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STEROIDS OF THE SPIROSTAN AND FUROSTAN SERIES FROM PLANTS OF THE GENUS *Allium*.

XXVIII. ALLIOGENONE, ANZUROGENIN D, AND KARATAVIOSIDES A AND B FROM *Allium suvorovii* AND *A. stipitatum*

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Continuing a study of the collective fruit and the bulbs of *Allium suvorovii* Rgl. and *A. stipitatum* Rgl. (fam. Liliaceae) [1], we have isolated two genins (**1**) and (**2**) and also two glycosides A and B having close R_f values.

As a result of the chromatography and rechromatography of the nonpolar fractions of the total material (**2**) obtained in [1] on columns of silica gels KSK (particle size 40-100 μm) and L (63-100 μm) in the chloroform−methanol (20:1) and (10:1) systems, we isolated two genins ((**1**) and (**2**)). The characteristic color reaction with vanillin/phosphoric acid and the IR spectrum permited the genins to be assigned to derivatives of the (25R)-spirostan series.

Genin (1) (130 mg), $C_{27}H_{42}O_6$, mp 309-311°C (methanol), $[\alpha]_D^{23}$ $-94.6 \pm 2°$ (s 1.21; pyridine), M^+462. ν_{max}^{KBr} (cm^{-1}): 870, 910 > 925, 990 (spiroketal chain of the 25R series), (C=O), 3250-3500 (OH). ORD (s 0.71; ethanol): $[M]_{323} = -5090,°$ $[M]_{281} = +1560$, $a = -66°$. PMR spectrum (C_5D_5N, δ, ppm., WM-250 Bruker): 0.62 (d, $J_{27,25} = 7.0$ Hz, CH_3-27); 0.74 (s, CH_3-18); 0.89 (s, CH_3-19); 1.05 (d, $J_{21,20} = 7.0$ Hz, CH_3-21); 2.12 (1H, dd, $J_{1a,2a} = 12.0$ Hz, $J_{1a,2e} = 5.0$ Hz, H-1); 2.17 (1H, dd, H-7); 2.33 (1H, m, H-1); 2.42 (1H, dd, $J_{4a,4e} = 13.0$ Hz, $J_{4e,3a} = 5.0$ Hz, H-4); 2.64 (1H, dd, H-4); 3.05 (1H, t, H-7); 3.41 (1H, t, $J_{26a,26e} = 10.5$ Hz, H-26); 3.52 (1H, dd, $J_{26e,25a} = 3.5$ Hz, H-26); 4.22 (1H, m, H-2); 4.48 (1H, m, H-16); 4.62 (1H, m, H-3). For the ^{13}C NMR spectrum, see Table 1*.

On the basis of its spectral characteristics, genin (**1**) was identified as alliogenone − (25R)-2α,3β,5-trihydroxy-5α-spirostan-6-one. It must be mentioned that this is the first time that this compound has been isolated from a plant: alliogenone has been obtained previously by the oxidation of alliogenin with N-bromosuccinimide in aqueous dioxane [2].

Genin (2) (30 mg), $C_{27}H_{44}O_5$, mp 290-292°C (methanol), $[\alpha]_D^{20}$ $-86.4 \pm 2°$ (s 1.24; ethanol), M^+ 448. ν_{max}^{KBr} (cm^{-1}): 880, 905 > 925, 987 (spiroketal chain of the 25R series), 3300-3500 (OH). PMR spectrum (C_5D_5N, δ, ppm, WM-250 Bruker): 0.60 (d, $J_{27,25} = 7.0$ Hz, CH_3-27); 0.79 (s, CH_3-18); 1.05 (d, $J_{21,20} = 7.0$ Hz, CH_3-21); 1.48 (s, CH_3-19); 1.84 (1H, m, H-7); 2.34 (1H, t, $J_{4a,4e} = 13.5$ Hz; $J_{4e,3a} = 5.0$ Hz, H-4); 2.85 (1H, dd, H-4); 3.39 (1H, t, $J_{26a,26e} = 10.5$ Hz, H-26); 3.52 (1H, dd, $J_{26e,25a} = 3.5$ Hz, H-26); 4.09 (1H, t, $J_{6,7} = 6.0$ Hz, H-6); 4.45 (1H, td, $J_{16,15} = 6.0$ Hz, $J_{16,17} = 8.0$ Hz, H-16); 4.76 (1H, m, H-3). For the ^{13}C NMR spectrum, see Table 1*.

On the basis of the facts given, genin (**2**), which we have called anzurogenin D, was identified as (25R)-5α-spirostan-3β,5,6β-triol, synthesizd previously from diosgenin [3].

By column chromatography of the polar fractions of the total material (**2**) obtained in [1] on silica gel KSK (particle size 10-100 μm) in the chloroform−methanol−water (65:22:4) system we obtained a purified mixture of two glycosides, A and B, having close R_f values. These compounds were separated by high-performance liquid chromatography in stainless-steel columns filled with the silica gels Silpearl (Czechoslovakia, particle size 10-30 μm) and L (20-30 μm). As eluents we used the systems chloroform−methanol−water (65:15:2) and (65:22:4).

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*The table has been omitted from the original — Translator.

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Glycoside A (200 mg), $C_{50}H_{80}O_{23}$, mp 285-287°C, decomp. (methanol), $[\alpha]_D^{20}$ $-75.1 \pm 2°$ (s 1.11; $CHCl_3-CH_3OH$. ν_{max}^{KBr} (cm^{-1}): 870, 905 > 925, 990 (spiroketal chain of the 25R series), 3300-3500 (OH). PMR spectrum (C_5D_5N, δ, ppm, JNM-4H-100): 0.60 (d, $J_{27,25}$ = 6.0 Hz, CH_3-21); 4.71 (1H, m, H-16); 5.10 (4H, m, anomeric protons of sugars); 5.39 (1H, m, H-6).

Glycoside B, $C_{56}H_{88}O_{27}$, mp 223-225°C, decomp, (methanol), $[\alpha]_D^{20}$ $-71.3 \pm 2°$ (s 1.08; DMSO). ν_{max}^{KBr} (cm^{-1}): 875, 905 > 920, 990 (spiroketal chain of the 25R series), 1740 (C=O), 3350-3500 (OH). PMR spectrum (C_5D_5N, δ, ppm, JNM-4H-100): 0.58 (d, $J_{27,25}$ = 6.0 Hz, CH_3-27); 0.67 (s, CH_3-18); 0.81 (s, CH_3-19); 1.00 (d, $J_{21,20}$ = 6.0 Hz, CH_3-21); 1.45 (s, CH_3 of the acyl moiety); 2.72 (br.m., 2 × CH_2 of the acyl moiety); 4.73 (1H, m, H-16); 5.14 (4H, anomeric protons of sugars); 5.40 (1H, m, H-6).

Methanolysis, followed by the gas-liquid chromatographic analysis of the sugars showed that both glycosides contained residues of D-glucose, D-xylose, and D-galactose in a ratio of 2:1:1. The aglycon was yuccagenin, $C_{27}H_{42}O_4$, mp 244-246°C (methanol), $[\alpha]_D^{22}$ $-124.3°C \pm 2°C$ (*c* 1.12; chloroform), M^+ 430. The aglycon obtained was identical with an authentic specimen of yuccagenin in terms of R_f values and IR, mass, and PMR spectra.

All the results reported above, and also the chromatographic mobilities of glycosides A and B (thin-layer chromatography) and the absence of a depresssion of the melting point of mixtures with authentic samples, showed the identity of the compounds under investigation as karataviosides A and B, respectively. Karataviosides A and B were first isolated from the inflorescences of *Allium karataviense* Rgl. [4, 5].

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