FLAVONOIDS OF *HAPLOPAPPUS RENGIFOANUS* REMY IN GAY

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ABSTRACT.—Eight flavonoids, including the new scutellarein 6-β-D-glucoside, were isolated from the leaves of *Haplopappus rengifoanus* Remy in Gay (Compositae). The known compounds are apigenin, luteolin, quercetagetin 3-methyl ether, quercetagetin 3,7-dimethyl ether, isorhamnetin and its 3-β-D-galactoside, and 3-β-D-glucoside.

The present report of the flavonoids in *Haplopappus rengifoanus* represents the initial chemical investigation of South American *Haplopappus* as part of an extensive morphological, chemical, cytological, and palynological study of this genus. Although little work has previously been carried out on South American species (1), much is known about North American taxa formerly considered congeneric with *Haplopappus* (2–5). The chemical data are expected to aid in resolving long-standing questions concerning the generic limits of *Haplopappus*.

EXPERIMENTAL[1]

PLANT MATERIAL.—The leaves of *H. rengifoanus* were collected 20 km north of La Serena, Prov. Coquimbo, Chile, in January, 1979. A voucher specimen (Clark and Brown 1285) is deposited in the Arizona State University Herbarium.

EXTRACTION AND ISOLATION OF THE FLAVONOIDS.—Dried and powdered leaves (200 g) of *H. rengifoanus* were extracted with 85% aqueous ethanol followed by 50% ethanol and water. The combined extracts were evaporated to a small volume *in vacuo*. The aqueous syrup was extracted with *n*-hexane, chloroform, and ethyl acetate. The three extracts were evaporated to dryness *in vacuo* to yield 1.6 g, 10.3 g, and 5.8 g of residue, respectively. The remaining aqueous portion yielded 22.8 g of a brown syrup. Two-dimensional paper chromatography showed that only the ethyl acetate and aqueous fractions contained flavonoids; since no additional flavonoids were detected in the latter fraction, only the ethyl acetate fraction was examined in detail.

A polyclar column (5 x 40 cm) was used for the separation of flavonoids from the ethyl acetate fraction. The elution was initiated with ethanol and was continued with increasing amounts of water up to 100%.

SCUTELLAREIN 6-β-D-GLUCOSIDE (5 MG).—Hydrolysis of the new glycoside with both 0.1 N TFA for 2 hrs. and β-glucosidase yielded glucose and scutellarein (6-hydroxyapigenin) (uv spectra and tlc comparison with a standard sample). The compound appeared purple when viewed on paper under uv light (366 nm) and yellow-green with NH_3 and appeared brownish when sprayed with NA reagent on a cellulose plate. Since the NaOMe uv spectral data for the glucoside established a 4'-OH (Band I exhibited a bathochromic shift of 55 nm with an increase in intensity relative to Band I in the MeOH spectrum) and a 7-OH (Band III at 328 nm), the glucosyl moiety must be at the 6-OH. This was confirmed by the $AlCl_3$/HCl spectrum in which Band I exhibited a bathochromic shift of 19 nm relative to Band I in MeOH, as expected for flavones with a 6-OR group (6). After hydrolysis, this same reagent gave a shift of 26 nm in accord with a 6-OH group. Thus the compound must be scutellarein 6-β-D-glucoside. The complete spectral data for this new glycoside are: uv λ max (MeOH), 336, 276,

[1]Spectra were recorded with the following instruments: uv, Varian Techtron model 635; pmr, Varian 90 MHz; ms, DuPont 21-491. Adsorbents for cc and tlc were from E. Merck and Macherey-Nagel.

NaOMe, 391, 328, 276; $AlCl_3$, 355, 303, 280; $AlCl_3$/HCl, 355, 305, 276 (sh); NaOAc 350, 296, 276; NaOAc/H_3BO_3, 355, 276; pmr (as TMS derivative in CCl_4), δ 7.72, d, J=9Hz for H-2' and H-6'; 6.95, d, J=9Hz, for H-3' and H-5', 6.58, s, for H-8, 6.54, s, for H-3, glucosyl H-1 at δ 5.0, d, J=7Hz; other sugar protons appeared between δ 3.5–4.0; ms (underivatized) M^+ 286; A_1 168; (A_1–H_2O), 150; B_1, 118.

APIGENIN (5 MG), LUTEOLIN (5 MG) AND ISORHAMNETIN (20 MG).—Uv, ms, pmr (for isorhamnetin) and direct tlc comparisons with standard samples established these compounds.

ISORHAMNETIN 3-β-D-GLUCOSIDE (5 MG).—Hydrolysis with acid and β-glucosidase yielded glucose and isorhamnetin (uv, pmr, ms and tlc comparison with an authentic sample). The uv spectral data for this glucoside (7), colors on paper under uv light before and after hydrolysis, and the chemical shift of the glucosyl H-1 in pmr (δ 5.9) established a 3-O linkage. Direct tlc comparison with authentic isorhamnetin 3-β-D-glucoside confirmed the structure assignment.

ISORHAMNETIN 3-β-D-GALACTOSIDE.—The uv spectral properties (8) as well as colors on paper under uv light were similar to those observed for isorhamnetin 3-glucoside; however, this compound afforded isorhamnetin and galactose when hydrolyzed with acid and β-galactosidase. Since the R_f values were essentially the same as those observed for isorhamnetin 3-glucoside, this compound can be assigned a monogalactoside structure.

QUERCETAGETIN 3-METHYL ETHER.—Although this compound was present in the plant in only trace amounts, tlc comparison with an authentic sample showed it to be quercetagetin 3-methyl ether (9).

QUERCETAGETIN 3,7-DIMETHYL ETHER.—The uv and ms spectral properties as well as tlc comparison with a standard sample showed that this trace compound was quercetagetin 3,7-dimethyl ether (10).

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