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FLAVONOID GLYCOSIDES OF *LATHYRUS PRATENSIS* (LEGUMINOSAE)

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Key Word Index—*Lathyrus pratensis*; Leguminosae; flavonoids; flavonol glycosides; flavone glycosides; tricetin 7-diglucoside; myricetin 3-diglucoside.

Abstract—Eight flavonoid glycosides have been identified in the leaves of *Lathyrus pratensis*, two of which are new glycosides.

INTRODUCTION

In the course of a chemotaxonomic investigation of the Leguminosae, we examined the flavonoid glycosides from *Lathyrus pratensis*. A two-dimensional TLC from the EtOAc fraction of the leaves and stems of *Lathyrus pratensis* revealed 17 spots due to flavonoid glycosides. Of these twelve were isolated and identified [1–4]. Previous investigations on the flavonoid glycosides of *Lathyrus pratensis* [5–9] have revealed the presence of tricetin 3′-glucoside, luteolin 4′-glucoside, quercetin 3-glucoside and luteolin 7-glucoside. The occurrence of kaempferol, quercetin and myricetin glycosides has also been reported, but without further identification [6–12].

RESULTS AND DISCUSSION

Six glycosides of flavonols were isolated and identified: quercetin 3-diglucoside, myricetin 3-diglucoside, quercetin 3-arabinoside, myricetin 3-arabinoside, quercetin 3-glucoside and kaempferol 3-glucoside. Their identification was realized through their chromatographic and spectrophotometric properties before and after acid hydrolysis. The sugars were identified by GC of their silylated derivatives; the number and position of sugars were determined by the UV spectroscopy, and by chromatographic comparison with reference samples.

Six flavone glycosides were separated: luteolin 3′-glucoside, luteolin 4′-glucoside, luteolin 7-diglucoside, tricetin 3′-glucoside, tricetin 7-diglucoside and apigenin 7-diglucoside; for this last compound, the quantity isolated was too small to be sure of the identification. These identifications were determined in the same way as for the flavonol glycosides.

The present results are a substantial contribution to our knowledge of *Lathyrus pratensis* flavonoid glycoside pattern. On the chemotaxonomic side, the occurrence of tricetin in *Lathyrus pratensis* is significant; two glucosides of this rare flavone [5–8] were identified. One of them (tricetin 7-diglucoside) is, to our knowledge, a new natural product. In addition, the relative importance of flavones with a B-ring glycosylation and of myricetin glycosides must be noted. Also, myricetin 3-diglucoside appears to be a new product [10]. Most of the other flavonoid glycosides have a relatively widespread distribution in the Leguminosae [9–11].

EXPERIMENTAL

Plants were collected in France and vouchers are retained in the laboratory. Dried, powdered aerial parts (leaves and stems, 250 g) were extracted 3 ×, in cold, with MeOH–H_2O (7:3) for 72 hr. The MeOH–H_2O extracts were concd under red. pres. and the residue was extracted with boiling H_2O. When cold, the H_2O-soluble fraction was filtered, then extracted several times with EtOAc. The EtOAc extract was concd to dryness under red. pres. and dissolved in MeOH. This MeOH extract was separated by PC (Whatman No. 3) in HOAc–H_2O (3:20). Chromatographic bands were eluted with MeOH, then separated again by prep. TLC (C_6H_6–MeCOEt–MeOH 4:3:3 or H_2O–MeOH–MeCOEt–Ac_2CH_2, 40:15:8:7). Chromatographic bands were eluted with MeOH.

The identity of flavonoid glycosides was determined by chromatography together with authentic samples and by UV spectrophotometry, before and after acid hydrolysis. Hydrolysis was performed with 2 N HCl at 100° for 10–90 min according to the position of sugars. Sugars were identified by GC after silylation with C_5H_5N and BSTFA + 1% HMDS on Gas Chrom Q, 80–100 mesh, with 5% SE 52. Myricetin 3-diglucoside: UV λ_{max} nm: MeOH 257–361; +NaOAc 272–390; +H_3BO_3 259–385; $AlCl_3$ 272–428; +HCl 272–365–405; NaOMe 268–385. Tricetin 7-diglucoside; UV λ_{max} nm: MeOH 268–338; +NaOAc (272) 350; +H_3BO_3 265–372; $AlCl_3$ 272–423; +HCl 272–360–395.

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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