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POLYPHENOLS FROM *ACHYROCLINE SATUREIOIDES**

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Key Word Index—*Achyrocline satureioides;* Compositae; galangin; galangin 3-methyl ether; quercetin 3-methyl ether; protocatechuoylcalleryanin; caffeoylcalleryanin.

Abstract—Galangin, galangin 3-methyl ether, quercetin, quercetin 3-methyl ether, caffeic acid and two esters of calleryanin (3,4-dihydroxybenzylalcohol 4-glucoside), with caffeic acid and protocatechuic acid, have been isolated from aerial parts of *Achyrocline satureioides*.

Achyrocline satureioides DC. (Lam.), which is distributed in dry regions of South America [1], is used in folk medicine [2–4]. Previously, Wagner *et al.* reported the isolation of isognaphaliin (3,7-dimethoxy-5,8-dihydroxyflavone) [5] and Ricciardi and Cassano described the components of the essential oil [6]. The present paper reports the isolation of galangin, galangin 3-methyl ether, quercetin, quercetin 3-methyl ether, caffeic acid and two esters of calleryanin (3,4-dihydroxybenzyl alcohol 4-glucoside) with caffeic acid and protocatechuic acid. Calleryanin was previously isolated from *Pyrus calleryana* [7] but this is the first report of its occurrence in the Compositae. Caffeic acid and its esters have been proved to increase bile flow in rats. The beneficial properties of *A. satureioides* are presumably related to the high content of caffeic acid esters [8].

* Part 12 in the series "Flavonoids from Argentine Medicinal Plants". For Part 11 see Ferraro, G. E., Martino, V. S. and Coussio, J. D. (1977) *Phytochemistry* **16**, 1618.

EXPERIMENTAL

Plants were collected in Concepción del Uruguay, Province de Entre Rios, Argentina. Voucher specimens are deposited in the University Herbarium (Museo de Botánica, Universidad de Buenos Aires).

Extraction. Air-dried, ground aerial parts of *A. satureioides* (1.1 kg) were extracted with 50% aq. MeOH at room temp., the extracts evapd to dryness, taken into hot H_2O and partitioned with C_6H_6, CH_2Cl_2, Et_2O and EtOAc. The C_6H_6 extract was evapd to dryness and passed twice through a column packed with Sephadex LH20 and eluted with C_6H_6, $CHCl_3$ and MeOH. The $CHCl_3$ afforded 5,8-dihydroxy-3,7-dimethoxyflavone. The $CHCl_3$–MeOH eluates gave 5,7-dihydroxy-3-methoxyflavone (galangin 3-methyl ether). Spectral values and colour reactions for this compound were identical with previously reported values [9]. The Et_2O extract was evapd to dryness and passed through a column packed with polyamide. 3,5,7-Trihydroxyflavone (galangin) and quercetin crystallized from different fractions and were identified by mp, mmp, TLC and UV by comparison with authentic samples [9]. The EtOAc extract of *A. satureioides* was concd and run on 1D PC (Whatman No. 3) in

H_2O, giving bands of caffeic acid, caffeoylcalleryanin and protocatechuoylcalleryanin which were eluted with MeOH and taken to dryness.

Caffeic acid (yield 0.5%) was crystallized from MeOH and determined by mp, mmp, TLC, PC and UV by comparison with an authentic sample [10].

Caffeoylcalleryanin (ester of caffeic acid with 3,4-dihydroxybenzyl alcohol 4-glucoside). Pale yellow amorphous powder. UV: pale blue; UV/NH_3: greenish grey. PC Whatman No. 1: 2% HOAc, H_2O, 0.1 N HCl and PhOH–H_2O (4:1) R_fs: 0.19, 0.10, 0.13 and 0.60, respectively. Found: C, 56.21; H, 5.22; $C_{22}H_{24}O_{11}$ requires: C, 56.89; H, 5.17%. UV λ_{max}^{MeOH} nm: 244, 292 sh., 332; NaOMe: 267, 300 sh., 378 [7, 11].

Protocatechuoylcalleryanin (ester of protocatechuic acid with 3,4-benzyl alcohol 4-glucoside). Pale yellow amorphous powder. UV: very pale blue, UV/NH_3: yellow. Colour reactions: NH_3, yellow; $FeCl_3$, greenish grey. PC Whatman No. 1, 2% HOAc; H_2O; 0.1 N HCl and PhOH–H_2O (4:1) R_fs: 0.40, 0.48, 0.53 and 0.51, respectively. Found: C, 50.07; H, 5.62. $C_{20}H_{22}O_{11}\cdot 2H_2O$ requires: C, 50.63; H, 5.48%. UV λ_{max}^{MeOH} nm: 260, 282 sh, 300; NaOMe: 240, 320.

Alkaline hydrolysis: Both caffeoylcalleryanin and protocatechuoylcalleryanin gave 3,6-dihydroxybenzyl alcohol 4-glucoside (calleryanin) on alkaline hydrolysis with 10 N KOH at room temp. for 30 min. Calleryanin was determined by the method of Challice and Williams [7]. Protocatechuic acid (3,4-dihydroxybenzoic acid) was determined by TLC, PC, UV spectroscopy and by comparison with an authentic sample. Caffeic acid (3,4-dihydroxycinnamic acid), extracted with Et_2O from the hydrolysate, was determined by the method of Nichiforescu–Coucou [10] and by UV, mp and mmp.

Enzymatic hydrolysis. Both caffeoylcalleryanin and protocatechuoylcalleryanin were hydrolysed with β-glucosidase, pH 5.0, at room temp. for 24 hr. Caffeic and protocatechuic acids and 3,4-dihydroxybenzyl alcohol were identified as above. Glucose was determined by descending PC by comparison with an authentic sample.

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