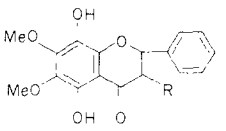

1 R = OMe
2 R = H

H-4′ and H-5′), 11.30 (1H, *br s*, 5-OH, exchangeable with D_2O). ^1H NMR [$CDCl_3$ + Eu(fod)$_3$] $\Delta Eu = \delta_{Eu}^{n=1} - \delta_{Eu}^{n=0}$ where n is the molar ratio of shift reagent to solute; ΔEu values: 4.40(OMe-6), 0.40(OMe-7), 0.30(OMe-3). MS *m/z* (%): 344 $[M]^+$ (81.0), 329 $[M-Me]^+$ (100.0), 301 $[M-COMe]^+$ (12.5), 212 $[A_1]^+$ (2.5), 213 $[A_1+H]^+$ (2.0), 197 $[A_1-Me]^+$ (4.5), 170 $[A_1+H-COMe]^+$ (28.0), 105 $[PhCO]^+$ (26.5), 77 $[Ph]^+$ (19.0).

Methylation of **1**. This was carried out with ethereal CH_2N_2 in MeOH in the usual manner to give 3,6,7,8-tetramethoxy-5-hydroxyflavone [2].

5,8-*Dihydroxy*-6,7-*dimethoxyflavone* (**2**). Its spectral data agreed with those previously reported [4].

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ORICIOPSIN, A NEW RING-D CLEAVED TETRANORTRITERPENOID, AND FLINDERSIAMINE FROM *ORICIOPSIS GLABERRIMA*

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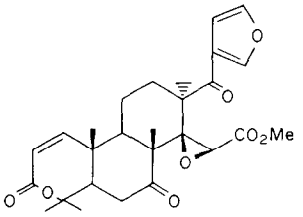
Key Word Index—*Oriciopsis glaberrima*; Rutaceae; tetranortriterpenoid; oriciopsin; alkaloid; furoquinoline; flindersiamine.

Abstract—A novel ring-D cleaved tetranortriterpenoid, oriciopsin and flindersiamine have been isolated from the whole plant extracts of *Oriciopsis glaberrima*. The structure of the new limonoid was determined from its ^1H NMR and ^{13}C NMR spectra and by mass spectrometry.

Oriciopsis glaberrima Eng. (Rutaceae) is a monotypic genus endemic to the humid rain forests of Cameroon[1]. It co-occurs with *Vepris louisii* in shady areas and the two species have been considered to be very closely related morphologically [1]. After our detailed study of *Vepris louisii* [2–5] we considered it of interest to study chemically extracts of *O. glaberrima* in order to see whether a phytochemical relationship paralleling the ecological and morphological one exists between these two species. We now report the isolation and structural elucidation of a novel totally cleaved ring-D tetranortriterpenoid, provisionally named oriciopsin, and the furoquinoline alkaloid, flindersiamine, from the whole plant extracts of *Oriciopsis glaberrima*. The structure of flindersiamine was confirmed by comparison with an



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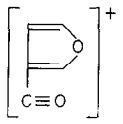

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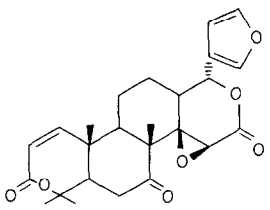

3

authentic sample obtained from *Teclea verdoorniana* [6].

Oriciopsin (**1**), $C_{27}H_{32}O_8$, $[\alpha]_D^{23} - 60.5°$ (acetone), mp 242–244°, had absorptions for cyclohexanone, acetate, ketone, and α,β-unsaturated lactone absorption in its IR spectrum ($\nu_{max}^{CCl_4}$ cm^{-1}: 1767, 1735 sh, 1718, and 1662). The ^1H NMR spectrum showed resonances for five tertiary methyl groups (δ 0.94, 1.10, 1.24, 1.37 and 1.40), a base epoxidic proton (3.50, *s*, H-15), a carbomethoxy group (3.77, 3H, OMe), a disubstituted double bond (5.97 and 6.44, *ds*, $J = 12$ Hz, H-1 and H-2), and the characteristic β-substituted furan (8.40, 7.42 and 6.87). One of the α-furan ring protons was shifted very far down-field (8.40) probably by the deshielding anisotropic effect of the C-17 carbonyl group. The ^{13}C NMR spectrum (see Experimental) confirmed the presence of two free keto-groups, a lactone, an ester carbonyl and a secondary tertiary ether. This spectroscopic information could be satisfactorily interpreted to give structure **1** for oriciopsin. Convincing support for the proposed structure **1** was obtained from the mass spectrum of oriciopsin which showed in addition to the parent peak $[M]^+$ at *m/z* 484 prominent signals at *m/z* 389 $[M-95]^+$, 374 $[M-95-15]^+$ and 95, the first two fragments representing respectively the loss of fragment **2** and the loss of **2** plus a methyl group from the parent ion. The UV spectrum λ_{max}^{EtOH} nm: 257 was also in perfect agreement with structure **1**.

Several cleaved tetranortriterpenoids have recently been reported from plants of the families Rutaceae and Meliaceae. Notable among these are ochinal [7], the antifeedant toonacilin [8], and calamin [9], which represent respectively ring-C, ring-B and ring-A cleaved tetranortriterpenoids. Apart from the complex procerin [10], oriciopsin (**1**) to our knowledge is the first simple ring-D cleaved member of this group and is biogenetically interesting since it represents simple ring-D cleavage of obacunone (**3**) followed by methylation of the resulting acid and oxidation at C-17.

From our study, there is no apparent phytochemical similarity between *Vepris louisii* and *Oriciopsis glaberrima*.

EXPERIMENTAL

All mps were determined on a Büchi 251 mp apparatus and are uncorr. ^1H NMR and ^{13}C NMR were measured at 60 and 25.16 MHz, respectively. MS were recorded by direct inlet at 70 eV, and optical rotations were recorded with 10-cm cells with an AA-100 polarimeter.

Extraction and isolation. Dried whole plants of *Oriciopsis glaberrima* (1.5 kg) collected at Djaposten in the Eastern Province of Cameroon during December 1979 were exhaustively extracted with CH_2Cl_2 in a Soxhlet apparatus. Concn of the extract afforded a green syrup (40 g) which was chromatographed over Si gel (Merck; 70–230 mesh) in hexane. Elution with Et_2O yielded flindersiamine (20 mg) in the first three fractions, colourless prisms from CH_3COCH_3–$CHCl_3$, mp 206–208°, lit. [6] 206–207°; IR ν_{max}^{KBr} cm^{-1}: 3142, 3120 (β-substituted furan), 1460, and 940 (methylenedioxy); UV λ_{max}^{EtOH} nm (ϵ_{max}): 245 (40,000), 253 (51,200), and 338 (5600); ^1H NMR ($CDCl_3$): δ 4.27 (3H, *s*, OMe), 4.38 (3H, *s*, OMe) 6.08 (2H, *s*, OCH_2O) 7.02 (1H, *d*, $J = 2$ Hz, H-3), 7.20 (1H, *s*, H-5), and 7.59 (1H, *d*, $J = 2$ Hz, H-2). MS *m/z* (rel. int.): 273 $[M]^+$ (100), 272 (48), 258 (30), 244 (22), 228 (52) and 172 (23). Later fractions of the Et_2O eluate gave oriciopsin (**1**) (105 mg), colourless rods from $CHCl_3$–Et_2O, mp 242–244°, $[\alpha]_D^{23} - 60.5°$ (CH_3COCH_3, *c* 0.8); UV λ_{max}^{EtOH} nm (ϵ_{max}): 257 (Found: C, 66.82; H, 6.72. $C_{27}H_{32}O_8$ requires : C, 66.94; H, 6.61%.) ^{13}C NMR (25.16 MHz): δ 205.7 (*s*, C-7), 196.6 (*s*, C-17), 168.0 (*s*, C-16), 166.5 (*s*, C-3), 150.9 (*d*, C-1), 149.5 (*d*, C-21), 143.0 (*d*, C-23), 126.7 (*s*, C-20), 120.7 (*d*, C-2), 110.3 (*d*, C-22), 83.4 (*s*, C-4), 70.20 (*s*, C-4), 70.2 (*s*, C-14) 57.4 (*d*, C-15), 55.9 (*d*, C-5), 53.9 (*s*, C-13), 52.6 (*s*, C-8), 52.4 (*q*, OMe), 44.2 (*s*, C-10), 39.5 (*t*, C-6), 35.4 (*t*, C-12), 31.2 (*q*, Me) 24.9 (*q*, Me), 24.1 (*q*, Me), 19.7 (*q*, Me), and 15.8 (*q*, Me).

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