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# STEROIDAL SAPOGENINS FROM *Allium rotundum*

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*Allium rotundum* L. (Alliaceae) is widely distributed in Georgia, is readily cultivated, and can provide an industrial base for preparing steroidal sapogenins, starting material for the synthesis of hormonal preparations.

We previously isolated and characterized from flowers of *A. rotundum* the sapogenins diosgenin, $\beta$-chlorogenin, yuccagenin, and agigenin [1]. The goal of the present communication was to study the genin composition of the upper 10-15 cm of the flower spikes. Plant material was collected near the town of Kojori.

Sapogenins were isolated by hydrolyzing saponins directly in the raw material [2]. Extracts were combined. Solvents were distilled to afford total sapogenins (7.5 g), which was 1.5% of the material (500 g).

TLC of total sapogenins on Silufol plates ($CHCl_3$:MeOH, 15:1) detected seven compounds that we designated in order of increasing polarity **1-7** ($R_f$ 0.95, 0.82, 0.63, 0.48, 0.38, 0.30, and 0.12, respectively). Then total sapogenins were chromatographed preparatively over an $Al_2O_3$ column with elution successively by benzene, benzene:MeOH (in various ratios), and MeOH. Crystals of genins were isolated from combined and condensed fractions containing pure compounds by filtration and recrystallization from MeOH, benzene, or acetone. The sapogenins produced this way were identified using chromatographic mobilities, physical constants, comparison of IR and NMR spectroscopy data with those of authentic samples, and literature data.

**Sapogenin 1**, $C_{27}H_{44}O_3$ (*m/z* 416 $[M]^+$), prismatic crystals (acetone), mp 202-204°C, $[\alpha]_D^{20}$ -68.5° (*c* 1.0, $CHCl_3$). IR spectrum (KBr, ν, $cm^{-1}$): 3300, 1212, 1158, 1036, 1025, 995, 961, 921, 900, 870 (intensity of 900 > 921, *R*-configuration of C-25). Acetate of **1**, mp 206-208°C, $[\alpha]_D^{20}$ -75° (*c* 1.0, $CHCl_3$). The chromatographic mobility, physical constants, and IR and NMR spectral data correspond with those of tigogenin, (25*R*)-5$\alpha$-spirostan-3$\beta$-ol [3, 4].

**Compound 2**, $C_{27}H_{42}O_3$ (*m/z* 414 $[M]^+$), white needlelike crystals (MeOH), mp 201-203°C, $[\alpha]_D^{20}$ -123° (*c* 1.0, $CHCl_3$). IR spectrum (KBr, ν, $cm^{-1}$): 3400-3500, 1665, 1050, 988, 930, 910, 871, 790 (910 > 930, 25*R*-configuration). Acetate of **2**, mp 196-198°C, $[\alpha]_D^{20}$ -119.0°. Comparison of the experimental physical constants and NMR spectroscopy data with those in the literature [4-6] allowed **2** to be assigned the structure (25*R*)-spirost-5-en-3$\beta$-ol or diosgenin.

**Sapogenin 3** had chromatographic mobility on TLC that coincided with that of authentic (25*R*)-5-spirostan-3$\beta$-ol-12-one or heckogenin. Judging from the nature of the spot, it was present in a very small amount. During further preparative chromatography, traces of it were lost. Because **3** could not be isolated pure, we could not unambiguously confirm that it was heckogenin due to a lack of information.

**Compound 4**, $C_{27}H_{44}O_4$ (*m/z* 432 $[M]^+$), white needlelike crystals (MeOH), mp 266-268°C, $[\alpha]_D^{20}$ -73° (*c* 0.8, $CHCl_3$). IR spectrum (KBr, ν, $cm^{-1}$): 3430, 1060, 1038, 968, 940, 916, 900, 866 (900 > 916, 25*R*-configuration of C-25). Acetylation by acetic anhydride in pyridine produced the acetate of **4**, mp 241-243°C, $[\alpha]_D^{20}$ -98° (*c* 1.0, $CHCl_3$). A mixed sample with authentic gitogenin gave one spot on TLC. The physical constants and a comparison of the experimental NMR spectra with those in the literature [3, 7] confirmed that **4** was (25*R*)-5$\alpha$-spirostan-2$\alpha$,3$\beta$-diol or gitogenin.

**Sapogenin 5**, $C_{27}H_{44}O_4$ (*m/z* 432 $[M]^+$), white needlelike crystals (benzene), mp 238-241°C, $[\alpha]_D^{20}$ -71.2° (*c* 1.32, $CHCl_3$). IR spectrum (KBr, ν, $cm^{-1}$): 3670-3420, 2940, 1454, 1060, 981, 920, 900, 875 (900 > 920, 25*R*-configuration of asymmetric C-25). Acetlation by acetic anhydride in pyridine produced the diacetate, mp 181-182°C, $[\alpha]_D^{20}$ -92.3° (*c* 1.80, $CHCl_3$). Comparison of the aforementioned constants and NMR data with those in the literature [8-10] indicated that **5** was (25*R*)-5$\alpha$-spirostan-3$\beta$,6$\beta$-diol or $\beta$-chlorogenin.

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**Compound 6**, $C_{27}H_{42}O_4$ (*m*/*z* 430 $[M]^+$), white needlelike crystals (MeOH), mp 242-244°C, $[\alpha]_D^{20}$ -119.0° (*c* 1.2, $CHCl_3$). IR spectrum (KBr, ν, $cm^{-1}$): 3420, 983, 925, 905, 870 (905 > 925, 25-*R*-spiroketal). Acetylation gave the diacetate, mp 176-178°C, $[\alpha]_D^{20}$ -138.6° (*c* 1.66, $CHCl_3$). A mixed sample with authentic yuccagenin did not depress the melting point and gave one spot on TLC. The physical constants and NMR spectral data of **6** were identical to those of (25*R*)-spirostan-5-en-2$\alpha$,3$\beta$-diol or yuccagenin [5, 11].

**Compound 7**, $C_{27}H_{44}O_5$ (*m*/*z* 448 $[M]^+$), white needlelike crystals (MeOH), mp 264-266°C, $[\alpha]_D^{20}$ -72.7° (*c* 1.33, $CHCl_3$). IR spectrum (KBr, ν, $cm^{-1}$): 3600-3500, 990, 930, 905, 870 (905 > 930, 25*R* spiroketal). Acetylation of **7** produced the triacetate, mp 197-201°C, $[\alpha]_D^{20}$ -111.4° (*c* 1.31, $CHCl_3$). The physicochemical properties and NMR spectral data identified it as (25*R*)-5-spirostan-2$\alpha$,3$\beta$,6$\beta$-triol or agigenin [12, 13].

Thus, in addition to the genins previously reported [1], tigogenin and gitogenin were isolated and traces of heckogenin were observed for the first time from tops of flower spikes of *A. rotundum*.

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