## **Brief Reports**

Dried and ground roots of A. incanescens (280 g) were extracted successively at room temperature with hexane/Et<sub>2</sub>O and Et<sub>2</sub>O as described by Greger *et al.* (6). The combined extracts were concentrated and chromatographed on Si gel (elution with hexane/Et<sub>2</sub>O 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. <sup>13</sup>C nmr of coniferyl alcohol (CDCl<sub>3</sub>, 50.32 MHz, 27°):  $\delta$  146.67 (C-3), 145.60 (C-4), 131.35 (Ar-CH=), 129.26 (C-1), 126.15 (=CH-CH<sub>2</sub>OH), 120.29 (C-6), 114.50 (C-5), 108.42 (C-2), 63.79 (CH<sub>2</sub>OH), 55.87 (OMe). Numbers refer to aromatic carbons.

IDENTIFICATION.—All products were identified by their mps, spectral data, (ir, uv, <sup>1</sup>H and <sup>13</sup>C 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 *Carpbochaete bigelovii* A. Gray (1) [Asteraceae, Tribe: Eupatorieae, Subtribe: Piqueria K & R (2)]. The genus *Carpbochaete* 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 'irst 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 the have been reported from a number of species of the Asteraceae (10, 11).

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## EXPERIMENTAL

PLANT MATERIAL AND EXTRACTION.—Collection and extraction of leaf material of C. bigelovii (260 g) are described in Meurer et al. (1). Voucher ADZ 2368 is deposited in the Plant Resources Center of the University of Texas at Austin.

Flavonoid fractions were enriched by partitioning the  $CH_2Cl_2$  extract against hexane (yield of concentrate: 13.5 g). A detailed description of the purification of all flavones can be requested from the senior author. The flavones were identified by their uv and their <sup>1</sup>H-nmr spectra (12) and their eims fragmentation patterns.

6,7,4',5'-TETRAMETHOXY-5,3'-DIHYDROXYFLAVONE.—Tlc: Rf on cellulose (microcrystalline, Avicel, Macherey & Nagel, Düren, F.R.G.): S<sub>1</sub> (40% HOAc): 0.71; S<sub>2</sub> (Forestal: HOAc-H<sub>2</sub>O-37% HCl, 30:10:3): 0.96; on polyamide layers (DC-6, Macherey & Nagel): S<sub>3</sub> (toluene-MeOH, 7:3): 0.88. Spot color (350 nm): purple,  $+NH_3$ : purple, +Na-reagent (2-aminoethyl diphenylborinate): brown. Uv  $\lambda$  max (MeOH) 275, 330; (NaOMe) 276, 370, no decomposition; (AlCl<sub>3</sub>) 285, 352; (AlCl<sub>3</sub>+HCl) idem; (NaOAc) 277, 371; (NaOAc+H<sub>3</sub>BO<sub>3</sub>) 276, 330. <sup>1</sup>H nmr (200 MHz, DMSO-d<sub>6</sub>)  $\delta$  7.34 (s, 2H, H-2', H-6'), 7.04 (s, 1H, H-8), 6.68 (s, 1H, H-3), 3.9 (s, 6H, 2 -OCH<sub>3</sub>, B-ring), 3.77 and 3.75 (s, 3H, -OCH<sub>3</sub> on C-6 and C-7). Eims *m*/z 374 (M<sup>+</sup>) (100%), 359 (M<sup>+</sup>-15) (72%), 344 (M<sup>+</sup>-30) (25%), 197 (A<sup>+</sup>+1) (8.4%), 178 (B<sup>+</sup>) (27%). Supplemental data for the four known flavones are available upon request from the senior author.

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