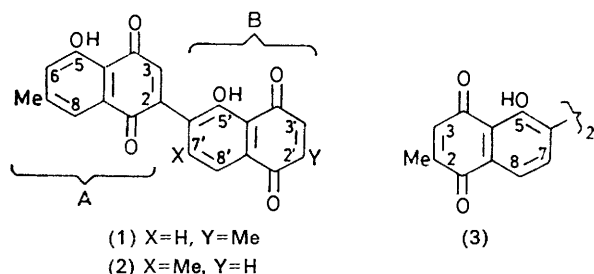


Ebenaceae Extractives. Part 6.¹ Ehretione, a Bisnaphthoquinone derived from Plumbagin and 7-Methyljuglone

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Ehretione (1), isolated from *Diospyros ehretioides*, is the first example of a natural quinone which contains both plumbagin and 7-methyljuglone units.

In the course of separating the pigments² of the wood of *Diospyros ehretioides* Wall we have obtained a new bisnaphthoquinone, C₂₂H₁₄O₆, for which we propose the name 'ehretione' and the structure (1). Ehretione undergoes little fragmentation in the mass spectrometer but the formation of ions with *m/e* 134 and 106 suggests¹ that it contains a 7-methyljuglone unit. The n.m.r. spectrum confirms this, the signals at δ 2.46, 7.11, 7.51, and 11.86 resembling closely those¹ from unit A of diospyrin (2). The OH chemical shift (δ 11.86) indicates³ that unit A of ehretione carries an aryl group at C-2, and the remaining signals establish that this substituent is a plumbagin unit, as in structure (1). Thus the signals at δ 2.23 and 6.85 resemble closely those shown by the methyl and olefinic protons of elliptinone (3), and the



position of the AB quartet centred at δ 7.63 and 7.73 resulting from the aryl protons at C-7' and C-8' is similar to that (δ 7.73) of the singlet produced by the corresponding protons of elliptinone. The δ value (12.44) of the C-5' hydroxy-proton signal of ehretione is considerably higher than that calculated³ (δ 12.22) on the basis of the observed shift (δ 12.11) for the corresponding

hydroxy-proton of diospyrin. We attribute this anomaly to the absence of a methyl group at C-7' of ehretione, which results in a decrease in the twisting of the bisnaphthoquinone system. Both the enhanced mesomeric effect of the quinonoid substituent at C-6' and the proximity of the C-1 carbonyl group would help to deshield the hydroxy-proton.

EXPERIMENTAL

Ehretione (5,5'-Dihydroxy-2',7-dimethyl-2,6'-bisnaphthoquinone) (1).—The band located between lupeol and mamegakinone in the thin-layer chromatogram² of the soluble material from *Diospyros ehretioides* afforded a solid which crystallised from light petroleum to give *ehretione* (5 mg) as orange needles, m.p. 232° (decomp.) (Found: *M*, 374.0785. C₂₂H₁₄O₆ requires *M*, 374.0790), ν_{\max} (KBr) 1665 and 1642 (quinone C=O and hydrogen-bonded quinone C=O), and 1602 cm⁻¹ (C=C), λ_{\max} (EtOH) 431 nm (log ϵ 3.41), λ_{inf} 245 nm (log ϵ 3.89), δ (CDCl₃) 2.23br (3 H, s, 2'-CH₃), 2.46 (3 H, s, 7-CH₃), 6.85br (1 H, s, H-3'), 7.07 (1 H, s, H-3), 7.11br (1 H, s, H-6), 7.51br (1 H, s, H-8), 7.63 and 7.73 (2 H, ABq, *J* 8 Hz, H-7' and -8'), 11.86 (1 H, s, 5-OH), and 12.44 (1 H, s, 5'-OH), *m/e* 374 [100%, (*M*)⁺], 346 [9%, (*M* - CO)⁺], 187 [6%, (*M*)²⁺], 134 (5%), and 106 (5%).

Elliptinone showed δ (CDCl₃) 2.22br (6 H, s, 2- and 2'-CH₃), 6.86br (2 H, s, H-3 and -3'), 7.73 (4 H, s, H-7, -7', -8, and -8'), and 12.48 (2 H, s, 5- and 5'-OH).

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¹ Part 5, T. J. Lillie, O. C. Musgrave, and D. Skoyles, *J.C.S. Perkin I*, 1976, 2155.

² O. C. Musgrave and D. Skoyles, *J.C.S. Perkin I*, 1974, 1128.

³ T. J. Lillie and O. C. Musgrave, *J.C.S. Perkin I*, in the press.