

Diosquinone, a Naphthoquinonylnaphthoquinone Epoxide

By TERENCE J. LILLIE, OLIVER C. MUSGRAVE,* and RONALD H. THOMSON

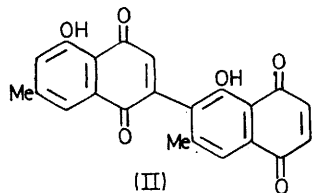
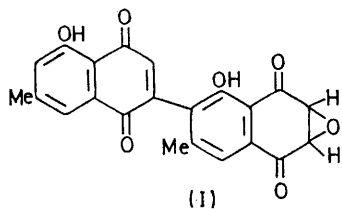
(Chemistry Department, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland)

Summary Diosquinone, previously thought to be 8-hydroxy-1,2-naphthoquinone, is an enantiomer of diospyrin epoxide (I).

DIOSQUINONE, which occurs in the bark of *Diospyros tricolor* Hiern, was formulated as 8-hydroxy-1,2-naphthoquinone in 1955 by Nogueira Prista.¹ This structure lacks the methyl group which is characteristic² of the naphthoquinones present in *Diospyros* species and we have now

established that the pigment is, in fact, the naphthoquinone epoxide (I).

Diosquinone, m.p. 200—200.5°, has the molecular formula C₂₂H₁₄O₇, and undergoes fragmentation in the mass spectrometer with the initial loss of an oxygen atom. Its i.r. spectrum shows bands at 1698, 1665—1645 and 1642 cm⁻¹ typical of aryl ketone, quinone and hydrogen-bonded aryl ketone, and hydrogen-bonded quinone carbonyl groups, respectively. It gives n.m.r. signals corresponding to two *peri*-hydroxy, three aromatic, one quinonoid, six methyl, and two methine protons. The last-named appear as an



AB quartet centred at δ 4.02 and 3.98 (J 3.5 Hz) having the same chemical shifts and coupling constant (in CDCl_3) as the methine protons in 5-hydroxy-1,4-naphthoquinone 2,3-epoxide.³ Treatment of diosquinone with zinc, sodium iodide, and sodium acetate in acetic acid⁴ removes the epoxide group and affords diospyrin (II), so establishing the relationship between the two compounds. The epoxidation of diospyrin using sodium perborate³ gave a product whose spectral properties in solution are identical with those of diosquinone but whose m.p. (236°, decomp.) is considerably higher. As diosquinone is optically active ($[\alpha]_D^{22} -106^\circ$) and exhibits circular dichroism it must be one of the two enantiomers represented by structure (I), while synthetic diospyrin epoxide is the corresponding racemic compound.

(Received, 16th May 1973; Com. 693.)

¹ L. Nogueira Prista, *Anais. Fac. Farm. Porto*, 1955, **15**, 73; see also R. Paris and L. Prista, *Ann. pharm. franç.*, 1954, **12**, 375; L. Nogueira Prista, *Anais. Fac. Farm. Porto*, 1954, **14**, 67; L. Nogueira Prista and H. Romeira Prista, *ibid.*, p. 91.

² R. H. Thomson, 'Naturally Occurring Quinones', 2nd edn., Academic Press, London, 1971.

³ A. Raschid and G. Read, *J. Chem. Soc. (C)*, 1967, 1323.

⁴ J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 1959, 112.