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STRUCTURE OF DIOSPYRIN

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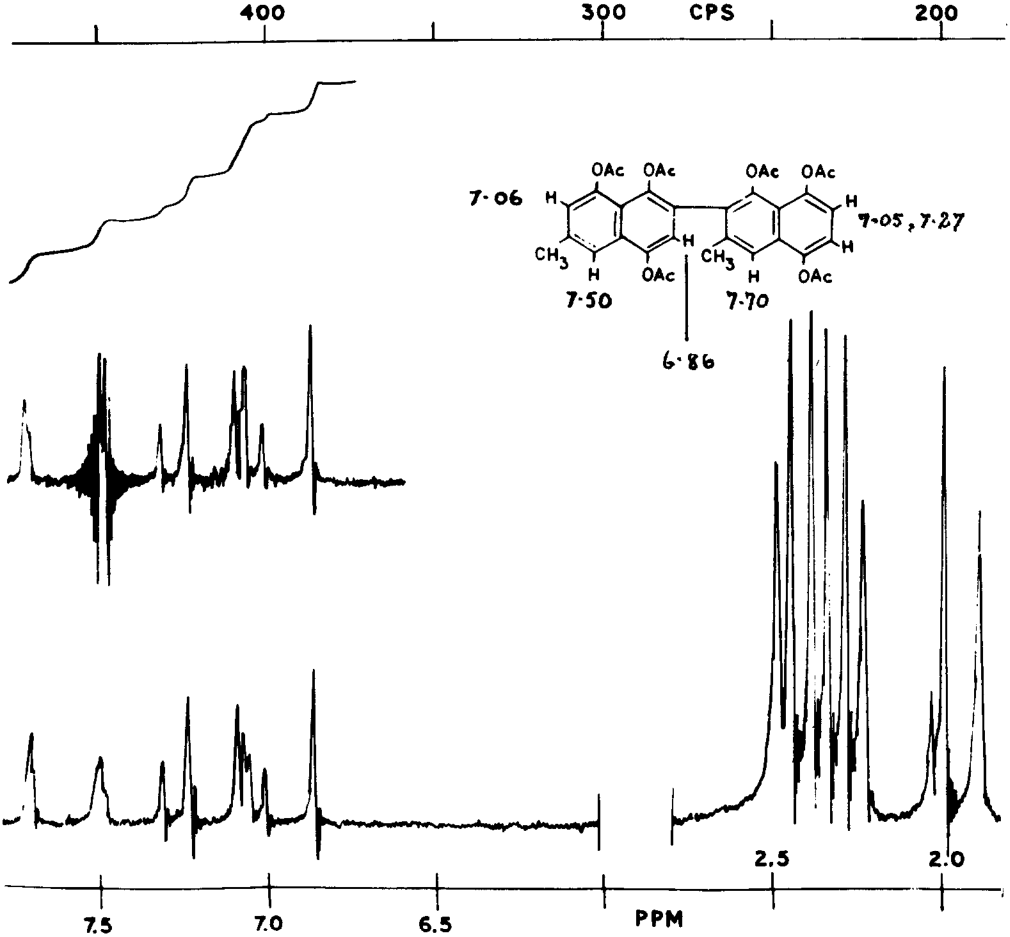
Diospyrin ($C_{22}H_{14}O_6$) was first isolated by R.S. Kapil and M.M. Dhar (1) and assigned structure (I) by A.K. Ganguly and T.R. Govindachari (2). Our results clearly show that it has structure (II). Whether the linkage is between C-2 and C-6′ or C-3 and C-6′ cannot yet be decided. Our conclusions are based on the following findings.

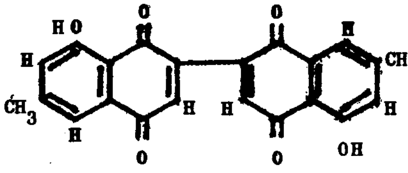
(i) The P.M.R. spectra of diospyrin (CF_3CO_2H; 60 Mc) and its dimethyl ether (III) ($CDCl_3$; 100 Mc) show the presence of <u>three</u> vinylic protons. The two C-methyl groups have different chemical shifts as also the two methoxy methyls in the dimethyl ether. In contrast, dianellinone (IV) has the same chemical shifts for its two C-methyl groups (3).

(ii) The P.M.R. spectrum of diospyrin leucohexaacetate, m.p. 225° (fig. 1; $CDCl_3$; 100 Mc) clearly shows the presence of two <u>ortho</u>-coupled protons. These can also be seen in the 60 Mc spectrum, but the two side limbs are rather small and can be confused with the background noise.

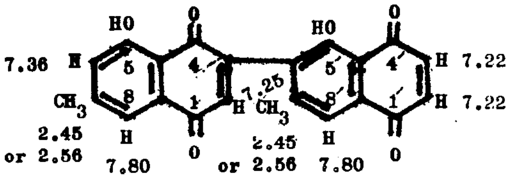
FIG. 1



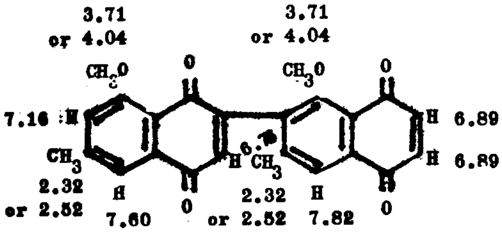
(iii) Oxidation of diospyrin with alkaline H_2O_2 gives a mixture of two acids which can be separated by preparative paper chromatography. One of these, m.p. 235-237°, is identical with a synthesised sample of isococchinillic acid (V), (4). The second acid on treatment with diazomethane gives a ether-ester identified as (VI) by its P.M.R. and mass spectra (M.W. 238; main fragments m/e 207, 175, 148, 89).



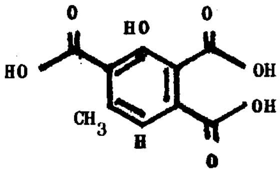
I



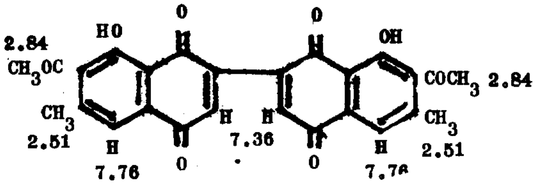
II



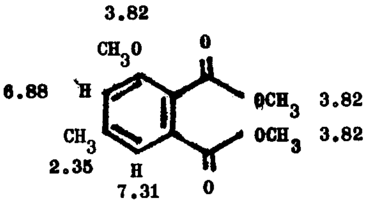
III



V



IV



VI

Chemical shifts in δ = ppm relative to TMS as internal standard

A further alternative structure for diospyrin, in which the methyl and hydroxyl are interchanged is ruled out in so far as the two hydroxyl groups in diospyrin occupy peri positions as indicated by its I.R. spectrum, (no OH band; CO bands at 1660 and 1632 cm^{-1}, unbonded and bonded respectively).

The dimethyl ether of diospyrin, (CO band at 1650 cm^{-1}) prepared by shaking it with methyl iodide and silver oxide in chloroform at room temperature, crystallises in yellow needles, m.p. 256° from petroleum ether/methylene chloride; (M.W. 402 by mass spectrum; found C 71.70 H 4.46 O 23.70 %; $C_{24}H_{18}O_6$ requires

C 71.63 H 4.51 O 23.86 %; 2 OCH_3 groups by P.M.R. spectroscopy).

Kapil and Dhar (1) methylated diospyrin by refluxing it with methyl sulphate and potassium carbonate in dioxane and obtained a red methyl ether m.p. 230 . Ganguly and Govindachari also prepared this red methyl ether and their structure of diospyrin is based on the oxidation of this compound. Diospyrin is unstable to alkali and we suspected the red methyl ether to be a rearrangement product. We also prepared it by the same method (1) and our suspicion was confirmed when its mass spectrum showed it to have M.W. 416. It has thus three methoxy groups [$C_{22}H_{11}O_3(OCH_3)_3$]. T.L.C of the crude product showed the presence of the compound III also. We will comment on its structure in a subsequent publication.

Our diospyrin is identical with that of Ganguly and Govindachari (2) as shown by direct comparison with a sample kindly supplied by Prof. Govindachari. Diospyrin has been isolated in our laboratory from Diospyros chloroxylon also, where it co-occurs with 7-methyl juglone (5).

We would like to thank Dr. U. Scheidegger, Varian A.G., Zurich for the 100 Mc P.M.R. spectra, Dr. B.C. Das, Institut de Chemie des Substances Naturelles, Gif, Paris for the mass spectra, and Dr. S.K. Pradhan for helpful discussions.

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