

EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *A. tomentella* were collected 7 mi south of the border with Puebla along Hwy. 190 from Huajuapán to Izúcar, Oaxaca, Mexico, on October 5, 1984. Voucher material (Sundberg and Lavin 3035) is deposited in the Plant Resources Center at the University of Texas at Austin, Austin, Texas.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Ground, dried leaves and flowers (1.6 kg) were extracted with CH_2Cl_2 . The CH_2Cl_2 extracts were evaporated in vacuo until dry. The concentrated CH_2Cl_2 extract (126.8 g) was dissolved in CH_2Cl_2 and adsorbed onto a minimum amount of silica gel. After drying, the resulting powder was charged onto a silica gel column packed in hexane. The column was eluted with hexane and gradually increased to pure EtOAc in 10% increments. All fractions were further separated over Sephadex LH-20 using hexane- CH_2Cl_2 -MeOH (7:4:1). All compounds were purified over Sephadex LH-20 in 100% MeOH prior to analysis by uv, ^1H nmr, ms, color reactions on paper under uv light [7], and comparisons with authentic samples.

Details of the isolation and identification are available upon request to the major author.

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FLAVONOIDS FROM *GUTIERREZIA WRIGHTII*

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In our earlier chemotaxonomic studies in the *Gutierrezia-Xanthocephalum* complex (Compositae, tribe Astereae) (1-5), we reported that the two woody species, *Gutierrezia grandis* and *Gutierrezia microcephala*, produce large quantities of flavonoids, mostly with 6,8-oxygenation. In contrast, *Gutierrezia alamanii* var. *megalcephala*, a perennial herbaceous species, yields only a few flavonoids, all without 6,8-oxygenation and all in relatively low amounts. In our present study, we found that *Gutierrezia wrightii* A. Gray, an annual herbaceous species, contains mainly flavonoids without 6,8-oxygenation and, like *G. alamanii* var. *megalcephala*, does not produce them in large amounts. Fifteen flavonoids were isolated from *G. wrightii* including kaempferol and its 3-O- β -D-glucoside, quercetin and its 3-O- β -D-glucoside and 3-O- β -D-glucuronide, isorhamnetin and its 3-O- β -D-glucoside, 5,7,4'-trihydroxy-3,6-dimethoxyflavone, 3,5,7,3',4'-pentahydroxy-6-methoxyflavone, 3,5,7,4'-tetrahydroxy-6,3'-dimethoxyflavone, 5,7,4'-trihydroxy-3,6,8-trimethoxyflavone, 5,7-dihydroxy-3,6,8,4'-tetramethoxyflavone, 5,7,4'-trihydroxy-3,6,8,3'-tetramethoxyflavone, luteolin, and chrysoeriol. We present previously unreported spectral data for quercetin 3-O- β -D-glucuronide (6), 5,7,4'-trihydroxy-3,6,8-trimethoxyflavone (1), and 5,7-dihydroxy-3,6,8,4'-tetramethoxyflavone (7).

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Comparison of the ^1H -nmr spectra of the trimethylsilyl (TMSi) ether derivatives of the 3-*O*- β -*D*-glucuronide and 3-*O*- β -*D*-glucoside of quercetin indicated that the signal at δ 6.28 for H-8 in the spectrum of the TMSi ether of quercetin 3-*O*- β -*D*-glucuronide appears at higher field than for other similarly derivatized quercetin 3-*O*-glycosides (8). Moreover, in this same spectrum the signal for the C-1" proton does not appear as a sharp doublet but instead gives a complex multiplet perhaps indicating the presence of rotomers.

EXPERIMENTAL

PLANT MATERIAL.—*G. wrightii* (Barrie #977) was collected in the state of Chihuahua, Mexico in September 1984. Voucher material is deposited in The Plant Resources Center at The University of Texas at Austin, Austin, Texas.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Air-dried leaves and stems (800 g) of *G. wrightii* were exhaustively extracted with 85% and 50% aqueous MeOH. The two extracts were concentrated and combined, and the aqueous solution was partitioned against CH_2Cl_2 and EtOAc. The concentrates from the CH_2Cl_2 (94 g) and the EtOAc (22.6 g) extracts were chromatographed over Polyclar AT (GAF Corp.) using columns packed initially in toluene and gradually altered in 10% increments to 100% MeOH and, finally, concluded with $\text{Me}_2\text{CO}-\text{H}_2\text{O}$ (1:1). Fractions were collected on the basis of monitoring the columns with uv light; material from each fraction was further separated by paper chromatography using 15% HOAc on Whatman 3 MM paper. Final purification of each compound for spectral analysis was by standard procedures (8) using 75% or 100% MeOH over Sephadex LH-20 columns. The EtOAc fraction yielded kaempferol 3-*O*-glucoside, quercetin, quercetin 3-*O*-glucoside, quercetin 3-*O*-glucuronide, isorhamnetin 3-*O*-glucoside, 3,5,7,3',4'-pentahydroxy-6-methoxyflavone, luteolin, and chrysoeriol, while 3,5,7,4'-tetrahydroxy-6,3'-dimethoxyflavone, 5,7-dihydroxy-3,6,8,4'-tetramethoxyflavone, and 5,7,4'-trihydroxy-3,6,8,3'-tetramethoxyflavone were obtained from the CH_2Cl_2 extract. Kaempferol, isorhamnetin, 5,7,4'-trihydroxy-3,6-dimethoxyflavone, and 5,7,4'-trihydroxy-3,6,8-trimethoxyflavone were detected in both the CH_2Cl_2 and EtOAc fractions.

Previously unreported data are listed below for previously described compounds.

QUERCETIN 3-*O*- β -*D*-GLUCURONIDE.—Uv λ max (MeOH) 256, 267sh, 300sh, 354, λ max (MeOH+NaOMe) 271, 330sh, 397, λ max (MeOH+ AlCl_3) 268, 305sh, 375, λ max (MeOH+ AlCl_3/HCl) 267, 300, 355, 400sh, λ max (MeOH+NaOAc) 269, 325sh, 378, λ max (MeOH+NaOAc/ H_3BO_3) 261, 300sh, 372; ^1H nmr (as TMSi ether, CCl_4 , TMS) δ 3.40-3.80 (4H, m), 5.67 (1H, dd, $J=7$ and 2.5 Hz), 6.18 (1H, d, $J=2.5$ Hz), 6.28 (1H, d, $J=2.5$ Hz), 6.86 (1H, d, $J=8.5$ Hz), 7.55 (1H, dd, $J=8.5$ and 2.5 Hz), 7.60 (1H, d, $J=2.5$ Hz).

5,7,4'-TRIHYDROXY-3,6,8-TRIMETHOXYFLAVONE.—Uv λ max (MeOH) 277, 340, λ max (MeOH+NaOMe) 280, 334, 404, λ max (MeOH+ AlCl_3) 254, 285, 307sh, 362, λ max (MeOH+ AlCl_3/HCl) 250, 286, 307sh, 357, λ max (MeOH+NaOAc) 281, 315, 395, λ max (MeOH+NaOAc/ H_3BO_3) 280, 340; ^1H nmr (as TMSi ether, CCl_4 , TMS) δ 3.76 (3H, s), 3.90 (3H, s), 3.93 (3H, s), 6.91 (2H, d, $J=8.5$ Hz), 8.08 (2H, d, $J=8.5$ Hz).

5,7-DIHYDROXY-3,6,8,4'-TETRAMETHOXYFLAVONE.—Uv λ max (MeOH) 277, 336, λ max (MeOH+NaOMe) 280, 305sh, 377, λ max (MeOH+ AlCl_3) 285, 310sh, 358, λ max (MeOH+ AlCl_3/HCl) 289, 310sh, 357, λ max (MeOH+NaOAc) 280, 310sh, 380, λ max (MeOH+NaOAc/ H_3BO_3) 280, 335; ^1H nmr (as TMSi ether, CCl_4 , TMS) δ 3.76 (3H, s), 3.86 (3H, s), 3.91 (6H, s), 6.95 (2H, d, $J=8.5$ Hz), 8.10 (2H, d, $J=8.5$ Hz).

TRIMETHYLSILYLATION.—This was carried out as described in reference (8).

HYDROLYSIS OF QUERCETIN 3-*O*- β -*D*-GLUCURONIDE.—Hydrolysis by both β glucuronidase and standard acid hydrolysis (1 N HCl for 45 min) produced an aglycone and glucuronic acid.

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