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STEROID GLYCOSIDES OF *Solanum nigrum*

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The total steroid glycosides, amounting to 2%, have been obtained from the air-dry epigal parts of black nightshade *Solanum nigrum* L. (Solanaceae) growing in the Dusheti region of Georgia. Repeated chromatography on a column of silica gel KSK 50/90 with elution by the solvent system chloroform—methanol—water (65:35:8) yielded two individual glycosides: (1) with mp 215-218°C, $[\alpha]_D^{20}$ −95° (*c* 0.5; methanol), and (2) with mp 245-248°C, $[\alpha]_D^{20}$ −48° (*c* 0.3; pyridine). They gave positive reactions with the Sannié reagent [1] and negative reactions with the Ehrlich reagent [2]. Their IR spectra contained absorption bands in the 850-980 cm^{-1} region characteristic for a spiroketal grouping, which showed their spirostanol nature [3].

The acid hydrolysis of 0.1 g of glycoside (1) with 8% H_2SO_4 (20 ml at 100°C for 4 h) led to the isolation of an aglycon in the form of a white crystalline powder which, after recrystallization from methanol, melted at 204-207°C, $[\alpha]_D^{20}$ −120° (*c* 0.5; chloroform); ν_{max} (KBr): 3400, 3020, 2845, 960, 915, 895, 850 cm^{-1} (895 > 915). A mixture of the aglycon with an authentic sample of diosgenin gave no depression of the melting point. On the basis of these facts, the aglycon was identified as diosgenin [3, 4]. The acid hydrolysis of glycoside (2) under the same conditions yielded an aglycon which, after recrystallization from methanol, melted at 204-206°C; $[\alpha]_D^{20}$ −65° (*c* 1.0; chloroform). ν_{max} (KBr): 3300, 1050, 980, 965, 920, 895, 865 cm^{-1} (895 > 920). On the basis of these results the aglycon was identified as tigogenin [3, 4].

In the carbohydate moiety of glycoside (1), by TLC in the solvent system butanol—methanol—water (5:3:1) we identified *D*-glucose and *L*-rhamnose, and, for glycoside (2), *D*-xylose, *D*-glucose, and *D*-galactose. The hydrolysates were reduced with sodium tetrahydroborate at room temperature (12 h) and were then acetylated in 4 ml of a mixture of acetic anhydride and pyridine (1:1) at room temperature (12 h). By GLC in comparison with authentic samples, for glycoside (1) we identified rhamnitol and sorbitol acetates in a ratio of 1:1, and, for glycoside (2), *D*-sorbitol, dulcitol, and xylitol acetates in a ratio of 2:1:1.

From the amounts of the aglycons and the sugar moieties, and also from their physicochemical constants, glycosides (1) and (2) were characterized as uttronins B and A, respectively, from black nightshade growing in India [5, 6] and having the chemical structures of (25R)-spirosten-3β-ol 3-O-[O-β-*D*-glucopyranosyl-(1→4)-α-*L*-rhamnopyranoside] and (25R)-5α-spirostan-3β-ol3-O-{[(O-β-*D*-glucopyranosyl)-(1→2)]-[O-β-*D*-xylopyranosyl)-(1→3)]-O-β-*D*-glucopyranosyl-(1→4)-β-D-galactopyranside}.

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