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STRUCTURE OF DIOSPYRIN*

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The isolation of diospyrin from Diospyros montana Roxb. has been reported by earlier workers (1), but no definite structural proposals have been made, except that it could be a bis-1:4-naphthoquinone derivative. In this present investigation, diospyrin was obtained as orange red cubes, m.p. 286-288°. It shows an UV absorption spectrum typical of 1:4-naphthoquinones. The presence of two phenolic hydroxyl groups is shown by the formation of a dimethylether, $C_{24}H_{18}O_6$, m.p. 330°, and a diacetate, $C_{26}H_{18}O_8$, m.p. 160°. Reductive acetylation yields a crystalline hexaacetate $C_{34}H_{30}O_{12}$ (mol. wt. by mass spectrum) leading to the molecular formula $C_{22}H_{14}O_6$ for diospyrin itself.

Oxidation of diospyrin dimethyl ether with alkaline hydrogen peroxide yields an acid, giving a crystalline anhydride identical with 2-methoxy-4-methyl phthalic anhydride by comparison with an authentic sample. This proves the orientation of the methyl and hydroxyl groups on the benzenoid rings and

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* Contribution No.53

also that dimerisation should have occurred at positions on the quinonoid rings of the molecule.

Additional support for the above conclusions is provided by the NMR spectrum of diospyrin leucohexaacetate ($CDCl_3$, 60 Mc) which shows the presence of

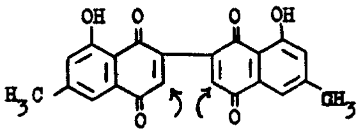
i) two aromatic methyl singlets at δ 1.9 and 2.0

ii) six singlets at δ 2.25, 2.3, 2.35, 2.45, 2.5 and 2.55 ascribed to the six acetoxyl methyl protons

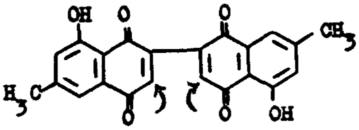
iii) two aromatic hydrogen singlets at δ 6.9 and 7.35

iv) four doublets at δ 7.15, 7.25, 7.5 and 7.75 ($J = 2\text{-}3$ cps) ascribed to two pairs meta-oriented aromatic protons.

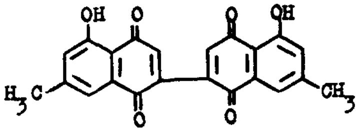
The absence of any signals for ortho-coupled protons would rule out the possibility of dimerisation: a) between the quinonoid and a second benzenoid position of the two naphthoquinone rings; b) between two benzenoid positions of the two naphthoquinone rings. These observations suggest that diospyrin could have one of the following three structures, (I), (II) and (III).



I



II



III

The leucoacetate derived from structure I could be symmetrical whereas that from structure II could be unsymmetrical. The protons marked with arrow could be expected to have identical chemical shifts in the leucoacetate derived from I, whereas in reality they have quite different chemical shifts at δ 6.9 and 7.5. If this difference was not due solely to inhibition of rotation about the central bond, the NMR evidence would favour (II) as the most probable structure for diospyrin.

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Reference

1) R.S. Kapil and M.M. Dhar, J.S.I.R., 20B, 498 (1961).