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COLOMBIAN PLANTS OF THE GENUS *GNAPHALIUM*

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Key Word Index—*Gnaphalium pellitum*; Compositae; 5-hydroxy-7,8-dimethoxyflavone; (+) pinitol.

The present work deals with a study of the chemistry of the flowers of *Gnaphalium pellitum*, a small abundant plant growing on the plain of Bogotá (2500–2700 m altitude). The plants were collected in November 1975 and May 1976. Classification was carried out by the Herbario Nacional, Universidad Nacional de Colombia. This plant is used to reduce swelling [1] and as an ornamental.

EXPERIMENTAL

The dried and ground plant material (2 kg) was exhaustively extracted with petrol (60–80°) the extract treated with EtOH (96%), and the soln was evapd under vacuum to dryness. The resulting dark brown residue was chromatographed on Si gel, using C_6H_6 as eluent. The first fraction gave 27 mg of a flavonoid (*A*) identified as 5-hydroxy-7.8-dimethoxyflavone on the basis of its spectral characteristics. The pure compound was obtained by fractional crystallization from Et_2O as yellow needles, Mp 173–175°. The flavonoid on TLC eluated with C_6H_6–Me_2O (9:1) gave a spot R_f 0.9 which appeared reddish under UV light. The same result was observed with NH_3/UV. With $CoCl_2$ a yellow visible spot appeared. The acetate derivative melted at 164–166°. Tests with $FeCl_3$; Mg/HCl [2, 3] and the Wilson reagent [4] were positive. UV: λ_{max} (MeOH) 275, 294 nm; $AlCl_3$ 275, 294 nm. IR ($CHCl_3$) ν_{max} 3330, 1740, 1650, 1450, 1270, 850, 720 cm^{-1}. MS [5]: 298 (M^+), 283, 280, 267, 166, 148, 113, 105. NMR (TMS, in $CDCl_3$) δ = 2.9 (*s*, 2-OMe); δ = 6.42 (*s*, 6H); δ = 6.65 (*s*, 3H); δ = 7.45–7.60 (*m*, 3H 3′, 4′, 5′); δ = 7.85–8.0 (*m*, 2H-2′, 6′); δ = 12.7 (*s*, OH). [2, 6]. The second fraction gave 160 mg of a compound *B*, with a sweet taste, identified as (+)pinitol as compared to an authentic sample [7]. The ethereal extract afforded 70 mg of a compound identified as Sitosterol.

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NEW FLAVONOIDS FROM *EUPATORIUM INULAEFOLIUM**

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Key Word Index—*Eupatorium inulaefolium*; Compositae; 5,6,3′-trihydroxy-7,4′-dimethoxyflavone; pedalitin.

As a part of our chemical investigation of Argentine medicinal plants, we have examined *Eupatorium inulaefolium* var. *suaveolens* H.B.K. Hier., a perennial shrub of northeastern Argentina which is commonly known as 'sanalotodo' or 'yerba de Santa María' [1]. It is used externally for lavages of sores and pimples [2]. From this plant we have isolated and identified a new natural flavone (**1**), previously synthesized [3]; and

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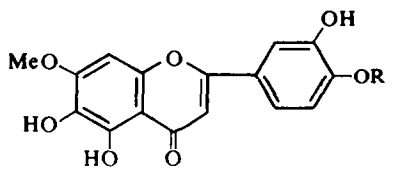
pedalitin (2), which it has been previously reported only as glycoside [4, 5].

The new flavone isolated from a $CHCl_3$ extract has been assigned structure (1) because it gives a positive Sr^{2+}–NH_3 test [6] for 5,6-dihydroxylation and shifts in the UV spectrum are consistent with this oxygenation pattern. A bathochromic shift with NaOMe with decrease in intensity indicates that the 4'-hydroxyl group is substituted. The absence of shift with either NaOMe or $NaOAc/H_3BO_3$ preclude the presence of 7-hydroxyl group or *o*-dihydroxyl group [7]. A shift in band I with $AlCl_3/HCl$ of about 20 nm indicates the presence of a hydroxyl function at the 6 position [8]. The NMR spectrum of (1) in DMSO-d_6 showed signals at δ 4.0 corresponding to two methoxyl groups, singlets at δ 6.7 (H-3), δ 6.9 (H-8) and δ 7.5 (H-2',6') and a doublet at δ 7.1 (H-5'). Peaks in the MS spectrum at 330(M^+), 315 (M-17) and 285 *m/e* (M-49) are in agreement with this structure. After methylation with Me_2SO_4 both (1) and (2) afforded 5-hydroxy-6,7,3',4'-tetramethoxyflavone (mp, UV, NMR) [4, 5].

The Et_2O extract (see Experimental) yielded pedalitin (mp, UV, NMR).



(1) R = Me, 5,6,3'-trihydroxy-7, 4'-dimethoxyflavone

(2) R = H, pedalitin

EXPERIMENTAL

Eupatorium inulaefolium was collected at Colonia Benítez, Province of Chaco, Argentina, February 1976 and a voucher specimen is deposited in the University Herbarium (Museo de Botanica, Universidad de Buenos Aires, Argentina). Air dried ground material (900 g) was extracted (24 hr) at room temp. with aq. MeOH. The aq. MeOH were evapd to dryness, redissolved in hot H_2O and partitioned with petrol, $CHCl_3$ and Et_2O. The petrol extract contained no flavonoids and was discarded. The $CHCl_3$ extract was evapd to dryness and passed twice through a column packed with Sephadex LH_{20} and eluted with C_6H_6, $CHCl_3$ and MeOH. The $CHCl_3$–MeOH eluates afforded 5,6,3'-trihydroxy-7,4'-dimethoxyflavone which crystallized from MeOH as yellow crystals (mp 245–247°). The Et_2O extract was applied to a polyamide column and upon elution with H_2O–MeOH (7:3) afforded 5,6,3',4'-tetrahydroxy-7-methoxyflavone which crystallized from MeOH (mp 295–297°) (lit. 300–301°) [4].

5,6,3'-Trihydroxy-7,4'-dimethoxyflavone. Purple (UV) to yellow-brown (UV/NH_3); R_fs: TBA 0.7, 15% HOAc = 0.02: UV λ_{max} (nm): MeOH, 232*sh*, 253*sh*, 285, 340; NaOMe, 260, 320*sh*, 367; $AlCl_3$, 240*sh*, 262*sh*, 302, 372; $AlCl_3$/HCl, 242*sh*, 257*sh*, 302, 367; NaOAc, 235, 290, 337; $NaOAc/H_3BO_3$, 235, 290, 337. NMR (60 MHz), (DMSO-d_6) using TMS as internal standard, signals at δ 7.5 (2H, *d*, J = 4 Hz), δ 7.1 (1H, *d*, J = 9 Hz), δ 6.9 (1H, *s*), δ 6.7 (1H, *s*) and δ 4.0 (6H, 2Me). MS, principal peaks at 330 (8%) (M^+), 312 (2.4%) ($M^+ - 17$), 283 (3.5%) ($M^+ - 49$), 268 (3.1%) ($M^+ - 64$) and 207 *m/e* (13%) ($M^+ - 125$). The IR and NMR spectra were identical to those of the synthetic compound, kindly provided to us by Prof. H. Wagner.

Methylation with Me_2SO_4 [4] afforded 5-hydroxy-6,7,3',4'-tetramethoxyflanone, yellow crystals from aq. MeOH (mp 188–189°) (lit. 189–190°) [4]. UV λ_{max} (nm), MeOH, 242, 275, 339 [5].

5,6,3',4'-tetrahydroxy-7-methoxy flavone (pedalitin). Purple (UV) to yellow-brown (UV/NH_3); R_fs TBA = 0.66, 15% HOAc = 0.02. Positive test with Sr^{2+}/NH_3. UV λ_{max} (nm): MeOH, 245*sh*, 285, 345; NaOMe, 264, 385; $AlCl_3$ 270, 300, 420; $AlCl_3$/HCl, 257*sh*, 295, 370; NaOAc, 260*sh*, 290, 360; $NaOAc/H_3BO_3$, 260*sh*, 290, 360. NMR (60 MHz) (DMSO-d_6) using TMS as internal standard, signals at δ 7.45 (2H, *d*, J = 3 Hz), δ 6.95 (1H, *d*, J = 9 Hz) δ 6.85 (1H, *s*), δ 6.65 (1H, *s*) and δ3.9 (3H, 1Me). Methylation with Me_2SO_4 afforded 5-hydroxy-6,7,3',4'-tetramethoxyflavone.

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ISOLATION OF STRICTOSIDINE (ISOVINCOSIDE) LACTAM FROM *NAUCLEA LATIFOLIA*

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Key Word Index—*Nauclea latifolia*; Rubiaceae; indole alkaloid glycoside; strictosamide; artifact production.

Nauclea latifolia heartwood, collected in the environs of Ahmadu Bello University, Zaria, Nigeria, was macerated and extracted with methanol. The orange residue left after removal of the solvent, was further