CH_3), 30%; 396 (M − H_2O), 37.2%; 385 (M − C_2H_5), 17.2%; 381 (M − CH_3 − H_2O), 26.2%; 367 (M − C_2H_5 − H_2O), 14.8%; 329, 23.7%; 303, 28.2%; 273 (M − side chain), 24.0%; 255 (273 − H_2O), 26.2%; 231 (273 − C_3H_6), 24.0%; 213 (273 − C_3H_6 − H_2O), 37.2%.

SUMMARY

It has been shown that the unsaponifiable fraction of the oil of *Erysimum cuspidatum* contains β-sitosterol and campesterol, and the oil of *Erysimum diffusum* contains β-sitosterol.

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STEROID SAPONINS AND SAPOGENINS OF *Allium*

XI. NEOALLIOGENIN FROM *Allium turcomanicum*

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Continuing a study of the steroid spirostans of *Allium turcomanicum* Rgl. [1], we have investigated a methanolic extract of the skins of the bulbs of this plant.

From the total extractive substances we isolated the known spirostans neoagigenin (I) [2] and alliogenin [3], and new steroid sapogenin (VI) with the composition $C_{27}H_{44}O_6$.

The IR spectrum of the spirostan (VI) has the absorption of hydroxy groups (3300-3500 cm^{-1}), and also bands characteristic for sapogenins with the 25S configuration − 925 cm^{-1} (strong), 900 cm^{-1} (weak), and 855 cm^{-1} [4, 5]. The peak of the molecular ion with m/e 464 and the absence from the IR spectrum of absorption in the region of carbonyl groups and double bonds shows that the genin (VI) is a tetrahydroxysapogenin.

By acetylating the spirostan (VI) we obtained the triacetate (VII), in the PMR spectrum of which resonance lines of the C-26 protons at 3.22 and 3.88 ppm confirm, by their positions and multiplicities, the assignment of the genins under consideration (VI) and (VII) to the 25S series [6].

The good agreement of the values of the chemical shifts of C-18 (0.72 ppm) and C-19 (1.18 ppm) of the methyl groups in the PMR spectrum of the acetate (VII) with the indices for the angular methyls in the spectrum of alliogenin triacetate (C-18, 0.74; C-19, 1.19 ppm) [3] permit the assumption that the genin (VI) is the 25S isomer of alliogenin.

To prove the structure suggested we synthesized (VI), which we have called neoalliogenin, from lilagenin (V). The lilagenin was obtained in the following way. From the mixture of the products of the selective acetylation of neoagigenin (I) we isolated, separately, the 2,3,6-triacetate (III) and the 2,3-diacetate (II) of neoagigenin. The acetate (II) was subjected to dehydration with phosphorus oxychloride in pyridine [7]. This gave the spirostan diacetate (IV), the constants of which corresponded to those of lilagenin diacetate [8, 9]. The saponification of (IV) with a 1% methanolic solution of caustic potash led to lilagenin (V) [8. 9].

It is known [10, 11] that the hydroxylation of steroids containing a 5(6)-double bond with hydrogen peroxide in the presence of formic acid leads to 5α,6β-dihydroxy derivatives. Lilagenin (V) was oxidized under similar conditions, giving a 2α,3β,5α,6β-tetrahydroxyspirostan identical in its melting point, specific rotation, and IR spectrum with the native neoalliogenin. Acetylation of the tetraol synthesized gave a triacetate (VII) identical in its physicochemical constants and spectral characteristics with neoalliogenin triacetate.

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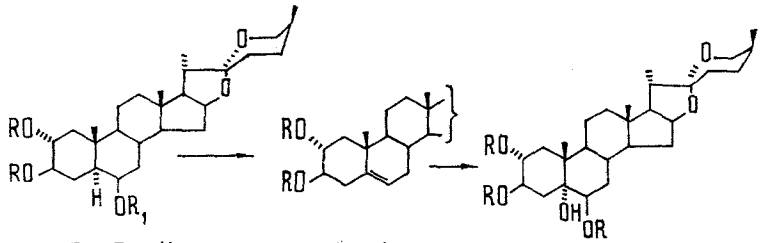

I R = R₁ = H
II R = Ac, R₁ = H
III R = R₁ = Ac

IV R = Ac
V R = H

VI R = H
VII R = Ac

Thus, neoalliogenin (VI) is (25S)-5α-spirostan-2α,3β,5α,6β-tetraol.

EXPERIMENTAL

For general remarks, see [3].

Isolation of the Total Sapogenins. The air-dry skins of the bulbs of *Allium turcomanicum* Rgl. collected in the budding phenophase in May, 1976 (Turkmen SSR, environs of the village of Babadurmex, Kopet Dagh range) (600 g) were extracted with methanol. The combined extractive substances (42 g) obtained after the solvent had been distilled off were chromatographed on a column of SiO_2. Washing the column with the solvent mixture chloroform–methanol–water (65:35:8) gave the total sapogenins (20 g), which were reseparated on a column of SiO_2. On elution with chloroform–methanol (7:1) the following fractions were isolated: 1 — 2.4 g; 2 — 80 mg; 3 — 100 mg; 4 — 120 mg; and 5 — 300 mg.

Neoagigenin (I) and Alliogenin. The recrystallization of fraction 1 from methol yielded 2.1 g of the genin (I) with mp 266-269°C, $[\alpha]_D^{24}$ — 72.5 ±3° [c 1.12; chloroform–methanol (10:1)], identical with neoagigenin [2]. The yield from the air-dry raw material was 0.33%.

Fraction 2 yielded 60 mg of a compound with mp 320-322°C (methanol), $[\alpha]_D^{20}$ — 67.5 ±3° (c 0.92; pyridine), identical with alliogenin [3].

Fractions 3 and 4 consisted of mixtures of alliogenin and neoalliogenin.

Neoalliogenin (VI). The recrystallization of fraction 5 from methanol yielded compound (VI), $C_{27}H_{44}O_6$, mp 315-317°C, $[\alpha]_D^{23}$ — 61.9 ±2° (c 0.92; pyridine); ν_{max}^{KBr}, 3300-3500 (OH), 990, 925 > 900, 855 cm^{-1} (spiroketal chain of the 25S series). Mass spectrum m/e (%): M^+ 464 (2.6), 405 (1.4), 395 (2.1), 392 (5.2), 350 (2.2), 335 (2.1), 332 (8.8), 321 (6.1), 139 (100), 115 (11.5). The total yield of alliogenin and neoalliogenin calculated on the weight of the air-dry raw material was 0.1%.

Neoalliogenin Triacetate (VII) from (VI). A solution of 100 mg of neoalliogenin (VI) in a mixture of 50 ml of pyridine and 5 ml of acetic anhydride was kept for two days and was then diluted with water and extracted with chloroform. The chloroform extract yielded 72 mg of the acetate (VII), $C_{33}H_{50}O_9$, mp 234-236°C (methanol), $[\alpha]_D^{20}$ — 93.06 ±2° (c 1.01; chloroform); ν_{max}^{KBr}, cm^{-1}: 3400-3500 (OH), 1720 (C=O of an acetyl group), 990, 925 > 900, 855 (spiroketal chain of the 25S series); PMR spectrum ($CDCl_3$, HMDS, δ, ppm): 0.72 (3 H at C-18, s), 0.92 (3 H and C-27, d, j = 6 Hz), 1.01 (3 H at C-21, d, j = 7 Hz), 1.18 (3 H at C-19, s), 1.97, 2.04 (3 Ac at C-2, C-3, and C-6, s), 3.22 (H at C-26, doublet with broadened components, J_{gem} = 11 Hz, $J_{vic} \approx$ 3 Hz), 3.88 (H at C-26, doublet with broadened components, J_{gem} = 11 Hz, $J_{vic} \approx$ 4 Hz), 4.35 (H at C-16, m), 4.77 (H at C-6; $W_{1/2}$ = 5 Hz), and 5.15 (2 H at C-2 and C-3, m); M^+ 590.

Neoagigenin 2,3,6-Tri-O-acetate (III) and 2,3-Di-O-acetate (II). A solution of 0.5 g of neoagigenin in 50 ml of pyridine was treated with 0.5 ml of acetic anhydride, and the reaction mixture was left at room temperature for 48 h, after which another 0.2 ml of acetic anhydride was added. After 24 h, the reaction products were poured into water and extracted with chloroform. The chloroform extract was separated on a column of SiO_2 with elution bh banzene–menthanol (100:1). This gave 50 mg of neoagigenin triacetate (III) [2], $C_{33}H_{50}O_8$, mp 145-146°C (from methanol), $[\alpha]_D^{25}$ — 122.7 ±3° (c 1.45; chloroform). (In the literature [2], $[\alpha]_D$ for neoagiogenin 2,3-diacetate has been given erroneously as —177.3° instead of —117.3°).

The subsequent saponification of the same mixture gave 300 mg of neoagigenin diacetate (II), $C_{31}H_{48}O_7$, mp 279-282°C (methanol), $[\alpha]_D^{22}$ − 99.5° (c 1.06; chloroform; ν_{max}^{KBr}, cm^{-1}: 3540 (OH), 1720 (>C=O of an acetyl group), 990, 925 > 900, 855 (spiroketal chain of the 25S series); PMR spectrum ($CDCl_3$, HMDS, δ, ppm): 0.74 (3 H at C-18, s), 0.94 (3 H at C-27, d, J = 7 Hz), 1.02 (3 H at C-21, d, J = 7 Hz, 1.10 (3 H at C-19, s), 1.96, 1.98 (2 Ac at C-2 and C-3, s), 3.24 (H at C-26, doublet with broadened components, J_{gem} = 10 Hz, J_{vic} ≈ 3 Hz), 3.82 (H at C-6; m, $W_{1/2}$ < 7 Hz), 3.86 (H at C-26, doublet with broadened components, J_{gem} = 11 Hz, J_{vic} ≈ 4 Hz), 4.36 (H at C-16, m), and 4.90 (2 H at C-2 and C-3, m); M^+ 532.

Lilagenin (V) from (II). A solution of 260 mg of the diacetate (II) in 3 ml of pyridine was treated with 1 ml of $POCl_3$. The reaction mixture was left at room temperature for 5 h. Then it was diluted with chloroform, poured into ice water, and extracted with chloroform. Recrystallization from methanol of the dry residue from the chloroform extract yielded 210 mg of lilagenin diacetate (IV) with mp 153-156°C, $[\alpha]_D^{22}$ − 130.8 ±2° (c 0.81; chloroform); M^+ 514. Literature information for (IV): mp 155°C [8, 9].

A mixture of 200 mg of the diacetate (IV) and 25 ml of 1% KOH solution was left at room temperature for 4 h. Then the reaction products were poured into water and extracted with chloroform. Recrystallization of the dry residue from methanol yielded 170 mg of lilagenin (V) with mp 243-245°C, $[\alpha]_D^{22}$ − 110.7 (c 0.92; chloroform); M^+ 430. Literature information for lilagenin: mp 246°C [8, 9].

Neoalliogenin (VI) from (V). A solution of 150 mg of lilagenin (V) in a mixture of 2.5 ml of tetrahydrofuran and 1.5 ml of 80% formic acid was heated in the boiling water bath for 15 min. After the reaction mixture had been cooled to 40°C, 1 ml of 30% H_2O_2 in 2 ml of tetrahydrofuran was added. The mixture was left at room temperature for 24 h, and it was then diluted with water and the precipitate that deposited was filtered off. This precipitate was boiled with 0.15 g of caustic potash in 4 ml of methanol and 0.2 ml of water for 15 min. The reaction mixture was diluted with water and the methanol was distilled off. The precipitate that deposited was filtered off and recrystallized from methanol, giving 80 mg of compound (VI), $C_{27}H_{44}O_6$, with mp 316-318°C, $[\alpha]_D^{23}$ − 63.7 ±3° (c 0.69; pyridine). The R_f value and IR spectrum of the spirostan compound synthesized coincided completely with the analogous indices for natural neoalliogenin.

The acetylation of 70 mg of synthetic neoalliogenin (VI) in 2 ml of acetic anhydride and 20 ml of pyridine for 24 h gave 50 mg of the triacetate (VII) with mp 235-237°C (methanol), $[\alpha]_D^{23}$ − 100.6 ±2° (c 1.12; chloroform). The spectral characteristics (IR, mass, and NMR) of the compound described proved to be identical with those of the triacetate (VII) obtained from natural neoalliogenin.

SUMMARY

In addition to the known spirostans neoagigenin and alliogenin, we have isolated from the skins of the bulbs of *Allium turcomanicum* Rgl. a new steroid sapogenin — neoalliogenin, which is (25S)-5α-spirostan-2α,3β,5α,6β-tetraol.

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