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SHORT COMMUNICATION

A NEW BINAPHTHAQUINONE FROM *DROSERA RAMENTACEA*

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Abstract—The naphthaquinones plumbagin, 7-methyljuglone (ramentacéone) and biramentaceone have been isolated from *Drosera ramentacea*. Biramentaceone is the 2,2′-dimer of 7-methyljuglone.

Peri-hydroxynaphthaquinones occur regularly in the Droseraceae. These include[1] plumbagin (I; R = H), droserone (I; R = OH) and hydroxydroserone (II; R = OH), and very recently Bendz and Lindberg[2] have found 3-chloroplumbagin (I; R = Cl) and 2-methylnaphthazarin (II; R = H) in *Drosera intermedia* and *D. anglica*. We now report the presence of two further quinones in the Malagasian species *D. ramentacea* Burch.

Paris and Delaveau[3] previously isolated a quinone, ramentacéone, $C_{11}H_8O_3$, m.p. 124–125°, from *D. ramentacea* and it seemed to us from its u.v.-vis. absorption and other properties, that it was probably 7-methyljuglone (III). In our hands, extraction of whole plants has yielded four naphthaquinones of which the major product fitted the description[3] of ramentacéone and was identical with 7-methyljuglone. It is probably also a constituent of *D. intermedia* and *D. longifolia*.[2] Another was identified as plumbagin (I; R = H) while the third, biramentaceone, is new.

Biramentaceone, $C_{22}H_{14}O_6$, m.p. 235° (dec.), is isomeric with but (by direct comparison) different from the three dimers diospyrin (V),[4] isodiospyrin (VI)[5, 6] and elliptinone (VII)[6] isolated from *Diospyros* spp. It shows light absorption typical for a juglone [λ_{max} (EtOH) 270, 430 nm; ν_{max} (KBr) 1662, 1639 cm^{-1}], gives a purple colour in alkaline solution [λ_{max} (EtOH/HO$^-$) 550 nm] and is clearly another methyljuglone dimer. The NMR spectrum† is very simple and comprises singlets at τ 7·58 (Ar—CH_3), 3·03 (Q—H) and −1·78 (*peri*-OH) and doublet signals from *meta*-coupled aromatic protons centred at τ 2·55 and 2·92 (*J*, *ca.* 2 Hz). Biramentaceone is therefore a symmetrical dimer of 7-methyljuglone, the two halves being linked by a carbon–carbon bond between the quinonoid rings, i.e. the structure must

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† 100 MHz in $CDCl_3$. The spectrum was too weak for satisfactory integration but the intensities were of the right order by visual inspection.

[1] R. H. THOMSON, *Naturally Occurring Quinones*, Butterworths, London (1957).

[2] G. BENDZ and G. LINDBERG, *Acta Chem. Scand.* **22**, 2722 (1968).

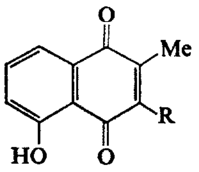
[3] R. PARIS and P. DELAVEAU *Ann. Pharm. Franç.* **17**, 585 (1959).

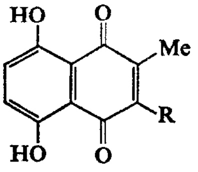
[4] R. S. KAPIL and M. M. DHAR, *J. Sci. Ind. Res.* (*India*) **20b**, 498 (1961); G. S. SIDHU and M. PARDHASARADHI, *Tetrahedron Letters* 1313 (1967).

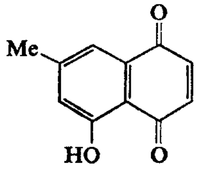
[5] G. S. SIDHU and K. K. PRASAD, *Tetrahedron Letters* 2905 (1967).

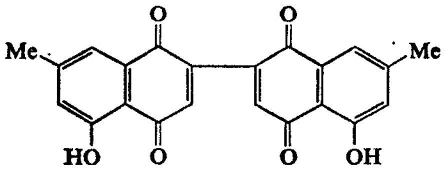
[6] A. L. FALLAS and R. H. THOMSON, *J. Chem. Soc.* (*C*) 2279 (1968).

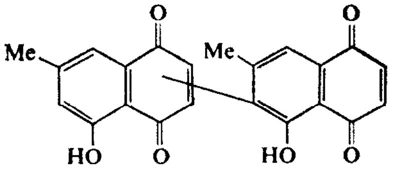
be (IV) or (VIII). On this basis the fragmentation shown on p. 1593 would be expected on electron impact by analogy with previous experience.[6,7] All these ions are, in fact, represented in the mass spectrum (intensities and metastable peaks as indicated) together with peaks at *m/e* 359 (3) (M—Me), 357 (26) (M—HO), 331 (2) (M—Me—CO), 303 (5) (M—Me—2CO) and *m/2e* 187 (12), providing appropriate agreement with the mass spectra[6] of (V), (VI) and (VII). The absence of a doublet at M-54 and M-56 confirms that both quinonoid rings are substituted,[7] and the absence of ions *a* and *b* and their decomposition products rules out all other dimeric structures involving an internuclear link to a benzenoid ring.

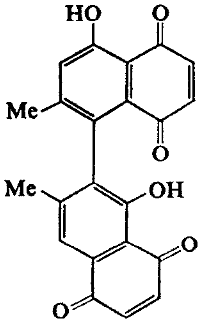

(I)

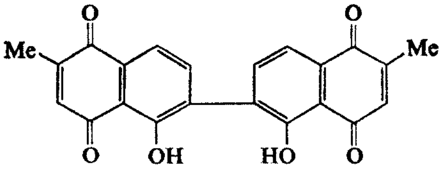

(II)

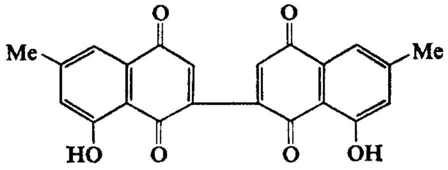

(III)


(IV)


(V)


(VI)


(VII)


(VIII)

Thus the mass spectrum confirms that biramentaceone is either (IV) or (VIII). The latter has previously been obtained[8] by oxidation of diospyrol (IX) and its u.v., i.r. and NMR* spectra are virtually the same as those of biramentaceone. However, (VIII) has m.p. 253° and direct comparison by TLC showed that it differed slightly in R_f from biramentaceone and hence we conclude that the new quinone has structure (IV). This suggests that the

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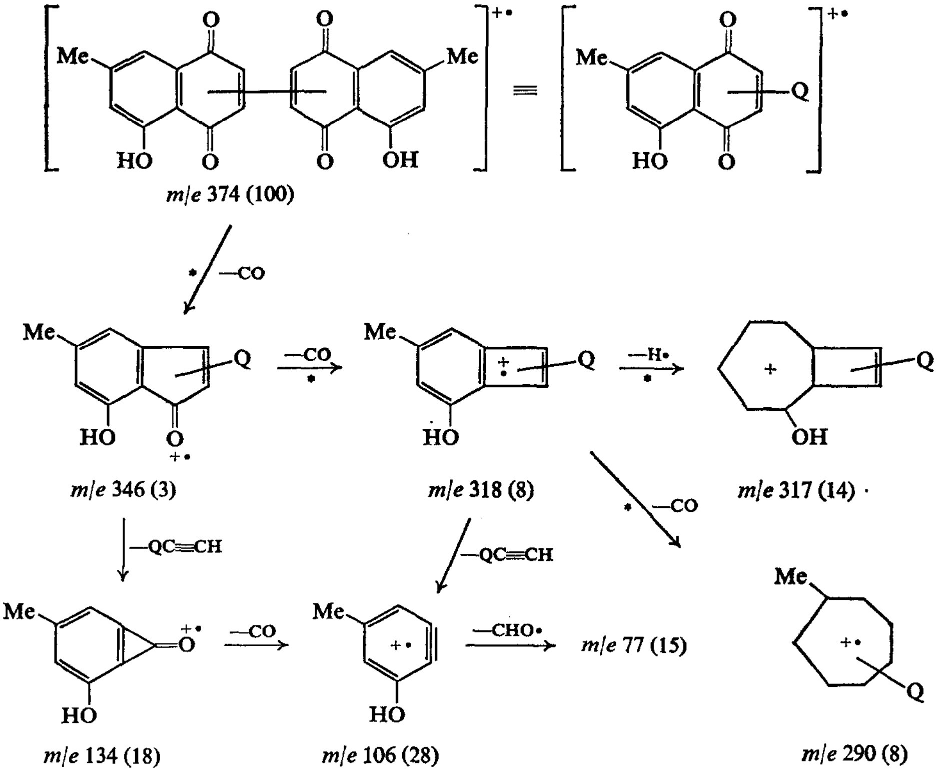
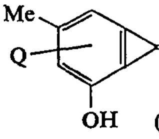
* Allowing for solvent shifts.

[7] J. H. BOWIE, D. W. CAMERON and D. H. WILLIAMS, *J. Am. Chem. Soc.* **87**, 5094 (1965).

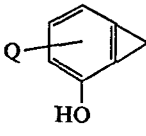
[8] K. YOSHIHARA, S. NATORI and P. KANCHAPEE, *Tetrahedron Letters* 4857 (1967).

dimerization step takes place *in vivo* not at the naphthalenediol stage as (presumably) in the biogenesis of diospyrol (IX) but at the naphthalenetriol level, i.e. after the formation of the

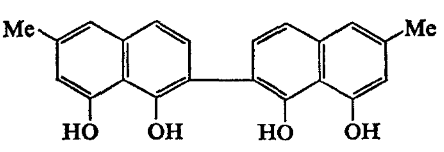




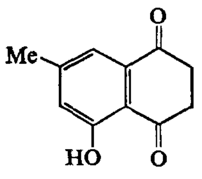
(*a*)
m/*e* 320



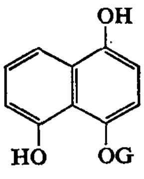
(*b*)
m/*e* 306



(IX)



(X)



(XI)

quinol of 7-methyljuglone. The latter occurs as its diketo tautomer (X) along with (III) in *Diospyros ebenum*[9] while juglone itself exists in *Juglans regia* as the quinol-4-β-D-glucoside

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[9] R. G. Cooke and H. Dowd, *Australian J. Sci. Res.* 5A, 760 (1952).

(XI).[10] A fourth quinone, not obtained pure, appeared to be very similar to methylnaphthazarin.

EXPERIMENTAL

Plumbagin and 7-methyljuglone were identified by direct comparison (i.r., u.v., TLC) with authentic specimens.

Dried *Drosera ramentacea* plants (500 g) were ground and extracted with petroleum ether (b.p. 60–80°) and then $CHCl_3$, the quinones being mainly in the latter. The residue from the $CHCl_3$ extract was chromatographed on a column of silica gel eluting with petroleum ether containing increasing proportions of benzene. Appropriate fractions were further purified by TLC. *Biramentaceone* was isolated from a fraction eluted with benzene alone, rechromatographed on silica gel plates (containing 3% oxalic acid) in benzene–$CHCl_3$, and finally crystallized from MeOH–$CHCl_3$ in orange-yellow rods, m.p. 235° (dec.) (7 mg), λ_{max}^{EtOH} 215, 270, 430 nm (log ϵ 4·54, 4·32, 3·85), $\lambda_{max}^{EtOH/OH^-}$ 550 nm (log ϵ 3·97), λ_{max}^{KBr} 1662, 1640 cm^{-1}.(Found: M, 374·07924. $C_{22}H_{14}O_6$ required: M, 374·07903.)

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[10] C. DAGLISH, *Biochem. J.* **47**, 452 (1950); W. RUELIUS and A. GAUHE, *Annalen* **571**, 69 (1951); N. F. HAYES and R. H. THOMSON, *J. Chem. Soc.* 904 (1955).