3-METHOXY-5-HYDROXYFLAVONOLS FROM *TILLANDSIA PURPUREA*

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The chemistry of *Tillandsia* (Bromeliaceae) has been but little explored, with work reported on triterpenoids and steroids (1), a variety of flavonoids (2,3) from *T. usneoides* and *T. utriculata* and polysaccharides (4) from *T. aeranthos*. Flavonoids from these and 15 other *Tillandsia* species were also identified (5) in an extensive report dealing with the systematics of the Bromeliaceae. It was reported (6) that *T. mooreana* is considered by the Tarahumara of northern Mexico to be a companion plant to peyote. Several *Tillandsia* species, including *T. purpurea* Ruiz and Pav., are depicted on pre-Incan Mochica pottery of northern Peru (7), and it has been suggested[1] that these depictions are often in a context which can be interpreted as having "magic" connotations.

Alkaloid tests on *T. purpurea* by a differential pH extraction and tlc screening with iodoplatinate visualization were negative. The crude MeOH extract showed the presence of many flavonoids by tlc and ^{1}H-nmr spectroscopy. Two of the flavonoids were isolated and shown to be retusin (5-hydroxy-3,7,3′,4′-tetramethoxyflavone) and artemetin (5-hydroxy-3,6,7,3′,4′-pentamethoxyflavone) by ^{1}H nmr, uv, and tlc in comparison with literature values and standard samples. The ^{1}H-nmr spectrum of an additional fraction suggested that one further component was penduletin 4′-*O*-methyl ether (5-hydroxy-3,6,7,4′-tetramethoxyflavone), but a standard sample was not available. The remainder of the complex mixture was composed of several additional highly methoxylated 5-hydroxyflavones as evidenced by the ^{1}H-nmr spectrum. Although the flavonoids isolated are not particularly rare, none has previously been reported (2,3,5) from *Tillandsia* species.

The biological activity of these compounds is not known, but it was recently shown (8) that the antiviral activity of some flavones correlated with the presence of a 3-methoxy-5-hydroxy substituent pattern, and highly methoxylated 5,6-hydroxyflavones were the major constituents in two *Thymus* species used widely in folk medicine (9,10).

EXPERIMENTAL

PLANT MATERIAL AND EXTRACTION.—Plants of *T. purpurea* were colleced in bloom March 24, 1982, at Cajamarquilla near Lima, Peru with assistance and identification by Dr. R. Ferreyra, Museo Historia Naturales, Universidad de San Marcos (voucher specimen FR 5313, Colorado State Herbarium). They were grown in a greenhouse (Colorado) until 1985 when extractions were made. Fresh plant material was extracted cold with MeOH, and the residue after evaporation was partitioned between Et_2O and H_2O. The H_2O layer contained a mixture of α- and β-glucose. The Et_2O layer residue was triturated with H_2O, then with $CHCl_3$ and the $CHCl_3$-soluble flavonoids were separated and purified by chromatography. Details of isolation and compound identification are available from F.R. Stermitz.

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FLAVONOIDS FROM *AGERATINA SALTILLENSIS*

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In a continuation of our chemotaxonomic studies in the tribe Eupatorieae (Compositae) (1-5), we investigated the flavonoids of *Ageratina saltillensis* (B.L. Robinson) R.M. King & H. Robinson. Thirteen 6-methoxylated and non-6-methoxylated flavonol derivatives have been isolated, namely: 6-methoxykaempferol and its 3-*O*-glucoside and 3-*O*-rhamnoside, 7-methyl ether and 7-methyl ether 3-*O*-rhamnoside; quercetin and its 3-methyl ether and 3-*O*-glucoside; 6-methoxyquercetin and its 3-methyl ether, 3,4′-dimethyl ether, 3-*O*-glucoside and 7-methyl ether 3-*O*-rhamnoside. The earlier studies of the genus *Ageratina* have shown that the 6-methoxylation, 7-methoxylation, and 6,7-dimethoxylation are characteristic of the main evolutionary line in the genus *Ageratina* (1-7). In our present study, we found that *A. saltillensis* contains mainly flavonoids with 6-methoxylation and 6,7-dimethoxylation (see Experimental section), which provides support for its alignment with the other species placed in *Ageratina* (1-7).

EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *A. saltillensis* (1400 g) were collected 9.2 mi northeast of San Antonia Tena Nevada on the road to Zaragosa, Nuevo Leon Mexico, on October 7, 1984. Voucher material (Ayers No. 489) is deposited in the Plant Resources Center of the University of Texas at Austin.

EXTRACTION, ISOLATION, AND IDENTIFICATION.—Ground, dried leaves and flowers of *A. saltillensis* were extracted sequentially with 90% MeOH and 50% MeOH. After filtration the extracts were combined and concentrated to an aqueous layer under reduced pressure, and the concentrate was partitioned against CH_2Cl_2 and EtOAc. The concentrate from the CH_2Cl_2 and the EtOAc extracts were chromatographed over Polyclar AT (GAF Corp.) columns packed initially in toluene; during elution the solvent was gradually altered in 10% increments to 100% MeOH and finally concluded with Me_2CO-MeOH (1:1). Fractions, which were collected by monitoring the column with uv light, were further separated by paper chromatography using 15% HOAc on Whatman 3MM paper. The EtOAc fraction yielded all the compounds [6-methoxykaempferol (10 mg) and its 3-*O*-glucoside (42 mg) and 3-*O*-rhamnoside (16 mg), quercetin (18 mg) and its 3-*O*-glucoside (21 mg), 6-methoxyquercetin (30 mg) and its 3-*O*-glucoside (2,565 mg) and 7-methyl ether 3-*O*-rhamnoside (568 mg) except for 6-methoxykaempferol 7-methyl ether (74 mg), quercetin 3-methyl ether (8 mg), and 6-methoxyquercetin 3,4′-dimethyl ether (26 mg) which were isolated from the CH_2Cl_2 extract and 6-methoxykaempferol 7-methyl ether 3-*O*-rhamnoside (3,884 mg) and 6-methoxyquercetin 3-methyl ether (15 mg) which were detected in both the CH_2Cl_2 and EtOAc fractions.

All compounds were purified over Sephadex LH-20 in 80% or 100% MeOH prior to analysis by uv, ^{1}H nmr (as TMSi ethers), color reactions on paper under uv light (8), and comparisons with authentic samples.

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