

then by polyamide cc (C₆H₆ up to C₆H₆-MeOH, 95:5) to lead to Z-3-(2-hydroxybutylidene)phthalide (1.5 mg) and Z-9-hydroxyiligustilide (2.5 mg) separated by semi-preparative hplc on Lichrosorb Si 60 (*n*-hexane-*i*PrOH, 98:2) and to Z-4-hydroxy-3-butylidene-phthalide (4 mg) also purified by hplc but with *n*-hexane-CHCl₃-*i*PrOH-MeOH (95:3:1:1). Fraction 4 was directly subjected to the last hplc system to yield Z-5-hydroxy-3-butylidene-phthalide (14 mg). After filtration through a Sephadex LH 20 column, fraction 7 was first treated by SiO₂ cc and then by cctlc on silica gel (*n*-hexane-CHCl₃-*i*PrOH-MeOH, 36:2:1:1) to afford Z-*cis*-6,7-dihydroxyiligustilide (13 mg). Fraction 8 was subjected to SiO₂ cc (CHCl₃-MeOH, 90:10), then to Sephadex LH 20 (MeOH) to isolate Z-*trans*-6,7-dihydroxyiligustilide (11 mg) purified by cctlc on silica gel (*n*-hexane-CHCl₃-*i*PrOH-MeOH, 80:10:5:5).

Identification of the isolated phthalides was performed by analysis of their spectral data. Additional details of the spectral properties may be obtained from the senior author.

LITERATURE CITED

1. D. Barron, M. Kaouadji, and A.M. Mariotte, *Z. Naturforsch.*, **39c**, 167 (1984).
2. D. Barron, M. Kaouadji, and A.M. Mariotte, *J. Nat. Prod.*, **47**, 737 (1984).
3. M. Kaouadji, A.M. Mariotte, and H. Reutenauer, *Z. Naturforsch.*, **39c**, 872 (1984).
4. W. Pushan, G. Xuanliang, W. Yixiong, Y. Fukuyama, I. Miura, and M. Sugawara, *Phytochemistry*, **23**, 2033 (1984).
5. M. Kobayashi, M. Fujita, and H. Mitsunashi, *Chem. Pharm. Bull.*, **32**, 3770 (1984).
6. M. Puech-Baronnat, M. Kaouadji, and A.M. Mariotte, *Planta Med.*, **50**, 105 (1984).
7. M. Kaouadji, M. Puech-Baronnat, and A.M. Mariotte, *Pl. Méd. et Phyt.*, **17**, 147 (1983).

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FLAVONOLS FROM *GUTIERREZIA ALAMANII* VAR. *MEGALOCEPHALA*

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As part of a chemosystematic study of the *Gutierrezia-Xanthocephalum* complex in North America (1), we previously reported the isolation of 34 flavonoids from *Gutierrezia grandis* (see 2) and 51 from *Gutierrezia microcephala* (3); from a different population of the latter species, other workers reported 21 flavonoids (4). Most compounds of these two woody species have 6,8-oxygenation. Here we report our results from *Gutierrezia alamanii* A. Gray var. *megaloccephala* (Fern.) M.A. Lane, a perennial herbaceous plant. Eight flavonoids were obtained, namely quercetin, quercitrin, rutin, kaempferol, quercetin-3,7-dimethyl ether, quercetin-3,7,4'-trimethyl ester (ayanin), 5,7-dihydroxy-3,3',4',5'-tetramethoxyflavone, and 5,3',5'-trihydroxy-3,7,4'-trimethoxyflavone. The chemical data support a separation of the herbaceous species of *Gutierrezia* from the woody members that produce 6,8-oxygenated flavonoids. Previously, in 1964, 5,3',5'-trihydroxy-3,7,4'-trimethoxyflavone was isolated from *Rhizinocarpus stylosus* (Euphorbiaceae) (5); we present spectral data (ms, uv, ¹H nmr) of this compound, not included in the earlier report.

EXPERIMENTAL

PLANT MATERIAL.—The aerial parts of *G. alamanii* var. *megaloccephala* were collected at Municipio Ciudad Guerro, 32 km N of San Juanito, on the road to Creel, Chihuahua, Mexico, on September 10, 1984. A voucher specimen (Fred R. Barrie & Mark E. Leidig no. 993) is on deposit in the Herbarium of the University of Texas at Austin.

EXTRACTION, ISOLATION AND IDENTIFICATION.—Dried aerial parts of *G. alamanii* var. *megaloccephala* (400 g) were extracted three times with 80% and 50% aqueous MeOH. The concentrated extract was partitioned against CH₂Cl₂ and EtOAc. The CH₂Cl₂ fraction was chromatographed over a Polyclar column using a CH₂Cl₂-EtOAc gradient with increasing amounts of EtOAc. The following compounds were sequentially obtained: 5,7-dihydroxy-3,3',4',5'-tetramethoxyflavone, quercetin-3,7,4'-trimethyl ether (ayanin), 5,3',5'-trihydroxy-3,7,4'-trimethoxyflavone, and quercetin-3,7-dimethyl ether. The EtOAc fraction, which was also chromatographed over a Polyclar column using a CH₂Cl₂-MeOH gradient with increasing amounts of MeOH, afforded kaempferol, rutin, quercitrin, and quercetin. All compounds, which were purified over Sephadex LH-20 (100% MeOH) prior to spectral analysis, were identified by uv, ¹H nmr, and color reactions (6). Mass spectra were recorded for 5,7-dihydroxy-3,3',4',5'-tetramethoxyflavone, quercetin-3,7,4'-trimethyl ether, 5,3',5'-trihydroxy-3,7,4'-trimethoxyflavone, and quercetin-3,7-dimethyl ether.

Previously unreported data for 5,3',5'-trihydroxy-3,7,4'-trimethoxyflavone: uv λ maxima (nm) in MeOH 262, 344; +NaOMe 262, 302(sh), 366; +AlCl₃ 274, 302, 350, 395; +AlCl₃/HCl 275, 303, 345, 395; +NaOAc 262, 348; +NaOAc/H₃BO₃ 262, 350; ¹H nmr (TMSi ether, 90 MHz, CCL₄, TMS) δ 3.82 (3H, s), 3.87 (6H, s), 6.17 (1H, d, $J=2.5$ Hz), 6.46 (1H, d, $J=2.5$ Hz), 7.21 (2H, s); ms m/z (rel. int.) 360 [M]⁺ (100), 345 [M-15]⁺ (26), 167 [B₂]⁺ (23), 166 [A₁]⁺ (13).

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LITERATURE CITED

1. M.A. Lane, *Systematic Botany*, **10**, 7 (1985).
2. N. Fang, T.J. Mabry, and N. Le-Van, *Phytochemistry*, **25**, 235 (1986).
3. N. Fang, M. Leidig, and T.J. Mabry, *Phytochemistry* (in press).
4. J.N. Roitman and L.F. James, *Phytochemistry*, **24**, 835 (1985).
5. A. Henrick and P.R. Jefferies, *Aust. J. Chem.*, **17**, 934 (1964).
6. T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," Springer Verlag, New York, 1970.

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