

## FLAVONOIDS OF GALIUM FAGETORUM. I.

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In the herb Galium fagetorum Klok. (collected in the environs of the village of Verkhnyaya Kutuzovka, Crimea region) by two-dimensional chromatography on paper and by qualitative reactions we have detected eight flavonoid substances with the following  $R_f$  values:  $\Phi_1$  0.36,  $\Phi_2$  0.50,  $\Phi_3$  0.66,  $\Phi_4$  0.23,  $\Phi_5$  0.84,  $\Phi_6$  0.95,  $\Phi_7$  0.15,  $\Phi_8$  0.09 [in an ethyl acetate-formic acid-water (10:2:3) system].

When an ethanolic extract was separated on Kapron using ethanol-chloroform (20:80) and isopropanol as eluants, the individual compounds  $\Phi_1$  and  $\Phi_6$  were obtained.

Substance  $\Phi_1$   $C_{26}H_{20}O_{11}$ . Mp 248-252° C (isopropanol),  $[\alpha]_D^{22}$  -41° (c 0.1, dimethylformamide), UV spectrum:  
 $\lambda_{max}^{ethanol}$  362 and 257 m $\mu$ ,  $\lambda_{max}^{ethanol + CH_3COONa}$  363 and 262 m $\mu$ .

Hydrolysis with 10%  $H_2SO_4$  (6 hr) gave the aglycone  $C_{15}H_{10}O_6$ , mp 330-331° C, identical with substance  $\Phi_6$  and a sugar identified by paper chromatography as D-glucose. The melting point of the osazone was 202-204° C (from 50% ethanol).

On the basis of the bathochromic shifts in the UV spectrum in the presence of ionizing and complex-forming reagents, and also the absence of a depression of the melting point of a mixture with an authentic sample, the aglycone was identified as luteolin [1, 2]. The D-glucose is attached in position 7, as is shown by the absence from the UV spectrum of the substance of a bathochromic shift of the long-wave maximum when sodium acetate is added. The flavonoid under investigation is hydrolyzed by an enzyme preparation from Aspergillus orizae. This shows the  $\beta$ -configuration of the glycoside bond. A comparison of the molecular rotations of the glycoside with the corresponding phenyl glycosides and differential IR spectroscopy (bands at 756, 920, and 890  $cm^{-1}$ ) permit the conclusion that the D-glucose is present in the pyranose form.

Thus, substance  $\Phi_1$  is mainly luteolin 7-O- $\beta$ -D-glucopyranoside (cynaroside), and 7, 5, 3', 4'-tetrahydroxyflavone (luteolin).

## REFERENCES

1. N. P. Maksyutina and V. I. Litvinenko, Phenolic Compounds and their Biological Functions [in Russian], Moscow, p. 7, 1968.
2. T. A. Geisman, The Chemistry of Flavonoid Compounds, Pergamon Press, New York, 107, 1962.

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