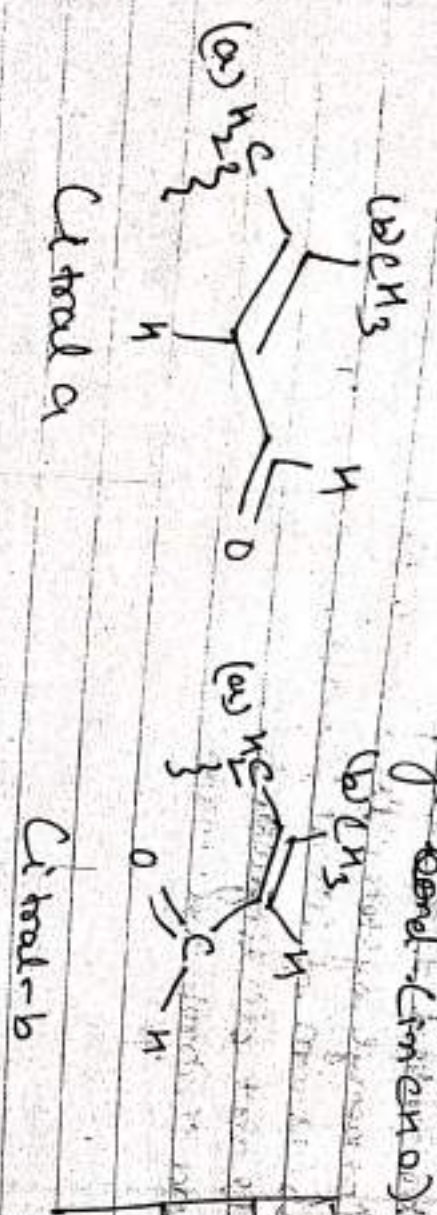


trans - (or E) form, cis - (or Z) form

Citral-a; geraniol Citral-b; nerol



⇒ Structure have been confirmed by the NMR spectra of citral = (A) and citral = (B) (Cinnamaldehyde).  
 Thus, for example, the Z value of  $\text{CH}_2=\text{CH}$  and  $\text{CH}_3\text{CH}=\text{CH}$  are different due to the different magnetic shielding effects of the carbonyl bond. (Cinnamaldehyde)



	$\text{CH}_2$	$\text{CH}$
Citral-a	7.06	7.84
Citral-b	7.14	7.82

⇒ Rosenzweig was very much used by the classical workers in the determination of structures of terpenoids. In most cases, this method predicted two types of products, one arising from the terminal isopropylidene group, one acetone, and the other arising from the terminal isopropylidene group,  $\text{CH}_2=\text{CH}-$  (to give formaldehyde). Because of this, it was originally believed that many alicyclic monoterpenoids were mixtures of both structures.

⇒ However, infrared spectroscopic studies show the presence of enantiomers (or almost enantiomers) the isopropyl pyridone groups.

⇒ It might also be noted that the presence of the  $\alpha, \beta$ -unsaturated carbonyl system is shown from the UV absorption spectrum of the compound; however, it does not distinguish between the isopropylidene and isopropenyl forms.