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# STEROID GLYCOSIDES.

## XVIII. THE STRUCTURE OF FUNKIOSIDES C AND D FROM THE LEAVES OF *Funkia ovata (Hosta caerulea)*

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We have previously reported the isolation from *Funkia (Hosta)* of nine steroid glycosides and have described the structure of funkiosides A and B [1]. In the present paper we give information to show the structures of another two glycosides of this plant – funkiosides C and D.

The individual compounds – funkioside C with mp 258-262°C, $[\alpha]_D^{20}$ −78° (c 0.58; $CH_3OH$), and funkioside B with mp 188-202°C, $[\alpha]_D^{20}$ −60° (c 0.35; $CH_3OH$) – were obtained by repeated chromatography of the combined material on a column of $SiO_2$ in the chloroform–methanol–water (65:25:10) system. Each of the glycosides mentioned was hydrolyzed with 2.5% $H_2SO_4$ at 120°C for 15 h in sealed tubes in order to determine the monosaccharide composition. In the carbohydrate moiety of the first of them, glucose and galactose (1:1) were detected by gas–liquid and paper chromatography, and the same monosaccharides but in a ratio of 2:1 in the second compound. In both cases the aglycone was identified as diosgenin (from its melting point, specific rotation, chromatographic mobility in a thin layer, and IR spectrum).

The sequence of attachment of the carbohydrates was determined by partial hydrolysis (1% $H_2SO_4$, 100°C, 5 h), as a result of which diosgenin galactoside (mp 230-235°C, $[\alpha]_D$ −91° (c 1.1; $CH_3OH$) was obtained as a progenin of funkioside C, and for funkioside D hydrolyzed under the same conditions we detected, in addition to the galactoside, a galactoglucoside of diosgenin (mp 258-261°C, $[\alpha]_D$ −75° (c 0.58; $CH_3OH$).

Methylation by Kuhn's method [2] followed by methanolysis showed the position of the bonds of the monosaccharides in the carbohydrate chain. From funkioside C we obtained methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside and methyl 2,3,6-tri-O-methyl-D-galactopyranoside, and from funkioside D, in addition, methyl 3,4,6-tri-O-methyl-D-glucopyranoside.

When the funkiosides under study were subjected to periodate oxidation, not one of the monosaccharides remained unattacked, which also agrees with the results of methylation concerning the absence of branching in the carbohydrate chain and 1→3 bonds.

The configurations of the glycosidic centers were determined by means of Klyne's rule [3].

The facts given, and also the results of a study of the progenins obtained on partial hydrolysis have permitted the following structures to be assigned to funkiosides C and D:

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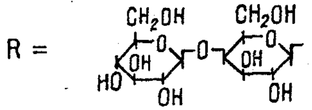
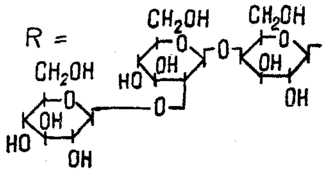
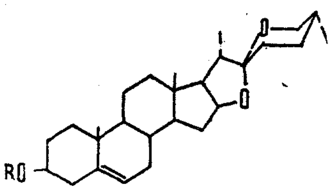


Funkioside C



Funkioside D



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## C-GLYCOSIDES FROM THE LEAVES OF *Crocus reticulatus*

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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 $\lambda_{max}$, 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, $\lambda_{max}$, 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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