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5,8-DIHYDROXY-3,6,7-TRIMETHOXYFLAVONE FROM *GNAPHALIUM GAUDICHAUDIANUM*

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Key Word Index—*Gnaphalium gaudichaudianum*; Compositae; 5,8-dihydroxy-3,6,7-trimethoxyflavone; 5,8-dihydroxy-6,7-dimethoxyflavone.

Abstract—5,8-Dihydroxy-3,6,7-trimethoxyflavone and 5,8-dihydroxy-6,7-dimethoxyflavone were isolated from aerial parts of *Gnaphalium gaudichaudianum* and identified by spectral data.

Gnaphalium gaudichaudianum DC. is an annual herb found in the humid Pampas and in the sandy, distrubed soils of the semi-arid zone of Argentina. No chemical investigations on this species have been previously reported although the flavonoid constituents of *G. pellitum* [1]; *G undulatum*; *G. wrightii* [2] and *G. elegans* [3] have been studied. The present paper deals with the isolation and identification of 5,8-dihydroxy-3,6,7-trimethoxyflavone (**1**) and 5,8-dihydroxy-6,7-dimethoxyflavone (**2**). To our knowledge **1** has not been reported previously from any natural source. However the related substance, **2** has been isolated from *Helichrysum herbaceum* [4].

The presence of 5,6,7,8-tetrasubstituted flavonoids may be of chemotaxonomical importance since these compounds have been described in other *Gnaphalium* species.

From the methanolic extract of aerial parts of *G. gaudichaudianum* two flavonoids, **1** and **2**, were isolated by chromatographic procedures. High resolution mass spectrometry of **1** exhibited a molecular ion at *m/z* 344.08963 for $C_{18}H_6O_7$. ^{1}H NMR signals indicated the presence of three methoxyls (singlets at δ 3.88, 3.98 and 4.03), two hydroxyls (broad singlets at δ 6.58 and 11.30 interchangeable with D_2O) and an unsubstituted B-ring (two multiplets at 7.46 and 8.08 integrating for 2H and 3H, respectively). The position of these substituents was determined by mass spectral data. Peaks at *m/z* 212 (A_1) and *m/z* 105 (B_2) evidenced the presence of two hydroxyls and two methoxyls in ring A and the absence of substitution in ring B [5], respectively. The intense peak at *m/z* 329 $[M-Me]^+$ indicated that one methoxyl is located either at C-6 or C-8 [5]. The methanolic UV spectrum exhibited a weak Band I in the range for flavonols with the 3-hydroxyl substituted [6]. The structural question remaining was to determine the positions of the methoxyl and hydroxyl groups in ring A. A bathochromic shift of the UV spectrum with aluminium chloride which persisted with concentrated hydrochloric acid suggested that one of these hydroxyls is at the C-5 position [6]. This placement was supported by the D_2O-exchangeable signal at δ 11.30 in the ^{1}H NMR spectrum. The absence of Band III in the sodium methoxide spectrum [7] and the absence of a sodium acetate shift indicated a 7-*O*-substituent. From ^{1}H NMR spectra recorded in the presence of Eu(fod)$_3$ [8] the remaining methoxyl group was assigned to C-6. Finally methylation with diazomethane yielded 3,6,7,8-tetramethoxy-5-hydroxyflavone, which was identified by comparison with physical and spectroscopic literature data [2]. Thus these results clearly demonstrate that **1** must be 5,8-dihydroxy-3,6,7-trimethoxyflavone.

From mass spectrometry ^{1}H NMR data it was concluded that **2** has an unsubstituted B-ring and the same A-ring substitution as **1**, but no methoxyl at C-3. Therefore, **2** is 5,8-dihydroxy-6,7-dimethoxyflavone [4].

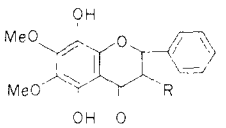
EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were recorded at 60 MHz in $CDCl_3$ with TMS as int. standard. High and low resolution MS were determined on a Varian Mat 112 S at 70 eV. High resolution work was performed by the peak matching technique.

Plant material. Aerial parts of *G. gaudichaudianum* (voucher INTA V.M. 2906) were collected in San Luis, Argentine.

Isolation, purification and identification of **1** *and* **2**. Dried ground plant material was throughly extracted with MeOH. The MeOH extract was concd and chromatographed on a Si gel column packed in C_6H_6 and eluted with C_6H_6–EtOAc mixtures of increasing polarity. Elution with C_6H_6–EtOAc (19:1) yielded a mixture of **1** and **2** that were separated on a Sephadex LH-20 column with MeOH as eluent (yield: 1.10 g of **1** and 0.26 g of **2**).

5,8-*Dihydroxy*-3,6,7-*trimethoxyflavone* (**1**). Mp 177–178° High resolution MS, M^+ 344.08963 ($C_{18}H_6O_7$ requires M^+ 344.08959). UV λ_{max}^{MeOH} nm: 277, 324(sh), 375(sh); +NaOMe: 282, 380; + $AlCl_3$; 252(sh), 291, 341, 420(sh); + $AlCl_3$–HCl: 252 (sh), 291, 342, 420(sh); + NaOAc: 280, 375; NaOAc–H_3BO_3: 277. ^{1}H NMR ($CDCl_3$) δ: 3.88, 3.98, 4.03 (3H each, *s*, 3-, 6-, 7-OMe, respectively), 6.58 (1H, *br s*, 8-OH, exchangeable with D_2O), 7.46 (2H, *m*, H-2′ and H-6′), 8.08 (3H, *m*, H-3′,



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