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FLAVONOL AND COUMARIN GLYCOSIDES FROM *ARTEMISIA INCANESCENS*

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In the course of our research on the chemotaxonomy of the genus *Artemisia* (Compositae), we previously reported (1) on the isolation of several 3-methoxyflavones and coumarins from the ether-soluble portion of a MeOH extract of *Artemisia incanescens* Jordan [syn. = *A. alba* Turra, *A. camphorata* Vill., *A. lobelii* All., and *A. suavis* Jordan (2)]. We now report the results of our studies on the more polar fraction of the MeOH extract, which enabled the isolation of four flavonol aglycones, six flavonol glycosides, and two coumarin glycosides. Furthermore, we report the results of our investigation on a root extract, which yielded coniferyl alcohol and the coumarins scopoletin and isofraxidin. Sesquiterpene lactones and coumarin-sesquiterpene ethers (3) were not found.

Within the genus *Artemisia* flavonol derivatives appear to be specially abundant in the sect. *Abrotanum*, whereas the species of the sect. *Absinthium* form predominantly flavones and only a few classes of flavonols (4). The rich variety of flavonols we have isolated from *A. incanescens* (1) would perhaps support its inclusion into the sect. *Abrotanum* rather than *Absinthium*, as proposed by Greger (3) for the synonymous *A. alba*.

PLANT MATERIAL, EXTRACTION, AND ISOLATION.—The plant material and methods have been described previously (1). The EtOAc extract (1) was concentrated to dryness (11 g) and chromatographed on Polyamide MN SC6 (500 g). Elution with H₂O to MeOH gave, after inspection by tlc, two main fractions A (4.3 g) and B (4.1 g). Fraction A was rechromatographed on polyamide (elution with toluene-MeOH-MeCOEt, 3:1:1). This gave successively isorhamnetin (4 mg), 6-methoxykaempferol (3 mg), kaempferol (15 mg), quercetin (20 mg), kaempferol 3-glucoside (13 mg), isorhamnetin 3-glucoside (5 mg), a ca. 1:1 mixture of quercetin 3-glucoside and 3-galactoside (90 mg), kaempferol 3-rutinoside (27 mg), and quercetin 3-rutinoside (78 mg). The crude products were percolated through Sephadex LH-20 (elution with MeOH) and crystallized from MeOH/H₂O mixtures. Fraction B was rechromatographed on Si gel (elution with CHCl₃-MeOH, 4:1). In this way scopoletin 7-glucoside (105 mg) and esculetin 6-glucoside (15 mg) were successively eluted. ¹³C nmr of scopoletin-7-glucoside (DMSO-*d*₆, 50.32 MHz, 27°): δ 160.58 (C-2), 149.91 (C-7), 148.93 (C-9), 146.02 (C-6), 144.25 (C-4), 113.31 (C-3), 112.30 (C-10), 109.70 (C-5), 103.04 (C-8), 99.65 (C-1'), 77.15, 76.77 (C-3', C-5'), 73.11 (C-2'), 69.66 (C-4'), 60.71 (C-6'), 56.06 (OMe). For numbering, see Sankar *et al.* (5).

Dried and ground roots of *A. incanescens* (280 g) were extracted successively at room temperature with hexane/Et₂O and Et₂O as described by Greger *et al.* (6). The combined extracts were concentrated and chromatographed on Si gel (elution with hexane/Et₂O mixtures), which enabled the isolation of isofraxidin (30 mg), scopoletin (25 mg), and coniferyl alcohol (80 mg). No more definitive compounds were found, apart from waxes and other unpolar components. ¹³C nmr of coniferyl alcohol (CDCl₃, 50.32 MHz, 27°): δ 146.67 (C-3), 145.60 (C-4), 131.35 (Ar-CH=), 129.26 (C-1), 126.15 (=CH-CH₂OH), 120.29 (C-6), 114.50 (C-5), 108.42 (C-2), 63.79 (CH₂OH), 55.87 (OMe). Numbers refer to aromatic carbons.

IDENTIFICATION.—All products were identified by their mps, spectral data, (ir, uv, ¹H and ¹³C nmr, ms) and, in most cases (except 6-methoxykaempferol) by direct comparison with authentic samples. The sugar residue of the glycosides was identified by acid hydrolysis, separation of aglycone and sugar fraction, and gc of the silylated derivative of the latter. Details are available upon request to senior author.

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6-METHOXYLATED FLAVONES FROM *CARPHOCHAETE BIGELOVII*

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We recently reported the terpenoids of *Carphochaete bigelovii* A. Gray (1) [Asteraceae, Tribe: Eupatorieae, Subtribe: Piqueria K & R (2)]. The genus *Carphochaete* includes five species all restricted to the southwestern U.S. and Mexico.

We now describe the identification of five 6-methoxylated flavones from a leaf surface extraction. One of these flavones, 6,7,4',5'-tetramethoxy-5,3'-dihydroxyflavone, while known synthetically (3), has never been reported from nature. The known naturally occurring compounds are 6,7,4'-trimethoxy-5,3'-dihydroxyflavone (eupatorin), 6,3',5'-trimethoxy-5,7,4'-trihydroxyflavone, 6,3'-dimethoxy-5,7,4'-trihydroxyflavone (jaceosidin), and 6-methoxy-5,7,4'-trihydroxyflavone (hispidulin). All compounds are structurally closely related by their 5,6,7,4'-oxygenation patterns.

All the spectral data for 6,7,4',5'-tetramethoxy-5,3'-dihydroxyflavone corresponded to those of the synthetic flavone with the same substitution pattern (3). Moreover, the structure assignment was further supported by comparison of the spectral data with those for a flavone containing a 4',5'-dimethoxy-3'-hydroxy-B-ring [scaposin, (4), as well as the 4',5'-dimethoxy-5,7,3'-trihydroxyflavone (5)]. The other polymethoxylated flavones have been described from several genera of the Asteraceae (6). Eupatorin was first identified from *Eupatorium semiserratum* DC. (7), while 6,3',5'-trimethoxy-5,7,4'-trihydroxyflavone found in *Conoclinium coelestinum* (L.) DC. (8) and *Artemisia frigida* Willd. (9). Jaceosidin and hispidulin have been reported from a number of species of the Asteraceae (10, 11).

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