Verbena is source of Myrcene

Lemmon grass is source of Citral

CITRAL, *3,7-Dimethyl-2,6-octadien-1-al,* $C_{10}H_{16}O$

Citral is widely distributed and occurs to the extent of 70 to 80 per cent in lemongrass oil. It is also found in oil of orange, oil of lemon (6 to 7 per cent) and in citronella oil.

ISOLATION

The essential oil containing citral is treated with sodium bisulfite solution, when crystalline citral bisulfite derivative is obtained. This derivative is then hydrolysed with sodium carbonate to give pure citral.

STRUCTURE OF CITRAL

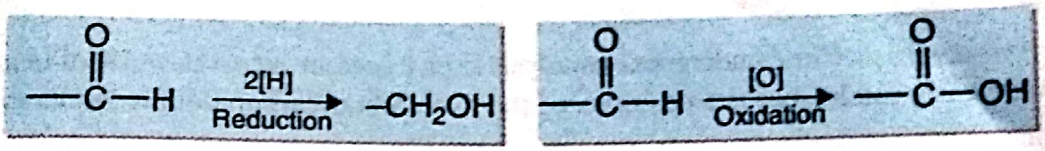
The structure of citral has been deduced from the consideration of facts and conclusions such as the following :

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

(2) Citral reacts with bromine (2 molecules) to form a tetrabromide derivative. This indicates the presence of two carbon-carbon double bonds in the citral molecule.

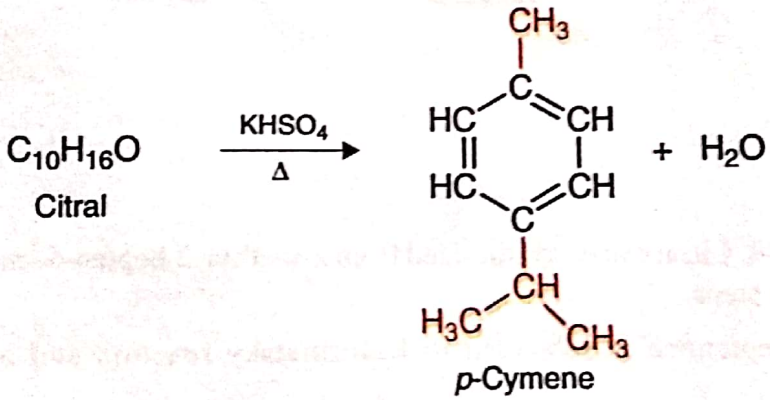
(3) Citral reacts with hydroxylamine to form an oxime. It also adds sodium bisulfite. These reactions indicate the presence of an aldehyde (–CHO) or a ketone (–CO–) group.

(4) Citral undergoes reduction with sodium amalgam and water to give a primary alcohol *geraniol*, $C_{10}H_{18}O$. It undergoes oxidation with the silver oxide to yield *geranic acid*, $C_{10}H_{16}O_2$, containing the same number of carbons. These reactions indicate the presence of an aldehyde group.

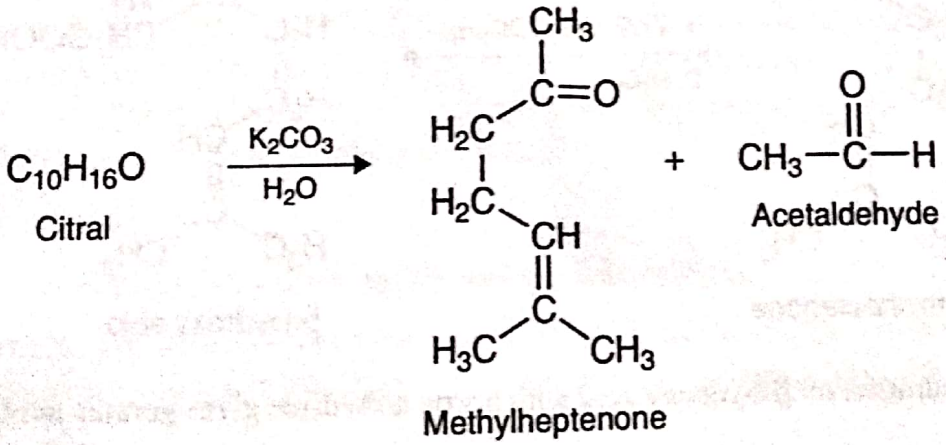


UV Studies indicate that the aldehyde group in citral is present as a part of an α,β-unsaturated carbonyl system.

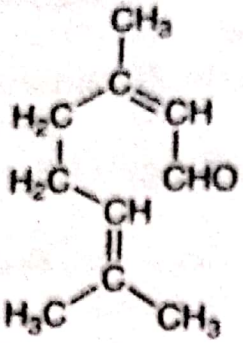
(5) When citral is heated with potassium bisulfate, it is converted to *p*-cymene. This indicates the relative positions of methyl and isopropyl groups in the citral molecule.



(6) Citral undergoes hydrolysis with potassium carbonate to give 2-methyl-2-hepten-6-one (methylheptenone) and acetaldehyde.

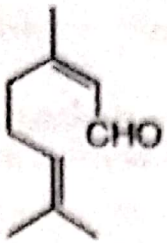


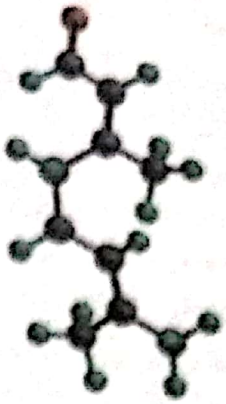
The above evidence indicates that citral has the following structural formula :



Citral

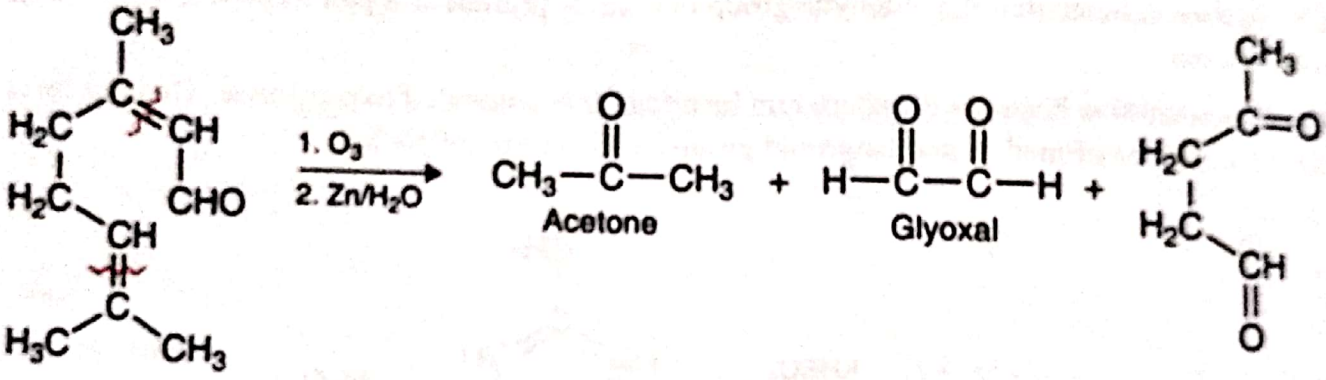
Can be written as





This structure of citral has been confirmed by its ozonolysis and synthesis from 2-methyl-2-hepten-6-one.

Ozonolysis of Citral. Citral undergoes ozonolysis to give acetone, glyoxal, and levulinic aldehyde. This reaction clearly establishes the positions of the two carbon-carbon double bonds in the citral molecule.

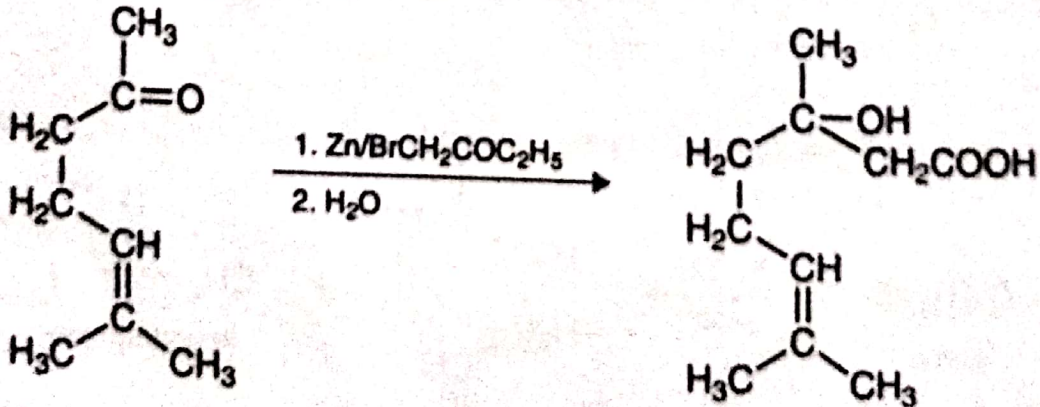


Citral

Levulinic aldehyde

Synthesis of Citral. Citral can be synthesized from 2-methyl-2-hepten-6-one (methylheptenone) by the following three steps.

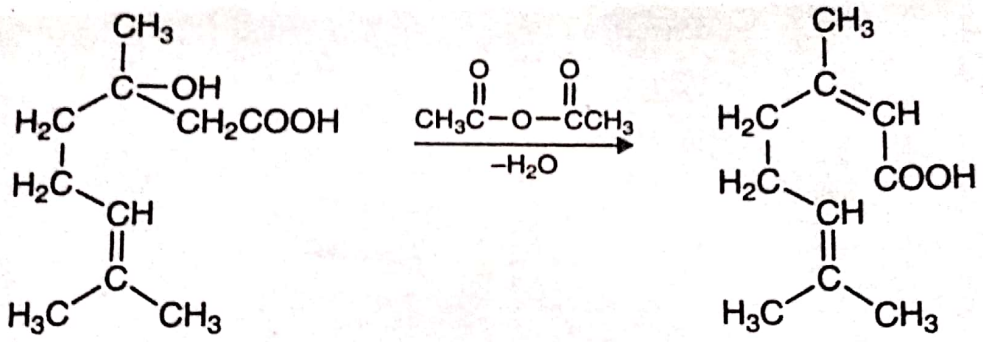
Step 1. Methylheptenone is subjected to Reformatsky reaction and hydrolysis to give a β-hydroxy acid.



Methylheptenone

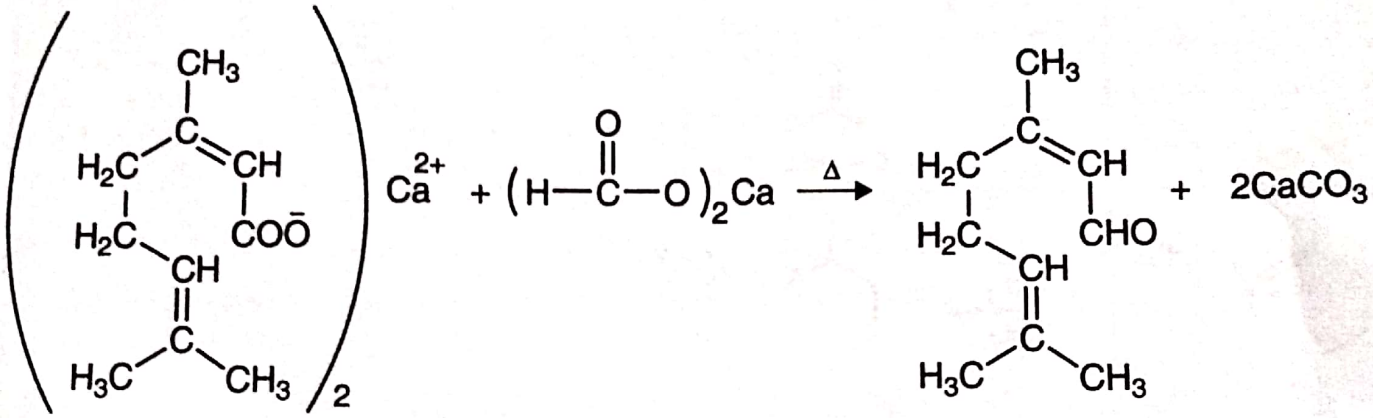
β-Hydroxy acid

Step 2. Dehydration of β-hydroxy acid with acetic anhydride gives geranic acid.



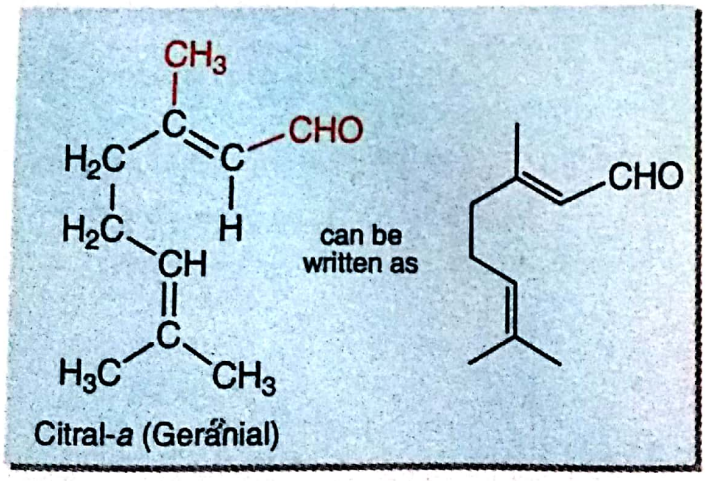
β-Hydroxy acid — Geranic acid

Step 3. Distillation of a mixture containing the calcium salt of geranic acid and calcium formate yields citral.

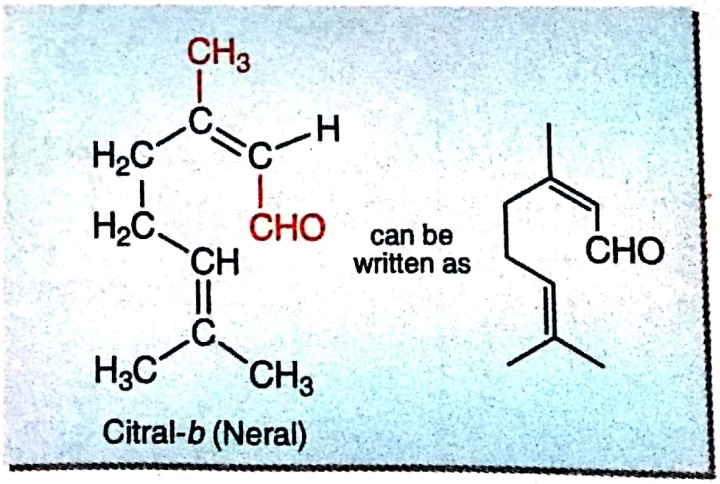


Calcium salt of geranic acid — Calcium formate — Citral

Geometrical Isomerism in Citral. Citral exists in two geometrical forms, known as citral-*a* (*geranial*) and citral-*b* (*neral*).



Citral-*a* (Geranial)



Citral-*b* (Neral)

In geranial the methyl and the aldehyde groups are *cis* to each other and in neral they are *trans*. Both these forms occur together in varying amounts in natural oils. The unqualified term citral usually refers to the mixture. The configurations of these two isomers have been determined from a consideration of the rate of cyclization of their corresponding alcohols.