6-OXYGENATED FLAVONOIDS[1] FROM *NEUROLEANA MACROPHYLLA*

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ABSTRACT.—Of twelve flavonoids isolated from *Neurolaena macrophylla* three, luteolin 7-β-D-glucoside, 6-hydroxykaempferol 3,6,4'-trimethyl ether, and 6-hydroxykaempferol 6-methyl ether 7-β-D-glucoside were found in this genus for the first time. The other known flavonoids were 6-hydroxyluteolin 7-β-D-glucoside, quercetagetin 3,7-dimethyl ether, quercetagetin 3,6-dimethyl ether, quercetagetin 6-methyl ether 7-β-D-glucoside, quercetagetin 7-β-D-glucoside, quercetagetin 3-methyl ether 7-β-D-glucoside, 6-hydroxykaempferol 7-β-D-glucoside, kaempferol 3-β-D-glucoside, and kaempferol.

In a continuation of our chemical investigation of the genus *Neurolaena* (Compositae-Heliantheae) (1–3), we report the isolation and characterization of twelve flavonoids from *N. macrophylla* Greenm. from Guatemala. We previously described fifteen flavonoids from *N. oaxacana* (1), seven from *N. venturana* (2), twelve from *N. lobata* (3) and six from *N. macrocephala* (3).

The leaves of *N. macrophylla* were first extracted in a Soxhlet with benzene, chloroform and ethanol and, later, with aqueous ethanol. Two dimensional paper chromatography showed that most of the flavonoids were in the chloroform extract; the other extracts contained only traces of some of the same compounds. The chloroform extract yielded luteolin 7-β-D-glucoside (4), 6-hydroxyluteolin 7-β-D-glucoside (5), quercetagetin 3,7-dimethyl ether (6), quercetagetin 3,6-dimethyl ether (7), quercetagetin 6-methyl ether 7-β-D-glucoside (8), 6-hydroxykaempferol 6-methyl ether 7-β-D-glucoside (9), quercetagetin 7-β-D-glucoside (10), 6-hydroxykaempferol 7-β-D-glucoside (9), 6-hydroxykaempferol 3,6,4'-trimethyl ether (11), quercetagetin 3-methyl ether 7-β-D-glucoside (1), kaempferol 3-β-D-glucoside (1) and kaempferol.

EXPERIMENTAL[1]

PLANT MATERIAL.—Leaves of *N. macrophylla* were collected in Guatemala, Quetzaltenango Department, upper reaches of the Pirineos, 5 km below Santa Maria de Jesus, at km post 197, Highway C.A. 95 on January 20, 1980. Voucher specimens J. MacDougal No 603 are deposited in the Herbaria of Duke University and the University of Texas at Austin.

EXTRACTION AND IDENTIFICATION OF FLAVONOIDS.—General chromatographic techniques were described in a previous paper (1). Ground leaves of *N. macrophylla* (585 g) were extracted in a Soxhlet with benzene, chloroform, ethanol, and aqueous ethanol.

CHLOROFORM EXTRACT.—The concentrate from the chloroform extract was chromatographed over a polyclar column (4x50 cm). Elution was initiated with Egger's solvent (methylene chloride-methanol-2 butanone-acetone, 20:10:5:1), and the polarity was gradually increased by reduction of the amount of methylene chloride.

LUTEOLIN 7-β-D-GLUCOSIDE (2 mg), 6-HYDROXYLUTEOLIN 7-β-D-GLUCOSIDE (2 mg).—Uv data taken both before and after hydrolysis, ms data of underivatized compounds, both acid (0.1 N TFA) and enzyme hydrolysis, as well as tlc comparison with standard samples established the structures.

[1]Spectra were recorded with the following instruments: uv Varian Techtron model 635; pmr Varian 90 MHz and Varian 200 MHz; ms DuPont 21-491. Adsorbants for cc and tlc were from E. Merck and Macharey-Nagel.

6-HYDROXYKAEMPFEROL 6-METHYL ETHER 7-β-D-GLUCOSIDE (16 mg), 6-HYDROXYKAEMPFEROL 7-β-D-GLUCOSIDE (10 mg), KAEMPFEROL 3-β-D-GLUCOSIDE (20 mg).—Each of these compounds yielded the expected aglycones and sugars when hydrolyzed with both acid (0.1 N TFA) and enzyme. The pmr and uv spectral data taken both before and after hydrolysis, ms of underivatized compounds, and standard sample comparisons showed the structures.

QUERCETAGETIN 6-METHYL ETHER 7-β-D-GLUCOSIDE (18 mg), QUERCETAGETIN 7-β-D-GLUCOSIDE (10 mg).—The colors under uv light (366 nm) indicated free 3-OH groups for both compounds. Hydrolysis with acid (0.1 N TFA) and enzyme yielded quercetagetin 6-methyl ether and quercetagetin as aglycones and glucose as sugar for both compounds. Pmr and uv spectral data before and after hydrolysis, ms of the underivatized compounds and direct comparison with authentic samples established the identities of the two compounds.

QUERCETAGETIN 3-METHYL ETHER 7-β-D-GLUCOSIDE (9 mg).—Uv data before and after hydrolysis, ms data of underivatized compound as well as standard sample comparisons proved the structure.

QUERCETAGETIN 3,7-DIMETHYL ETHER (10 mg), QUERCETAGETIN 3,6-DIMETHYL ETHER (15 mg), 6-HYDROXYKAEMPFEROL 3,6,4'-TRIMETHYL ETHER (15 mg) AND KAEMPFEROL (5 mg).—Uv, pmr and ms data and standard sample comparison (except 6-hydroxykaempferol 3, 6, 4'-trimethyl ether) proved the structures of the compounds.

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