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STEROID SAPONINS AND SAPOGENINS OF Allium

X. NEOAGIGENIN 6-O-BENZOATE FROM Allium turcomanicum

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Continuing a systematic study of the steroid spirostans of plants of the genus Allium [1], we have investigated A. turcomanicum Rgl. The present paper gives information on the steroid sapogenins of the epigeal part of this plant.

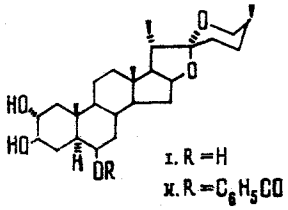
From the total sapogenins obtained by the hydrolysis of the extractive compounds we isolated the known genins yuccagenin, neoagigenin, alliogenin, and 2α,3α-dihydroxy-(25S)-5α-spirostan-6-one. This is the first time that the last-mentioned compound, which we have called neoagigenone, has been isolated from plants. It has been obtained previously by the selective oxidation of neoagigenin [2].

From the same combined product we obtained a new steroid sapogenin (II) with the composition $C_{34}H_{48}O_6$. Judging from the ratio of the intensities of the absorptions bands in the IR spectrum at 930 cm^{-1} (strong) and 900 cm^{-1} (weak), the genin (II) must be assigned to the steroid spirostans of the 25S series [3, 4]. The existence of ester absorption at 1720 and 1280 cm^{-1} and of frequencies relating to a benzene ring (1600, 1585, and 718 cm^{-1}) permit the assumption that the molecule of the sapogenin (II) contains an ester grouping of aromatic character.

The nature of this grouping is shown by the mass spectrum of compound (II) in which, together with ions characteristic for spirostan sapogenins there are strong peaks of ions with m/e 122 ($C_7H_6O_2$) and 105 (C_7H_5O) characteristic of benzoic acid.

When the sapogenin (II) was subjected to alkaline saponification, the neutral fraction was found to contain neoagigenin (I), and benzoic acid was identified by TLC in the acid fraction of the hydrolyzate.

The facts given show that the spirostan (II) is a neoagigenin benzoate. The NMR spectrum of the sapogenin (II) has a one-proton signal with $W_{1/2}$ = 6 Hz at δ 5.16 belonging to an equatorial proton geminal to a benzoate group, and therefore the benzoic acid must have esterified the hydroxyl at C-6.



I. R = H
II. R = C_6H_5CO

The proposed structure is confirmed by the preparation of the spirostan (II) from neoagigenin (I). For this purpose, neoagigenin was converted by benzoylation into the tribenzoate which, without being isolated in the pure form, was subjected to selective saponification. The neoagigenin 6-O-benzoate isolated from the reaction products was identical in melting point, specific rotation, and spectral properties, with the sapogenin (II) isolated from the plant raw material.

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EXPERIMENTAL

For general observations, see [5].

Isolation of the Combined Sapogenins. The air-dry epigeal part of A. turcomanicum collected in the budding phenophase in May, 1973 (Turkmen SSR, environs of the village of Babadurmez, Kopet-Dagh range) (2.5 kg) was extracted with methanol. The residue of combined extractive substances after the evaporation of the solvent (170 g) was dissolved in 500 ml of 50% aqueous methanol, containing 5% of hydrochloric acid, and the solution was boiled on the water bath for 7 h. The hydrolyzate was diluted with twice its amount of water and the methanol was distilled off as completely as possible. The precipitate that deposited was filtered off and extracted with chloroform on a Soxhlet apparatus. After the elimination of the chloroform, the residue was chromatographed on a column of Al_2O_3 and elution was performed with chloroform–methanol (20:1). The purified combined genins (4 g) were rechromatographed on a column of SiO_2. When the column was washed with benzene–methanol (80:1) the following fractions were obtained: 1, 230 mg; 2, 45 mg; 3, 80 mg.

Neoagigenin 6-O-Benzoate (II). Recrystallization of fraction 1 from ether–hexane yielded 200 mg of compound (II), $C_{34}H_{48}O_6$, mp 138-140°C, $[\alpha]_D^{20}$ −63.7° (c 1.57; chloroform). ν_{max}^{KBr}, cm^{-1}: 3400-3500 (OH); 1720, 1280 (ester grouping); 1600, 1585, 718 (benzene ring); 900, 930 > 900, 860 (spiroketal chain of the 25S series). NMR spectrum ($CDCl_3$, HMDS, δ, ppm): 0.72 (3H at C-18, s, 0.93 (3H at C-27, d, J = 6 Hz), 1.00 (3H at C-21, d, J = 7 Hz), 1.11 (3H at C-19, s), 3.30 (3H at C-2, C-3, and C-26, m), 3.86 (H at C-26, doublet with broadened components, J_{gem} = 11 Hz, J_{vic} = 3 Hz), 4.27 (H at C-16, m), 5.16 (H at C-6, $W_{1/2}$ = 6 Hz); the aromatic protons (5H) resonate in the form of two multiplets at δ 7.35 and 7.93 ppm. Mass spectrum, m/e (%): M^+ 552(14.5), 493(2.8), 483(3.2), 480(10.8), 438(1.6), 430(1.0), 423(1.5), 409(3.9), 361(6.6), 343(3.2), 325(2.3), 316(47.6), 301(2.1), 298(4.4), 287(6.8), 280(2.2), 139(100), 122(7.12), 115(23.8), 105(35.7).

Yuccagenin. The recrystallization of fraction 2 from methanol gave 30 mg of a sapogenin with mp 238-242°C, $[\alpha]_D^{20}$ −96.5° (c 0.92; chloroform), which was identified as yuccagenin [6, 7].

Neoagigenone. The recrystallization of fraction 3 from methanol gave 50 mg of a sapogenin $C_{27}H_{42}O_5$ with mp 236-238°C, $[\alpha]_D^{23}$ −97.5° (c 0.64; chloroform) was identified from the results of IR, mass, and NMR spectroscopy as 2α,3α-dihydroxy-(25S)-5α-spirostan-6-one [2].

Neoagigenin and Alliogenin. When the silica gel column was eluted with mixtures of benzene and methanol (50:1 and 30:1), fractions 4 and 5 (720 mg and 55 mg, respectively) were obtained.

The recrystallization of fraction 4 from methanol yielded 700 mg of a compound with mp 266-269°C, $[\alpha]_D^{23}$ −71.7° [c 0.92; chloroform–methanol (10:1)], which was identical with neoagigenin [2].

Fraction 5 yielded 20 mg of a sapogenin with mp 320-322°C (from methanol) $[\alpha]_D^{20}$ −65.2° (c 0.92; pyridine) which was identical with alliogenin [5].

Hydrolysis of Neoagigenin 6-O-Benzoate(I) from (II). A mixture of 100 mg of the genin (II) and 100 ml of 2% methanolic KOH solution was heated at 100°C for 3 h. Then the reaction mixture was poured into water and extracted with chloroform. The chloroform extract yielded 20 mg of compound (I), M^+ 448, which was identical in melting point (263-265°C, from methanol), chromatographic mobility on TLC [SiO_2/gypsum; chloroform–methanol (15:1)], and IR spectrum with neoagigenin (I).

After acidification with hydrochloric acid, the residual aqueous solution was extracted with chloroform. The chloroform extract was shown by chromatography to contain benzoic acid [TLC; SiO_2; ethanol–ammonia–water (10:1.4:1.2)].

Neoagigenin 6-O-Benzoate (II) from Neoagigenin (I). A solution of 150 mg of neoagigenin in 20 ml of pyridine was treated with 2 ml of benzoyl chloride and the mixture was left at room temperature for 24 h, after which it was diluted with water and extracted with chloroform. After the solvent had been driven off, the tribenzoate was obtained in the form of a viscous oily product which, without purification, was dissolved in 1% methanolic KOH and the solution was kept at 0°C for 4 h. The reaction products were poured into water and extracted with chloroform. The solvent was distilled off and the residue was recrystallized from ether–hexane to give 40 mg of the sapogenin (II), M^+ 552, mp 135-138°C, $[\alpha]_D^{20}$ −61.3° (c 1.10; chloroform). The R_f value and the features of the IR spectrum of the benzoate synthesized also coincided with the corresponding indices for the neoagigenin 6-O-benzoate isolated from the plant material.

SUMMARY

From the epigeal parts of Allium turcomanicum Rgl., in addition to the known spirostans yuccagenin, neoagigenin, neoagigenone, neoagigenin, and alliogenin, we have isolated a new steriod sapogenin the structure of which has been established as neoagigenin 6-O-benzoate.

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NEOCONVALLATOXOLOSIDE – A CARDENOLIDE GLYCOSIDE FROM Convallaria majalis

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The isolation from the seeds of Convallarium majalis L. (lily of the valley) collected in the Khar'kov oblast of polar glycosides – lokundjoside, convalloside, and convallatoxoloside – has been reported previously [1]. On investigating the leaves of this plant, Ya. Bochvarov isolated three polar cardenolides [2] which were provisionally denoted as substances (I), (II_1), and (II_2).

The present paper gives a proof of the structure of the glycoside (II_1), which we have called neoconvallatoxoloside (I).

The glycoside isolated was not reduced by sodium tetrahydroborate. Its UV spectrum showed only one maximum, in the 220 nm region (log ε 4.18), which is characteristic for the butenolide ring of a cardenolide; the optical rotatory dispersion (ORD) spectrum had the form of a smooth curve: 600 nm (−8°), 589 nm (−11°), 520 nm (−12°), 440 nm (−12°), 306 nm (−10°), 300 nm (+40°), and 294 nm (+120°). These facts show the absence of a carbonyl group in the steroid skeleton of the substance under investigation. On acid hydrolysis according to Mannich and Siewert [3], neoconvallatoxoloside (I) was cleaved into D-glucose (V), L-rhamnose (IV), and a number of products of aglycone nature, two (II and III) of which present in predominating amount.

To isolate these substances, the aglycone fraction of the hydrolyzate was separated by partition chromatography on silica gel using chloroform as the mobile phase and formamide as the stationary phase. As a result, strophanthidol (II) and a substance similar in its physicochemical properties to 5(6)-anhydrostrophanthidol (pachygenol) [4] was isolated in the crystalline state. To confirm its structure we obtained 5(6)-anhydrostrophanthidin (IX) from strophanthidin (VII) and reduced it with sodium tetrahydroborate to 5(6)-anhydrostrophanthidol (III).

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