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Iridoids from *Galium aparine*

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Abstract

The isolation and UV, IR, ^{1}H- and ^{13}C-NMR data of asperulosidic acid, 10-deacetylasperulosidic acid from *Galium aparine* L. aerial parts are reported.

Keywords: *Galium aparine*, iridoid glucosides, asperulosidic acid, 10-deacetylasperulosidic acid, Rubiaceae.

Introduction

The medicinal plant genus *Galium* L. (Rubiaceae) is represented in Turkey by 101 species gathered in 10 sections (Ehrendorfer et al., 1982).

Galium species are traditionally used to coagulate milk because of an enzyme in their chemical composition. For this reason, this plant is known as "Yoğurt herb" (Ergun et al., 1999).

Galium aparine L. is a climbing plant and widely spread in Anatolia, and is known by the common name of "Tırmanıcı Yoğurt Otu" (Baytop, 1963, 1984).

Extracts from this plant have long been used in folk medicine for a variety of purposes, mainly as a diuretic, choleretic and in the treatment of some stomach, gout and epilepsy diseases (Temizer et al., 1996).

Material and Methods

General experimental procedures

Optical rotations were measured on a Rudolph Autopol IV polarimeter A 7040-12 Model. IR spectra were determined on a Perkin-Elmer 257 instrument in KBr pellets. UV spectra were recorded on a Beckman DU 650 spectrophotometer; spectroscopic grade MeOH (Merck). ^{1}H and ^{13}C-NMR spectra were obtained using a FT mode Bruker WM 300 spectrometer (300.133 MHz and 75.47 MHz, respectively). FAB-MS were recorded with a Kratos AEI-MS 50 mass spectrometer. Vacuum liquid chromatography and Kieselgel 60 (0.063–0.200 mm, Art.7734, Merck) were used for column chromatography and Kieselgel 60 F_{254} (Merck) prepared plates for TLC. Spots were detected by UV fluorescense and/or spraying with 1% vanillin/H_2SO_4 followed by heating at 100 °C for 5–10 min. MPLC was carried out in the reversed phase mode using a Büchi system. The column (18.5 × 352 mm) was packed with LiChroprep RP-18 (solvent system: MeOH : H_2O mixtures).

Plant material

Galium aparine L. aerial parts were collected in Ankara-Çankırı, Esenboğa, ca. 850 m, in June 1997. A voucher specimen is deposited in the Herbarium of the Pharmacognosy Department, Faculty of Pharmacy, Gazi University, Ankara (GÜE No. 864).

Extraction and isolation

The dried and powdered aerial parts of the plant (650 g) were percolated with 80% ethanol (10 L) several times at room temperature, the extract was concentrated *in vacuo* at 30 °C, diluted with water, filtered and exhaustively defatted with petroleum ether (40–60 °C). The aqueus extract was then concentrated to give 15.06 g of solid extract (yield 2.32%).

The water phase (15.06 g) was applied to vacuum liquid chromatography on normal-phase silica gel material (Kieselgel 60, 0.063–0.200 mm, Art. 7734 Merck), using $CHCl_3$-MeOH-H_2O mixtures (80 : 20 : 1 → 50 : 50 : 5, 100 ml/fraction) to yield 6 main fractions; Fr. 4 was studied. Fraction 4 was subjected separately to MPLC using H_2O-MeOH mixtures to give Fr. 5–7 (591.02 mg) and Fr. 41–46 (22.60 mg). Fr. 5–7 was chromatographed on silica gel eluting with $CHCl_3$: MeOH : H_2O (61 : 32 : 7) and MeOH : H_2O (50 : 50) to give compound **2** (38.12 mg). Fr. (41–46)

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was also chromatographed on silica gel eluting with $CHCl_3$: MeOH : H_2O (80 : 20 : 2 → 61 : 32 : 7) to give compound **1** (9.92 mg).

Two iridoid glycosides were isolated from the aerial parts of *G. aparine*. Asperulosidic acid (**1**) (0.191%), and 10-deacetylasperulosidic acid (**2**) (0.571%). Additionally, in this study, chlorogenic acid (0.117%), reported to be isolated from *G. aparine*, was also isolated by using the MPLC technique and its structure was elucidated by spectral methods (Tzakou et al., 1990). The yields are based on dry plant weight.

Asperulosidic acid (1)

$[\alpha]_D^{29} = -106.95°$ (MeOH: c 0.2). UV (MeOH): $\lambda_{max} = 235$. IR (KBr): $\nu_{max} = 3390, 1680, 1630$. ^{1}H-NMR (300 MHz, CD_3OD): $\delta = 7.61$ (1H, br s, H-3), 6.01 (1H, br s, H-7), 5.03 (1H, d, $J = 9$ Hz, H-1), 4.97 (1H, br s, H-10a), 4.92 (1H, br s, H-10b), 3.62 (1H, dd, $J = 12/6$ Hz, H-6), 3.03 (1H, t, $J = 6.6$ Hz, H-5), 2.63 (1H, t, $J = 8$ Hz, H-9), 1.29 (3H, br s, CH_3), 4.71 (1H, d, $J = 7.80$ Hz, H-1′), 3.36 (1H, t, $J = 9$ Hz, H-3′), 3.21–3.42 (H-2′/4′/5′/6′, signals unclear due to overlapping). ^{13}C-NMR (75.5 MHz, CD_3OD): δ = 172.54 (OAc), 154.61 (C-3), 146 (C-8), 131.86 (C-7), 109.50 (C-4), 101.17 (C-1), 75.57 (C-6), 63.83 (C-10), 46.41 (C-9), 42.71 (C-5), 100.58 (C-1′), 77.92 (C-5′), 78.57 (C-3′), 74.96 (C-2′), 71.61 (C-4′), 63.01 (C-6′). FAB-MS: *m/z* = 433.2 $[M + H]^+$, 455.2 $[M + Na]^+$.

10-Deacetylasperulosidic acid (2)

$[\alpha]_D^{29} = +28.9°$ (MeOH: c 1.09). UV (MeOH): $\lambda_{max} = 236$. IR (KBr): $\nu_{max} = 3375, 1675, 1630$. ^{1}H-NMR (300 MHz, CD_3OD): $\delta = 7.55$ (1H, br s, H-3), 6.00 (1H, br s, H-7), 5.00 (1H, d, $J = 8.9$ Hz, H-1), 4.48 (1H, br s, H-10a), 4.43 (1H, br s, H-10b), 3.36 (1H, dd, $J = 13/6.5$ Hz, H-6), 3.03 (1H, t, $J = 7.30$ Hz, H-5), 2.55 (1H, t, $J = 8$ Hz, H-9), 4.73 (1H, d, $J = 7.80$ Hz, H-1′), 3.16–3.49 (H-2′/3′/4′/5′/6′, signals unclear due to overlapping). ^{13}C-NMR (75.5 MHz, CD_3OD): δ = 173.98 (COOH), 154.13 (C-3), 151.98 (C-8), 130.18 (C-7), 100.80 (C-1), 75.45 (C-6), 62.21 (C-10), 46.60 (C-9), 43.70 (C-5), 101.65 (C-1′), 78.92 (C-5′), 78.27 (C-3′), 76.20 (C-2′), 72.10 (C-4′), 63.27 (C-6′).

Results and Discussion

Compounds **1** and **2** were elucidated by IR, UV, optical rotations, ^{1}H-, ^{13}C-NMR, FAB-MS. Previous studies reported the isolations of monotropein, asperuloside, aucubin, protopine, harmine, (±)-vasicinone, (−)-1-hydroxydeoxypeganine, (−)-8-hydroxy-2,3-dehydrodeoxypeganine, *p*-hydroxybenzoic, chlorogenic, salisilic, cafeic, *p*-coumaric acid, flavonoid, anthraquinon, cholesterol, campestrol, stigmasterol, sitosterol, Δ^5-avenasterol, Δ^7-stigmasterol, Δ^7-avenasterol from the aerial parts of *G. aparine* (Ergun et al., 1986; Şener et al., 1988; Tzakou et al., 1990).

In the current research, two iridoid glycosides were isolated from the aerial parts of *G. aparine* and identified by spectral methods (optical rotation, UV, IR, NMR and MS) as asperulosidic acid and 10-deacetylasperulosidic acid. Their spectrometric data were compared with published data (Chaudhuri et al., 1979, 1980; Bianco et al., 1983; Ersöz et al., 1997). This is the first report on the isolation of asperulosidic acid and 10-deacetylasperulosidic acid from *Galium aparine*.

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