

## Details of Module

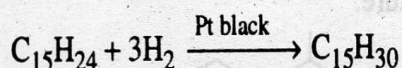
Subject	Chemistry
Course Name	M. Sc. IVth Semester
Paper No.	Paper-14 (Organic Chemistry Special) (Chemistry of Natural Products)
Module Name/Title	Terpenoids (Lecture-3)
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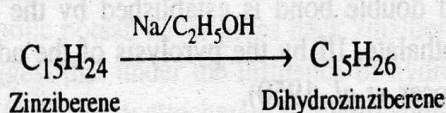
#### (1) Structure of zinziberene

**Constitution :** 1. Its molecular formula is  $C_{15}H_{24}$ .

2. On catalytic (platinum black) hydrogenation, zinziberene takes up three moles of hydrogen to form hexahydrozinziberene indicating the presence of three double bonds and hence zinziberene is monocyclic.



3. Its molecular refraction value is 61.37 which is higher than that for monocyclic sesquiterpenoids (67.87) and thus zinziberene exhibits optical exaltation and hence in zinziberene at least two double bonds must be conjugated. The conjugation in zinziberene is confirmed by its ultraviolet absorption spectrum ( $\lambda_{\text{max}}$  260 $\mu$ ) and formation of adduct with maleic anhydride. Moreover, zinziberene on reduction with sodium and alcohol forms dihydrozinziberene further confirming that in zinziberene two of the double bonds are conjugated.

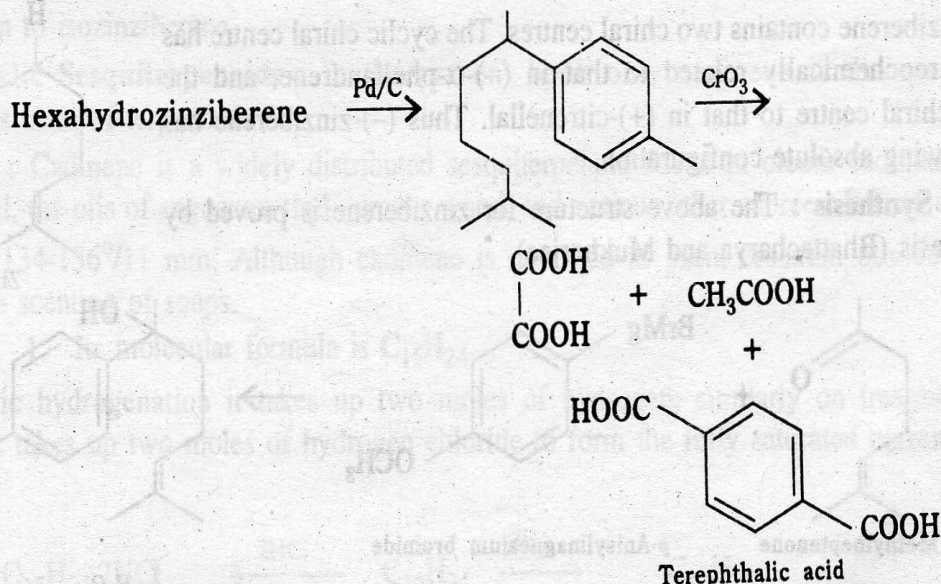
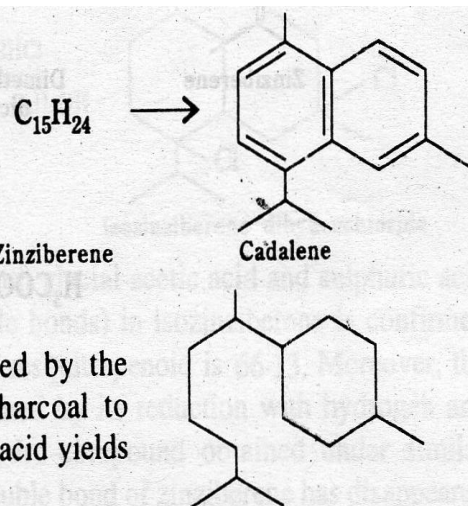


Furthermore, the dihydrozinziberene has molecular refraction value as 68.37 which is similar to calculated value (68.25) of dihydrozinziberene on the assumption that the latter has two isolated double bonds; and hence dihydrozinziberene must be having two isolated double bonds and is produced by the reduction of one of the conjugated double bonds of zinziberene.

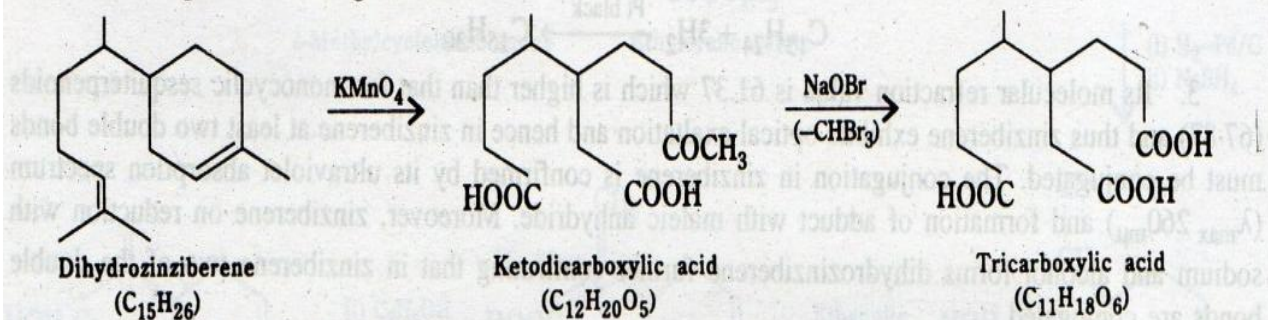
4. Zinziberene of dehydrogenation forms cadalene which gives insight about the carbon skeleton of zinziberene.

5. Zinziberene, on ozonolysis, gives the same products as obtained by bisabolene, viz. acetone, laevulinic acid and succinic acid, indicating that the former has the same skeleton as the latter; and thus ignoring the position of the double bonds the carbon framework drawn on side may be assigned to zinziberene.

The above carbon skeleton of zinziberene is confirmed by the dehydrogenation of hexahydrozinziberene over palladised charcoal to 6-*p*-tolyl 2-methylheptane<sup>1</sup>, I, which on oxidation with chromic acid yields acetic, oxalic and terephthalic acids.

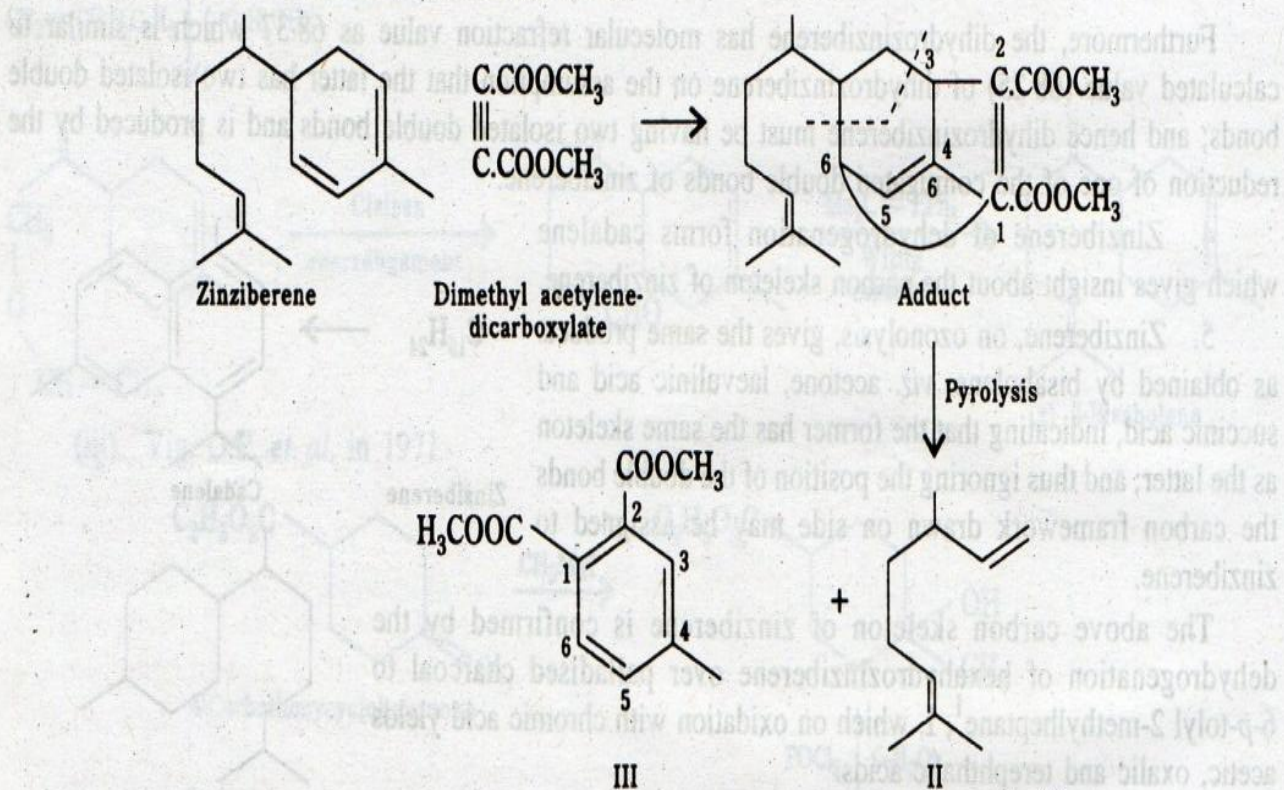


6. Now as acetone is formed as one of the products during ozonolysis, one of the double bonds must be present as isopropylidene group. Further the dihydrozinziberene, obtained by the sodium-ethanolic reduction of zinziberene, on potassium permanganate oxidation gives a ketodicarboxylic acid,  $C_{12}H_{20}O_5$  which on further oxidation with sodium hypobromite forms a tricarboxylic acid,  $C_{11}H_{18}O_6$ , along with bromoform, indicating that the ketodicarboxylic acid has a  $-COCH_3$  group. Hence the dihydrozinziberene must be having the following structure.





7. The position of the third double bond is established by the formation of 2, 6-dimethylocta-2, 7-diene, II and methyl-4-methylphthalate, III by the pyrolysis of the adduct of zinziberene with dimethyl acetylene dicarboxylate (Eschenmoser *et al.* 1950).



Zinziberene contains two chiral centres. The cyclic chiral centre has been stereochemically related to that in  $(-)\text{-}\alpha\text{-phellandrene}$ , and the acyclic chiral centre to that in  $(+)\text{-citronellal}$ . Thus  $(-)\text{-zinziberene}$  has the following absolute configuration.

8. **Synthesis :** The above structure for zinziberene is proved by its synthesis (Bhattacharya and Mukherjee).

