

THE STRUCTURE OF THE NEW DITERPENE HYDROCARBON ISOLATED FROM THE ESSENTIAL OIL OF THE WOOD OF *ERYTHROXYLON MONOGYNUM* ROXB.—PART II

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In an earlier paper (Gupta and Muthana, *J. Indian Inst. Sci.*, 1954, 36A, 76), while reporting the examination of the essential oil obtained from the wood of *Erythroxylon monogynum* Roxb., the presence of a new diterpene hydrocarbon had been recorded. The present paper deals with some aspects of the investigations on the structure of this hydrocarbon, and on the basis of the experimental evidence obtained a provisional structure (I) has been proposed.

The hydrocarbon has the following physical constants : b.p. 149–50° C./1.5 mm. ; d_{28}^{28} 0.9647 ; n_D^{28} 1.5155 ; $[\alpha]_D^{27}$ +18 ; $[R_L]_D$ 85.33. The molecular weight (270.3) and elemental analysis indicate that the compound has the molecular formula $C_{20}H_{32}$. The molecular refractivity (85.33) points out the presence of four rings with one double bond. The presence of one double bond was further confirmed with perbenzoic acid titration. The dibromide of the compound, m.p. 155–56° C. mol. wt. (417.2), further supports the presence of one double bond only.

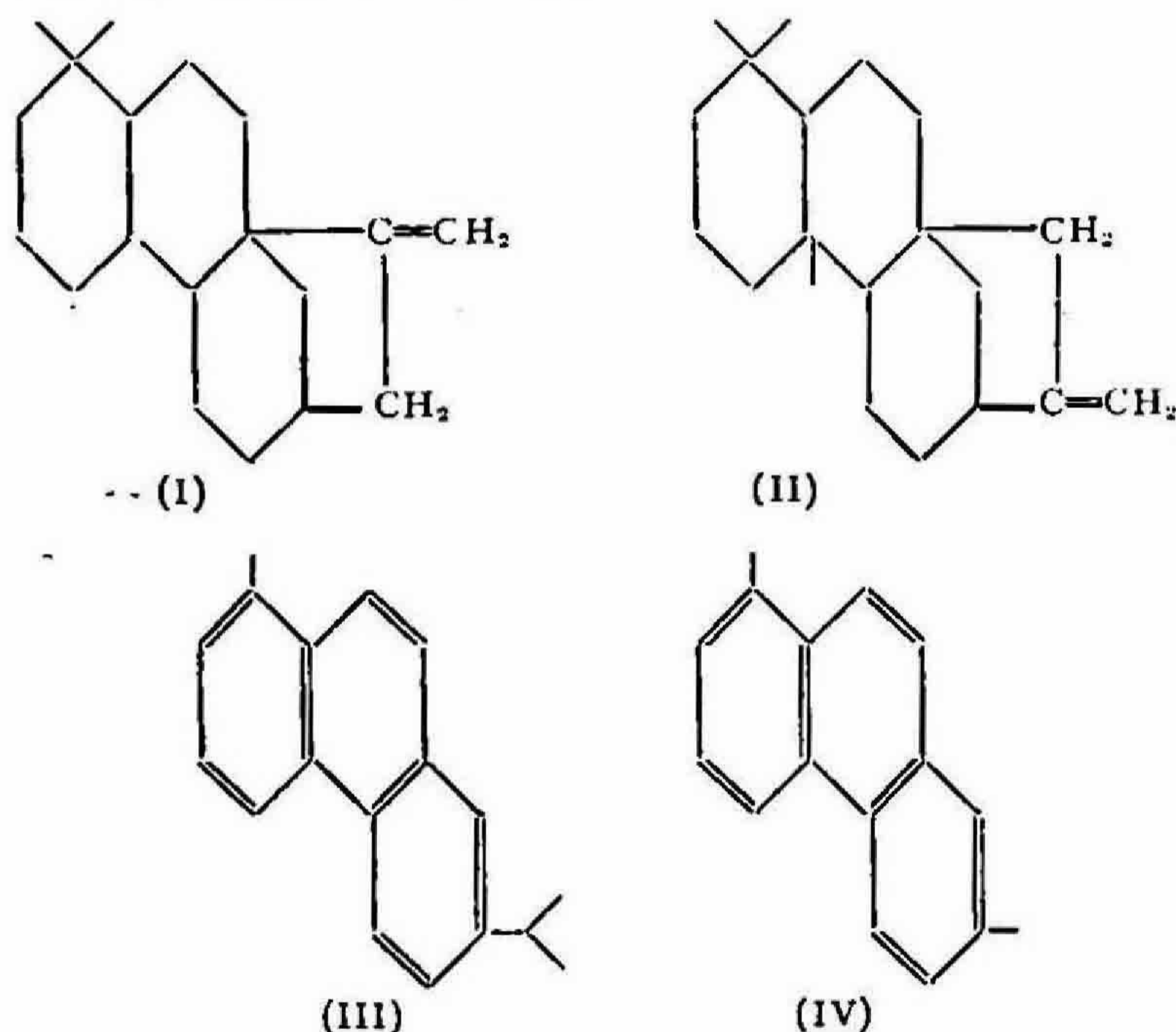
On ozonolysis of the diterpene hydrocarbon, formaldehyde was detected by its dimedone derivative, m.p. 188° C., indicating the presence of exocyclic double bond. The ozonised product after decomposition and purification was found to be a saturated ketone ; b.p. 160–70° C./1 mm. The ozonised compound did not give any test for aldehyde, acid or methylketo group. The combustion values indicate that the ketone has the formula $C_{19}H_{30}O$. Semicarbazone of the ketone was obtained as an amorphous powder and all attempts to get it in a crystalline form failed ; m.p. Ca, 153–54° C.

The hydrocarbon, on dehydrogenation with selenium, furnished pimanthrene, m.p. 85° C., and a non-picrate forming liquid which was not further investigated. Pimanthrene was characterised by its picrate, m.p. 128° C. (cf. pimanthrene picrate, m.p. 127° C. Beath, *J. Soc. Chem. Ind.*, 1933, 52, 122)

338), styphnate (m.p. 158–59° C.) (cf. pimanthrene styphnate, m.p. 159° C.; Ruzicka and Balas, *Helv. Chim. Act.*, 1923, 6, 677) and T.N.B. compound, m.p. 156–7° C. (cf. T.N.B. compound of pimanthrene, m.p. 155° C., Harris and Sandersons, *J. Am. Chem. Soc.*, 1948, 70, 3870).

The colour test with sulphuric acid and acetic anhydride was characteristic of diterpene hydrocarbons.

All the experimental facts stated above can be satisfactorily explained by the formula (I) for the diterpene hydrocarbon. On the basis of similar experimental evidence Brandt (*Am. Che. Abs.*, 1939, p. 551) has proposed the structure (I) and (II) for phyllocladene. It was observed that phyllocladene gave both retene (III) and pimanthrene (IV) on dehydrogenation with selenium. The formation of retene is better explained by the formula (II) for phyllocladene. The exclusive formation of pimanthrene (IV) on dehydrogenation of the diterpene hydrocarbon investigated by us, points towards the validity of the formula (I) for it.



Further work is in progress to substantiate these investigations and will form the subject of future communication.

EXPERIMENTAL

Physical constants and combustion values.— d_{28}^{28} 0.9647; n_D^{28} 1.5155; $[\alpha]_D^{27}$ +18; $[R_L]_D$ 85.33. mol. wt. [Found : 270.3; (by cryoscopic method), $C_{20}H_{32}$ requires 272]. Found : C, 88.06; H, 11.8; $C_{20}H_{32}$ requires C, 88.23; H, 11.77 per cent.

Estimation of double bonds.—The presence of one double bond was determined by perbenzoic acid method. The value obtained after one hour being 1.030 and after 24 hours 1.1.

Ozonolysis.—Ozone was bubbled through a solution of the diterpene hydrocarbon (10 g.) in carbon tetrachloride for 8 hours, till the solution showed no yellowish-brown coloration with tetranitromethane. The escaping gases were absorbed in a trap containing water and cooled in ice. Formaldehyde was detected by its dimedone derivative (m.p. 188° C.) in the water solution of the trap. Carbon tetrachloride was removed from the ozonised solution by suction with the water pump. The ozonide was decomposed by first gently warming with water (250 c.c.) and then heating for six hours on boiling water-bath. A viscous liquid separated, which was extracted with ether. After drying the ether extract over anhydrous sodium sulphate, ether was removed and the ketone purified by distilling under reduced pressure, b.p. 160–70° C./1 mm. (pale yellow). (Found: C, 83.6; H, 11.06; $C_{19}H_{30}O$ requires C, 83.20; H, 10.95 per cent.). Semicarbazone of the ketone was prepared in the usual manner and crystallised from dilute alcohol in amorphous powder; m.p. Ca, 153–4° C. (Found: N, 12.56; $C_{20}H_{33}N_3O$ requires N, 12.688).

Dehydrogenation.—The diterpene hydrocarbon (10 g.) was dehydrogenated with selenium (17 g.) by heating at 300–50° C. for 60 hours. The dehydrogenated product was extracted with benzene and after removing the solvent, was purified by repeatedly distilling over sodium. Pimanthrene (0.5 g.) was isolated after cooling in ice and crystallised from alcohol, m.p. 85° C. (Found: C, 93.29; H, 6.86; $C_{16}H_{14}$ requires C, 93.2; H, 6.8 per cent.). Picrate, m.p. 128° C., styphnate, m.p. 159° C. T.N.B. compound, m.p. 156–7° C.

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