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NAPHTHOQUINONE DERIVATIVES FROM *DIOSPYROS* SPP.: BISISODIOSPYRIN, A TETRAMERIC NAPHTHOQUINONE

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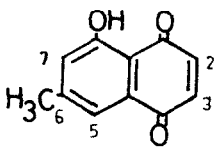
NAPHTHOL and naphthoquinone derivatives have been proved to occur widely in Ebenaceae extractives.[1-5] Our investigations on the constituents of Asian *Diospyros* plants[1] now revealed the presence of a tetrameric naphthoquinone.

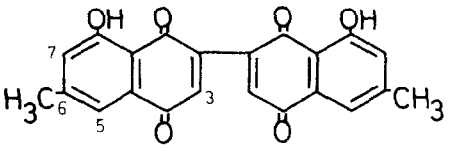
Chloroform extracts of the roots of *Diospyros lotus* L. (Japanese name: mamegaki) afforded, after column and preparative layer chromatographic separation, four naphthoquinones, 7-methyljugulone (I), a quinone of m.p. ca. 256° (decomp.) (II), isodiospyrin[2,3] (IIIa), and a quinone of m.p. > 320° (IVa), besides three triterpenoids, taraxerol, betulinic acid, and oxyallobetulin.[6] The quinone (II), named mamegakinone, was assigned as 8,8'-dihydroxy-6,6'-dimethylbinaphthoquinonyl-2,2' and identified with the sample[1] obtained by the oxidation of diospyrol(V).

The structure (IIIa) of isodiospyrin, m.p. 233°, $[\alpha]_D^{20}$ - 150° (c = 0.27, $CHCl_3$),* was suggested chiefly by the spectral properties.[2,3] Slight ambiguity existed in the assignment of the NMR spectra has now been eliminated by the precise examination of the spectra and the nuclear Overhauser effects(NOE) observed in the dimethyl ether (IIIb). The two quinoid protons at 2' and 3', reported to show equivalent chemical shifts,[2,3] now appear in a pair of doublets (τ 3.08 and 3.13, J = 10 Hz). The NOE observed by the irradiation at the two methyl and the methoxyl protons disclosed the relative positions

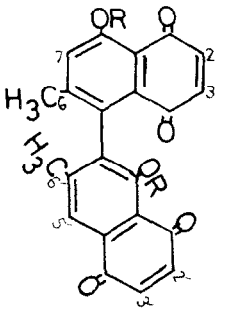
* Although the identity of ours with the authentic sample kindly supplied by Professor R. H. Thomson[3] was firmly established by a mixed fusion, IR, and t.l.c., the $[\alpha]_D$ value is higher than the reported value ($[\alpha]_D^{23}$ - 16.6° ± 1° (c = 0.27, $CHCl_3$)).[3]



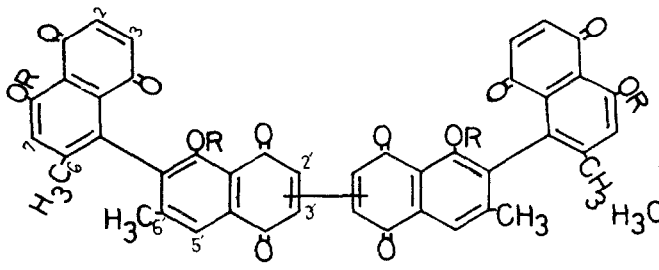
(I)

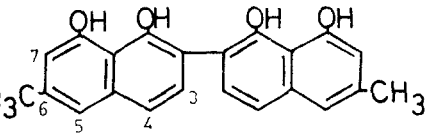


(II)



(IIIa) R: H
(IIIb) R: CH_3





(V)

(IVa) R: H
(IVb) R: CH_3

of those on the aromatic rings. These observations made the assignemnt of the spectra of IIIa and IIIb beyond any doubt as shown in Table 1.

The quinone (IVa), orange prisms of m.p.$>$ 320°, $[\alpha]_D^{21}$ - 678° (c = 0.14, $CHCl_3$), has a molecular formula $C_{44}H_{26}O_{12}$ (M^+ 746.142 m/e, calcd. 746.142), which was also supported by an osmometric determination. Since IVa and its tetramethyl ether (IVb), m.p. 223° (decomp.), show nearly the same UV (IVa, $\lambda_{max}^{CHCl_3}$ 257, 444 mμ (log ε 4.69, 4.25); IVb, $\lambda_{max}^{CHCl_3}$ 260, 405 (log ε 4.87, 4.20)) and IR absorptions(IVa, ν_{KBr} 1658, 1639, 1601 cm^{-1}; IVb, ν_{KBr} 1655, 1583 cm^{-1}) with 7-methyljugulone (I) and isodiospyrin (IIIa) and the methyl ethers,[2,3] IV is assumed to be 7-methyljugulone tetramer from the molecular formula.

The comparison of the NMR spectra of IVa and IVb with those of IIIa and IIIb showed the striking similarity as shown in Table 1 and indicated the symmetrical feature of the molecule of IV. In the spectra of IVa and IVb one of the two signals of the nearly identically situated quinonoid protons in IIIa and IIIb disappears and the other shifts to a lower field

Table 1 NMR Spectra of Naphthoquinones
(τ in $CDCl_3$, 60 MHz)

compound	2-H and 2'-H	3-H and 3'-H	5-H and 5'-H	6-CH_3 and 6'-CH_3	7-H and 7'-H	8-OH or OMe and 8'-OH or OMe
I	3.02 s	3.02 s	2.50 d (J=1.5 Hz)	7.64 s	2.86 d (J=1.5 Hz)	-1.91
II[a]	____	2.82 s	2.37 d (J=0.8 Hz)	7.49 s	2.78 d (J=0.8 Hz)	(----)[c]
IIIa	3.06 d (J=10 Hz)	3.23 d (J=10 Hz)	____	7.95 s	2.65 s	-2.12 and
	3.02 s	3.02 s	2.33 s	7.98 s	____	-2.50
IIIb[b]	3.17 d (J=10 Hz)	3.34 d (J=10 Hz)	____	7.96 s[d]	2.67 s	5.94 s[e]
	3.08 d and (J=10 Hz)	3.13 d (J=10 Hz)[h]	2.13 s	8.01 s[f]	____	6.53 s[g]
IVa[a]	3.04 d (J=10 Hz)	3.22 d (J=10 Hz)	____	7.94 s	2.67 s	(----)[c]
	____	2.91 s	2.27 s	7.94 s	____	(----)[c]
IVb	3.12 d (J=10 Hz)	3.30 d (J=10 Hz)	____	7.93 s	2.66 s	5.93 s
	____	2.95 s	2.05 s	7.99 s	____	6.52 s

(a) in $CDCl_3$ + CF_3COOH

(b) determined at 100 MHz

(c) not observed by the addition of CF_3COOH

(d) The irradiation at the signal decreases the width and increases the area (12 %) of the signal of 7-H proton.

(e) The irradiation decreases the width and increases the area (15 %) of 7-H.

(f) The irradiation decreases the width and increases the area (21 %) of 5'-H.

(g) No effect was observed by the irradiation.

(h) At 60 MHz the signals overlap and appear in a siglet(2H).

(cf. 3-H in I, 3.02τ; 3-H in II, 2.82 τ). All these facts clearly show that the quinone (IVa) must be the dimer of isodiospyrin (IIIa) bonded symmetrically at 2'- or 3'-position, in which 2'-position is more likely from the analogy with other naphthol and naphthoquinone dimers from the same genus.[1-3]

Since the ORD curve of the quinone (IVa) shows the same sign with that of isodiospyrin (IIIa) as shown in Fig. 1, the quinone (IVa) is assumed to be formed by the dimerization of IIIa.

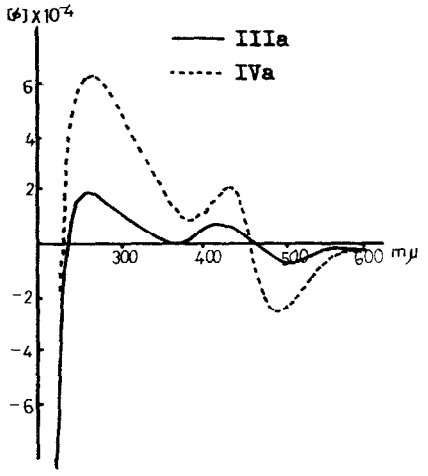


Fig. 1
ORD Curves of Isodiospyrin (IIIa) and Bisisodiospyrin (IVa) (in dioxane)

The quinone (IVa) has also been isolated from the roots of Diospyros japonica Sieb. et Zucc. (Japanese name: shinanogaki) and D. Morrisiana Hance (Japanese name: tokiwagaki) along with isodiospyrin (IIIa).[7] As far as the authors are aware IVa is the first example of a tetrameric quinone isolated as plant constituents.

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