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THE STRUCTURE OF THE SO CALLED RED "METHYL ETHER" OF DIOSPYRIN

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The structure of diospyrin (I) has recently been established by us (1). We showed during the course of this work that diospyrin dimethylether (II) is a yellow compound (m.p. 256°) and that the red compound (m.p. 320°) reported by Kapil and Dhar (2) and by Govindachari and Ganguli (3) to be the dimethylether of diospyrin has a molecular weight of 416. Hence it must be a trimethylether of a rearrangement product formed by the action of alkali on diospyrin.

To get an insight into its structure it was necessary to (a) assign the chemical shifts (3.71 and 4.04)* between the two methoxyl groups of diospyrin dimethylether (II), and (b) to prepare the two possible monomethylethers (III and IV) of diospyrin (I).

The chemical shifts of the methyl and methoxyl groups of 7-methyl-5-methoxy-1,4-naphthaquinone are 2.48 and 4.00 respectively. The 7-methyl and 5-methoxyl groups of II can respectively be expected to have nearly the same chemical shifts and the signals at 2.52 and 4.04 in the P.M.R. spectrum of II can, therefore, be assigned to the 7-methyl and 5-methoxyl groups respectively. It follows that the signals at 2.32 and 3.71 in II must be due to the 7'-methyl and 5'-methoxyl groups respectively. This significant shielding of the 7'-methyl and 5'-methoxyl groups is to be expected, if the two naphthaquinone moieties occupy roughly perpendicular planes in the preferred conformation thereby bringing the 7'-methyl and 5'-methoxyl within the shielding zone of the trisubstituted quinone ring.

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* all chemical shifts are in δ = ppm relative to TMS as internal standard.

The two diospyrin monomethylethers (III and IV) were prepared by partial methylation of diospyrin with methyl iodide and silver oxide and separated by elution with chloroform on a silica gel column.

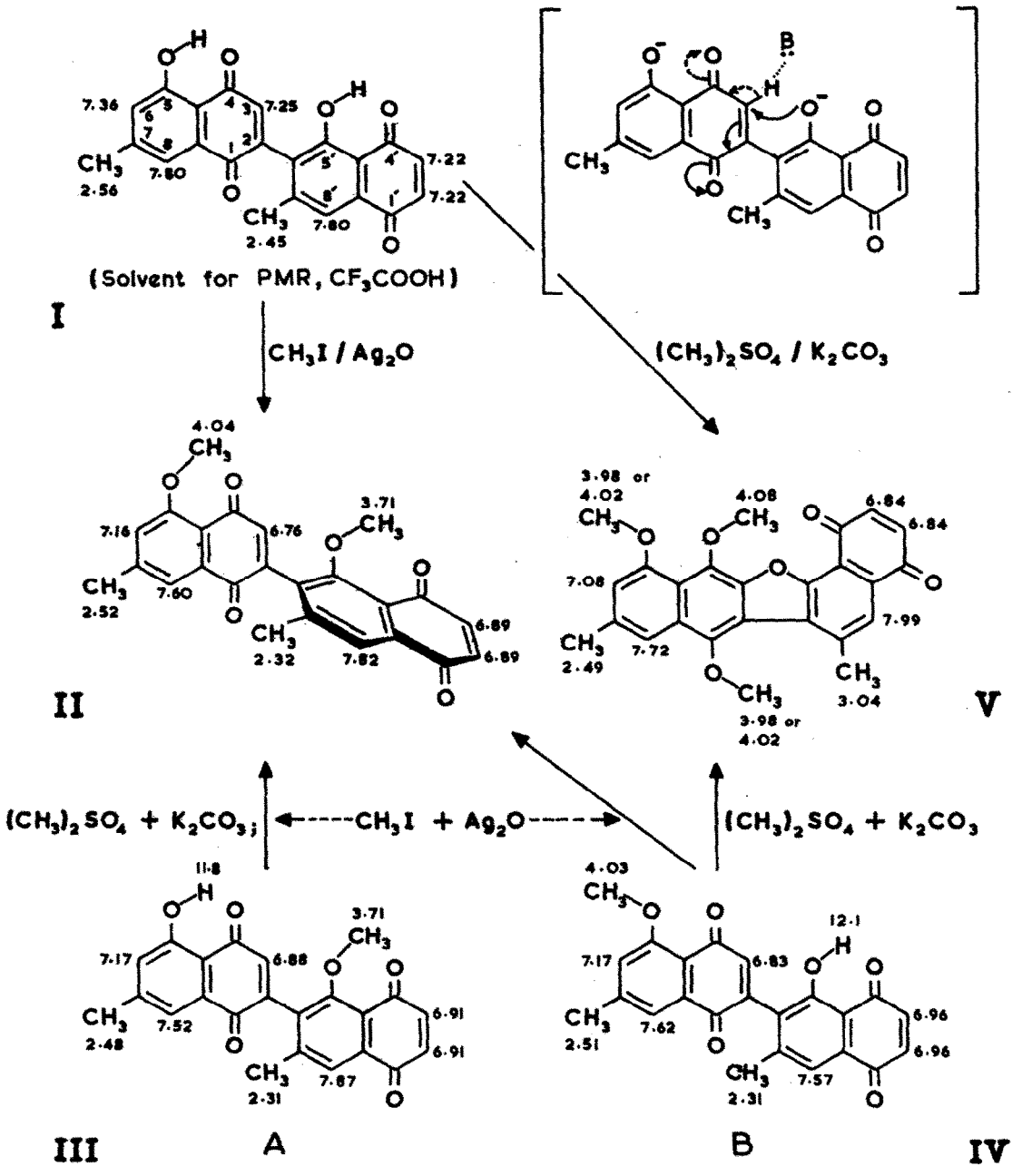
Monomethylether 'A': Orange-red plates m.p. 244°; found C 71.09 H 4.42; $C_{23}H_{16}O_6$ requires C 71.13 H 4.15 %; one OCH_3 group by P.M.R. spectroscopy; I.R. 1650 cm^{-1} and 1630 cm^{-1}; U.V. $\lambda_{max}^{dioxane}$ 216, 252, 362 and 427 (log ϵ 4.6, 4.4, 3.9 and 3.6).

Monomethylether 'B': Yellow crystals m.p. 257-8°; found C 70.50 H 4.36; one OCH_3 group by P.M.R. spectroscopy; I.R. 1650 cm^{-1} and 1630 cm^{-1}; U.V. $\lambda_{max}^{dioxane}$ 216, 252 and 416 (log ϵ 4.6, 4.3 and 3.0).

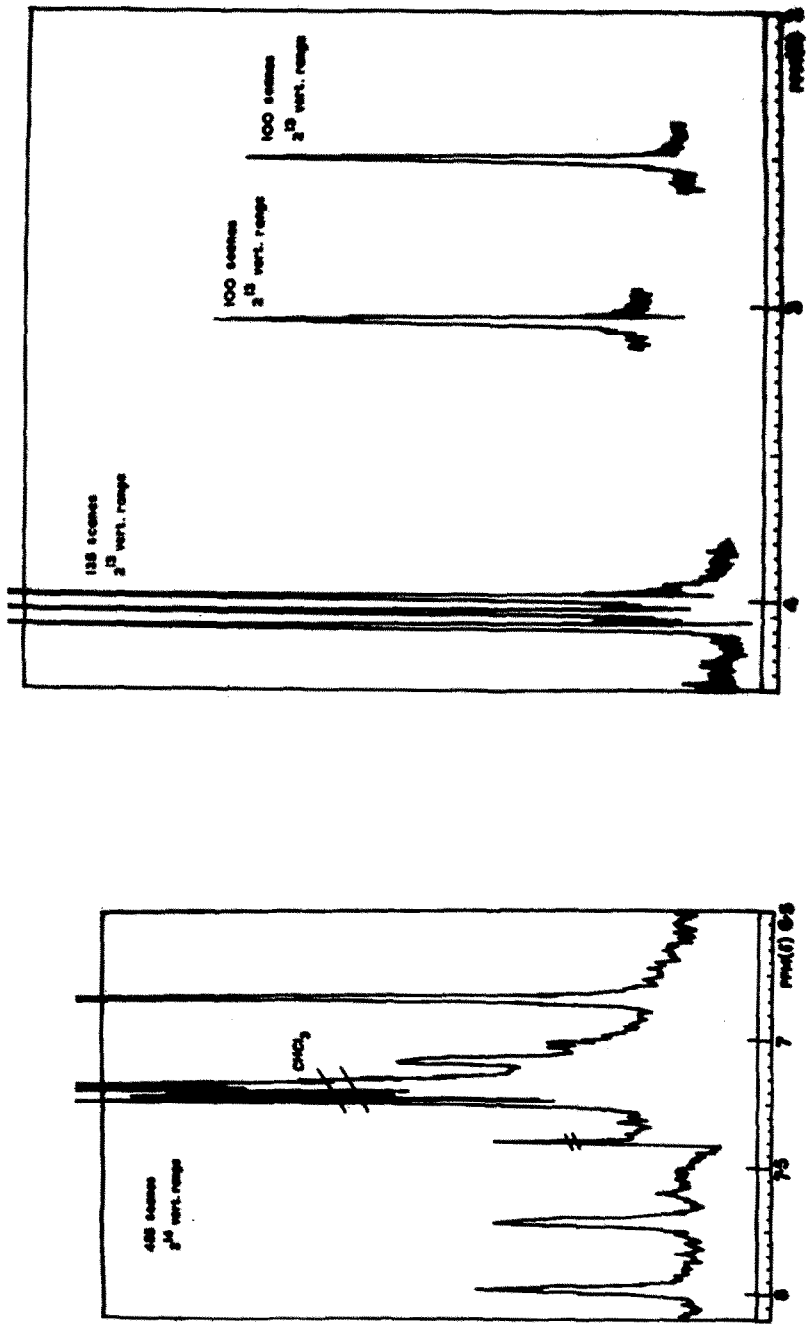
The methoxyl group of monomethylether 'B' has the chemical shift 4.03 and 'B' would, therefore, have structure (IV); structure (III) can be assigned to the monomethylether 'A' in which the methoxyl has the chemical shift 3.71.

Both the monomethylethers on treatment with methyl iodide and silver oxide yield the yellow dimethylether (II). But on methylation with methyl sulphate and potassium carbonate, only the monomethylether 'A' (III) gives (II). Monomethylether 'B' (IV) gives the red compound (V) (m.p. 330°). The formation of the red compound, therefore, requires the 5'-OH to be free. The anion formed from this hydroxyl by the action of base can presumably add intramolecularly at the β-position of the $\alpha:\beta$-unsaturated carbonyl part of the quinone ring. The addition should be facile as it leads to the formation of a five-membered ring. Subsequent enolization followed by methylation of the resulting hydroquinone leads to structure (V) having three methoxyl groups and a molecular weight of 416. found C 71.2, 71.5 H 4.83, 4.92 O 22.4 OCH_3 21.1 ; $C_{22}H_{11}O_3(OCH_3)_3$ requires C 72.10 H 4.84 O 23.06 OCH_3 22.34 %.

The physical evidence given below is in complete accord with the proposal that the red compound has structure (V). The U.V. spectrum of this red compound, $\lambda_{max}^{dioxane}$ 220, 231, 276 290, 349 and 427 (log ϵ 4.3, 4.32, 4.55, 4.00, 3.65 and 3.55) resembles that of trimethylisodianellinone (4) $\lambda_{max}^{dioxane}$ 272, 295, 358 and 470 (log ϵ 4.73, 4.16, 3.62 and 3.79). The I.R. spectrum indicates the absence of hydrogen bonded quinone carbonyls, the $-\overset{|}{C}=O$ stretching absorption being seen at 1670 and 1650 cm^{-1}, but with diminished intensity compared to I and II. No peak for a hydroxyl group is seen.



Scheme 1. Chemical shifts (δ=ppm) shown alongside the protons. Solvent $CDCl_3$ except for I



100 Mc N.M.R. spectrum of the "red compound"(V) in $CHCl_3$; repetitive scanning with Sat 1004

In the P.M.R. spectrum of the red compound (V) (100 Mc; $CDCl_3$)* only two vinylic protons are seen as a singlet at 6.84. There are only three other protons attached to aromatic rings. One gives a downfield signal at 7.99 and is obviously the peri-proton at 8' position. The other two are the meta-coupled protons at 7.08 and 7.72. There are signals for three methoxyls at 3.98, 4.02 and 4.08. [The 4.08 signal can probably be assigned to the C-4 methoxy group, which is deshielded by the furan oxygen; compare Methylated Laccaic Acid III (5)]. The two methyl groups resonate at 2.48 and 3.03. The downfield methyl group at 3.03 compares well with the methyl group at 2.97 in 9-methyl anthracene (6). "Inside" methyl groups in condensed aromatic systems are known to be highly deshielded by proximate aromatic rings (7).

Alternative structures for all compounds, in Scheme 1, where the linkage between the two halves of the diospyrin molecule is between C-3 and C-6', cannot be ruled out.

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