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FLAVONOIDS OF Hedysarum sericeum AND H. caucasicum

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UDC 547.972:582,971

We have made a preliminary phytochemical investigation of the seeds of species of the genus *Hedysarum* L. (family *Fabaceae* L.) of the Georgian flora.

The air-dry comminuted herbage of *Hedysarum sericeum* was extracted with 80% ethanol. The ethanol was distilled off, and the aqueous residue was purified with chloroform. On PC in the solvent systems 1) BAW (4:1:2); 2) 5% acetic acid; 3) tetrahydrofuran—chloroform (1:1); and 4) ethyl acetate—ethanol—water (100:16.5:13.5), we found seven dominating spots of flavonoids and flavone and xanthone derivatives [1, 2] in the extract and, in addition, we detected amino acids, hydroxycoumarins, and isoprenoids. The flavonoids of low polarity were isolated with ethyl acetate from the extract obtained. The ethyl acetate was distilled off and the total flavonoids were chromatographed on a column of polyamide. Two individual flavonoids (1 and 2) were isolated, and from the residual aqueous solution by fractionation on polyamide sorbent, four substances (3-6) were isolated.

- Substance (1)  $C_{15}H_{10}O_7$ , mp 308-312°C (ethanol), was characterized as quercetin [2, 3].
- Substance (2)  $-C_{15}H_{10}O_6$ , mp 273-276°C (ethanol), was identical with kaempferol [3].
- Substance (3)  $C_{21}H_{20}O_{12}$ , mp 238-240°C,  $[\alpha]_D^{20}$  —58° (c 0.1; ethanol). On acid hydrolysis (2%  $H_2SO_4$ , 100°C, 60 min) it was split into D-galactose and the aglycone quercetin,(68%) [3]. On the basis of its physicochemical properties, substance (3) was identified as hyperoside [3].
- Substance (4)  $C_{21}H_{20}O_{12}$ , mp 222-225°C,  $[\alpha]_D^{20}$  —10° (c 0.1; ethanol), was identified as isoquercitrin [3].
- Substance (5)  $C_{27}H_{30}O_{16}$ , mp 215-218°C,  $[\alpha]_D^{20}$  —117° (c 0.5; ethanol). UV spectrum:  $\lambda_{\max}^{\text{ethanol}}$  362, 269, 258 nm. On acid hydrolysis (2%  $H_2SO_4$ , 100°C, 2 h) it gave quercetin (47%), L-rhamnose, and D-glucose. From its physicochemical properties and the IR and UV spectra of the glycoside itself and of its transformation products, substance (5) was identified as quercetin 3-0- $\beta$ -glucopyranoside 7-0- $\alpha$ -rhamnofuranoside (antoside) [4].
- Substance (6)  $C_{19}H_{18}O_{11}$ , mp 258-261°C,  $[\alpha]_D^{20}$  +42° (c 0.45; DMFA). UV spectrum:  $\lambda$  ethanol 364, 315, 257, 240 nm. On the basis of chemical transformations, spectral characteristics, and literature information, it may be concluded that substance (6) was mangiferin [5-7].

Similarly, from *Hedysarum caucasium* we isolated and characterized kaempferol, quercetin, and antoside [1-7]. The chemical study of the other species is continuing. This is the first time that any of these substances has been isolated from the given species. The sample of mangiferin was kindly supplied by G. G. Nikolaeva.

I. G. Kutateladze Institute of Pharmacochemistry of the Academy of Sciences of the Georgian SSR, Tbilisi. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 646, September-October, 1983. Original article submitted March 23, 1983.

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## POLYPHENOLIC COMPOUNDS OF POTATO FLOWERS

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UDC 547.972

In folk medicine, the flowers of the potato (Solanum tuberosum L.) have been used since antiquity as an antipyretic agent in diseases of the liver and kidneys, and in cases of constipation and tumors [1-3].

We have investigated the flowers of potatoes of the variety "Rozovyi rannii" ["early pink"] gathered in the Novo-Vodolazhskii Region of Khar'kov province.

The comminuted flowers were extracted with a fivefold volume of 80% ethanol with steeping for 24 h (three times) at room temperature. The combined extracts were evaporated in vacuum to small volume and centrifuged, and the resinous precipitate that had deposited was filtered off. After a day, an amorphous precipitate giving no reaction for flavonoids deposited from the extract obtained. Chromatography on paper in systems 1) butan-1-ol—acetic acid—water (4:1:2) and 2) 15% acetic acid showed the presence in the purified extract of not less than 9 substances of phenolic nature. In the products of the acid hydrolysis of the extract (5% ethanolic solution of hydrochloric acid, on the boiling water bath for 4 h), we found kaempferol, quercetin, myricetin, luteolin, and caffeic acid.

When the purified extract was stored in the refrigerator (5-6°C) a precipitate was formed of a substance in the form of pale yellow needles with the composition  $C_{21}H_{20}O_{11}$ , mp 256-258°C,  $[\alpha]_D^{20}$  -100.0°. UV spectrum:  $\lambda_{\rm max}$  257, 268, 350 nm (substance (1)).

Chromatography on polyamide columns with elution by 30% ethanol gave a compound consisting of light yellow acicular crystals with the composition  $C_{27}H_{30}O_{16}$ , mp 191-193°C,  $[\alpha]_D^{20}$  -32.0°. UV spectrum:  $\lambda_{\rm max}$  258, 264, 362 nm (substance (II)).

When using as eluent chloroform—ethanol (9:1), a substance was isolated in the form of yellow acicular crystals with the composition  $C_{21}H_{20}O_{12}$ , mp 229-231°C,  $[\alpha]_D^{20}$  -33.0°. UV spectrum:  $\lambda_{\text{max}}$  258, 264, 360 nm (substance (III)), and on elution with water heated to 40°C, we obtained a compound with the composition  $C_{16}H_{18}O_9$ , mp 202-204°C  $[\alpha]_D^{20}$  -31.9°. UV spectrum:  $\lambda_{\text{max}}$  240, 328 nm (substance (IV)).

On the basis of the results of a chemical investigation of the compounds obtained and of the products of their hydrolysis, and also of a comparison with authentic samples, substance (I) was identified as luteolin 7-0- $\beta$ -D-glucopyranoside (cynaroside); (II) as quercitin 3-[0- $\alpha$ -L-rhamnopyranosyl-(1+6)- $\beta$ -D-glucopyranoside] (rutin); (III) as quercetin 3-0- $\beta$ -D-glucopyranoside (isoquercitrin); and (IV) as 5-0-caffeyl-D-quinic (chlorogenic) acid.

Ukrainian Institute for the Advanced Training of Physicians, Kiev. Khar'kov Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 647, September-October, 1983. Original article submitted April 7, 1983.