STEROID COMPOUNDS OF *Erysimum*

XI. STEROLS OF *Erysimum diffusum* AND *E. cuspidatum*

R. U. Umarova, V. A. Maslennikova, and N. K. Abubakirov

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Hitherto we have studied various species of *Erysimum* mainly for their content of cardenolide glycosides. Assuming that the steroid compounds of plants are biogenetically interrelated, we have studied the sterols of the unsaponifiable fraction of the seed oils of *E. diffusum* Ehrh. and *E. cuspidatum* (M.B.) DC.

The seed oils of the plants studied were extracted with petroleum ether. The unsaponifiable fractions, obtained by the usual method [1], contained a number of other compounds besides sterols. The sterols were precipitated from the mixture in the form of the digitonin complexes. The complexes were decomposed by means of dimethyl sulfoxide as described by Isidorides et al. [2].

The total amount of sterols in the oils of *E. cuspidatum* was 0.88%, and in *E. diffusum* 0.11%. On the basis of mass-spectrometric results [3, 4], the sterol from *E. diffusum* was identified as β-sitosterol. *E. cuspidatum* was found to contain a mixture of sterols consisting of β-sitosterol (67.7%) and campesterol (32.3%).

EXPERIMENTAL

The seeds of the *Erysimum* species investigated were defatted with petroleum ether until there was no more oil in the extracts. The yield of oil was 33% of *E. cuspidatum* and 28% for *E. diffusum*.

The oil of *E. cuspidatum* (10 g) was boiled with a 2 N ethanolic solution of caustic potash for 1 h. After cooling, 50 ml of water was added to the solution, and the ethanol was evaporated off in vacuum. The residue was extracted with diethyl ether (8 × 15 ml). The combined ethereal extracts, after being washed with water, drying, and evaporation yielded 0.10 g of unsaponifiable fraction. This was dissolved in 50 ml of ethanol, and 45 ml of 1% solution of digitonin in 80% ethanol was added. For completeness of precipitation, the reaction mixture was left at +5°C for 24 h. Then the precipitate was filtered off (filter with a No. 2 porous plate) and was washed with 80% ethanol, hot water, acetone, and chloroform. The yield of digitonin complex was 0.38 g.

A mixture consisting of the sterol digitonides and 5 ml of dimethyl sulfoxide was heated on the boiling-water bath for 15 min. Then the reaction mixture, together with the precipitate that had formed, was extracted with hexane (6 × 15 ml). The hexane solution was dried with sodium sulfate, filtered, and evaporated to dryness. The residue was dried to constant weight at 100°C and was recrystallized from hot methanol. The mixture of sterols obtained was chromatographed preparatively on a plate coated with silica gel in the hexane—ether (5:2) system. This gave 0.082 g of a mixture of sterols with mp 130°C.

The mass spectrometry of the mixture showed the presence of fragments of β-sitosterol: M^+ 414, 100%; m/e 399 (M − CH_3), 29.5%; 396 (M − H_2O), 36.3%; 385 (M − C_2H_5), 13.6%; 381 (M − CH_3 − H_2O), 22.7%; 367 (M − C_2H_5 − H_2O), 11.3%; 329, 29.5%; 303, 43.1%; 273 (M − side chain), 29.5%; 255 (273 − H_2O), 34.0%; 231 (273 − C_3H_6), 22.7%; 213 (273 − C_3H_6 − H_2O), 22.7% and of campesterol: M^+ 400, 100%; m/e 385 (M − CH_3), 28.5%; 382 (M − H_2O), 42.8%; 367 (M − CH_3 − H_2O), 23.8%; 315 − 33.3%; 289, 47.6%; 273 (M − side chain), 61.9%; 255 (273 − H_2O), 71.4%; 231 (273 − C_3H_6), 47.6%; 213 (273 − C_3H_6 − H_2O), 47.6%.

Evaporation of the dimethyl sulfoxide layer to dryness yielded 0.21 g of digitonin.

The unsaponifiable fraction of the oil of the seeds of *E. diffusum* was analyzed similarly. The mass spectrum contained fragments of β-sitosterol alone: M^+ 414, 100%; m/e 399 (M −

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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*

G. V. Pirtskhalava, M. B. Gorovits, and N. K. Abubakirov

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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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