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EUCLEOLATIN: A DIMERIC METHYLNAPHTHAZARIN FROM *EUCLEA LANCEOLATA*

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Key Word Index—*Euclea lanceolata*; Ebenaceae; common name; naphthaquinones; eucleolatin; 8′-hydroxydiospyrin.

Abstract—8,8′-Dihydroxy-4,4′-dimethoxy-6,6′-dimethyl-2,2′-binaphthyl-1,1′-quinone, 7-methyljuglone, 8′-hydroxydiospyrin, and eucleolatin have been isolated from the root bark of *E. lanceolata*. Eucleolatin is the 3,6′- or 3,7′- dimer of 2-methylnaphthazarin.

THE GENUS *Euclea* has only attracted the attention of phytochemists since 1969 when the first study[1] of naphthaquinones of a *Euclea* sp. appeared. Recently, such compounds have been isolated from *E. crispa*,[2] *E. crispa* var. *crispa*,[2] *E. undulata*,[2] *E. undulata* var. *myrtina*,[2] *E. pseudebenus*,[3] and *E. lanceolata* E. Mey ex DC.[4] The last named species grows in the districts of Malange, Bié, and Huíla, in Angola,[5] where it is known by the vernacular names Mboto, Mumboto, Otinu and Omundine; it is used in folk medicine as a purgative in some African regions.[6]

The known compounds isolated[4] from *E. lanceolata* include 8,8′-dihydroxy-4,4′-dimethoxy-6,6′-dimethyl-2,2′-binaphthyl-1,1′-quinone (**1**),[7] 7-methyljuglone (**2**),[8] mamegakinone (**3**),[9] and 8′-hydroxydiospyrin (**4**).[10] In addition, two unidentified naphthaquinones were also isolated and we now report that one of these appears to be the first example of a dimeric methylnaphthazarin to be found in Nature.

RESULTS AND DISCUSSION

Maceration in chloroform of the powdered root bark of *E. lanceolata* previously treated with dilute HCl gave an extract from which three naphthaquinones A–C were isolated by column chromatography and preparative TLC. A seems to be a naphthazarin derivative but has not yet been identified while B was identified as 8′-hydroxydiospyrin (**4**) by direct comparison with an authentic sample.[10]

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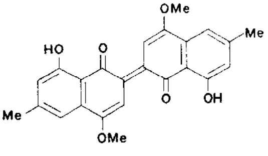
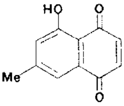
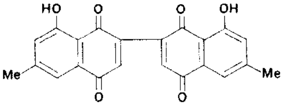
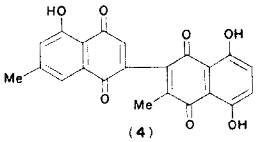
Compound C, $C_{22}H_{14}O_8$, for which we propose the name eucleolatin, crystallized from C_6H_6 as a red–violet solid, m.p. 250° (decomp.). It shows light absorption typical of a naphthazarin and is clearly a dimeric methylnaphthazarin. Its 100 MHz N.M.R. spectrum (in $CDCl_3$–CF_3COOD) comprises singlets at τ 7·84 (3H, Me at C-2), 2·68 (2H, Ar–H at C-6 and C-7) and 2·80 (1H, Ar–H at C-6′ or C-7′), a quartet centred at τ 2·94, J, 1.5 Hz (1H, Q–H at C-3′) and a doublet at τ 7·70, J 1.5 Hz (3H, CH_3 at C-2′).

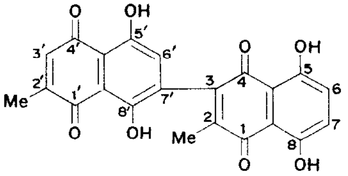

(1)

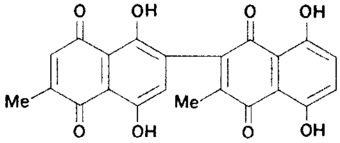

(2)


(3)


(4)

The methyl groups appear to be attached to quinonoid rings, as in 2-methylnaphthazarin, and the protons of one of them (at C-2′) exhibit allylic coupling with the proton at C-3′. It is evident that there is no proton at C-3 and hence the two methylnaphthazarin units are linked C-3 to C-6′ or C-3 to C-7′. The structure of eucleolatin must therefore be (**5**) or (**6**).


(5)


(6)

The fragmentation of eucleolatin in the mass spectrometer also provides support for these structures. The most important ions resulting from fragmentation are: *m/e* 391 (M–$\dot{C}H_3$), 390 (M–CH_4), 389 (M–$\dot{O}H$), 388 (M–H_2O), 374 (M–$\dot{O}H$–$\dot{C}H_3$), 361 (M–$\dot{O}H$–CO) and 360 (M–H_2O–CO), together with those with *m/e* 179, 151, 137, 136, 122 and 108. These last ions clearly result from the cleavage of an internal quinonoid ring and they can be accounted for by assuming that the eucleolatin molecule behaves in two tautomeric forms, possible fragmentation routes being represented as follows:[10]

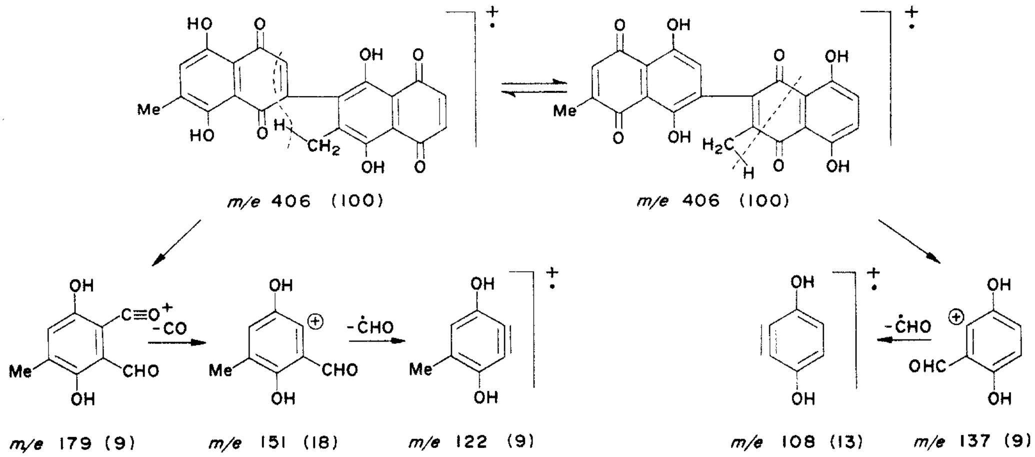


TABLE 1. MS OF EUCLEOLATIN*

m/e	406	391	390	389	388	376	374
I%	100	22	29	23	43	2·4	13
	363	362	361	360	333	228	203
	3·5	4·0	9	11	4·5	3·6	17
	200	179	165	159	151	137	136
	7	9	4	10	18	9	5
	122	115	108	106	79	77	65
	9	6	13	6	2·5	6·6	7
	63	55	54	53	52		
	6	6	4·5	4	8		

* Measured on an AEI MS902 mass spectrometer at 70 eV with the ion source at 240°.

EXPERIMENTAL

Powdered root bark of *E. lanceolata** collected in the Catholic Mission of Huila, Angola (750 g) was first extracted (Soxhlet) with light petrol. (b.p. 50–70°) to remove aliphatic matter and then repeatedly macerated in $CHCl_3$. The combined $CHCl_3$ extracts were evaporated and the residue (6·5 g) was chromatographed on a column of silicic acid using petrol., C_6H_6, and mixtures of C_6H_6 and $CHCl_3$ as eluants.

The C_6H_6 extracted a blue pigment along with a yellow one, which were separated by preparative TLC on silica gel using $CHCl_3$–C_6H_6 (24:1). The blue pigment was repeatedly washed with petrol. and MeOH and crystallized from $CHCl_3$ after addition of petrol. It proved to be identical with an authentic sample of 8,8'-dihydroxy-4,4'-dimethoxy-6,6'dimethyl-2,2'-binaphthyl-1,1'-quinone.[7] Elution of the column with mixtures of C_6H_6–$CHCl_3$ extracted two substances which were separated by repeated column chromatography and TLC. One of them proved to be identical with an authentic sample of 7-methyljuglone.

Another portion of powdered root bark of *E. lanceolata* (850 g) was extracted with boiling petrol. (50–70°) and then treated with dil. HCl and repeatedly macerated in $CHCl_3$. The combined $CHCl_3$ extracts were evaporated and the residue (30 g) was chromatographed on a column of silicic acid using mixtures of petrol. and C_6H_6 and finally C_6H_6 as eluent. The benzene eluted three substances, A–C (in order to their decreasing R_fs using silica gel–$CHCl_3$) which were purified by repeated column chromatography and preparative TLC on silica gel using $CHCl_3$.

A crystallized from $CHCl_3$ as a red solid, m.p. 215–220°. λ_{max}: (EtOH) 275, 281, 490 (sh), 520 and 558 nm. ν_{max}: (KBr) 1740, 1700, 1660, 1620, 1560, 1460, 1410, 1370, 1340, 1290, 1295, 1180, 1130, 1090, 1070, 1040, 990, 920, 890, 845, 800 and 755 cm^{-1}. B was identical (UV, IR, NMR, MS, TLC, m.m.p.) with an authentic sample of 8'-hydroxydiospyrin.[10] C, eucleolatin, crystallized from benzene as a dark red solid, m.p. 250° (decomp.) (Found: *M*, 406·0689; $C_{22}H_{14}O_8$ requires: *M*, 406·0689). λ_{max}: (EtOH) 218, 280, 492, 520 and 558 nm. ν_{max}: (KBr) 1620, 1575, 1450, 1400, 1315, 1300, 1260, 1240, 1220, 1205, 1190, 1165, 1130, 1085, 1050, 1020, 990, 890, 850, 825, 800, 770, 755, 725 and 690 cm^{-1}.

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* Herbarium specimens are kept at the Instituto de Investigação Científica de Angola, Luanda.