

IRIDOIDS AND A PHENYLPROPANOID GLYCOSIDE FROM *PENSTEMON ROSSEUS*¹

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As a part of our continuing studies on secondary metabolites of the genus *Penstemon* (Schrophulariaceae) of México, we have investigated *Penstemon rosseus* (Sweet) G. Don which is widely distributed in México.

From a methanolic extract of dried aerial parts of this plant, we have isolated two iridoid glucosides, namely boschnaloside and plantarenalosite, as well as acteoside, a phenylpropanoid glycoside. The last compound was isolated as the nonaacetyl derivative. This is the first report of these compounds in plants of this genus; their identification was accomplished by means of chemical and spectroscopic methods.

Boschnalosite and plantarenalosite have been previously reported as constituents of *Leuocarpus perfoliatus* (Schrophulariaceae) (1) and boschnalosite and acteoside of *Boschniaka rossica* (Orobanchaceae) (2,3). It is interesting to point out the coexistence of these compounds as constituents of *P. rosseus*.

EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *P. rosseus* (Sweet) G. Don were collected in July 1983, in Cerro del Ajusco, D.F., México. The plant was identified by Dr. Concepción Rodríguez (Botany Department, Escuela Nacional de Ciencias Biológicas, IPN), and a voucher specimen (reg. no. 345231) was deposited in the MEXU herbarium (Instituto de Biología, UNAM, México).

EXTRACTION AND FRACTIONATION.—Dried aerial parts (1 kg) were extracted with MeOH (10 liters) at room temperature for 3 days. The extract was concentrated under reduced pressure to a solid (60 g) that was suspended in H₂O (3 liters) and partitioned first with EtOAc (3 liters), and then with *n*-BuOH (3 liters × 2). The *n*-BuOH extract was concentrated in vacuo, and the residue (26.4 g) was chromatographed on a charcoal column developing with H₂O, H₂O-MeOH (1:1), and MeOH (ca. 3 liters each fraction); the H₂O eluate was discarded, and the others were concentrated under reduced pressure to yield Fraction A (6.86 g) and Fraction B (4.30 g), respectively.

SEPARATION AND ISOLATION.—Flash column chromatography of fraction A (1 g) on silica gel, using EtOAc-MeOH (9:1) as eluent, allowed the separation of boschnalosite and plantarenalosite. Fractions 1-6 afforded boschnalosite, which was crystallized from Me₂CO to yield 200 mg, mp=98-100° (uncorrected dec). The following fractions, a mixture of both iridoids, were rechromatographed as above with CH₂Cl₂-MeOH (8:2) as eluent. In this way, an additional 120 mg of boschnalosite and 11 mg of plantarenalosite were obtained.

Fraction B was shown by tlc to consist of two compounds. One of them was plantarenalosite and the other acteoside which was isolated as the acetyl derivative. Fraction B (1 g) was acetylated with pyridine (5 ml) and Ac₂O (5 ml) for 6 days at room temperature. Usual work-up followed by chromatography of the product (1.245 g) on silica gel (70-230 mesh) with development by hexane and EtOAc afforded two principal products. The first one was eluted by hexane-EtOAc (6:4) and was shown to be plantarenalosite tetraacetate (80 mg), and the second one was eluted by hexane-EtOAc (4:6) (660 mg). Because this product was a mixture (as indicated by ¹H-nmr analysis), an aliquot (160 mg) was rechromatographed by hplc (MICROPAK Si-10 column, 25 cm × 2.2 mm id.; mobile phase-hexane-EtOAc, 3:7; flow rate: 3.67 ml/min) to yield 99 mg of nonaacetyl as a white amorphous powder, mp 73-75° (uncorrected dec).

All compounds were identified by direct comparison with literature data (2-4) using accepted techniques (uv, ir, ¹H nmr, ¹³C nmr). Full details of the isolation and identification of these compounds are available from the senior author upon request.

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LITERATURE CITED

1. Y. Ozaki, S. Johne, and M. Hesse, *Helv. Chim. Acta*, **62**, 2708 (1979).
2. F. Murai and M. Tagawa, *Chem. Pharm. Bull.*, **28**, 1730 (1980).
3. T. Konishi and J. Shoji, *Chem. Pharm. Bull.*, **29**, 2807 (1981).
4. A. Bianco, M. Guiso, C. Iavarone, M. Massa, C. Trogolo, J. V. Oguakwa, and A. Francesconi, *Gazz. Chim. Ital.*, **112**, 199 (1982).

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BIFLAVONES FROM THE LEAVES OF *ARAUCARIA ARAUCANA*

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A number of biflavones have been reported from the leaves of *Araucaria bidwilli* (1-3), *Araucaria cookii* (3-7), *Araucaria cunninghamii* (3,6,8,9), *Araucaria excelsa* (10,11), and *Araucaria rulei* (1). The chemotaxonomic significance of the biflavones in the genus *Araucaria* (3) and their anticancer activity (N.U. Khan, N. Parveen, M. Parveen, and H.M. Taufeeq, unpublished results) prompted us to investigate *Araucaria araucana* (Molina) K. Kock (Araucariaceae). In the present communication we report the occurrence of several biflavones isolated by the method of Khan *et al.* (3). The major leaf constituents identified were 7-*O*-methylgathisflavone, 7ⁿ-*O*-methylamentoflavone, and 7,7ⁿ-di-*O*-methylcupressuflavone.

The minor constituents, di-*O*-methylgathisflavone, di-*O*-methylamentoflavone, tri-*O*-methylgathisflavone, tri-*O*-methylamentoflavone, and tri-*O*-methylcupressuflavone were tentatively identified based on their R_f values and characteristic colors in uv light with authentic samples (3,4).

EXPERIMENTAL

PLANT MATERIAL.—*A. araucana* was collected from Lylod Botanical Garden, Darjeeling, in March 1984 and identified by Dr. W. Husain, Reader, Department of Botany, A.M.U., Aligarh. A voucher specimen was submitted to the A.M.U. Herbarium, Aligarh (Voucher No. Husain-49601).

ISOLATION AND IDENTIFICATION.—Dried and powdered leaf material of *A. araucana* (1 kg), after being defatted with light petrol, was extracted with Me₂CO. The Me₂CO extract was concentrated, and the residue was refluxed with light petrol, C₆H₆, and CHCl₃, treated with boiling H₂O, and filtered. The yellow, solid, undissolved residue (2.5 g) yielded six chromatographically homogeneous fractions, AA-I to AA-VI, after development on a Si gel column and subsequent preparative tlc (Si gel, C₆H₆-pyridine-