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FLAVONOIDS AND ISOFLAVONOIDS FROM *Genista tricuspidata*

O. Boumaza,[1] R. Mekkiou,[1] R. Seghiri,[1] D. Sarri,[2] S. Benayache,[1] V. P. Garcia,[3] J. Bermejo,[3] and F. Benayache[1]

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Genista species contain a variety of secondary metabolites of various types, especially isoflavonoids, which have been shown to be biologically active [1, 2]. In a continuation of our study of Algerian medicinal plants, especially of the genus *Genista* [3], we report herein our search concerning the secondary metabolite content of *G. tricuspidata.*

In Algeria, the genus *Genista* (Fabaceae) is represented by 16 species from which 11 are endemic, distributed, in particular, in the eastern and southeastern parts of the country [4]. *G. tricuspidata* is endemic and has not been previously investigated.

Aerial parts of *G. tricuspidata* Desf. were collected during the flowering phase in May 2001 in eastern Algeria and authenticated by Dr. D. Sarri (Biology Department, University of M′Sila, Algeria) on the basis of Quezel and Santa [4].

The dried aerial parts of *G. tricuspidata* Desf. (1200 g) were macerated with EtOH–H_2O (70:30 v/v). After, filtration, the EtOH was evaporated at room temperature and the remaining aqueous solution extracted successively with petroleum ether, $CHCl_3$ and *n*-BuOH.

The *n*-BuOH extract was chromatographed on silica gel by gradient elution with hexane–EtOAc–MeOH, giving 30 fractions. The isolation and purification were performed by TLC on silica gel using CH_2Cl_2–acetone and $CHCl_3$–MeOH with different polarities as eluents and TLC on polyamide DC6 using toluene–MeOH–methylethylketone (4:3:3) and water–MeOH–methylethylketone–acetylacetone (13:3:3:1), leading to six compounds.

These compounds were identified by spectral analysis (UV, ^{1}H NMR, COSY and MS). All these results were in good agreement with the literature data [5, 6].

Compound (1): $C_{15}H_{10}O_5$, mp 298–300°C; UV (λ_{max}, MeOH, nm): 261, 323 (sh); +NaOH: 274, 321 (sh); +$AlCl_3$: 273, 306, 374; +$AlCl_3$/HCl: 273, 306, 374; +NaOAc: 269, 328 (sh); +NaOAc/H_3BO_3: 261, 322 (sh); ^{1}H NMR (250 MHz, CD_3OD, δ, ppm, J/Hz): 8.10 (1H, s, H-2), 7.35 (2 H, d, J = 8.8, H-2′, H-6′), 6.85 (2H, d, J = 8.8, H-3′, H-5′), 6.30 (1H, d, J = 2.2, H-8), 6.20 (1H, d, J = 2.2, H-6).

Identified as 4′,5,7-trihydroxyisoflavone (genistein).

Compound (2): $C_{21}H_{20}O_{10}$, mp 297°C; UV (λ_{max}, MeOH, nm): 263, 340 (sh); +NaOH: 275, 325 (sh); +$AlCl_3$: 272, 314, 368; +$AlCl_3$/HCl: 273, 315, 365; +NaOAc: 272, 329 (sh); +NaOAc/H_3BO_3: 262, 343 (sh); ^{1}H NMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 8.00 (1H, s, H-2), 7.35 (2H, d, J = 8.9, H-2′, H-6′), 6.83 (2H, d, J = 8.9, H-3′, H-5′), 6.26 (1H, d, J = 2.0, H-8), 6.16 (1H, d, J = 2.0, H-6), 4.78 (1H, d partially obscured by H_2O signal, H-1″), 3.20–3.65 (the other sugar protons).

Characterized as genistein 4′-glucoside (sophoricoside).

Compound (3): $C_{16}H_{12}O_5$, mp 238–240°C; UV (λ_{max}, MeOH, nm): 257, 319 (sh); +NaOH: 267, 299 (sh); +$AlCl_3$: 256, 317 (sh); +$AlCl_3$/HCl: 260, 322 (sh); +NaOAc: 264, 323 (sh); +NaOAc/H_3BO_3: 255, 319 (sh); ^{1}H NMR (250 MHz, CD_3OD, δ, ppm, J/Hz): 7.80 (1H, s, H-2), 7.30 (1H, d, J = 8.8, H-2′, H-6′), 6.80 (1H, d, J = 8.8, H-3′, H-5′), 6.35 (1H, d, J = 2.1, H-8), 6.30 (1H, d, J = 2.1, H-6), 3.90 (3H, s, OMe-5).

Characterized as 4′,7-dihydroxy-5-methoxyisoflavone (isoprunetin).

Compound (4): $C_{23}H_{24}O_{13}$, mp 245°C; UV (λ_{max}, MeOH, nm): 257, 271, 307, 361; +NaOH: 278, 334, 422; +$AlCl_3$:

1) Laboratoire de Phytochimie et Analyses Physico-Chimiques et Biologiques, Departement de chimie, Universite Mentouri, Constantine, Route Ain El Bey, 25000 Constantine, Algerie, fax 213 31 81 88 65, e-mail: ouahibaboumaza@yahoo.fr; 2) Departement de Biologie, Universite de M′Sila, Algerie; 3) Consejo Superior de Investigaciones Cientificas, Instituto de Productos Naturales y Agrobiologia, Tenerife, Spain. Published in Khimiya Prirodnykh Soedinenii, No. 6, pp. 595-596, November-December, 2006. Original article submitted November 1, 2005.

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276, 307 (sh), 367; +$AlCl_3$/HCl: 279, 309, 361, 417 (sh); +NaOAc: 281, 325, 413; +NaOAc/H_3BO_3: 256, 276, 373; ^{1}H NMR (250 MHz, CD_3OD, δ, ppm, J/Hz): 8.03 (1H, d, J = 2.2, H-2′), 7.77 (1H, dd, J = 8.8, 2.2, H-6′), 6.97 (1H, d, J = 8.8, H-5′), 6.21 (1H, s, H-6), 3.99, 3.94 (6H, s, OMe), 5.29 (1H, d, J = 8.8, H-1″), 3.90–3.20 (the other sugar protons).

Identified as 4′,5,7-trihydroxy-3′,8-dimethoxy-3-*O*-glucosylflavone.

Compound (5): $C_{22}H_{22}O_{12}$, mp 316°C; UV (λ_{max}, MeOH, nm): 255, 269, 358; +NaOH: 272, 319, 413; +$AlCl_3$: 268, 303, 358, 399; +$AlCl_3$/HCl: 268, 301, 357, 399; +NaOAc: 274, 316, 479; +NaOAc/H_3BO_3: 266, 357; ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 7.77 (1H, br.s, H-2′), 7.55 (1H, br.d, J = 8.5, H-6′), 6.75 (1H, d, J = 8.5, H-5′), 6.30 (1H, d, J = 2.1, H-8), 6.10 (1H, d, J = 2.1, H-6), 3.80 (3H, s, OMe-3′); 5.31 (1H, d, J = 9.3, H-1″), 3.70 (1H, dd, J = 11.9, 2.1, H-3″), 3.55 (1H, dd, J = 11.9, 5.4, H-4″), 3.44 (1H, m, H-2″), 3.32 (1H, m, H-6″), 3.22 (1H, m, H-5″).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 316 $[M]^+$ (97.9), 301 $[M-15]^+$ (1.9), 273 $[M-15-28]^+$ (6.0), 153 (2.9), 151 (4.6), 147 (8.0).

Identified as isorhamnetin 3-glucoside.

Compound (6): $C_{21}H_{20}O_{12}$, mp 242°C; UV (λ_{max}, MeOH, nm): 260, 365; +NaOH: 273, 334, 406; +$AlCl_3$: 274, 422; +$AlCl_3$/HCl: 270, 361, 402; +NaOAc: 270, 323, 399; +NaOAc/H_3BO_3: 264, 383; ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 7.71 (1H, br.s, H-2′), 7.58 (1H, br.d, J = 8.4, H-6′), 6.86 (1H, d, J = 8.4, H-5′), 6.39 (1H, br.s, H-8), 6.20 (1H, br.s, H-6), 5.24 (1H, d, J = 7.5, H-1″), 3.71 (1H, dd, J = 11.9, 2.1, H-3″), 3.55 (1H, dd, J = 11.9, 5.4, H-4″), 3.40 (1H, m, H-2″), 3.33 (1H, m, H-6″), 3.22 (1H, m, H-5″).

Identified as quercetin 3-glucoside (quercetrin).

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