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BATOCANONE, A NEW NAPHTHOQUINONYLNAPHTHOQUINONE EPOXIDE

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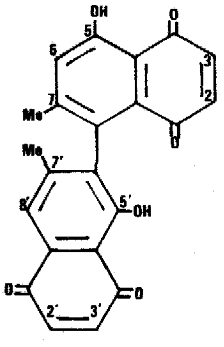
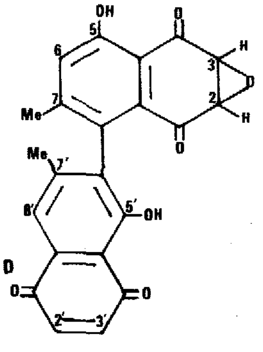
Batocanone is the second naphthoquinonyl-naphthoquinone epoxide to be isolated from higher plants, its structure corresponding to isodiospyrin 2',3'-epoxide.

In the course of separating the pigments of the root bark of Diospyros batocana Hiern we have obtained a new bisnaphthoquinone, $C_{22}H_{14}O_7$, for which we propose the name batocanone and structure (III). It has M^+390, m.p.127-130°C., ν_{CO} 1725, 1670-1652, 1645 cm^{-1}, λmax (MeOH)258(log ε 4.39), 306(sh)(log ε 3.64), 374(log ε 3.82) and 444(sh) nm (log ε 3.32). These spectral characteristics show that the substance has aryl ketone (normally 1700-1680 cm^{-1}, in this case shifted to 1725 cm^{-1} by the α-epoxide), quinone, hydrogen-bonded aryl ketone and hydrogen-bonded quinone carbonyl groups, and that the light absorption differs from the common peri-hydroxy-naphthoquinones in the absence of a maximum in the visible region, consistent with structure (III).

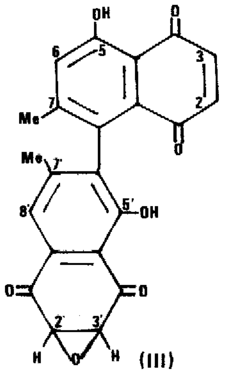
The M.W. of batocanone corresponds to a dimeric bismethyljuglone plus 16 mass units. However a naphthazarin derivative can be excluded on the basis of its visible absorption (1). The m.s. shows that batocanone loses methyl (m/e 375, 45.5%) and hydroxyl (m/e 373, 9.5%) radicals and a water molecule (m/e 372, 5%), and that it undergoes little direct cleavage of the quinonoid rings (m/e 362, 6.5%, M^+-CO; m/e 334, 3.5%, M^+-2CO). The absence of peaks at m/e 135, 134 and 106, which only arise from fragmentation of internal quinonoid rings, means that batocanone must be a dimeric naphthoquinone of the arene-to-arene type (2). Furthermore, the molecular ion loses one oxygen atom (m/e 374, 28%), an indication that it contains an epoxide function. Both this and the fact that the general pattern of batocanone fragmentation in the mass spectrometer closely resembles that of isodiospyrin (I)(3) show that it must be an epoxide of this dimeric naphthoquinone. So, as batocanone has M.W. 390, it follows that it corresponds to one of the mono-epoxides (II) or (III).



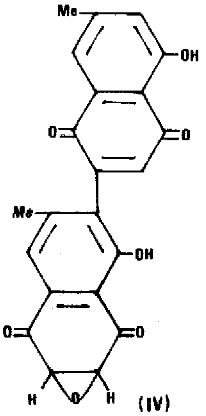
(I)



(II)



(III)



(IV)

TABLE N.m.r. signals for isodiospyrin and batocanone

Assignment	Isodiospyrin*(I)	Batocanone (III)
H-2	6.72,d, J=10	6.65,d, J=10
H-3	6.91,d, J=10	6.89,d, J=10
H-6	7.30,s	7.28,s
7-CH_3	2.03,s	2.04,s
5-OH	12.40,s	12.36,s
H-2'	6.94,s	4.02,d, J=3.5
H-3'	6.94,s	3.97,d, J=3.5
7'-CH_3	2.01,s	2.01,s
H-8'	7.60,s	7.56,s
5'-OH	12.02,s	11.40,s

Spectra run in $CDCl_3$ at 100MH$_z$. Chemical shifts in δ , using T.M.S. as internal standard.
*Data from reference (3).

The n.m.r. spectrum of batocanone (III) (see TABLE) shows signals for two o - coupled quinonoid protons, forming an AB quartet centred at δ 6.65 and 6.89(J 10H$_z$). Such a quartet is also present in the spectrum of isodiospyrin (I) (see TABLE) as well as in those of all known bisnaphthoquinones having a 7-methyljuglone unit linked via C-8 atom to the other half of their molecules, which is ascribed to the protons at C-2—C-3 (I) (3.4). On the other hand, the 2H signal for the quinonoid protons at C-2'—C-3' present in the isodiospyrin (I) spectrum (δ 6.94) does not appear in the batocanone (III) spectrum, but is replaced by a quartet from two methine protons centred at δ3.94 and 4.02 (J 3.5H$_z$), having practically the same chemical shifts and coupling constant as the methine protons in 5-hydroxy-1, 4-naphthoquinone 2,3-epoxide (5) and in diosquinone (IV) (6).

This clearly indicates that batocanone is isodiospyrin 2',3'-epoxide(III) and as it is optically active $\left[[\alpha]_D^{20} -163° \right]$ and exhibits circular dichroism, it must correspond to one of the enantiomers represented by structure (III). Batocanone is the second naphthoquinonyl-naphthoquinone epoxide to be isolated from Ebenaceae and it occurs in this plant simultaneously with diosquinone, this indicating that such compounds are normal metabolites of these plants, which is of interest from the biosynthetic point of view.

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