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FLAVONOIDS OF *Ferula schair* AND *F. samarkandica*

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We have studied the flavonoids of *Ferula schair* Borszcz. and *F. samarkandica*, family Apiaceae. An ethanolic extract of the epigeal part of *F. schair* collected in the environs of Alim-Tau (southern Kazakhstan) was concentrated in vacuum, diluted with water, and filtered. The filtrate was washed three times with chloroform. On cooling, the purified aqueous ethanolic solution deposited a precipitate which, after recrystallization from ethanol, had mp 240-242°C, $[\alpha]_D$ −27.6° (c 1.45: pyridine–methanol (1:1)), $\lambda_{max}^{ethanol}$, nm: 256, 268 (sh.), and 350 (I). The hydrolysis of (I) with 10% H_2SO_4 led to glucose and luteolin (mp 329-330°C, M^+ 286) in equimolar amounts. According to UV spectroscopy, the carbohydrate component was present in position 7.

The study of IR, UV, and PMR spectra, and also enzymatic hydrolysis with β-glucosidase, enabled us to characterize substance (I) as luteolin 7-O-β-D-glucopyranoside [1, 2]. From its mother liquor we isolated luteolin (II).

To extract flavonoids, the seeds of *Ferula samarkandica* collected in the Tashkent province were extracted with ethanol three times. The concentrated extract was diluted with water (1:2) and was freed from lipophilic substances by washing with petroleum ether and with benzene. Then the flavonoids were extracted with ethyl acetate. When the ethyl acetate extract was concentrated, a precipitate deposited the repeated crystallization of which from a mixture of ether and ethyl acetate yielded a new flavonoid (III).

The flavone (III) had the composition $C_{22}H_{22}O_{11}$, mp > 340°C, $[\alpha]_D^{20}$ +75° (c 0.8; pyridine–methanol (1:1)), R_f 0.44 in the toluene–ethyl acetate–ethanol (1:1:1) system. On the basis of Bryant's cyanidin reaction, compound (III) was assigned to the flavone glycosides [3]. This was confirmed by the presence in the PMR spectrum of (III) (Py-d_5) of the signal of the protons of a sugar residue (7 H in the interval 4.05-4.58 ppm) and of an anomeric proton (5.69 ppm, J = 6 Hz). The signal of a CH_3O group appeared at 3.72 ppm, and the protons of the flavone nucleus resonated in the region of aromatic protons [1, 4].

The UV spectrum of (III) had maxima at 255, 270, and 347 nm, which showed that it was a derivative of 3',4',5,7-tetrahydroxyflavone. According to the results of UV spectroscopy with various additives [5], there were free hydroxy groups in positions 3' and 5. When (III) was hydrolyzed with 5% HCl (80°C, 30 min), D-glucose was obtained together with an aglycone having mp 249-251°C, M^+ 300, which was identified on the basis of its mass and UV spectra as diosmetin [1, 6]. The absence of a shift of the maxima in the presence of sodium acetate showed the attachment of the glucose residue to position 7 of the aglycone. However, (III) differed from the known diosmetin 7-O-β-glucopyranoside [6]. The considerably greater hydrolyzability of (III) relative to known 7-O-glucopyranosides with dilute acids was probably due to the furanose form of the sugar residue [7]. This was confirmed by the presence of absorption bands at 1038, 1076, and 845 cm^{-1} in the IR spectrum, and also by the results of a Klyne calculation of molecular rotation, which showed the furanose form of the glucose and the α-configuration of the glucosidic bond [8].

On the basis of the facts given above, we propose for the flavone glycoside (III) the structure of 7-α-D-glucofuranosyloxy-3',5-dihydroxy-4'-methoxyflavone.

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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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