FLAVONOIDS OF Galium ruthenicum

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Continuing a chemical study of Galium ruthenicum Willd., we have isolated from the herbage of this plant by chromatography on Kapron columns another six individual flavonoids (substances 1-6), in addition to rutin and hyperoside [1, 2].

Substance 1 gives almost colorless crystals in the form of needles with mp 228-228°C (isopropanol), $[\alpha]_D^{22}-51°$ (c 0.1; dimethylformamide). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 270, 343 nm. In the products of acid (10% H_2SO_4) and enzymatic (emulsin) hydrolysis we identified D-glucose and apigenin (mp 345-347°C; triacetate with mp 178-182°C).

Substance 2 formed pale-yellow needles with mp 251-253°C (ethanol), $[\alpha]_D^{18}-86°$ (c 0.1; dimethylformamide). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 270 and 343 nm. Hydrolysis performed under the same conditions yielded apigenin, D-glucose, and L-rhamnose, while incubation with rhamnodiastase gave apigenin and rutinose. Partial hydrolysis (1% H_2SO_4, 3 h) gave L-rhamnose and substance 1.

Substance 3 forms pale-yellow needles with mp 256-258°C (70% ethanol), $[\alpha]_D^{20}-40.3°$ (c 0.1; dimethylformamide). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 257 and 362 nm. The products of hydrolysis were found to contain D-glucose and luteolin (mp 326-328°C; tetraacetate with mp 221-224°C).

Substance 4 forms almost colorless plates with mp 263-266°C, $[\alpha]_D^{22}-42.4°$ (c 0.1; dimethylformamide). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 257 and 355 nm. It is hydrolyzed by mineral acids and by enzymes to D-glucose and diosmetin (mp 255-257°C; triacetate with mp 194-197°C).

Substance 5 formed pale-yellow needles with mp 174-176°C (70% ethanol), $[\alpha]_D^{20}-57.5°$ (c 0.1; dimethylformamide). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 253 and 350 nm. Diosmetin, D-glucose, and L-arabinose were identified in the hydrolyzates after acid cleavage of the glycosides, while fermentation with rhamnodiastase led to diosmetin and a biose. Hydrolysis under mild conditions (1% H_2SO_4, 3 h) gave L-arabinose and substance 4.

Substance 6 forms yellow needles with mp 216-218°C (30% ethanol), $[\alpha]_D^{20}-28.1°$ (c 0.25; dimethylformamide). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 265 and 347 nm. Acid hydrolysis took place very readily (1% H_2SO_4) 30 min) leading to the formation of D-glucose, L-rhamnose, and kaempferol (mp 274-276°C; tetraacetate with mp 181-184°C). Cleavage with rhamnodiastase yielded kaempferol and rutinose.

On the basis of the results of our study of the physicochemical properties of the initial flavonoids and the products of their acid and enzymatic hydrolysis, and UV and PMR spectra, substance 1 was identified as apigenin 7-O-β-D-glucopyranoside, 2 as apigenin 7-O-α-L-rhamnopyranosyl-(1→6)-β-glucopyranoside, 3 as luteolin 7-O-β-D-glucopyranoside, 4 as diosmetin 7-O-α-D-glucopyranoside, 5 as diosmetin 7-O-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranoside and 6 as kaempferol 3-O-β-rutinoside.

LITERATURE CITED

1. M. I. Borisov and Yu. G. Borisyuk, Farmats. Zh., No. 3, 43 (1963).
2. M. I. Borisov and Yu. G. Borisyuk, Farmats. Zh., No. 4, 75 (1973).

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