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Constituents of *Gutierrezia mandonii* (Asteraceae)

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1. Subject and source

The genus *Gutierrezia* (Asteraceae) includes approximately 25 species which occur exclusively in the arid areas of América. Eighth species, *Gutierrezia baccharoides* Sch. Bip., *Gutierrezia gilliesii* Griseb., *Gutierrezia isernii* (Phil.) Phil., *Gutierrezia mandonii* (Sch. Bip.) Solbrig, *Gutierrezia pulviniformis* Cabrera, *Gutierrezia repens* Griseb., *Gutierrezia solbrigii* Cabrera, and *Gutierrezia spathulata* (Phil.) Kurtz, grow in Argentina (Freire, 1999). *G. mandonii* is a resinous shrub which grows naturally in the arid areas of northern Argentina and southern Bolivia (Cabrera, 1978).

The aerial parts of *G. mandonii* were collected during the flowering period in Salta, Argentina, on January 2004. The plant was identified by Ing. Julio Tolaba. A voucher specimen (no 3414) was deposited at the Museo de la Facultad de Ciencias Naturales, Universidad Nacional de Salta.

2. Previous work

Previous phytochemical investigations on genus *Gutierrezia* have been carried out. The most important constituents were diterpenes (Bohlmann et al., 1979, 1981, 1984; Gao et al., 1985, 1986; Gao and Mabry, 1987; Harraz and Doskotch, 1990; Jakupovic et al., 1985, 1986; Zdero et al., 1990, 1992) and flavonoids (Alarcón et al., 2007; Brittner et al., 1982, 1983; Dong et al., 1987; Fang et al., 1985a,b, 1986a,b,c; Lenherr et al., 1986; Li et al., 1987, 1988; Roitman and James, 1985). A previous phytochemical study of *G. mandonii* led to isolation of three diterpenes (Bohlmann et al., 1979). Insecticidal activity of the essential oil and extracts of aerial parts of *G. mandonii*, has been reported recently (Clemente et al., 2008).

3. Present study

Air-dried aerial parts (400 g) of *G. mandonii* were macerated in EtOH for 7 days at room temperature. After filtration, EtOH was evaporated to dryness under reduced pressure at 40 °C to yield 55.0 g of residue (crude extract) which was dissolved in

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H_2O–EtOH (1:1). The hydroalcoholic solution, after the evaporation of the EtOH, was exhaustively extracted with Cl_2CH_2 to afford 20.0 g of Cl_2CH_2 soluble fraction.

The Cl_2CH_2 soluble fraction was subjected to flash column chromatography on silica gel C-18, eluted with MeOH–H_2O 7:3 (*Fraction 1*) and MeOH (*Fraction 2*).

Fraction 1 (14.0 g), was subjected to flash column chromatography on silica gel with hexane (F_1), hexane–EtOAc 7:3 (F_2), hexane–EtOAc 1:1 (F_3), hexane–EtOAc 3:7 (F_4), EtOAc (F_5). F_2 (n-hexane:EtOAc 7:3, 165 mg) was chromatographed on a 230–400 mesh silica gel column eluting with a gradient of n-hexane–Et_2O to yield 13.0 mg of **1** (Krebs et al., 1990), 3.5 mg of **2** (Gijsen et al., 1992; Meira et al., 2008; Moreira et al., 2003), 5.0 mg de **3** (Markham and Geiger, 1994) and 6.5 mg de **4** (Markham and Geiger, 1994). F_3 (n-hexane–EtOAc 1:1, 1.50 g) was first purified by column chromatography on silica gel using mixtures (100 mL each) of Cl_2CH_2–Me_2CO of increasing polarity (5%), fractions of 10 mL were collected. Subfraction 21–34 (90 mg) were combined and chromatographed by CC on silica gel using mixtures (100 mL each) of hexane–EtOAc of increasing polarity (10%) followed by preparative TLC (C_6H_6–MeOH 2.9:0.1) affording 7.0 mg of **5** (Rf = 0.64) (Markham and Geiger, 1994), and 2.0 mg of **6** (Rf = 0.57) (Imre et al., 1977). F_4 (n-hexane:EtOAc 3:7, 250 mg) was subjected to silica gel column chromatography with a gradient of n-hexane–Et_2O, followed by preparative TLC (C_6H_6–MeOH 2.8:0.2) to give 9.0 mg of **7** (Rf = 0.24) (Rodríguez et al., 1972).

The isolated compounds were identified by spectroscopic methods (UV, ^1H and ^{13}C NMR). The NMR spectra were recorded on a Bruker Avance 400 (^1H at 400 MHz and ^{13}C at 100 MHz) spectrometer with TMS as internal reference. UV spectra were registered on a Shimadzu UV-260 instrument.

Spathulenol **1**, aromadendrane 4β,10α-diol **2**, naringenin **3**, kaempferol **4** and pectolaringenin **6** were identified by comparison of their spectral properties with those reported in literature. The structure of the compounds **5** and **7** were established on the basis of 1D NMR (^1H NMR, ^{13}C NMR) and 2D NMR (^1H–^1H COSY, HSQC, HMBC, NOESY). As far as we know, these compounds had been identified only by UV and ^1H NMR before.

3,5,7-trihydroxy-6,4′-dimethoxyflavone (**5**). Amorphous yellow solid, UV (MeOH) λ_{max} nm: 270, 302, 347; +NaOMe: 274, 393; +$AlCl_3$: 270, 362, 421; +$AlCl_3$/HCl: 270, 362, 421. RMN ^1H ($CDCl_3$): δ 12.01 (1H, *s*, 5-OH), 8.20 (2H, *d*, J = 9.0 Hz, H-2′ and H-6′), 7.06 (2H, *d*, J = 9.0 Hz, H-3′ and H-5′), 6.58 (1H, *s*, H-8), 4.08 (3H, *s*, OCH_3-C-6), 3.92 (3H, *s*, OCH_3-C-4′). RMN ^{13}C ($CDCl_3$): 146.8 (C-2), 130.4 (C-3), 174.8 (C-4), 151.3 (C-5), 129.9 (C-6), 154.4 (C-7), 93.4 (C-8), 154.4 (C-9), 104.8 (C-10), 124.0 (C-1′), 129.4 (C-2′ and C-6′), 114.1 (C-3′ and C-5′), 161.2 (C-4′), 61.0 (OCH_3-C-6), 55.4 (OCH_3-C-4′).

3,5,7-4′-tetrahydroxy-6-methoxyflavone (**7**). Amorphous yellow solid, UV (MeOH) λ_{max} nm: 270, 295, 340 (sh), 370; +NaOMe: 285, 325, 425; +NaOAc: 275, 335, 380; +$AlCl_3$: 275, 300, 365, 430; +$AlCl_3$/HCl: 275, 300, 365, 430. RMN ^1H (Me_2CO-d_6): δ 12.38 (1H, *s*, 5-OH), 8.17 (2H, *d*, J = 9.0 Hz, H-2′ and H-6′), 7.04 (2H, *d*, J = 9.0 Hz, H-3′ and H-5′), 6.64 (1H, *s*, H-8), 3.89 (3H, *s*, OCH_3). RMN ^{13}C (Me_2CO-d_6): 146.2 (C-2), 135.4 (C-3), 175.9 (C-4), 151.5 (C-5), 130.8 (C-6), 157.0 (C-7), 93.6 (C-8), 152.2 (C-9), 104.0 (C-10), 122.6 (C-1′), 129.6 (C-2′ and C-6′), 115.3 (C-3′ and C-5′), 159.2 (C-4′), 60.0 (OCH_3).

4. Chemotaxonomic significance

Compounds **1–7** were identified for the first time from *G. mandonii*, although **1** had been previously isolated from *G. solbrigii* (Jakupovic et al., 1985) and *G. spathulata* (Jakupovic et al., 1986), **3** from *Gutierrezia microcephala* (Roitman et al., 1985), **4** from *G. microcephala* (Fang et al., 1986a, b, c) and **6** from *Gutierrezia sphaerocephala* (Li et al., 1988). In addition **2**, **5** and **7** were characterized for the first time from the genus *Gutierrezia*.

Flavones and flavonols methoxylated are important groups of compounds in the genus *Gutierrezia*. These compounds are characterized by a combination of extra oxygenated A-rings, and several B-ring oxygenation patterns (Bohm and Stuessy, 2001). The presence of flavonoids **5–7** confirms that, like other members of genus *Gutierrezia*, *G. mandonii* is able to produce flavonoids with 5,7-dihydroxy-6-methoxy substitution in A-rings, and 4′-oxygenation in B-rings.

In *Gutierrezia*, only one aromadendrane sesquiterpenoid, spathulenol **1**, has been described. To the best of our knowledge, compound **2** has been reported previously in families Annonaceae (Moreira et al., 2005) and Convolvulaceae (Meira et al., 2008) but not in the Asteraceae.

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