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## FLAVONOLS AND FLAVONOL GLYCOSIDES FROM *EUPATORIUM AREOLARE* VAR. *LEIOCARPUM*

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In a continuation of our chemotaxonomic studies in the tribe Eupatorieae (Compositae) (1-8), we have investigated *Eupatorium areolare* var. *leiocarpum* B. L. Robins. Our work has focused upon finding chemical correlates with the generic limits proposed by King and Robinson in their taxonomic revision of the Eupatorieae (9, 10 and references therein). These authors recognize 180 genera (many of which they have created from the large genus *Eupatorium* L.) in a tribe where traditionally fewer than 50 genera have been accepted. The subject of this work, *E. areolare* var. *leiocarpum*, has not been directly treated by King and Robinson, but they would presumably include it within the small genus *Piptothrix* Gray (subtribe Oxylobinae) to which they have transferred the typical variety of this species, *E. areolare* DC. (11). In this

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study, we report sixteen 6-methoxylated and non-6-methoxylated flavonol derivatives, namely: 6-methoxykaempferol, patuletin (6-methoxyquercetin), eupatolitin (6,7-dimethoxyquercetin), quercetin, and their 3-*O*-glucosides and 3-*O*-galactosides, as well as penduletin (3,6,7-trimethoxykaempferol), ombuin (4′,7-dimethoxyquercetin), and eupalitin (6,7-dimethoxykaempferol) and its 3-*O*-galactoside. We also include the previously unreported $^{13}$C-nmr data for patuletin-3-*O*-galactoside.

If this variety is correctly placed in the genus *Piptothrix*, the flavonoids isolated, in accord with morphological affinities, would support a close relationship of *Piptothrix* to the large segregate genus *Ageratina*. The latter genus, which King and Robinson ally closely with *Piptothrix* (11), contains similar or identical 6-methoxylated, 7-methoxylated, and 6,7-dimethoxylated kaempferol and quercetin derivatives (12,13).

## EXPERIMENTAL

PLANT MATERIAL.—Leaves and heads of *E. areolare* var. *leiocarpum* (900 g) were collected near Huitzilac, State of Morelos, Mexico, on January 5, 1984. A voucher specimen (Gage and Calderon no. 1262) is on deposit at the Plant Resources Center of the University of Texas at Austin.

EXTRACTION, ISOLATION, AND IDENTIFICATION.—Ground leaves and heads of *E. areolare* var. *leiocarpum* were extracted sequentially with 90% aqueous MeOH and 50% aqueous MeOH. After filtration, the extracts were combined and concentrated in vacuo until only $H_2O$ remained. The aqueous syrup was partitioned first against $CH_2Cl_2$ and then EtOAc. The $CH_2Cl_2$ extract was concentrated and adsorbed onto celite. After drying, the resulting powder was charged onto a Polyclar (GAF Corp.) column packed in toluene. Flavonoids were eluted with a toluene/MeOH gradient with increasing amounts of MeOH. In the order of elution the following compounds were obtained: eupalitin, ombuin, penduletin, eupatolitin-3-*O*-glucoside, patuletin, and the 3-*O*-glucoside of 6-methoxykaempferol. The EtOAc extract was chromatographed over a Polyclar column using the same procedure described for the $CH_2Cl_2$ extract. This column afforded sequentially eupalitin-3-*O*-galactoside, eupatolitin-3-*O*-galactoside, eupatolitin, eupatolitin-3-*O*-glucoside, 6-methoxykaempferol-3-*O*-galactoside, patuletin-3-*O*-galactoside and 3-*O*-glucoside, quercetin-3-*O*-galactoside, quercetin, quercetin-3-*O*-glucoside, and finally patuletin. Patuletin-3-*O*-galactoside-$^{13}$C nmr (90.8 MHz, DMSO-$d_6$) 177.6 (s, C-4), 157.2 (s, C-7), 156.3 (s, C-2), 152.3 (s, C-5), 151.4 (s, C-9), 148.5 (s, C-4′), 144.8 (s, C-3′), 133.0 (C-3), 131.1 (s, C-6), 121.8 (s, C-1′), 121.1 (d, C-6′), 115.9 (d, C-5′), 115.1 (d, C-2′), 104.2 (s, C-10), 101.8 (d, C-1′), 93.8 (d, C-8), 75.7 (d, C-5″), 73.2 (d, C-3″), 71.2 (d, C-2″), 67.8 (d, C-4″), 60.4 (q, OMe), and 59.9 (t, C-6″).

All compounds were purified over Sephadex LH-20 (100% MeOH) prior to spectral analyses. Compounds were identified by uv, $^1$H nmr, ms (following acid hydrolysis for the glycosides), color reactions (14), and authentic sample comparisons. Details of the identifications are available upon request.

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