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FLAVONOIDS OF *Trigonella grandiflora* AND *T. tenuis*

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We have studied the epigeal parts of *Trigonella grandiflora* Bunge and *T. tenuis* Fisch. collected in the flowering period in the Chimganskii gorge, Tashkent province.

The comminuted air-dry raw material was exhaustively extracted with 90% ethanol on the boiling water bath. The combined extracts were evaporated to 1/3 of their initial volume and were diluted with water and freed from lipophilic impurities with the aid of chloroform. The flavonoids were extracted with ethyl acetate, and the combined ethyl acetate extracts were concentrated almost to dryness.

The combined flavonoids were separated on a column filled with cellulose powder, the eluents being increasing concentrations of ethanol in water. *T. grandiflora* yielded two substances in the individual state.

Substance (I) – light yellow crystals with mp 260-265°C. In the UV spectrum, λ_{max} (nm): C_2H_5OH: 270, 302 sh., 336; CH_3COONa: 280, 300 sh., 380; $AlCl_3$: 277, 305, 350, 385; $AlCl_3$ + HCl: 278, 303, 344, 384; CH_3COONa + H_3BO_3: 271 sh., 344.

In the IR spectrum (cm^{-1}): 3390, 3260 (OH groups); 1657 (C=O group); 1612, 1570, 1505 (π-conjugation of an aromatic nucleus); 1040, 1010 (C bond for a glycoside); 990, 972, 856, 780, 751, 701 (distribution in a lateral phenyl radical).

Substance (I) did not undergo hydrolysis in the presence of dilute mineral acids. When it was hydrolyzed with Kiliani's mixture apigenin, D-glucose, and a very small amount of L-arabinose were formed.

Thus, according to UV and IR spectroscopy and the products of acid hydrolysis, substance (I) was a C-glycoside of apigenin. In a mixture with an authentic sample of the C-glycoside vitexin it gave no depression of the melting point, which enables it to be identified as 8-C-D-glucopyranosylapigenin (vitexin).

The same compound was isolated from *T. tenuis*.

Substance (II) – light yellow crystals with mp 255-257°C. In the UV spectrum, λ_{max}(nm): C_2H_5OH: 255, 267, 294 sh., 346; $AlCl_3$: 276, 302, 430; $AlCl_3$ + HCl: 265 sh., 276, 296 sh., 357, 384; CH_3COONa: 278, 325, 386; CH_3COONa + H_3BO_3: 264, 275, 340 sh., C_2H_5ONa: 286, 378 sh., 405. In contrast to substance (I), under the action of solution of basic lead acetate the spots on the chromatogram acquired an orange coloration. R_f 0.76 in the butan-1-ol–CH_3COOH–H_2O (4:1:5) system.

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IR spectrum (cm^{-1}): 2900, 3550 (OH groups), 1657 (=CO group); 790, 815, 844 (presence of substitution in the lateral phenyl radical). There are absorption bands due to the deformation vibrations of the OH groups of a sugar residue in the 1000-1100 cm^{-1} region [1].

This substance was also difficult to hydrolyze. On acid hydrolysis in a mixture of conc. HCl + CH_3COOH + H_2O (10 + 3.5 + 5.5), after 4 h luteolin, D-glucose, and a very small amount of arabinose were formed.

On the basis of the results obtained, substance (II) was identified as orientin.

In the combined flavonoids, saponaretin (isovitexin) was detected by paper chromatography.

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INVESTIGATION OF THE FLAVONOIDS OF Scutellaria polyodon. II

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We have previously reported that the flowers of Scutellaria polyodon Juz., contain scutellarein and its 7-β-glucuronide [1].

Continuing to study the flavonoid composition, we subjected the comminuted freshly-gathered flowers to acetone extraction. After the raw material had been steeped for a day at room temperature, the acetone extract was evaporated to 1/3 of its initial volume and benzene was added until phase separation took place. When the system was left in the refrigerator, a bright yellow precipitate formed at the boundary of the two phases, and this was separated off and washed with ice water. In addition to this, we treated the raw material with liquid carbon dioxide at 20-22°C and a pressure of 5.8-6.18 MPa for 80 min, after which the flavonoids were extracted with methanol. In this case it was possible to increase the yield of flavonoid compounds from 2% by the procedure described previously [1] to 7%.

To isolate the individual compounds we used column chromatography on silica gel and on polyamide, and also gel filtration through Sephadex G-25.

Chromatography on silica followed by rechromatography on a polyamide sorbent yielded substances (IV-VI).

Substance (IV) consisted of pale yellow needles with mp 261-262°C (ethanol), $[\alpha]_D^0$ – 92° (c 0.1; dimethylformamide). According to UV spectroscopy in the presence of ionizing and complex-forming additives, the compound belonged to the flavone group and had no free hydroxy group at C-7. The PMR spectrum of the acetyl derivative in $CDCl_3$ contained the signals of the protons H-6, H-3, H-8, H-3', H-5' (2 H, d, 8 Hz), H-2', and H-6' (2 H, d, 8 Hz) and of the protons of acetyl groups, of a carbohydrate component, and of a CH_3 group in the 0.85 ppm region (d, 3 Hz).

D-Glucose, L-rhamnose, and apigenin were found in the products of acid hydrolysis (10% H_2SO_4).

To prove the structure of the carbohydrate component we performed the independent synthesis of various biosides of apigenin containing glucose and rhamnose from the corresponding naringenin glycosides. In its R_f values and the melting point of acetate, substance (IV) corresponded to synthetic apigenin 7-rutinoside, which was obtained from narirutin octaacetate by the method of Rösler et al [2].

Thus, the substance (IV) can be characterized as apigenin 7-O-[O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (isorhoifolin).

Substance (V) consisted of light-colored crystals with mp 260°C. UV spectrum, λ_{max}

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