The Constitution and Synthesis of Obtusaquinone, a New Quinone Methide

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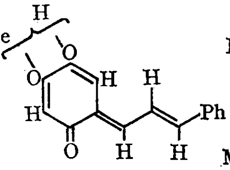
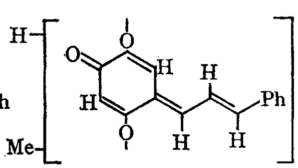
THE natural quinone methides[1] cover a range of structural types. We now describe a new type of *para*-quinone methide exemplified by obtusaquinone isolated from the heartwood of *Dalbergia obtusa*[2,3] Lecomte.

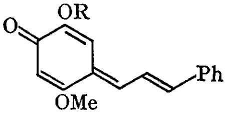
Obtusaquinone, $C_{16}H_{14}O_3$, was obtained as red needles, m.p. 155°, and its colour and absorption spectra [λ_{max} in EtOH 253 (ϵ 7060), 268 (ϵ 7270), 399 mμ (ϵ 43,800); ν_{max} 1605, 1600, 1580 cm.$^{-1}$] suggested a quinonoid structure; the failure to reduce obtusaquinone with sodium dithionite and the u.v. absorption ruled out a simple benzoquinone structure. The n.m.r. spectrum of obtusaquinone showed the presence of a phenyl group and three additional, highly-deshielded low-field olefinic protons [τ 2·4—3·0 (m, 8H)], two uncoupled (therefore 1,4-related) quinonoid protons [τ 3·16 (s, 1H), τ 4·13 (s, 1H)], a methoxy-group [τ 6·15(s, 3H)], and a hydroxy-group [τ 3·10 (broad s, 1H)]. This spectroscopic evidence suggested that obtusaquinone was an *o*- or *p*-benzoquinone methide derivative of partial structure (I) or (II).

(I)

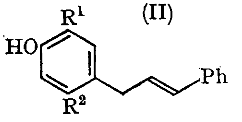




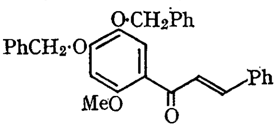
(II)



(III) R=H (IV) R=Me



(V) $R^1=R^2=OMe$
(VII) $R^1=OH$, $R^2=OMe$
(VIII) $R^1=R^2=H$
(IX) $R^1=H$, $R^2=OMe$



Methylation (methyl iodide–potassium carbonate) of obtusaquinone gave a monomethyl ether and catalytic hydrogenation (10% Pd–C, EtOH) of obtusaquinone gave a tetrahydro-derivative characterised by conversion into 3-(2,4,5-trimethoxyphenyl)-1-phenylpropane. The *p*-quinone methide structure (II) was shown to be correct by the synthesis of obtusaquinone monomethyl ether (IV) from the oxidation of violastyrene[2] (V) with lead dioxide in benzene. Finally, obtusaquinone was shown to have structure (III) by synthesis. The chalcone (VI), synthesised by the condensation of 4,5-dibenzyloxy-2-methoxyacetophenone with benzaldehyde, was reduced with lithium aluminium hydride–aluminium chloride to the cinnamylphenol (VII) which on oxidation with lead dioxide in benzene gave obtusaquinone (III).

The structural relationship between obtusaquinone (III) and the cinnamylphenols, obtusastyrene (VIII) and obtustyrene (IX), that are also found in *D. obtusa*,[2] shows that this new type of natural quinone methide may be considered[4] as a biogenetic oxidation product of a cinnamylphenol.

The stability of the quinone methides (III) and (IV) is not unexpected since they are vinylogues of the stable 7-aryl-*p*-quinone methides.[5]

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