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FLAVONOIDS FROM TWO ITALIAN *Genista* SPECIES: *Genista cilentina* AND *Genista sulcitana*

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The genus *Genista* L. (Leguminosae) is represented in Italy by about 30 species, with 16 endemic entities. Continuing our investigation on Mediterranean flora, two Italian endemic species growing in Sicily and Sardinia, *Genista cilentina* Valsecchi and *Genista sulcitana* Valsecchi, respectively, were analyzed.

Plants belonging to the genus *Genista* are known in the literature for the presence of flavonoids and quinolizidine alkaloids [1]. Many *Genista* species are traditionally employed as purgative and diuretic, and to treat gout, kidney stones, and rheumatism [2–4]; Etnean broom (*G. aetnensis*), like other *Genista* species, arrests erosion and incorporation of organic matter into the soil [5]; Dyer′s greenweed (*G. tinctoria*) was historically used as a natural yellow dye [6]. *G. cilentina* and *G. sulcitana* have not been investigated previously.

G. cilentina and *G. sulcitana* were collected in Sicily (July 2004) and Sardinia (May 2006), respectively. The plant material was authenticated by Dr. M. C. Loi (Dipartimento di Scienze Botaniche, Universita di Cagliari, Italy) for *G. sulcitana* and by Dr. A. Bader (Faculty of Pharmacy, Al-Zaytoonah Private University of Jordan) for *G. cilentina*. The phytochemical investigation of the two dried plant materials separately was carried out on a Soxhlet apparatus with *n*-hexane, chloroform, and methanol successively. The methanolic extracts were partitioned with EtOAc and *n*-BuOH, and the corresponding residues, submitted to different chromatographic techniques, such as silica gel columns, Sephadex LH-20, and p-TLC, led to the isolation and identification of nine flavonoids from *G. cilentina* and four compounds from *G. sulcitana*, sorted as: luteolin (**1**) [7], luteolin 7-*O*-glucoside (**2**) [8], vicenin-2 (**3**) [8], orobol (**4**) [7], genistein 7-*O*-glucoside (**5**) [7], biochanin A 7-*O*-glucoside (**6**) [7], genistein 4′,7-di-*O*-glucoside (**7**) [9], genistein 8-*C*-glucoside (**8**) [10], and pratensein 7-*O*-glucoside (**9**) [11] from *G. cilentina*, and luteolin (**10**), 7-*O*-glucoside (**2**), genistein 7-*O*-glucoside (**5**), genistein 8-*C*-glucoside (**8**), and *p*-coumaric acid (**11**) from *G. sulcitana*. D-pinitol (**10**), a chemotaxonomic marker of the Leguminosae family, was also isolated from *G. cilentina.*

All the purified known flavonoids (six isoflavones and three flavones, both in aglyconic and glycosidic forms), together with *p*-coumaric acid and D-pinitol, were identified by spectral analysis (^{1}H and ^{13}C NMR, ESI-MS) and by comparison with the literature data [7–11].

Vicenin-2 (3). $C_{27}H_{30}O_{15}$, yellow powder. ESI-MS *m/z* 593 $[M - H]^+$. ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm, J/Hz): 4.69 (1H, d, J = 10.2, 8G-1), 4.83 (1H, d, J = 10.2, 6G-1), 6.61 (1H, s, H-3), 6.87 (1H, d, J = 8.8, H-3′ and H-5′), 7.96 (1H, d, J = 8.8, H-2′ and H-6′). ^{13}C NMR (50.33 MHz, DMSO-d_6, δ): 60.5 (6G-6), 61.1 (8G-6), 69.7 (6G-4), 70.3 (8G-4), 70.7 (6G-2), 71.1 (8G-2), 71.4 (6G-1), 74.1 (8G-1), 78.5 (6G-3), 78.9 (8G-3), 80.9 (6G-5), 81.6 (8G-5), 102.0 (C-3), 102.1 (C-8), 102.8 (C-10), 107.9 (C-6), 115.8 (C-3′ and C-5′), 121.8 (C-1′), 128.6 (C-2′ and C-6′), 158.5 (C-5), 154.2 (C-9), 159.3 (C-4′), 160.9 (C-7), 162.8 (C-2), 179.5 (C-4).

Orobol (4). $C_{15}H_{10}O_6$, yellow powder. ESI-MS *m/z* 285 $[M - H]^+$. ^{1}H NMR (200.13 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.20 (1H, d, J = 1.8, H-6), 6.35 (1H, d, J = 1.8, H-8), 6.77 (2H, s, H-5′ and H-6′), 6.98 (1H, s, H-2′), 8.26 (1H, s, H-2). ^{13}C NMR (50.33 MHz, DMSO-d_6, δ): 93.6 (C-8), 99.0 (C-6), 104.4 (C-10), 115.4 (C-5′), 116.5 (C-2′), 119.9 (C-6′), 121.6 (C-1′), 122.3 (C-3), 144.9 (C-4′), 145.5 (C-3′), 153.9 (C-2), 157.2 (C-9), 161.6 (C-5), 162.0 (C-7), 180.2 (C-4).

Genistein 7-*O*-Glucoside (5). $C_{21}H_{20}O_{10}$, yellow powder. ESI-MS *m/z:* 431 $[M - H]^+$, 268 $[M - Glc]^+$. ^{1}H NMR (200.13 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.07 (1H, d, J = 7.1, G-1), 6.45 (1H, d, J = 2.0, H-6), 6.71 (1H, d, J = 2.0, H-8), 6.81

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(2H, d, J = 8.3, H-3′ and H-5′), 7.38 (2H, d, J = 8.3, H-2′ and H-6′), 8.41 (1H, s, H-2). ^{13}C NMR (50.33 MHz, DMSO-d_6, δ): 60.6 (G-6), 69.6 (G-4), 73.1 (G-2), 76.4 (G-5), 77.2 (G-3), 94.5 (C-8), 99.6 (C-6), 99.9 (G-1), 115.1 (C-3′ and C-5′), 121.0 (C-1′), 122.6 (C-3), 130.2 (C-2′ and C-6′), 154.6 (C-2), 157.3 (C-9), 157.6 (C-4′), 161.7 (C-5), 163.0 (C-7), 180.6 (C-4).

Biochanin A 7-*O*-Glucoside (6). $C_{22}H_{22}O_{10}$, yellow powder. ESI-MS *m/z* 445 $[M - H]^+$. ^{1}H NMR (200.13 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.76 (3H, s, OCH_3), 5.03 (1H, d, J = 6.8, G-1), 6.45 (1H, s, H-6), 6.68 (1H, s, H-8), 6.99 (1H, d, J = 8.9, H-3′ and H-5′), 7.49 (1H, d, J = 8.8, H-2′ and H-6′), 8.41 (1H, s, H-2). ^{13}C NMR (50.33 MHz, DMSO-d_6, δ): 55.6 (OCH_3), 60.7 (G-6), 69.7 (G-4), 73.1 (G-2), 76.4 (G-5), 77.3 (G-3), 94.7 (C-8), 99.9 (C-6), 100.1 (G-1), 106.4 (C-10), 113.9 (C-3′ and C-5′), 122.9 (C-3 and C-1′), 130.4 (C-2′ and C-6′), 154.8 (C-2), 157.5 (C-9), 159.4 (C-4′), 163.2 (C-7 and C-5), 180.5 (C-4).

Genistein 4′,7-di-*O*-Glucoside (7). $C_{27}H_{30}O_{15}$, yellow powder. ESI-MS *m/z* 593 $[M - H]^+$. ^{1}H NMR (200.13 MHz, DMSO-d_6, δ, ppm, J/Hz): 4.91 (1H, d, J = 6.7, 4′G-1), 5.06 (1H, d, J = 6.8, 7G-1), 6.47 (1H, br.s, H-6), 6.72 (1H, br.s, H-8), 7.09 (2H, d, J = 8.8, H-3′ and H-5′), 7.50 (2H, d, J = 8.8, H-2′ and H-6′), 8.42 (1H, s, H-2). ^{13}C NMR (50.33 MHz, DMSO-d_6, δ): 60.6 (7G-6 and 4′G-6), 69.7 (7G-4 and 4′G-4), 73.1 (4′G-2), 73.2 (7G-2), 76.4 (4′G-5), 76.6 (7G-5), 77.1 (4′G-3), 77.2 (7G-3), 94.7 (C-8), 99.7 (C-6), 99.8 (4′G-1), 100.3 (7G-1), 106.2 (C-10), 116.1 (C-3′ and C-5′), 122.2 (C-1′), 124.0 (C-3), 130.1 (C-2′ and C-6′), 155.0 (C-2), 157.3 (C-9), 157.4 (C-4′), 161.5 (C-5), 163.1 (C-7), 180.4 (C-4).

Genistein 8-*C*-Glucoside (8). $C_{21}H_{20}O_{10}$, yellow powder. ESI-MS *m/z*: 431 $[M - H]^+$, 283 $[M - Glc]^+$. ^{1}H NMR (200.13 MHz, DMSO-d_6, δ, ppm, J/Hz): 4.68 (1H, d, J = 9.8, G-1), 6.21 (1H, s, H-6), 6.89 (2H, d, J = 8.8, H-3′ and H-5′), 7.47 (2H, d, J = 8, H-2′ and H-6′), 8.40 (1H, s, H-2). ^{13}C NMR (50.33 MHz, DMSO-d_6, δ): 61.5 (G-6), 70.7 (G-2 and G-4), 73.3 (G-1), 78.8 (G-3), 81.8 (G-5), 99.0 (C-6), 104.3 (C-8), 104.5 (C-10), 115.1 (C-3′ and C-5′), 121.2 (C-1′), 122.0 (C-3), 130.2 (C-2′ and C-6′), 153.9 (C-2), 157.4 (C-9 and C-4′), 161.1 (C-5), 163.4 (C-7), 180.5 (C-4).

Pratensein 7-*O*-Glucoside (9). $C_{22}H_{22}O_{11}$, yellow powder. ESI-MS *m/z* 463 $[M + H]^+$. ^{1}H NMR (200.13 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.79 (3H, s, OCH_3), 5.06 (1H, d, J = 6.8, G-1), 6.46 (1H, d, J = 2.0, H-6), 6.70 (1H, d, J = 2.0, H-8), 6.96 (2H, br.s, H-5′ and H-6′), 7.04 (1H, s, H-2′), 8.42 (1H, br.s, H-2). ^{13}C NMR (50.33 MHz, DMSO-d_6, δ): 55.8 (OCH_3), 60.7 (G-6), 69.7 (G-4), 73.2 (G-2), 76.5 (G-5), 77.3 (G-3), 94.6 (C-8), 99.7 (C-6), 100.0 (G-1), 106.2 (C-10), 112.2 (C-5′), 116.5 (C-2′), 119.9 (C-6′), 122.5 (C-1′), 130.2 (C-3), 146.2 (C-3′), 147.9 (C-4′), 154.8 (C-2), 157.3 (C-9), 161.7 (C-7), 163.0 (C-5), 180.5 (C-4).

These flavonoids are characteristic compounds previously isolated in other *Genista species* [1, 12–15] and are in agreement also with the flavonoidic Genisteae patterns reported by Harborne [16]: high concentration of isoflavones, absence of leucoanthocyanidins, regular occurrence of glycoflavones, and presence of flavones.

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