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FLAVONOIDS OF *Reseda luteola*

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There are reports in the literature on the presence in the plant *Reseda luteola*, family Resedaceae (wild mignonette) of certain flavone glycosides, but they were not characterized [1, 2].

To isolate the flavonoids, the epigeal parts of the wild mignonette collected in the environs of Tashkumir (KirgSSR) in the vegetation period were extracted with ethanol. The concentrated ethanolic extracts were diluted with water (1:2) and were purified by washing with petroleum ether and with benzene. Then the flavonoids were extracted with ether, ethyl acetate, and butanol. Concentration of the ethereal extract led to the deposition of crystals with mp 240-242°C (ethanol). By a study of the products of acid and enzymatic hydrolysis and spectral characteristics (IR, UV, and PMR spectra) and also by polarimetric analysis, this substance was identified as luteolin 7-O-β-D-glucopyranoside (I) [3].

From the mother liquor of (I) we isolated luteolin and a flavone glycoside (II) with R_f 0.63 (on Silufol in the toluene—ethanol—ethyl acetate (1:2:2) system)).

Glycoside (II) had the composition $C_{21}H_{20}O_{11}$, mp 181-182°C (ethanol), $[\alpha]_D^{22}$ −2.2° (c 1.69; DMFA); $\lambda_{max}^{CH_3OH}$ 243, 270, 343 nm, $\lambda_{max}^{CH_3COONa}$ 270, 353 nm, $\lambda_{max}^{CH_3COONa/H_3BO_3}$ 269, 352 nm, $\lambda_{max}^{CH_3ONa}$ 268, 396 nm, $\lambda_{max}^{ZrOCl_2}$ 271, 368 nm; heptaacetyl derivative — mp 109-112°C. The UV spectral characteristics given above show the presence of free phenolic hydroxy groups in the 4', 5, and 7 positions. The acid hydrolysis of (II) (5% H_2SO_4, 1 h on the water bath) formed equimolar amounts of luteolin and glucose, a precipitate of the aglycone being observed only 5-10 min after the beginning of hydrolysis.

Consequently, (II) is a luteolin glucoside in which the glucose residue is attached to position 3' of the aglycone. This was confirmed by a comparison of the PMR spectra of (I) and (II) taken in deuteropyridine. In the spectrum of (II), the signals of the H-6 and H-8 protons (doublets at 6.60 and 6.69 ppm with an SSCC of 2 Hz) was shifted upfield in relation to the corresponding signals of compound (I) (6.67 and 6.84 ppm, doublets), which is due to the absence of a sugar residue in position 7 [3]. Furthermore, the spectrum of (II) contained the signals of the following protons: H-3 (6.78, ppm, singlet), H-2' (7.36 ppm), H-5' (7.11 ppm, doublet, J = 8.5 Hz), H-6' (7.36 ppm, doublet of doublets, J_1 = 8.5 Hz, J_2 = 2 Hz) and those of the sugar moiety (6 H, 3.94-4.54 ppm). The anomeric proton gave a broadened signal at 5.59 ppm.

The formation of luteolin under the action of the enzymes from the grape snail showed the presence of a β-glycosidic bond of the glucose with the aglycone. The presence in the IR spectrum of absorption bands at 1035 and 1076 cm^{-1} and the ready hydrolyzability of (II) by dilute acid showed the furanose form of the glucose [4, 5].

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Thus, (II) had the structure of luteolin 3'-O-β-D-glucofuranoside and is a new flavone glycoside.

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IDENTIFICATION OF 2',7-DIHYDROXY-4'-METHOXYISOFLAVAN (VESTITOL) IN THE ROOTS OF ALSIKE CLOVER

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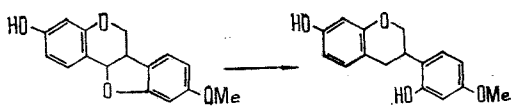
Trifolium hydribum (Alsike clover) differs from *Tr. pratense* (red clover) by a considerably greater resistance to unfavorable factors of the external environment and to fungal diseases [1]. In the search for compounds possessing antifungal activity and present in the roots of this plant — the organs subject to attack — we obtained an acetone extract and, by its separation on columns of silica gel in a benzene–acetone gradient system, we have isolated a small amount of a crystalline substance (I) with mp 156°C (chloroform) having the composition $C_{16}H_{16}O_4$.

The NMR spectrum of this substance taken in deuteroacetone solution contained a three-proton singlet of an aromatic methoxy group at 3.85 ppm, with two broadened one-proton singlets of OH groups at 8.06 and 8.51 ppm, and also a group of peaks of aromatic and aliphatic protons. These facts show the partial formula of the substance as $C_{15}H_{11}O(OH)_2(OMe)$. The absence from the IR spectra of the substance of the absorption of a C=O group and the presence of the characteristic system of proton signals for a $-CH_2-\underset{|}{CH}-CH_2$ group at 4.3-2.9 ppm [2] showed the isoflavan structure of the molecule. This was in agreement with the UV spectrum taken in MeOH solution: λ_{max} (nm) 206, 228, 285 (ε 45,500, 11,200, 5600).

The aromatic protons in the NMR spectrum of the substance taken in $CDCl_3$ solution formed an ABX system with the spin–spin coupling constants J_{AX} = 8 Hz, J_{AB} = 3 Hz, and J_{BX} = 0, which corresponds to 1,2,4-trisubstitution of both the aromatic rings of the molecule. The position of the methoxy group in it followed from the results of mass spectrometry: The spectra showed the presence of two high-intensity ions with m/e 150, having the composition $C_9H_{10}O_2$, and the m/e 137, having the composition $C_8H_9O_2$, formed from ring B of the isoflavan molecules [3] which corresponds to the presence of the methoxy group in this fragment. The choice between 2' and 4' positions for this group was made on the basis of the reductive decyclization of natural (−)-medicarpin (II) over 10% Pd/C (AcOH, 20°C). The substance formed by this reaction was completely identical (UV, NMR, and mass spectra) with compounds (I) that we had isolated.



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