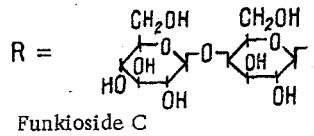
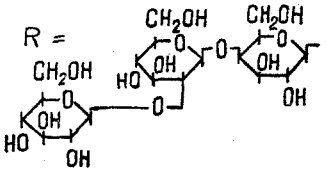
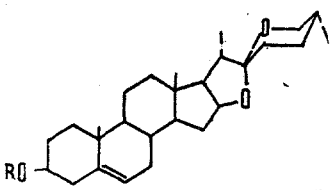


Funkioside C



Funkioside D



LITERATURE CITED

1. P. K. Kintya, N. E. Mashenko, N. I. Kononova, and G. V. Lazur'evskii, Khim. Prirodn. Soedin., 2, 267 (1976).
2. R. Kuhn and H. Trischmann, Chem. Ber., 96, 284 (1963).
3. W. Klyne, Biochem. J., 47, No. 4, xli (1950).

C-GLYCOSIDES FROM THE LEAVES OF *Crocus reticulatus*

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UDC 547.972

C-Glycosides have been isolated from the leaves of *Crocus reticulatus* Stev., family Iridaceae, collected in the flowering period in the environs of Pyatigorsk. The fresh comminuted leaves were steeped repeatedly with acetone at room temperature. The combined extract was concentrated and treated with benzene. This led to the deposition of a precipitate, which became larger on standing in the form of yellow clusters. These clusters were separated off and recrystallized from dilute ethanol. The product was a yellow crystalline substance (I), with mp 188-190°C, R_f 0.58 in BAW (4:1:5) (system 1); 0.60 in 15% acetic acid (system 2); and 0.43 in 2% acetic acid (system 3). The substance is soluble in methanol, ethanol, and water and insoluble in chloroform and ether. UV spectrum λ_{max}, nm: 348, 272, 250 (C_2H_5OH), 358, 335, 278 (CH_3COONa), 351, 273 ($CH_3COONa + H_3BO_3$), 360, 282, 264 ($AlCl_3$), 355, 280 ($AlCl_3 + HCl$), 393, 273 (C_2H_5ONa). On the basis of the characteristics of the UV spectrum of (I), the presence of free hydroxy groups at C_4', C_5, and C_7 and the absence of an ortho-diphenol grouping may be assumed. On partial hydrolysis of (I) with 3% hydrochloric acid for 2 h, substance (Ia) and L-rhamnose and D-glucose were obtained. The hydrolysis of (I) for a longer time or the use of more concentrated acids led to acid isomerization with the formation of two glycosides, (Ia) and (Ib). Substance (Ia) formed cream-colored crystals with mp 218-220°C, R_f 0.60, 0.32, 0.1 (in systems 1, 2, and 3, respectively). UV spectrum, λ_{max}, nm: 348, 272, 250 (C_2H_5OH), 362, 325, 280 (CH_3COONa), 348, 272 ($CH_3COOH + H_3BO_3$), 356, 280, 260 ($AlCl_3$), 352, 273, 260 ($AlCl_3 + HCl$), 390, 273 (C_2H_5ONa). Glycoside (Ia) was not hydrolyzed even with 30% H_2SO_4 in 6 h but underwent acid isomerization with the partial formation, probably, of a rotational isomer — the glycoside (Ib) [1]. Glycoside (Ib) was obtained from the hydrolyzate by preparative chromatography, R_f 0.32, 0.10, and 0.05 (in systems 1, 2, and 3, respectively); this glycoside has a UV spectrum close to that of the UV spectrum of (Ia). As in the case of the glycoside (I), in glycoside (Ia) and (Ib) there are free OH groups at C_4', C_5, and C_7. The Kiliani hydrolysis [2] of glycosides (Ia) and (Ib) for 10 h in the water bath gave the aglycone, D-glucose, and a small amount of L-arabinose. The aglycone was recrystallized from ethanol, mp 324-327°C.

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According to UV spectroscopy, the results of alkaline degradation, which led to phloroglucinaol and vanillic acid, and a mixed melting point with an authentic sample, the aglycone was identical with chrysoeriol. The behavior of the glycosides on acid hydrolysis, their IR spectra [3], and the fact that after hydrolysis no new hydroxy groups were liberated give grounds for assuming that the L-rhamnose and D-glucose are bound directly to the D-glucose forming a C-glycosidic bond, i.e., according to the results of our analysis compound (Ia) is probably chrysoeriol 8-C-β-D-glucopyranoside and (I) is a chrysoeriol 8-C-[(O-L-rhamnosyl-O-D-glucosyl)-β-D-glucopyranoside].

From the leaves of *C. reticulatus*, in addition to (I) after its recrystallization and removal from the mother solution by filtration, we isolated the glycoside (Ia). No less than seven O-glycosides were detected in the leaves among which we have shown the presence of kaempferol glycosides.

LITERATURE CITED

1. G. A. Drozd, Khim. Prirodn. Soedin., 443 (1972).
2. H. Kiliani, Ber., 63, 2866 (1930).
3. H. Wagner, in: Methods in Polyphenol Chemistry (ed. by J. B. Pridham), Vol. 2, Pergamon Press, Oxford (1964), p. 37.

GLYCOSYLATION OF CARDENOLIDES.

V. PERIPLOGENIN FUCOSIDE AND STROPHANTHIDOL DIRHAMNOSIDE

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Partial syntheses of periplogenin fucoside (I) and of strophanthidol dirhamnoside (II) has been performed by the orthoester method [1] in the same way as in previous work [2]. The syrupy glycosylating mixture, containing, according to its NMR spectrum, 50% of 3,4-di-O-acetyl-α-D-fucopyranose 1,2-O-(methyl orthoacetate) was obtained under the conditions described previously [3]. The condensation product formed in the reaction of this glycosylating mixture with periplogenin was saponified with a methanolic solution of ammonia and the resulting mixture of substances was chromatographed on a column of SiO_2. This gave with yield of 64.9% periplogenin β-D-fucoside (I), $C_{29}H_{44}O_9$, mp 169-175°C (from methanol); $[\alpha]_D^{24}$ +9.3 ± 3° [c 1.1; chloroform–ethanol (1:1)], $\lambda_{max}^{C_2H_5OH}$ 217 nm (log ε 4.21); ν_{max}^{KBr}, cm^{-1}: 3400-3550 (OH), 1780, 1745, 1633 (butenolid ring). NMR spectrum (C_5D_5N), ppm: 0.89 (3H at C_{18}, s); 0.93 (3H at C_{19}, s); 1.40 (3H at C_6', d, J = 7 Hz), 4.40 (H at C_3, m); 4.75 (H at C_1', d, J = 8 Hz — β-configuration of the glycosidic bond); 4.90, 5.20 (2H at C_{21}, q, centers of doublets, J = 18 Hz); 5.98 (H at C_{22}, s). Literature data [4]: mp 169-175°C; $[\alpha]_D^{23}$ +5.2 ± 1.5° (c 1.13; methanol).

3,4-Di-O-acetyl-β-L-rhamnopyranose 1,2-O-(methyl orthoacetate) was condensed with strophanthidol and the reaction products were saponified with a solution of ammonia in methanol. Subsequent chromatography on a column of SiO_2 gave a 35.8% yield of strophanthidol 3,19-di-α-L-rhamnoside (II), $C_{35}H_{54}O_{14}$, mp 200-201.5°C (from ethanol); $[\alpha]_D^{24}$ −29.5 ± 3° (c 0.87; methanol); $\lambda_{max}^{C_2H_5OH}$: 218 nm (log ε 4.20); ν_{max}^{KBr}, cm^{-1}: 3400-3500 (OH), 1780, 1740, 1630 (butenolide ring). NMR spectrum (C_5D_5N), ppm: 0.88 (3H at C_{18}, s); 1.54 (6H at C_6', and C_6'', m, [the single prime denotes the signals of the protons of the sugar residue at C_3 and the double prime that at C_{19}]; 4.87, 5.17 (2H at C_{21}, q, centers of doublets, J = 18 Hz); 5.12 (H at C_1'', br. s); 5.33 (H at C_1', br. s.); 6.00 (H at C_{22}, s). Literature data [5]: $[\alpha]_D^{19}$ −18 ± 2° (methanol).

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