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BRIEF COMMUNICATIONS

FLAVONOIDS OF THE EPIGEAL PART OF *Cicer flexuosum* AND *C. mogoltavicum*

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Continuing an investigation of the flavonoids of plants of the *Cicer* L. genus [1], we have studied the epigeal part of *C. flexuosum* Lipsky [2]. The raw material was gathered in the flowering period of 1993 in the area of the R. Aksak-ata, Tashkentskii Oblast, Republic of Uzbekistan. Kaempferol, pratensein, formononetin, daidzein, kaempferol 3-O-glucoside, isorhamnetin 3-O-glucoside, ononin, and daidzin have been detected in the epigeal part of *C. flexuosum* previously [3].

From various fractions of an alcoholic extract of the epigeal part, by chromatography on a column of silica gel we have isolated — in addition to formononetin and isorhamnetin 3-O-glucoside — four aglycons (**1-4**) and one glycoside (**5**). Flavonoids (**1-5**) were identified from the results of a study of UV, PMR, and mass spectra, and the performance of some chemical transformations, and also by direct comparison with authentic specimens.

Biochanin A (1) (5,7-dihydroxy-4′-methoxyisoflavone) — $C_{16}H_{10}O_4$ (M^+ 284), mp 213-214°C, λ_{max} 263, 335 nm [4].

Isorhamnetin (2) (3,4′,5,7-tetrahydroxy-3-methoxyflavone) — $C_{16}H_{12}O_7$ (M^+ 316) mp 305-307°C, λ_{max} 255, 266, 372 nm. The PMR spectrum (Py-d_5) contained the signals of protons at 3.87 (*s*, $-OCH_3$), 6.09 (1H, d, 2.5 Hz, H-6), 6.41 (1H, d, 2.5 Hz, H-8), 6.83 (1H, d, 8.5 Hz, H-5′), 7.54 (1H, d, 2.5 Hz, H-2′), 7.60 ppm (1H, dd, 2.5 and 8.5 Hz, H-6′) [5, 7].

Luteolin (3) (3′,4′,5,7-tetrahydroxyflavone) — $C_{15}H_{10}O_6$, mp 328-330°C (decomp.), λ_{max} 260, 274, 356 nm. The PMR spectrum (Py-d_5) showed the signals of protons at 6.58 (1H, d, 2.0 Hz, H-6), 6.67 (1H, d, 2.0 Hz, H-8), 6.79 (*s*, H-3), 7.08 (1H, d, 8.0 Hz, H-5′), 7.51 (br.s, H-2′), 7.56 ppm (1H, dd, 2.0 and 8.0 Hz, H-6′) [1].

Quercetin (4) (3,3′,4′,5,7-pentahydroxyflavone) — $C_{15}H_{10}O_7$ (M^+ 302), mp 313-315, λ_{max} 257, 267, 331 nm; $+CH_3COONa$, 270, 405 nm. The PMR spectrum (Py-d_5) showed the signals of protons at 6.56 (1H, d, 2.5 Hz, H-6), 6.63 (1H, d, 2.5 Hz, H-8), 7.24 (1H, d, 8.5 and 8.5 Hz, H-5′), 7.94 (1H, dd, 8.5 and 2.5 Hz, H-6′), 8.47 (1H, d, 2.5 Hz, H-2′), 11.75 (br.m, 3-OH), 13.81 ppm (br.m., 5-OH) [3, 5, 6].

Sissotrin (5) (biochanin A 7-O-glucoside) — $C_{22}H_{22}O_{13}$, mp 218-220°C, λ_{max} 265, 337 nm. The IR spectrum contained absorption bands of hydroxy groups (3409-3600 cm^{-1}), of a methoxy group (2897 cm^{-1}), of a γ-pyrone carbonyl (1659 cm^{-1}), of aromatic C=C bonds (1619, 1582, 1516 cm^{-1}) and of the CO vibrations of glycosides (1100-1000 cm^{-1}).

In the PMR spectrum the signals of protons appeared at 3.74 (*s*, OCH_3), 4.00-4.65 (protons of the carbohydrate moiety), 5.67 (1H, d, 6.0 Hz, H-1″), 6.58 (1H, d, 2.0 Hz, H-6), 6.66 (1H, d, 2.0 Hz, H-8), 6.99 (2H, d, 9.0 Hz, H-3′,5′), 7.64 (2H, d, 9.0 Hz, H-2′, 6′), 8.07 (*s*, H-2), 13.45 ppm (br.s, 5-OH).

The acid hydrolysis of glycoside (**5**) yielded biochanin A (**1**) and *D*-glucose.

When substance (**5**) was acetylated with acetic anhydride in pyridine, a pentaacetyl derivative was obtained, with mp 204-206°C the mass spectrum of which contained, together with the peak of the molecular ion at *m/z* 656, intense peaks of fragmentary ions of a tetraacetylhexose residue with *m/z* 331, 329, 271, and 169.

In the PMR spectrum of glycoside (**5**) a signal of the anomeric proton of *D*-glucose appeared at 5.67 ppm in the form of a doublet with a spin–spin coupling constant of 6.0 Hz, which showed a β-glycosidic bond of the carbohydrate residue with the aglycon [1].

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This is the first time that flavonoids (**1-5**) have been isolated from *C. flexuosum*. We previously isolated six flavonoids from the epigeal part of *C. mogoltavicum* A. Kor. [1]. Continuing the separation of the mixture of flavonoids from this plant, from an ethyl acetate fraction of an alcoholic extract we have isolated flavonoids (**6**) and (**7**).

Isorhamnetin 3-O-α-*L*-rhamnoside (6) — $C_{22}H_{22}O_{11}$, mp 155-157°C, λ_{max} 256, 266, 362 nm, which is characteristic for 3-O-substituted flavonols.

In the PMR spectrum (Py-d_5) there were the signals of the protons of the methyl group of *L*-rhamnose (1.38 ppm, d, 6.0 Hz), methoxyl group (3.75 ppm, s), protons from the sugar fraction (3.56-4.72 ppm), anomeric protons of L-rhamnose (5.10 ppm, br.s) and of aromatic protons at C-6 (6.65 ppm, d, 2.0 Hz), C-8 (6.82 ppm, d, 2.0 Hz), C-5′ (7.23 ppm, d, 8.0 Hz), C-2′ (8.17 ppm, br.s), C-6′ (8.27 ppm, dd, 2.0 and 8.0 Hz).

The acid hydrolysis of glycoside (**6**) yielded isorhamnetin and *L*-rhamnose [5, 8].

Isorhamnetin 3-O-β-*D*-glucoside (7) — $C_{22}H_{22}O_{12}$, mp 163-165°C, λ_{max} 257, 267, 360 nm. The acid hydrolysis of glycoside (**7**) formed isorhamnetin and *D*-glucose [5, 7, 8].

This is the first time that flavonoid (**6**) has been isolated from a plant of the *Cicer* L. genus, and flavonoid (**7**) from *C. mogoltavicum*.

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