The IR spectra were taken on a UR-10 spectrometer (in paraffin oil) the PMR spectra on a Brüker HX-90 spectrometer, and the mass spectra on a Hewlett-Packard-5980 A chromato-mass spectrometer. The melting points were determined on a Kofler block.

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NEW FLAVONOL GLYCOSIDES OF *Rhodiola algida*

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In a course of the study of the components of *Rhodiola algida* (Ledeb.) (Fisch. et Mey.), family Crassulaceae, collected in the Gorno-Altai Autonomous Oblast at the end of flowering, we have found flavonoids not previously described. For their isolation, the comminuted air-dry rhizomes were extracted three times with 95% ethanol, and the combined extracts were concentrated in vacuum, diluted with hot water, and extracted with chloroform, ether, ethyl acetate, and butanol.

The ethereal extract yielded lemon-yellow acicular crystals (I). After their removal, the residue was separated by chromatography on columns of polyamide. On elution with chloroform containing 5 and 7% of ethanol (by volume) and after fractional crystallization, three new flavonoid compounds were isolated (II)-(IV). From its physicochemical properties, compound (I) was similar to acetylrhodalgin. The PMR spectrum of the TMS ether of the acylglycoside, obtained by I. P. Kovalev (Kharkov Scientific-Research Institute of Pharmaceutical Chemistry), proved to be identical with the latter [1].

Substance (II), $C_{25}H_{24}O_{14}$, mp 182-183°C, $[\alpha]_D^{20}$ −68° (c 0.15; CH_3OH), $\lambda_{max}^{CH_3OH}$ 274, 329, 379 nm, R_f 0.27 and 0.66 (PC on FN-4; here and below in the 15 and 60% CH_3COOH systems).

Substance (III), $C_{25}H_{24}O_{14}$, mp 196-197°C, $[\alpha]_D^{20}$ −120° (c 0.1; CH_3OH), $\lambda_{max}^{CH_3OH}$ 275, 328, 385 nm, R_f 0.19 and 0.61.

The hydrolysis of these compounds with 2% HCl (100°C, 1 h) gave herbacetin with mp 295-297°C, D-glucose, and acetic acid. The latter was identified by paper chromatography in the presence of a marker, and also by the production of acethydroxamate. UV spectra with diagnostic reagents [2] showed the presence of free hydroxy groups in positions 3, 5, and 7; $\Delta\lambda^{+MeONa}$ 84 and 77 nm, respectively, but after 10 min the long-wave maximum disappeared, which shows the presence of a 4'-hydroxy group. A negative reaction with p-benzoquinone under the conditions of the gossypetone test, in contrast to the behavior of the aglycone, gave grounds for concluding that the carbohydrate components were attached to the C_8 atom of herbacetin. On chromatograms of the substances, a bright yellow fluorescence appeared in UV light, which showed the presence of a free hydroxy group at C_3 in each of them.

The IR spectra were very close: 3470-3280 cm^{-1} (OH), 1745 cm^{-1} (ester C=O), 1007 m^{-1} (O–C–O of a glycosidic bond), and 888 cm^{-1} (β linkage). The only difference appeared in the 1010-1110 cm^{-1} region: in the case of substance (II) three absorption bands were observed (1045, 1080, and 1090 cm^{-1} – the pyranose ring of glucose) and in the case of substance (III) only two absorption bands (1053 and 1080 cm^{-1}), which is characteristic for furanosides. The difference in the sizes of the oxide rings of the carbohydrate components of the flavonol glycosides was confirmed by the polarimetric method [3]. The results of the hydroxamic reaction with the glucosides and their aglycones and the comparison of the IR spectra confirms that the two acetoxy groups were present in the carbohydrate moiety.

Consequently, substances (II) and (III) are new compounds, not previously described in the literature, with the structures of 3,4',5,7,8-pentahydroxyflavone 8-O-(di-O-acetyl-β-D-glucopyranoside), which we have called rhodalgisin and 3,4',5,7,8-pentahydroxyflavone 8-O-(di-O-acetyl-β-D-glucofuranoside), for which we propose the name rhodalgiside.

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Substance (IV), $C_{25}H_{26}O_{15}$, mp 261-262°C, $[\alpha]_D^{20}$ 36° (c 0.15; CH_3OH), $\lambda_{max}^{CH_3OH}$ 275, 327, 372 nm ν_{CO} 1665 cm^{-1}, R_f 0.14 and 0.45. Quantitative acid hydrolysis yielded equimolar amounts of herbacetin, L-arabinose, and D-xylose. From the changes in the UV spectra of the flavonoid caused by ionizing and complex-forming reagents, it was established that in the glycoside there were substituents at the C_8 and C_4' atoms of herbacetin.

Stepwise acid hydrolysis formed a mixture of two monosides: herbacetin 4'-xyloside and herbacetin 8-arabinoside. Treatment of the diglycoside with β-hydrolase led to the splitting out of D-xylose. On the basis of its physicochemical properties, chemical transformations, and UV and IR spectra, for substance (IV) we suggest the structure of 3,4',5,7,8-pentahydroxyflavone 8-O-α-L-arabinopyranoside 4'-O-β-D-xylopyranoside and the name rhodalide.

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DIDYMIN FROM THE BLOSSOMS OF THE SATSUMA ORANGE

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We have investigated the blossoms of the satsuma orange (*Citrus unshiu* Marc., syn, *C. nobilis* Lour. var. *unshiu* Swingle), which is widely cultivated on the Black Sea slopes of the town of Batumi.

The blossoms were extracted with 70% ethanol and the presence of flavonoid compounds in the alcoholic extracts was found by two-dimensional chromatography on paper in the butan-1-ol—CH_3COOH—H_2O (4:1:5) and 30% CH_3COOH systems and by the revelation of flavonoid spots by chromogenic reagents.

Not less than five flavonoid compounds were found in the blossoms, of which two were flavanone glycosides (chromatogram stained with a saturated solution of sodium tetrahydroborate in isopropanol and with hydrochloric acid vapor) [1].

To isolate the individual compounds, the blossoms were dried at +60°C and were exhaustively extracted first with chloroform and then with 60% ethanol. The alcoholic extracts were concentrated, one third of a volume of water was added, and the mixture was cooled to +5°C. After a week, the light-colored precipitate that had deposited was separated off and washed with cold water, and after four recrystallizations from 70% acetic acid colorless crystals of substance (I) with mp 212°C were obtained. UV spectrum (C_2H_5OH), nm: λ_{max} 287, 332 sh. No bathochromic shift was observed in the presence of sodium acetate. The acetyl derivative, obtained by a method described previously [2], had mp 118°C, λ_{max} (C_2H_5OH), nm: 268, 311 sh.

Acid hydrolysis with 5% sulfuric acid for three hours gave a hydrolysate containing D-glucose and L-rhamnose (paper chromatography, spots revealed with the aniline phthalate reagent). On partial hydrolysis with 85% formic acid in cyclohexanol, only L-rhamnose was split out.

The aglycone — colorless crystals with mp 193°C — gave a brown coloration with a solution of ferric chloride and a pink-violet coloration with sodium tetrahydroborate in the presence of hydrochloric acid.

UV spectrum, nm: $\lambda_{max}^{C_2H_5OH}$ 291, 330 sh; +$AlCl_3$: Δλ + 16 nm; CH_3COONa; Δλ + 37. Its R_f values corresponded to those of isosakuranetin (5,7-dihydroxy-4'methoxyflavanone).

The PMR spectrum of the acetyl derivative of the glycoside in $CDCl_3$ (internal standard

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