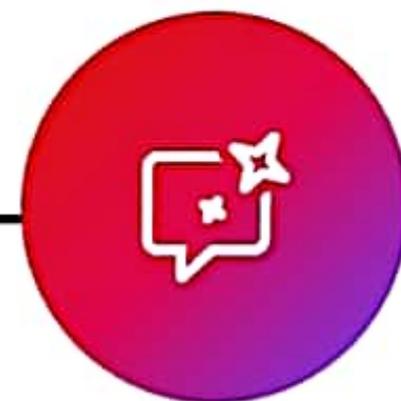


## **Citral**

Citral is an acyclic monoterpene. It is a major constituent of lemon grass oil in which it occurs to an extent of 60-80%. It is a pale yellow liquid having a 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.  $-77^{\circ}C$
  
- ii) Nature of Oxygen atom: Formation of oxime of citral indicates the presence of an oxo group in the citral molecule.



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 limonene 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  $\alpha,\beta$ -unsaturated ketones, UV spectroscopy is very useful tool. The values of  $\lambda_{max}$  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,  $\alpha,\beta$ -unsaturated esters, acids, lactones also have characteristic maxima.

b) **IR Spectroscopy:** IR spectroscopy is useful in detecting group such as hydroxyl group ( $-3400\text{cm}^{-1}$ ) or an oxo group (saturated  $1750-1700\text{cm}^{-1}$ ). 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.

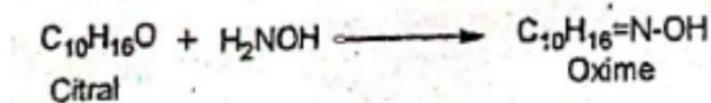
### **Citral**

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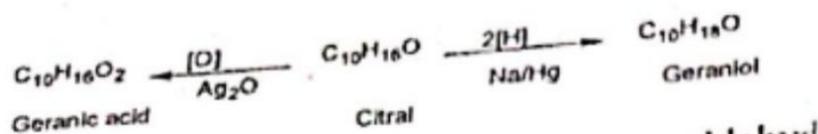
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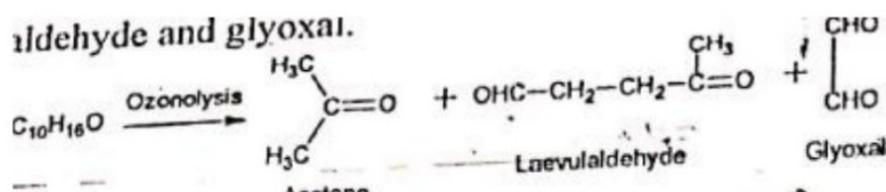


On reduction with Na/Hg it gives an alcohol called geraniol and on oxidation with silver oxide it give a monocarboxylic acid called Geranic acid without loss of any carbon atom.



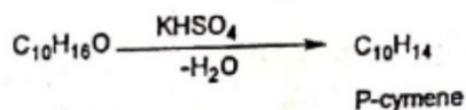
Both these reaction reveal that oxo group in citral is therefore an aldehyde group. Citral reduces Fehling's solution. further confirming the presence of aldehydic group.

iii) It adds on two molecule of Br<sub>2</sub> shows the presence of two double bonds. On ozonolysis, it gives acetone, laevulaldehyde and glyoxal.

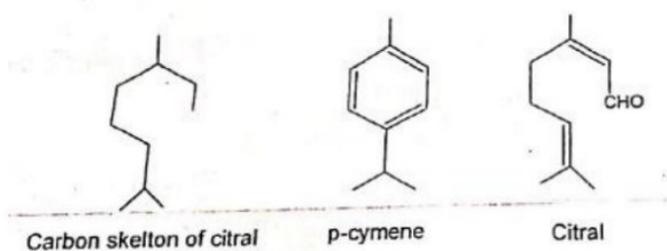


Formation of above products shows that citral is an acyclic compound containing two double bonds. Corresponding saturated hydrocarbon of citral (mol. Formula C<sub>10</sub>H<sub>22</sub>) corresponds to the general formula C<sub>n</sub>H<sub>2n+2</sub> for acyclic compounds, indicating that citral must be an acyclic compound.

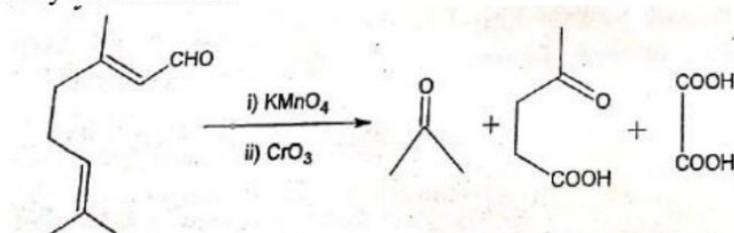
iv) Formation of *p*-cymene and product obtained from the ozonolysis reveals that citral is formed by the joining of two isoprene units in the head to tail fashion



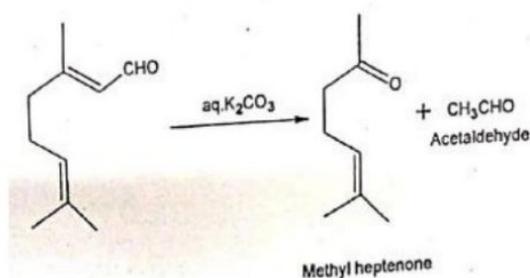
v) On the basis of above facts following structure was proposed for citral.



vi) Above structure was further supported by the degradation of citral on treatment with alkaline  $\text{KMnO}_4$  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.

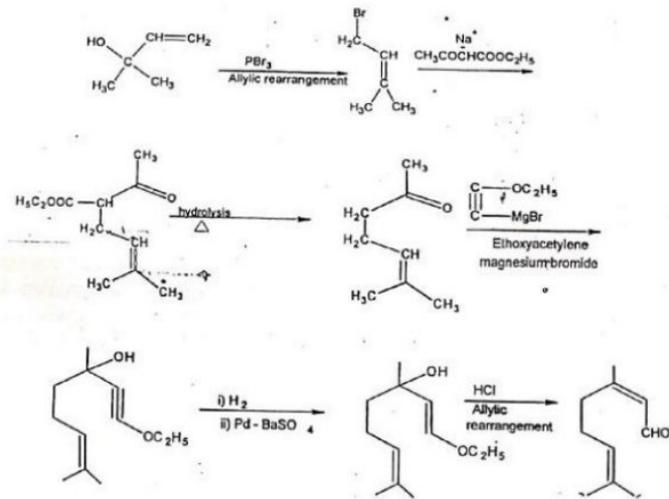


It Appears that citral is product of aldol condensation of these two.

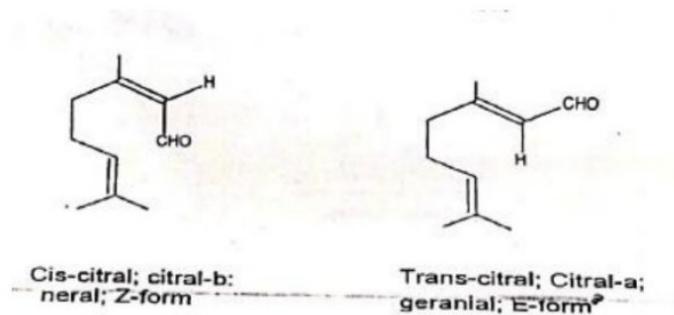
**Synthesis:** Finally the structure of citral was confirmed by its synthesis.

- 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.





**Isomerism of citral:** two geometrical isomers occur in nature.



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  $C_{10}H_{20}O$ .

