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THE STRUCTURE OF XANTHORRHOEIN

A.J.Birch, M.Salahud-Din and D.C.C.Smith
Department of Chemistry, The University, Manchester.

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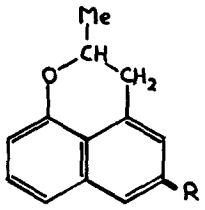
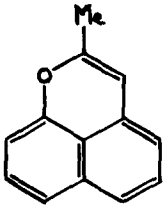
The neutral crystalline substance Xanthorrhoein, $C_{14}H_{14}O_2$, m.p.68-69°$[\alpha]_D^{13}$+55.6° (10% in benzene), from the resin of Xanthorrhoea Preisii,[1] and Xanthorrhoea reflexa,[2] contains one O-methyl,[1] one C-methyl,[3] no carbonyl or hydroxyl[1] and is not oxidised by potassium permanganate in acetone, nor reduced by catalytic hydrogenation over palladium.[3] Structural elucidation has been hindered because isolation of Xanthorrhoein could not be repeated,[3] and owing to scarcity of material further work has been limited to a micro-scale, but enables us now to propose structure I.

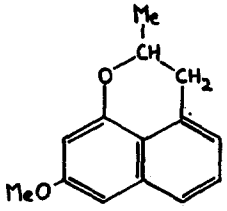


I R = OMe

VI R = H



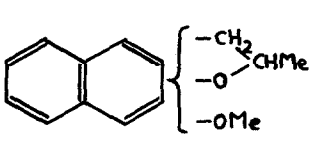
VII



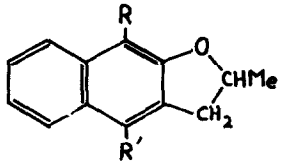
VIII

1. E.H.Rennie, W.T.Cooke and H.H.Finlayson, J.Chem.Soc. 117, 338 (1920).
2. H.H.Finlayson, J.Chem.Soc. 2763 (1926).
3. A.J.Birch and P. Hextall, Austral.J.Chem. 8, 263 (1955).

The ultraviolet spectrum [λmax 225,244,287,298,323,338 mμ (4.70,4,44,3.67,3.64,3.40,3.49)] indicates a naphthalene nucleus, and closely resembles the spectra of the dimethoxynaphthalenes (1,2-;1,3-;1,6-;and 1,7-) having one α and one β methoxyl, rather than the other isomers. Cleavage of the ether ring by potassium amide in ammonia, and catalytic hydrogenation to saturate the resulting ethylenic group, gave a crude naphthol. This was shown to contain a normal- rather than an iso-propyl side-chain, by partial oxidation with chromic acid, which afforded acetic, propionic, and butyric acids detectable by paper chromatography. Taken together with the presence of one C-methyl, this indicates the partial structure II.



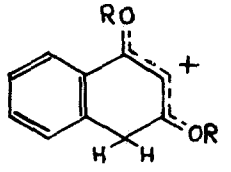
II



III R = R' = H

IV R = H,R' = OMe

V R = OMe,R' = H.



IX

The proton magnetic resonance spectrum confirms this position for the methyl on the heterocyclic ring: the methyl produces a doublet at τ 8.5 (J 7 c/s), the methylene a doublet at τ 7.0 (J 7 c/s), and the methine a multiplet at τ 5.7. 2,3-Dihydro-2-methylnaphtho-[2,3-b]furan(III),[4]

4. P.Emmott and R.Livingstone, J.Chem.Soc.4629 (1958).

and its 4- and 9-methoxy derivatives (IV and V respectively) were synthesised for comparison. In these compounds the bands attributable to the aliphatic ring protons are octets at τ 7.0,6.8 and 7.0 respectively from the methylene, and the multiplets at τ 5.2,5.2 and 5.3 respectively from the methine. Thus the methine band of Xanthorrhoein occurs at a significantly higher field, and the methylene band shows a strikingly different multiplicity than in compounds III - V; in compounds III - V these three protons constitute a typical ABX system, whereas in Xanthorrhoein they form a simpler A_2X system. This could arise if the heterocyclic ring were six-membered in Xanthorrhoein, and hence of greater conformational mobility. Accordingly, 2,3-dihydro-2-methyl-1-oxaphenalene (VI) was synthesised for comparison; it was obtained by catalytic hydrogenation of 2-methyl-1-oxaphenalene (VII).[5] Its spectrum strikingly resembles that of Xanthorrhoein: the methylene protons produce a doublet at τ 7.0 (J 7 c/s) and the methine proton produces a multiplet at τ 5.7.

Confirmation that Xanthorrhoein is a derivative of 1-oxaphenalene is found in the observation that two of the protons on the aromatic nucleus form an AB system (τ 3.0,3.2), and hence one of the naphthalene rings is disubstituted. Furthermore their coupling constant (2.5 c/s) is characteristic of protons in a meta relationship, so that only structures I and VIII need be considered for Xanthorrhoein.

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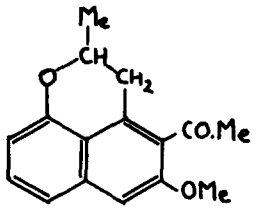
5. S.O'Brien and D.C.C.Smith, J.Chem.Soc.2907 (1963).

1,3-Dimethoxynaphthalene and compound IV give stable cations in cold sulphuric acid [λmax 265,336, mμ (4.11,4.16) and λmax 272,355 mμ (4.02,4.19) respectively], presumably due to C-protonation as in structure IX. Xanthorrhoein fails to show this behaviour, resembling in this respect 1,6-dimethoxynaphthalene, and so can be assigned structure I.

We have isolated from the weakly acidic fraction of the resin of X.Preisii, after methylation and chromatography, a substance $C_{16}H_{16}O_3$, m.p.124-125°, $[\alpha]_D^{20}$ + 127°(0.13% in $CHCl_3$), λmax 225,252,290,340 mμ (4.69,4.44,3.67,3.41). This has one O-methyl (singlet at τ 6.1), one C-acetyl (ν max 1695 cm^{-1} in CS_3, singlet at τ 7.5), one other C-methyl (doublet at τ 8.5, J 7 c/s), one methylene (unsymmetrical triplet at τ 7.0), and one methine group (multiplet at τ 5.8). The close correspondence with Xanthorrhoein makes it very likely that this substance is also a derivative of 2,3-dihydro-2-methyl-1-oxaphenalene. Furthermore, one of the protons on the aromatic nucleus gives rise to a singlet, τ 3.0, and no AB systems are present, so that the O-methyl and C-acetyl groups are attached to the same ring. The differing multiplicity of the bands due to the methylene group in Xanthorrhoein and in the acetyl compound could be due to the proximity of a hindered acetyl group that is not co-planar with the aromatic nucleus in the latter compound. Structure X is tentatively suggested as being consistent with these facts,



X

and with the probable biosynthesis from acetate of both Xanthorrhoein and the acetyl compound.

We are indebted to the Colombo Plan for a Scholarship (to M.S.). Dr. H.Duewell has informed us that he also has proposed a structure for Xanthorrhoein.