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STEROIDAL SAPONINS FROM *Allium waldsteinii*

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In continuation of studies of steroidal glycosides from plants of the genus *Allium* L. (Alliaceae, Liliaceae) in the flora of Georgia, we investigated the aerial part of *A. waldsteinii* Don. collected during flowering near Kodzhori.

We established previously that the principal active substances from this species were steroidal compounds. We isolated from them and characterized the sapogenins diosgenin, β-chlorogenin, and agigenin [1] and five glycosides **1-5**. Then, we found other chemical groups and identified the flavonoids kaempferol and quercetin; coumarins umbelliferone and scopoletin; amino acids among which dominated valine, α- and β-alanine, phenylalanine; alkaloids; thioglycosides; and polysaccharides [2].

Herein we report the structures of relatively slightly polar steroidal glycosides **1** and **2**. They were isolated by repeated chromatography of total glycosides (35 g) over silica-gel columns using $CHCl_3$:CH_3OH:H_2O (65:15:2 and 65:22:4) and collection of fractions containing chromatographically homogeneous compounds **1** and **2**. Recrystallization afforded **1** (0.45 g) and **2** (0.28 g), which were 0.03 and 0.019%, respectively, calculated for the air-dried raw material mass.

Both compounds were identified as derivatives of (25*R*)-spirostane based on a positive color reaction with vanillinphosphoric acid [3] and absorption in the IR spectrum characteristic of a spiroketal group.

Glycoside **1**: $C_{33}H_{52}O_8$, mp 260-262°C, $[\alpha]_D^{18}$ -104° (*c* 0.5, MeOH). IR spectrum (ν, cm^{-1}): 3660-3400 (OH), 985, 921, 902, 870, 840, 812.

Glycoside **2**: $C_{39}H_{64}O_{14}$, mp 292-294°C, $[\alpha]_D^{22}$ -67° (*c* 0.8, MeOH). IR spectrum (ν, cm^{-1}): 3450-3260 (OH), 985, 969, 927, 904, 876.

Acid hydrolysis of **1** and **2** produced their aglycons that were identified using authentic samples of diosgenin [4] and β-chlorogenin, respectively [1, 5].

Methylation of both glycosides by the Hakomori method [6] and methanolysis produced only methyl-2,3,4,6-tetra-*O*-methyl-D-glucopyranoside in **1** and also methyl-2,3,6-tri-*O*-methyl-D-galactopyranoside in **2** according to GC analysis with authentic samples.

^{13}C NMR spectra of the glycosides were compared with those of their aglycons to locate the site of attachment of the sugar units on C-3 because it exhibited the greatest paramagnetic shift in both instances: +7.1 ppm for **1** and +6.6 ppm for **2**.

^{13}C NMR spectra without decoupling but with the NOE determined the heteronuclear SSCC for the anomeric C atoms of the sugars. The values were J = 159 Hz for galactose and J = 160 Hz for glucose. These values are consistent with the β-configuration of the anomeric centers [7].

The results led to the conclusion that **1** was trillin [8, 9]; **2**, dideglucoeruboside B [10].

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