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BRIEF COMMUNICATIONS

FLAVONOIDS OF THE AERIAL PART OF *Trigonella grandiflora*

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Plants of the *Trigonella* L. (Fabaceae) genus are rich sources of flavonoids and saponins. Certain species are used in folk medicine as diuretics, analgesics, and antitumor agents for gout, ascites, and epilepsy [1, 2].

T. grandiflora Bge is an annual that grows on dry stony and gravelly slopes, in arid lands, in cultivation, and in fields in the lower mountainous band of Central Asia [3].

Ground and air-dried raw material (2.0 kg) collected during flowering (April 24, 1997) in the vicinity of the Alimtau mountains (Chimkentsk region, Republic of Kazakhstan) was exhaustively extracted with ethanol at room temperature. The combined extract was evaporated in vacuo. The condensed remainder was diluted with water and successively treated with $CHCl_3$, ethylacetate, and *n*-butanol. The solvents were removed to yield $CHCl_3$ (46.0 g), ethylacetate (22.0 g), and butanol (43.0 g) fractions.

The ethylacetate fraction was chromatographed over a silica-gel column with elution by $CHCl_3$—CH_3OH (97:3—85:15) to give **1-5**.

The butanol fraction was chromatographed over a silica-gel column with elution by $CHCl_3$—CH_3OH (90:10—85:15) to isolate flavonoids **6** and **7**.

The isolated compounds were identified using PMR, UV, and mass spectra in addition to chemical transformations and direct comparison with authentic samples of certain compounds.

Biochanin A (1) (5,7-dihydroxy-4′-methoxyisoflavone), $C_{16}H_{12}O_5$, $[M]^+$ 284, mp 213-214°C. UV spectrum (EtOH, λ_{max}, nm) 263, 335. According to the UV spectrum, **1** is an isoflavone derivative. The PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz) contains signals at 3.63 (3H, s, OCH_3), 6.55 (1H, d, J = 2.0, H-6), 6.63 (1H, d, J = 2.0, H-8), 6.96 (2H, d, J = 9.0, H-3′,5′), 7.62 (2H, d, J = 9.0, H-2′,6′), 8.05 (1H, s, H-2) [4].

Luteolin (2) (5,7,3′,4′-tetrahydroxyflavone), $C_{15}H_{10}O_6$, $[M]^+$ 286, mp 328-330°C (dec.). UV spectrum (EtOH, λ_{max}, nm) 260, 274, 356 [5, 6].

Quercetin (3) (3,5,7,3′,4′-pentahydroxyflavone), $C_{15}H_{10}O_7$, $[M]^+$ 302, mp 313-315°C. UV spectrum (EtOH, λ_{max}, nm) 257, 267, 371 [6, 7].

Cinaroside (4) (luteolin-7-O-β-D-glucoside), $C_{21}H_{20}O_{11}$, mp 240-242°C (dec.). UV spectrum (EtOH, λ_{max}, nm) 256, 268, 350; $+CH_3COONa$ 259, 267, 363, 403; $+CH_3COONa/H_3BO_3$ 259, 373; $+AlCl_3$ 274, 299, 330, 430; $+AlCl_3/HCl$ 272, 293, 356, 386; $+CH_3ONa$ 262, 301, 392. According to the UV spectrum, **4** is a flavone derivative.

The PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz) contains signals at 3.90-4.05 (sugar protons), 5.66 (1H, d, J = 7.0, H-1″), 6.67 (1H, d, J = 2.5, H-6), 6.77 (1H, s, H-3), 6.84 (1H, d, J = 2.5, H-8), 7.13 (1H, d, J = 8.0, H-5′), 7.38 (1H, dd, J = 8.0 and J = 2.5, H-6′), 7.74 (1H, d, J = 2.5, H-2′).

Acid hydrolysis of **4** produced luteolin and D-glucose. Acetylation of **4** by acetic anhydride in pyridine gave the heptaacetyl derivative of composition $C_{35}H_{34}O_{18}$ ($[M]^+$ 742), mp 121-123°C [5, 6].

Quercetin-7-O-β-D-glucopyranoside (5), $C_{21}H_{20}O_{12}$, mp 245-247°C, UV spectrum (EtOH, λ_{max}, nm) 257, 266, 374; $+CH_3COONa$ 256, 267, 378.

The PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz) contains signals at 3.87-4.60 (glucose protons), 5.73 (1H, d, J = 6.5, H-1″), 6.69 (1H, d, J = 2.5, H-6), 6.91 (1H, d, J = 2.5, H-8), 7.25 (1H, d, J = 8.5, H-5′), 7.96 (1H, dd, J = 2.5 and J = 8.5, H-6′), 8.50 (1H, d, J = 2.5, H-2′).

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Acid hydrolysis of **5** formed quercetin and D-glucose. The site of attachment of the carbohydrate was established by studying UV spectra recorded with diagnostic additives [6, 8].

Vitexin (6) (apigenin-8-C-β-D-glucopyranoside), $C_{21}H_{20}O_{10}$, mp 247-249°C. UV spectrum (EtOH, λ_{max}, nm) 285, 337. PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz): 4.05-4.55 (carbohydrate protons), 4.75 (1H, t, J = 8.0, H-2″), 5.79 (1H, d, J = 8.0, H-1″), 6.76 (1H, s, H-3), 7.07 (2H, d, J = 9.0, H-3′,5′), 7.35 (1H, s, H-6), 7.74 (2H, d, J = 9.0, H-2′,6′).

UV spectroscopy showed that the hydroxyls are in the 5-, 7-, and 4′-positions of the flavone core. Acid hydrolysis of **6** by Kiliani's mixture gave apigenin and glucose [6, 9].

Isoorientin (7) (luteolin-6-C-β-D-glucopyranoside), $C_{21}H_{20}O_{11}$, mp 233-235°C. UV spectrum (EtOH, λ_{max}, nm) 258, 271, 352. The PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz) of **7** contains signals at 3.92-4.55 (2H, m, H-3″,6″), 5.04 (1H, t, J = 9.0, H-2″), 5.72 (1H, d, J = 9.0, H-1″), 6.54 (1H, s, H-3), 6.76 (1H, s, H-8), 7.13 (1H, d, J = 8.5, H-5′), 7.39 (1H, dd, J = 8.5 and J = 2.0, H-6′), 7.75 (1H, d, J = 2.0, H-2′), 14.24 (1H, s, 5-OH).

According to the UV and PMR spectra, **7** contains phenolic hydroxyls in the 5-, 7-, 3′-, and 4′-positions of the flavone core. Acid hydrolysis of **7** by Kiliani's mixture gave luteolin and glucose [6, 10].

Flavonoids **1-7** are isolated for the first time from *T. grandiflora*.

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