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MAYURONE, A C_{14}-SESQUITERPENE KETONE*

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The presence of a crystalline, tricyclic sesquiterpene ketone, mayurone (m.p. 69.5 - 70°, $[\alpha]_D^{30}$ +253.4° in $CHCl_3$) in the essential oil of 'mayur pankhi' has been reported earlier[1]. We now find it to be a nor-ketone ($C_{14}H_{20}O$) and report on its structure.

Mayurone shows in its PMR spectrum[2] signals for the presence of three methyls (all quaternary, 3H singlet at 40, 68 and 80 cps) and two vinyl protons (an AB quartet centred at 345.5 cps with J_{AB} = 10 cps and $J_{AB}/\delta_B - \delta_A$ = 0.3). In the IR (Nujol) spectrum, it displayed bands for: C=O 1671; C=CH, 1640 (shoulder), 870 cm^{-1}.

Mayurone on hydrogenation (PtO_2, EtOH) gives a dihydroderivative (m.p. 106°, $[\alpha]_D$ +75.4°) which gives no colour with tetranitromethane. As expected, the PMR spectrum of the dihydroderivative showed no vinyl proton signals and, still displayed the presence of only three methyls (3H singlets at 38, 68 and 73 cps). Thus, the olefinic linkage in mayurone must be <u>cis</u>-disubstituted and the 870 cm^{-1} band in its IR spectrum must be assigned to this

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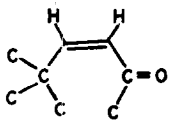
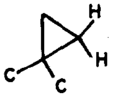
linkage[3]. Mayurone, thus, must contain the grouping I.

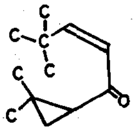
The UV spectrum of mayurone, at first sight, appeared to be in conflict with its being an αβ-unsaturated ketone, as it failed to display a maximum in the expected region (~237 mμ). However from the high end absorption of the UV spectrum (ϵ_{230}^{EtOH} , 7641) it was suspected that the λ_{max}^{EtOH} 217 mμ (ϵ, 11160) shown by mayurone might, in fact, be a summation peak of two absorptions. This was confirmed by the observation that dihydromayurone showed a maximum ~ 210 mμ (ϵ_{210} 6825) and by the substraction of the dihydromayurone absorption from that of mayurone, a substraction curve, showing λ_{max} 225 mμ (ϵ, 7843), was obtained.



I

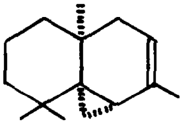


II

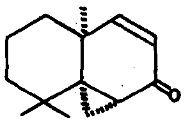


III

The chromophere present in dihydromayurone can reasonably be assigned to the conjugation of a cyclopropane ring with the carbonyl. This would appear to be supported by the occurrence of signals at 46, 50, 58 and 63 cps (~2H) in the PMR spectrum of mayurone and, which can be assigned to a methylene group in a cyclopropane ring. Compelling evidence for the presence of a cyclopropane ring was obtained as follows. Catalytic hydrogenation (PtO_2, AcOH; an uptake of ~ 3.2 mol. eq. of H_2) furnished a saturated alcohol (m.p. 112-113°), besides a mixture of saturated hydrocarbons. The PMR spectrum of this alcohol shows the presence of four quaternary methyls (48, 61, 61 and 64 cps); likewise, the major saturated hydrocarbon, isolated by preparative GLC, displays four quaternary methyl signals (46, 55, 60 and 65 cps) in its PMR spectrum. These results require the presence of grouping II in mayurone and in view of the splitting pattern of the cyclopropane methylene protons (which appears to be the AB part of an ABX system) and the previous conclusions, partial structure III follows for mayurone.



IV



V

The data presented, so far, require that either mayurone must possess an hitherto unknown sesquiterpene carbon-framework or else be a C_{14}-ketone[4], thus accounting for the presence of only three methyl groups. In view of the presence of thujopsene (IV)[5], as the main sesquiterpene hydrocarbon, in the 'mayur pankhi' oil, a nor structure based on IV became suggestive. Recently Nozoe et al[6] prepared V by the degradation of thujopsene and a sample of this compound, obtained by the courtesy of Prof.S.Ito[7], established its identity (IR, mixed m.p.) with mayurone. Thus, the absolute stereostructure of mayurone is established as V. Of the various pathways for the biogenesis of mayurene from thujopsene, the one simulating the laboratory degradation[6] appears to be especially attractive.

REFERENCES

1 G.L.Chetty and Sukh Dev, Tetrahedron Letters 73(1964).

2 All PMR spectra were measured in 10-20% solutions in CCl_4 on a Varian A-60 spectrometer; the signals are recorded in cps from tetramethylsilane as zero.

3 It must be pointed out that a vinylidene linkage on a strained system displays $\delta_{=CH_2}$ around 875 cm^{-1}.

4 This was first suggested by Prof. R.B.Bates and we are grateful to him for a stimulating discussion.

5 T. Norin, Acta. Chem. Scand. **17**, 738 (1963).

6 T. Nozoe, H. Takeshita, S. Ito, T. Ozeki and S.Seto, Chem. Pharm. Bull. (Tokyo) **8**, 936 (1960).

7 While supplying a sample of this compound, Prof.S. Ito kindly informed us that he has isolated this compound from *Thujopsis dolabrata* and it was mutually agreed to publish it simultaneously in the Tetrahedron Letters.