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EUCLEIN: A NEW BINAPHTHAQUINONE FROM *EUCLEA PSEUDEBENUS*

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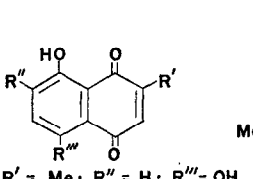
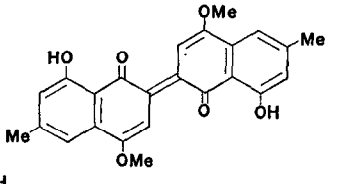
Key Word Index—*Euclea pseudebenus*; Ebenaceae; naphthaquinones; euclein; 7-methyljuglone; 2-methylnaphthazarin.

Abstract—7-Methyljuglone, 8,8′-dihydroxy-4,4′-dimethoxy-6,6′-dimethyl-2,2′-binaphthyl-1,1′-quinone, 2-methylnaphthazarin, mamegakinone and euclein have been isolated from *Euclea pseudebenus*. Euclein is the 3,6′-dimer of 7-methyljuglone.

THE GENUS *Diospyros* (Ebenaceae) has been extensively investigated for naphthaquinones but the other genera of this family are practically unexplored. Nevertheless, 2-methylnaphthazarin has been detected in *Euclea lanceolata* E. Mey. ex DC.[1] and Yoshihira *et al.* identified 8′-hydroxyisodiospyrin in *Maba buxifolia*.[2] We now report on the naphthaquinones in the Angolan species *Euclea pseudebenus* E. Mey. ex DC. This is a shrub growing in the South of Angola in Moçamedes, Maiombe and Giraul, and in the Porto Alexandre area, where it is known by the vernacular names of 'mumboto', mundine', 'musema' and 'amuzena'.[3] Its fruit, with an agreeable acidic taste, is edible and the heart-wood is black, being well suited for carved ornaments.



(I) $R' = Me$; $R'' = H$; $R''' = OH$
(III) $R' = R''' = H$; $R'' = Me$



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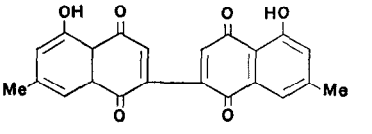


(IV)

RESULTS AND DISCUSSION

Extraction of the powdered roots of *E. pseudebenus* yielded five naphthaquinones. The first afforded red crystals, m.p. 179–180° from benzene, and was identified as 2-methylnaphthazarin (I) by comparison with an authentic sample. The second compound crystallized in long, dark blue needles and proved to be identical to 2,2′-binaphthyl-1,1′-quinone (II), previously isolated by Musgrave and Skoyles from *Diospyros buxifolia*.[4]

[1] CORREIA ALVES, A. CRUZ COSTA and M. A. FERREIRA, *Garcia de Orta, Lisbon* **17**, 299 (1969).
[2] K. YOSHIHIRA, M. TEZUKA, C. TAKAHASHI and S. NATORI, *Chem. Pharm. Bull. Tokyo* **19**, 851 (1971).
[3] J. GOSSWEILER, *Agronomia Angolana Luanda* **7**, 322 (1953).
[4] O. C. MUSGRAVE and D. SKOYLES, *Chem. Commun.* 146 (1970).

A third compound was recognized as a 7-methyljuglone dimer, but was different from diospyrin,[5] isodiospyrin[6,7] and elliptinone.[7] On the other hand, both MS and NMR spectra suggest that the substance is biramentaceone[8] (IV) or mamegakinone[9] (V). It was impossible to compare it directly with biramentaceone but it was different in its MS behaviour. This dimer must therefore be mamegakinone (see Table 1) and this was confirmed by UV, IR, NMR and TLC.

TABLE 1. MS OF MAMEGAKINONE* AND EUCLEIN†

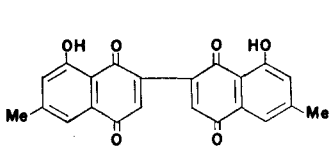
Mamegakinone										
m/e	51	52	53	55	57	63	69	71	76	77
I%	20	20	6	8	20	7	7	11	6	23
	78	83	85	105	106	107	128	133	134	
	18	8	7	7	43	7	6	6	20	
	135	156	187	189	219	261	262	289	290	
	10	6	12	5	7	9	11	6	30	
	291	303	317	318	319	346	357	358	374(M)	
	7	10	25	30	6	9	37	9	100	
	375	376								
	27	10								
Euclein										
m/e	51	52	63	76	78	89	101	102	105	106
I%	2·2	2	1·4	1·7	1·2	1·5	1	1	1·3	9
	107	127	128	133	134	135	136	139	165	173
	2·7	1·1	1	1	7	8	1·3	1	1·3	2·2
	178	187	189	202	213	215	238	239	243	247
	1	11	2	1	1·3	1	1·5	1·6	5	1
	248	275	289	290	300	301	302	303	317	318
	1	1·3	1·3	1·7	2·2	2·2	1·3	2·3	3	4
	319	328	329	330	331	332	345	346	347	357
	2	7	6	2·2	6·3	1·5	5	4	1	10
	358	359	360	374(M)		375	376			
	3·2	13·8	1	160		30	11			

* Run at 70 eV, inlet temp. 250°.
† Run at 70 eV, inlet temp. 200°.

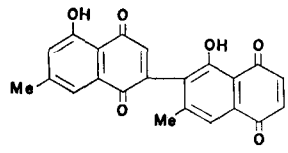
The major pigment, euclein, $C_{22}H_{14}O_2$, M 374, m.p. 249–251°, $[\alpha]_D = 0°$ ($CHCl_3$), is isomeric with but different from other dimers isolated from *Diospyros*. It shows light absorption typical of a juglone, λ_{max} (EtOH) 218, 255, 432 nm, gives a purple colour in alkaline solution, λ_{max} (EtOH–OH^-) 226, 288, 357 (sh), 548 nm, and has two absorption bands in the carbonyl region of the IR spectrum, ν_{CO} (KBr) 1670, 1640 cm^{-1}. The NMR spectrum (100 MHz in $CDCl_3$) shows two signals for Ar–Me (τ 7·56 and 7·70) which indicates that the substance is an asymmetric dimer, three vinyl protons (2H, τ 3·08 and 1H, τ 3·12), one isolated aromatic proton (τ 2·90) and two *meta*-coupled aromatic protons (τ 2·46 and 2·52).

[5] R. S. KAPIL and M. M. DHAR, *J. Sci. Ind. Res. India* **20B**, 498 (1961).
[6] G. S. SIDHU and K. K. PRASAD, *Tetrahedron Letters* 2905 (1967).
[7] A. L. FALLAS and R. H. THOMSON, *J. Chem. Soc.* **C**, 2279 (1968).
[8] V. KRISHNAMOORTHY and R. H. THOMSON, *Phytochem.* **8**, 1591 (1969).
[9] K. YOSHIHIRA, M. TEZUKA and S. NATORI, *Tetrahedron Lett.* 7 (1970); *Chem. Pharm. Bull. Tokyo* **19**, 2308 (1971).

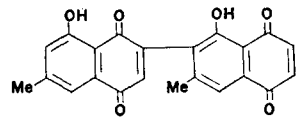
In accordance with these facts the compound from *E. pseudebenus* is either diospyrin (VI) or corresponds to structure (VII), but whether the linkage of the two methyljuglone moieties is C_2-C_6', or C_3-C_6', cannot be decided on the basis of the NMR spectrum.



(V)



(VI)



(VII)

The MS of euclein is similar to those of other methyljuglone dimers in its general pattern.[7] Nevertheless, it is different in some details from that of diospyrin,[7] the main difference being that all the ions have much lower intensities (see Table 1, euclein). However, since the IR spectra of the two compounds are different, it follows that euclein must have structure (VII).

EXPERIMENTAL

Dried powdered roots of *E. pseudebenus* plants* (800 g) were extracted with petrol (b.p. 50–70°) and then with $CHCl_3$, acidified $CHCl_3$, and acetone. The residue from the petrol extract (1·54%) was chromatographed on a column of silicic acid and eluted with petrol containing increasing proportions of benzene and benzene–$CHCl_3$. Benzene extracted the 2,2′-binaphthyl-1,1′-quinone, which was purified by washing with MeOH, the insoluble matter being crystallized from $CHCl_3$. Elution of the column with benzene–$CHCl_3$ (1:1–1:4) extracted three substances. The solvents were evaporated to dryness, and the residue submitted to preparative TLC on silica gel in $CHCl_3$. Three bands were obtained; the upper band was extracted with $CHCl_3$, and the residue, after crystallization from Et_2O, afforded mamegakinone, $\lambda_{max}^{CHCl_3}$ 256, 445 nm; ν_{max}^{KBr} 1660, 1642(sh), 1625, 1580, 1562, 1490, 1470, 1385, 1365(sh), 1310, 1280, 1260, 1242(sh), 1220, 1180, 1140, 1050, 1030, 930, 900, 870, 820, 750, 700, 675, 640 cm^{-1}. The NMR spectrum ($CDCl_3+CF_3CO_2H$) comprizes signals at τ 7·52 (Ar–Me), τ 2·77 and τ 2·44 from Ar–H and τ 2·89 from Q–H. $C_{22}H_{14}O_6$ requires: M, 374. Found: M, 374.

Euclein (250 mg) was eluted from the middle TLC band with $CHCl_3$, and purified by subsequent column chromatography on silicic acid in benzene. It crystallized from $CHCl_3$–Et_2O in orange cubes, m.p. 249–251°, λ_{max}^{EtOH} 218 (log ϵ 4·59), 255 (log ϵ 4·45), 432 nm (log ϵ 4·02); $\lambda_{max}^{EtOH\text{-}OH^-}$ 226 (log ϵ 4·74), 288 (log ϵ 4·30), 357(sh) (log ϵ 3·51), 548 nm (log ϵ 4·25); ν_{max}^{KBr} 1670, 1640, 1610, 1560, 1480, 1440, 1385, 1355, 1350(sh), 1330, 1260, 1210, 1175(sh), 1140(sh), 1090, 1050, 995, 980(sh), 910, 875, 852, 830, 810, 780(sh), 755 cm^{-1}. $C_{22}H_{14}O_6$ requires: M, 374·0790. Found: M, 374·0778.

The crude $CHCl_3$ extract (2·73%) was chromatographed on a silicic acid column. Elution with petrol–$CHCl_3$ (1:1) extracted 7-methyljuglone and other substances. TLC on silica gel in benzene–$CHCl_3$ (1:1) afforded 7-methyljuglone, identified by comparison with an authentic sample (TLC, UV, IR).

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* Plants from *E. pseudebenus* were collected at Giraul, Angola, and herbarium specimens are kept in the Institute of Scientific Research, Luanda.