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NAPHTHOQUINONE DIMERS AND TRIMERS FROM *EUCLEA NATALENSIS**

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Key Word Index—*Euclea natalensis*; Ebenaceae; naphthoquinones; natalenone; galpinone; 8′-hydroxydiospyrin; euclanone.

Abstract—The naphthoquinone dimers natalenone, 8′-hydroxydiospyrin and euclanone and the trimers galpinone and a compound with MW 562 were isolated from *E. natalensis* roots. Natalenone is a dehydrodimer of 7-methyljuglone with the two moieties linked by two C-C bonds to give a fused tetracyclic structure, one ring bearing a methylene bridge. Galpinone is a 7-methyljuglone linear trimer, the three units probably being linked C-8-C-6′ and C-3′-C-3″. Euclanone is a new dimer of 7-methyljuglone and methylnaphthazarin, isomeric with 8′-hydroxydiospyrin.

INTRODUCTION

In previous work on *Euclea natalensis* A. D. C., Ebenaceae, several triterpenoids [1, 2] and naphthoquinones have been identified in its stems and roots; the quinones isolated include 7-methyljuglone, diospyrin, isodiospyrin, methylnaphthazarin, biramentaceone, mamegakinone, diosindigo A and xylospyrin [3–5]. We now report on five further pigments isolated from the roots of this plant.

RESULTS

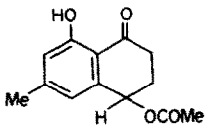
Identification of natalenone

From the petrol extract of *E. natalensis* roots a yellow crystalline substance (**5**), mp 229–231°, was isolated by PLC; it became violet in alkaline solution. The pigment is optically inactive (C.D.) and has λ_{max}^{EtOH} 226 (log ε 4·18), 294 (sh, log ε 3.83), 394 (sh, log ε 3.68), 440 (log ε 3.66) nm, $\lambda_{max}^{EtOH/OH^-}$ 275 (log ε 4.15), 292 (*sh*, log ε 3.94), 342 (*sh*, log ε 3.87), 568 (log ε 3.79) nm, ν_{max}^{KBr} 3523, 1670, 1640 and 1610 cm^{-1}. The ^{1}HNMR of (**5**) showed aromatic methyl signals at δ 2.37 and 2.40, two singlets from peri-hydroxy groups at δ 11.39 and 11.40, and four doublets for *m*-coupled aromatic protons at 6.70, 6.94, 7.02 and 7.43 (each 1 H, $J = 2$). The presence of a free hydroxyl is indicated by a peak at δ 4.69 exchanging with D_2O, along with a methine proton signal at δ 4.17 (1 H, *m*) coupled to a methylene resonance at δ 3 02 (2 H, *d*, $J = 3$).

The off-resonance decoupled ^{13}C NMR spectrum included a singlet at 82 p.p.m. (>C—O), a CH_2 triplet at 54 and a CH doublet at 52 p.p.m., together with signals for two aromatic methyl, two vinyl (singlets), twelve aromatic and three carbonyl carbon atoms (198, 188 and 181 p.p.m.).

The MS of (**5**) indicated a molecular formula of $C_{22}H_{16}O_6$ (Found: M^+/e, 376·0943, 79%; required: M^+, 376.0946). Ionic fragments were observed at *m/e* 358 (M^+—H_2O, 100%), 330 ($M^+ - H_2O$—CO, 35%), 302 (M^+–H_2O–2CO, 9%) and 274 (M^+–H_2O–3CO, 3%). Besides this, the MS also showed ions with *m/e* 163 (3%), 135 (10%), 134 (11%), 106 (16%) and 77 (14%), which clearly resulted from the cleavage of an internal quinonoid ring of a 7-methyljuglone dimer [6].

Natalenone (**5**) formed a triacetate by reaction at room temperature with Ac_2O–H_2SO4, λ_{max}^{EtOH} 354 nm, and when heated with HOAc–H_2SO_4 it gave a monoacetate, $\lambda_{max}^{CHCl_3}$ 448 nm, δ 3.66 (1H, *q*), which retained both *peri*-hydroxyls. The formation of a monoacetate supports the spectral evidence (ν 3523 cm^{-1} and δ = 4.69) for an alcoholic hydroxyl in natalenone. This is evidently tertiary because the methine proton in the parent compound (δ = 4.17) moved upfield† on acetylation instead of downfield, as, for example, in shinanolone monoacetate (**1**) [7].

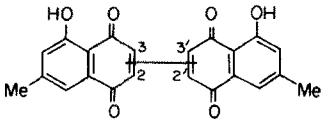


(**1**)

According to these data natalenone must be a dimeric methyljuglone but showing some differences compared to the usual compounds of this type [9, a–c]. In fact, natalenone has a MW of 376 instead of 374, as is observed in conventional compounds (**2**, a–c). Combined evidence suggests that natalenone is formed by two moieties, one of them being represented by 7-methyljuglone (**3**) linked through its quinonoid ring by >CH—CH_2– and >COH fragments to an aromatic ring bearing a methyl and a hydroxyl *peri* to a carbonyl group (**4**). As several structures are possible according to this evidence, the final

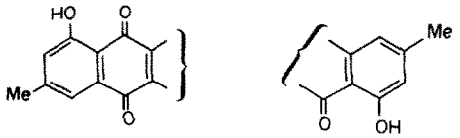
* Part of this work has been published in two preliminary communications [4, 8].

† Also observed in the triacetate.

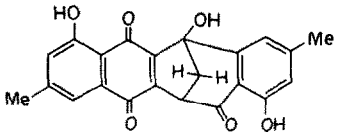


(2a) C-2–C-2′; biramentaceone
(2b) C-3–C-3′, mamegakinone
(2c) C-2–C-3′ rotundiquinone

elucidation was obtained by X-ray crystallographic analysis which showed natalenone as (5) [8].



(3) (4)



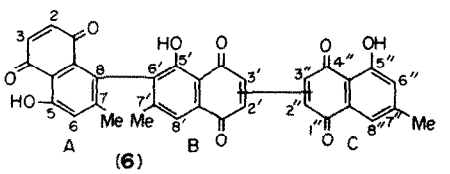
(5)

Identification of galpinone

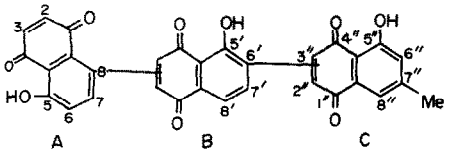
Compound (6), $C_{33}H_{20}O_9$, was isolated from the $CHCl_3$ extract as orange-red crystals, mp > 335°, λ_{max}^{EtOH} 216, 252, 434 nm, $\lambda_{max}^{EtOH/OH^-}$ 207, 228 (*sh*), 290, 558 nm, λ_{max}^{KBr} 1662, 1640, 1600 cm^{-1} [4], typical of a juglone. The NMR spectrum showed three aromatic methyls at 2·03 (3H, *s*), 2.04 (3H, *s*) and 2.44 (3H, *s*), two *o*-coupled quinonoid protons at δ 6.76 (1H, *d*, J = 10) and 6.86 (1H, *d*, J = 10), forming an AB quartet, and two quinonoid protons at δ 6.94 (1H, *s*) and 6.99 (1H, *s*). Four aromatic proton signals appeared at 7·10 (1H, *d*, J = 2), 7.28 (1H, *s*), 7.48 (1H, *d*, J = 2) and 7.64 (1H, *s*). The presence of three protons from *peri*-OH groups is indicated by peaks at 11.66 (1H, *s*), 11.85 (1H, *s*) and 12.35 (1H, *s*). In the MS major ions were observed at *m/e* 135(56%), 134(50%) and 106(71%), resulting from methyljuglone fragmentations and other peaks appeared at *m/e*. 562 (M^+ + 2, 40%), 561 (M^+ + 1, 31%), 560 (M^+, 100%), 545 (M^+ − Me, 32%), 543 (M^+ − OH, 25%), 532 (M^+ − CO, 11%), 504 (M^+ − 2CO, 11%), 517 (M^+ − Me–CO, 19%) and 489 (M^+ − Me–2CO, 14%). Therefore, according to its MW and NMR spectrum the substance must be a tris-(7-methyljuglone), the linkage among the three units having been made with elimination of two aromatic and two quinonoid protons.

As the NMR shows the existence of two *o*-coupled quinonoid protons, forming an AB quartet, this suggests that one of the end methyljuglone units must be linked via C-8 atom to the central unit. In fact, this structural situation occurs in all the known compounds presenting this feature [10–13] and, therefore, the trimer structure should be (6) or (7). Other possible structures are ruled out on the basis of the NMR spectrum.

As can be seen, in structure (6) A and B monomers are linked as in isodiospyrin (8) [10] and in bis-isodiospyrin (9) [11, 15], whilst B and C monomers are linked through their quinonoid rings. On the other hand, in structure (7)

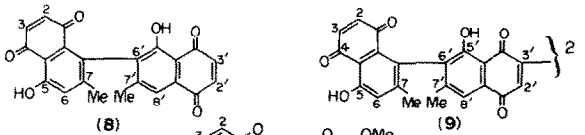


(6)

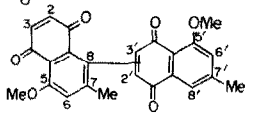


(7)

they are linked as in neodiospyrin dimethyl ether (10) [12] and in diospyrin [14]. From a comparison of the NMR



(8) (9)



(10)

spectra of these compounds (see Table 1) it is clear that A and B units in the trimer molecule are arranged as in isodiospyrin (8) and in bis-isodiospyrin (9). Supporting this conclusion there is a marked similarity among the chemical shifts of the C-7 and C-7′ methyls in all these compounds, while in neodiospyrin dimethyl ether [12] the methyl at C-7 (10) has a different chemical shift. In addition, the chemical shifts of the trimer quinonoid protons H-2′ or H-3″ (δ 6.94–6.99) do not agree with the δ value ascribed to H-2′ or 3′ (δ 6.45) in (10). On these grounds, structure (7) is ruled out.

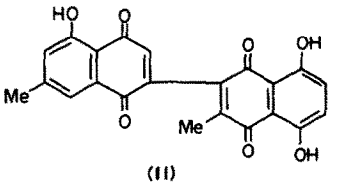
The B–C link in (6) must now be considered. There are three possibilities, namely C-2′–C-2″, as in biramentaceone (2a), C-3′–C-3″, as in mamegakinone (2b), or C-2′–C-3″, as in rotundiquinone (2c). In the first two cases the resulting compounds are symmetrical and their NMR spectra are practically coincident except in the chemical shift of the *peri*-OH protons (see Table 1), whereas the spectrum of rotundiquinone is asymmetrical and resembles that of an equimolecular mixture of biramentaceone and mamegakinone. [9C].

Taking into consideration the data from Table 1 it is evident that the trimer *peri*-OH proton at C-5″ (6) has practically the same chemical shift as the equivalent proton of mamgakinone (2b). This fact suggests that the C unit is most probably linked through C-3″ to the B moiety. However, whether this bond is C-2′–C-3″ or C-3′–C-3″ was impossible to determining with certainty in spite of the latter seeming to be the most probable. In favour of this it may be pointed out that it has just been established that bis-isodiospyrin is the 3-3′ dimer of isodiospyrin [15] and that mamegakinone has already been identified in this plant [4], while rotundiquinone has not. Therefore, B and C units must be linked via C-3′–C-3″, the slight difference observed between the chemical shifts of B and C quinonoid protons being due to the influence of A unit on B, because of asymmetry in the trimer. On these grounds it is evident that this substance is identical to galpinone, recently isolated from *Diospyros galpinii*

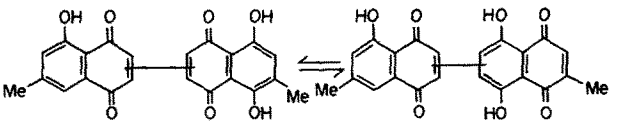
by Vijver [16] and for which this author also ascribes structure (6).

Identification of 8′-hydroxydiospyrin

From the acetone extract of *E. natalensis* roots a substance was isolated by PLC, mp 255–260°, which proved to be identical to an authentic sample of 8′-hydroxydiospyrin (11) (TLC, IR) [6].



(11)



(12) (12a)

comes from the absence of ions at *m/e* 136 and 108 in the MS, which are normally found if the dihydroxyaromatic ring of naphthazarin has no substituents [17], and the presence of ions at *m/e* 150 and 122, which can be accounted for by the fragmentation indicated above.

Structure (12) is tautomeric and a methyl group favoured the formation of a quinonoid ring in a naphthazarin [18]. Thus, euclanone is more appropriately represented by the tautomeric forms (12) and (12a).

Table 1. Comparison of the NMR spectrum of galpinone with those of isodiospyrin [10], bis-isodiospyrin [11], biramentaceone [9a], mamegakinone [9c], rotundiquinone [9c] and neodiospyrin dimethyl ether [12]

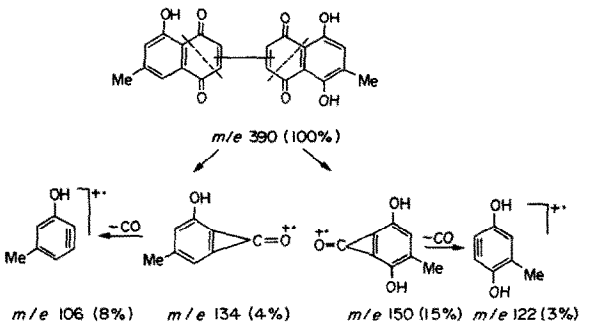
Assigment	Trimer* (6)	Isodiospyrin* (8)	Bis-isodiospyrin (9)	Biramentaceone* (2a)		Mamegakinone* (2b)		Rotundiquinone* (2c)	Neodiospyrin dimethyl ether (10)
2-H	6.86*d* $J = 10$	6.98*d* $J = 10$	6.96*d* $J = 10$	—	—	6.96 §*s*	6.99*s*	—	6.57*d*
3-H	6.76*d* $J = 10$	6.74*d* $J = 10$	6.78*d* $J = 10$	6.97†*s*	7.02‡*s*	—	—	7.02*s*	6.71*d* $J = 10$
5-OH	11.85*s*	12.08*s*	12.10*s*	11.78*s*	11.81*s*	11.64*s*	11.71*br*	11.81*s*	—
6-H	7.28*s*	7.33*s*	7.36*s*	7.02*d* $J = 2$	7.13*br*	7.11*d* $J = 2$	7.13*br*	7.13*br*	7.18*s*
7,7′-Me	2.02 *s*, 2.04 *s*	2.02 *d*	2.06 *s*, 2.07 *s*	2.42 *s*	2.46 *s*	2.44 *s*	2.46 *s*	2.46 *s*	2.30 *s*, 2.49 *s*
8-H	—	—	—	7.45 *d* $J = 2$	7.50 *br* $J = 2$	7.45 *d*	7.50 *br*	7.50 *br*	—
2′-H, 2″-H	6.94 *s* or 6.99 *s*	6.98 *s*	7.09 *s*	—	—	6.96 *s*	6.99 *s*	6.99 *s*	6.45 *s*
3′-H, 3″H	6.94 *s* or 6.99 *s*	6.98 *s*	or 7.09 *s*	6.97 *s*	7.02 *s*	—	—	—	or 6.45 *s*
5′-OH	12.35 *s*	12.46 *s*	12.51 *s*	11.78 *s*	11.81 *s*	11.64 *s*	11.71 *br*	11.71 *br*	—
6′-OH	—	—	—	7.02 *d* $J = 2$	7.13 *br*	7.11 *d* $J = 2$	7.13 *br*	7.13 *br*	7.06 *d* $J = 2$
8′-H	7.64 *s*	7.67 *s*	7.73 *s*	7.45 *d* $J = 2$	7.50 *br*	7.45 *d* $J = 2$	7.50 *br*	7.50 *br*	7.56 *d* $J = 1.5$
5″-OH	11.66 *s*	—	12.51 *s*	—	—	—	—	—	—
6″-H	7.10 *d* $J = 2$	—	—	—	—	—	—	—	—
7″-Me	2.44 *s*	—	2.06 *s*	—	—	—	—	—	—
8″-OH	7.48 *d* $J = 2$	—	7.73 *s*	—	—	—	—	—	—

The assigments to the formulae on p. 118. *The spectra of these compounds were run in $CDCl_3$ at 100 MH; chemical shifts are in δ. †Figures taken from [9a]; ‡figures taken from [9c]; §unpublished figures recorded by us; ¶figures taken from [9c].

Identification of euclanone

A second pigment, $C_{22}H_{14}O_7$, isolated from the acetone extract, gave red crystals (from $CHCl_3$) mp 260–263°, $\lambda_{max}^{CHCl_3}$ 224, 266 (*sh*), 284 (*sh*), 454 (*sh*), 492, 522 (*sh*), 562 (*sh*) nm, ν_{max}^{KBr} 1640, 1610 cm^{-1}. The NMR spectrum showed signals for two aromatic methyls at 2.28 and 2.45, two quinonoid protons at δ 6.94 (1H, *s*) and 7.06 (1H, *s*), two *m*-coupled aromatic protons at 7.12 (1H, *d*, $J = 2$) and 7.50 (1H, *d*, $J = 2$) and a singlet at 7.24 (1H, *s*). Three protons from *peri*-OH groups resonated at δ 11.81, 12.34 and 12.84. The MS showed peaks at *m/e* 392 ($M^+ + 2$, 11%), 391 ($M^+ + 1$, 16%), 390 (M^+, 100%), 362 ($M^+ - CO$, 3%), 334 ($M^+ - 2CO$, 13%) and 306 ($M^+ - 3CO$, 8%). Other ions were observed at *m/e* 150 (1·5%), 135 (5%), 134 (4%) and 122 (3%).

All these data suggest that euclanone (12) is clearly a dimer of 7-methyljuglone and methylnaphthazarin. Therefore, as there is no evidence of allylic coupling, since both methyl groups appear as very sharp singlets, euclanone must have structure (12). Further support



Compound MW 562

From the petrol extract another substance, $C_{33}H_{22}O_9$, was isolated by PLC, mp >350°, $\lambda_{max}^{CHCl_3}$ 245, 264, 302 (*sh*), 328, 449 nm, ν_{max}^{KBr} 3500, 1667, 1610 cm^{-1}. It was impossible to obtain the NMR spectrum of the substance because of its insolubility and a more soluble derivative could not be prepared due to lack of material. From its MS it seems to be a 7-methyljuglone derivative (ions at *m/e* 135, 134 and 106).

* We thank Dr. L. M. v.d. Vijver for kindly confirming this by direct comparison of substance with her galpinone specimen.

EXPERIMENTAL

Plant material. Plants from *E. natalensis* were collected near the Catholic Mission, Huila, Angola, by Dr. A. Figueira de Sousa and voucher specimens are kept in the Herbarium of the Institute for Scientific Research, Luanda, Angola.

Isolation of natalenone. Dried powdered roots of *E. natalensis* (1.5 kg) were Soxhlet extracted with petrol (bp 50–60°) giving 33.0 g crude material (2.2%) after evaporation of the solvent. The extract (1.7 g) was submitted to PLC on silica in $CHCl_3$, giving eight bands. Band B (the second in order of increasing R_f values was removed and rechromatographed in the same system, giving rise to 2 bands. The band with lower R_f afforded natalenone as pale yellow needles ($CHCl_3$) (12·5 mg), mp 229–231°.

Natalenone monoacetate. Natalenone (11 mg) was boiled with HOAc (10 ml) and conc. H_2SO_4 (2 drops) for 2 h. The crude product separated by PLC on silica in $CHCl_3$ into unchanged natalenone and the monoacetate. The latter crystallized from MeOH–$CHCl_3$ as long orange sticks, mp 255–257°, $\lambda_{max}^{CHCl_3}$ 244, 269, 299, 325 (*sh*), 448 nm (log 4.30, 4.27, 3.96, 3.78, 3.76), ν_{max}^{KBr} 1760, 1678, 1640, 1610, 1570 cm^{-1}, NMR (100 MH_z, $CDCl_3$) δ 2.30 (3H, *s*), 2.38 (6H, *s*), 2.90 (1H, *d*, J = 10 Hz), 3.68 (1H, *q*, J_1 = 10, J_2 = 5 Hz), 4.20 (1H, *d*, J = 5 Hz), 6.74 (1H, *d*, J = 2 Hz), 7.00 (1H, *d*, J = 2 Hz), 7.02 (1H, *d*, J = 2 Hz), 7.42 (1H, *d*, J = 2 Hz), 11.44 (1H, *s*), 11.68 (1H, *s*). Found: M^+ 418.1052, $C_{24}H_{18}O_7$ requires: M^+ 418.1052. MS: peaks at *m/e* 418 (M^+, 0,3%), 376 (M^+–CH_2CO, 32%), 358 (M^+–CH_2CO–H_2O, 100%), 330 (M^+–CH_2CO–H_2O–CO, 15%), 302 (M^+–CH_2CO–H_2O–2CO, 2,5%).

Natalenone triacetate. Natalenone was treated with Ac_2O (2 ml) and conc. H_2SO_4 (1 drop) at room temp. for 8 days. The product was purified by TLC on silica in $CHCl_3$, λ_{max}^{EtOH} 260, 296 (*sh*), 354 nm, ν_{max}^{KBr} 1780, 1750, 1695, 1665, 1630, 1605 cm^{-1}, NMR (100 MH_z, $CDCl_3$) δ 2.29. (3H, *s*), 2.32 (3H, *s*), 2.38 (3H, *s*), 2.44 (6H, *s*), 2.91 (1H, *d*, J = 10 Hz), 3.62 (1H, *q*, J_1 = 10, J_2 = 5 Hz), 4.13 (1H, *d*, J = 5 Hz), 6.86 (1H, *d*, J = 2 Hz), 7.10 (1H, *d*, J = 2), 7.46 (1H, *d*, J = 2), 7.80 (1H, *d*, J = 2). Found: 504 (M^+ + 2); $C_{29}H_{22}O_9$ requires: M^+, 502. MS: peaks at *m/e* 504 (M^+ + 2, 0.4%), 460 (M^+—CH_2CO, 0·9%), 418 (M^+—2 CH_2-CO, 22%), 376 (M^+—3CH_2CO, 10%), 358 (M^+—3CH_2 CO–H_2O, 100%), 330 (M^+—3CH_2CO–H_2O—CO, 19%), 302 (M^+—3CH_2CO–H_2O—2CO, 5%), 274 (M^+—3 CH_2CO–H_2O—3CO 2%).

Isolation of galpinone. The powdered roots, after having been extracted with petrol, were dried in air and Soxhlet extracted with $CHCl_3$ to give 20·4 g (1,36%) crude material. The extract (14.5 g) was submitted to repeated column chromatography on silicic acid. Elution with petrol–C_6H_6 in varying proportions separated some of the compounds already isolated from the petrol extract and further elution with C_6H_6 afforded galpinone (7.1 mg), mp > 335°. Found: M^+, 560.1103; $C_{33}H_{20}O_9$ requires: M^+, 560.1107.

Isolation of 8′-hydroxydiospyrin. Powdered roots, after extraction with petrol and $CHCl_3$, were subsequently Soxhlet extracted with Me_2CO. The extract was concentrated to a small volume and submitted to PLC on silica in $CHCl_3$ giving rise to 2 bands. The band with higher R_f afforded, after purification, 8′-hydroxydiospyrin, identified by comparison with an authentic sample (mp, IR, UV, TLC).

Isolation of euclanone. The second band obtained by PLC of acetone extract (lower R_f) afforded a substance, mp 260–263° (from $CHCl_3$). Found: M^+, 390.0738; $C_{22}H_{14}O_7$ requires: M^+ = 390.0739.

Isolation of compound MW 562. The band with higher R_f resulting from rechromatography of band B (see isolation of natalenone) was run again on silica in $CHCl_3$ to give an orange-red substance, mp > 350°, $\lambda_{max}^{CHCl_3}$ 245, 265, 302 (*sh*), 332 (*sh*), 446 nm (log ε 4.26, 4.23, 3.75, 3.63, 3.59) ν^{KBr} 3500, 2925, 2860, 1670, 1635, 1610, 1570 cm^{-1}. Found: M^+, 562.1270; $C_{33}H_{22}O_9$ requires: M^+, 562.1264.

Acknowledgements—We thank Professor R. H. Thomson for helpful criticism, Dr. I. H. Sadler for natalenone ^{13}C NMR spectrum and Dr. P. M. Scopes for natalenone circular dichroism measurement. We also thank the "Instituto de Alta Cultura" for financial support (Research Project PFR/7).

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