FLAVONOID GLYCOSIDES OF *Astragalus cicer*

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A comparative study has been made of the chemical composition of *Astragalus cicer* L. growing on the territory of the Georgian and Armenian SSRs (villages of Tianeti and Chkalovka, respectively).

The analysis of the two populations showed a difference in the qualitative and quantitative compositions of the flavonoids of the leaves, stems, and flowers. The flavonoids of *A. cicer* from Tianeti were characterized by a high degree of glycosylation. Both populations synthesize kaempferol, quercetin, and isorhamnetin derivatives, and also coumarins — scopoletin and umbelliferone.

From an air-dry extract of the epigeal parts of *A. cicer* growing in Tianeti we isolated three individual flavonoids [1, 2].

Substance (1), composition $C_{33}H_{40}O_{19}$, mp 190-194°C, $[\alpha]_D^{22}$ −61.7° (c 1.0; ethanol); $[M]_D$ 476.8; mol. wt. 740 (spectrometrically) [3]. UV spectrum, $\lambda_{max}^{ethanol}$: 350, 260 (log ε 4.4), (+$Zr(NO_3)_4$) 360, 270; ($Zr(NO_3)_4$ + citric acid) 345, 260 nm; (+ C_2H_5ONa) 395, 270. IR spectrum (in paraffin oil; cm^{-1}): 3600-3200 (OH), 1610-1600 (γ-pyrone), 1380 (—CH—), 920, 980 (—CH=CH—). The acid hydrolysis of (I) formed the aglycone kaempferol, and D-glucose and L-rhamnose were detected in the sugar moiety. It was cleaved by enzymes to a monoside — kaempferol 7-rhamnoside [2] — and a biose identified as rutinose [3, 4].

From the results obtained, substance (I) was identified as kaempferol 7-O-α-L-rhamnopyranoside 3-O-β-rutinoside [4].

Substance (2) had the composition $C_{22}H_{22}O_{12}$, mp 168-170°C, $[\alpha]_D^{25}$ −29.3° (c 0.5; dimethylformamide). UV spectrum, $\lambda_{max}^{ethanol}$: 355, 255, (log ε 3.8); (+ CH_3COONa) 375, 275; (+ $Zr(NO_3)_4$) 400, 255, 260; (+ $Zr(NO_3)_4$ + citric acid) 355, 255 nm. It was cleaved by acid into D-glucose and an aglycone (63%) with the composition $C_{16}H_{12}O_7$, mp 303-306°C, identified as isorhamnetin from its UV spectrum ($\lambda_{max}^{ethanol}$ 375, 255 nm) and the products of alkaline cleavage.

On the basis of UV and IR spectral characteristics and the results of analyses of transformation products, substance (2) was characterized as isorhamnetin 3-O-β-D-glucopyranoside [5-8, 10].

Substance (3), $C_{26}H_{27}O_{14}$, mp 188-190°C, $[\alpha]_D^{27}$ −129° (c 0.4; ethanol). UV spectrum, $\lambda_{max}^{ethanol}$, nm: 330, 270 (log ε 4.2); (+ C_2H_5ONa) 370, 285; (+ CH_3COONa) 330, 270. The glycoside was hydrolyzed by a 10% solution of sulfuric acid, forming an aglycone (47%) which was characterized by its physicochemical properties, a mixed melting point, and transformation products as apigenin, while in the carbohydrate moiety D-glucose and D-apiose were detected. Mol. wt. 547.3 (spectroscopically) [3].

The results obtained, the mobilities on PC in various solvent systems, and also literature information permit substance (3) to be characterized as apigenin 7-O-β-apiosylglucoside [5, 1, 9, 11, 12].

This is the first time that any of these substances have been isolated from *A. cicer* and described.

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FLAVONOIDS OF *Astragalus levieri* AND *A. sevangensis*

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Continuing an investigation of plants of the genus *Astragalus*, family Fabaceae [1], we have studied the chemical composition of two species: *Astragalus levieri* Freyn O. B. L. (Levier's milk vetch) and *Astragalus sevangensis* Grossh., belonging to the section *Onobrychium* Bge. [2]. The plants were collected in the flowering period from the territory of Georgia and Armenia.

To obtain the total flavonoids, 200.0 g of the air-dry herbage of each plant was extracted with 70% ethanol in an apparatus of the Soxhlet type. The ethanolic extracts were evaporated to an aqueous residue and treated with chloroform. The purified aqueous extract was exhaustively reextracted with ethyl acetate, and the ethyl acetate extract was evaporated and the total flavonoids were precipitated with chloroform.

The individual compounds were isolated by preparative chromatography on Filtrak FN-3 paper in the BAW (4:1:5) and 15% CH_3COOH systems and by column chromatography on polyamide. From *A. levieri* six flavonoid compounds were isolated, and their chemical compositions were established.

Substance (1), $C_{27}H_{30}O_{16}\cdot 2H_2O$, mp 187-189°C (from ethanol), $[\alpha]_D^{20}$ −12.5° (c 0.68; methanol), λ_{max} 359, 363 nm, was characterized as quercetin 3-O-rutinoside (rutin) [3].

Substance (2), $C_{21}H_{20}O_{12}$, mp 232-235°C (from ethanol), $[\alpha]_D^{20}$ −60° (c 0.15; methanol), λ_{max} 259, 365 nm, was quercetin 3-O-β-D-galactopyranoside (hyperoside) [4].

Substance (3), $C_{21}H_{20}O_{11}$, mp 179-181°C (ethanol), $[\alpha]_D^{20}$ −69° (c 0.5; ethanol), λ_{max} 350, 266 nm, was kaempferol 3-glucoside (astragalin) [5].

Substance (4), $C_{15}H_{10}O_7$, mp 310-313°C (from methanol), λ_{max} 256, 370 nm, was characterized as quercetin [6].

Substance (5), $C_{33}H_{40}O_{19}$, mp 189-191°C, $[\alpha]_D^{20}$ −120.4° (pyridine–ethanol (1:1)), λ_{max} 350, 265 nm, was identified as robinin [7].

Substance (6), $C_{28}H_{32}O_{11}\cdot 2H_2O$, mp 180-182°C, $[\alpha]_D^{20}$ −32.2° (c 0.31; dimethylformamide), λ_{max} 354, 266 nm, consisted of narcissin [8].

From *A. sevangensis*, we isolated rutin, hyperoside, astragalin, and narcissin.

The structures of all the compounds isolated were confirmed by the results of elementary analysis, UV and IR spectroscopy, and the results of a study of the products of acid and alkaline hydrolyses, and also by comparison with authentic samples.

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