Reduction of the Aglycon (VI) with $LiAlH_4$ Followed by Acetylation. The aglycon (VI) (4 mg) was reduced by the procedure described above. This gave 1 mg of derivative (VII), amorphous, $[\alpha]_D^{20}$ +20°C (c 0.04; chloroform).

CONCLUSIONS

From psolusodide B — a minor glycoside of *Psolus fabricii* — the genin onekotanogenin has been obtained. Its structure has been determined as 20(S)-acetoxy-3β,16-dihydroxylanost-7-en-18-oic acid 18,16-acetone . It has been shown that the native aglycon of psolusoside B is 20(S)-acetoxy-3β-16-dihydroxylanosta-3,25-dien-18-oic acid 18-16-lactone.

Aglycon (VI) from *Cucumaria fraudatrix* was made available to us by Sh. Sh. Afiyatullov.

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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*

XII. 5α-ECDYSTERONE 22-O-BENZOATE FROM *Silene scabrifolia*

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The new phytoecdysteroid 5α-ecdysterone 22-O-benzoate (I), $C_{34}H_{48}O_8$, mp 262-274°C (methanol—water) $[\alpha]_D^{20}$+45.8° (methanol), has been isolated from the epigeal organ of *Silene scarbiofolia* Kom. The alkaline hydrolysis of (I) led to 5α-ecdysterone (II) and benzoic acid. The isomerization of ecdysterone (0.6% $KHCO_3$ in CH_3OH) has yielded (II). Details of the IR, mass, and NMR spectra of compound (I) are given.

We have previously detected 2-deoxy-α-ecdysterone (I), ecdysterone (II), ecdysterone 22-O-benzoate (III) [1], and 2-deoxy-α-ecdysone 3-acetate (IV) in the plant *Silene scabrifolia* Kom. (family Caryophyllaceae) [2]. By rechromatographing the mother solution obtained on the isolation of ecdysterone 22-O-benzoate (III) on a column of silica gel we have isolated a new phytoecdysteroid (VI) with the composition $C_{34}H_{48}O_8$.

Bands in the IR spectrum at 1710, 1720, and 1280 cm^{-1}, in combination with the absorption characteristic of a benzene ring (1610, 1580, 725 cm^{-1}), and also strong peaks of ions with m/z 122 ($C_7H_6O_2$), 105 (C_7H_5O) and 77 (C_6H_5) in the mass spectrum indicated that the ecdysteroid (VI) contained a benzoic acid residue. The signals of five aromatic protons at 7.40 ppm (3 H) and 8.26 ppm (2 H) in the PMR spectrum showed the presence of a single benzoate group.

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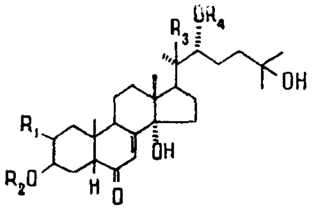

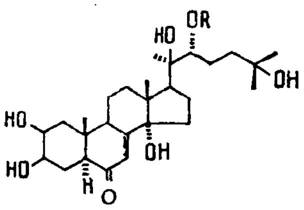

I. $R_1=R_2=R_3=R_4=H$
II. $R_1=R_3=OH$; $R_2=R_4=H$
III. $R_1=R_3=OH$; $R_2=H$; $R_4=C_6H_5CO$
IV. $R_1=R_3=R_4=H$; $R_2=Ac$

V. $R=H$
VI. $R=C_6H_5CO$

It can be seen from Table 1 that the 20-O-benozate group causes a downfield shift in the signal of the 21-methyl group by 0.23 ppm (δ_{III} = 1.78 ppm, δ_{II} = 1.55 ppm, $\Delta\delta$ = 0.23 ppm). The signals of the protons of the 21-methyl group in the PMR spectrum of compound (VI) were shifted downfield in comparison with those of ecdysterone by 0.24 ppm, appearing at 1.79 pm. This fact, together with the results of a comparison of the chemical shifts of the protons of the side chain of ecdysteroid (VI) with the analogous indices of ecdysterone 22-O-benzoate (III), permitted the conclusion that compound (VI) had the side chain of ecdysterone and that the benzoic acid residue was attached to the hydroxy group at C-22. It follows from a further comparison of the PMR spectra of substances (III) and (VI) that all the indices agreed well with the exception of the values of the chemical shifts of the resonance lines of the 19-methyl groups. In compound (VI), the 19-methyl group resonated at 1.44 ppm, while in the benzoate (III) it did so at 1.10 ppm. The observed paramagnetic shift by 0.34 ppm can be explained by the trans-linkage of rings A/b in compound (VI). It is known that the signal of the 19-methyl group in 5α-ecdysterone is shifted downfield [3] (see Table 1).

We subjected benzoate (VI) to alkaline saponification and in the neutral fraction we found an ecdysteroid identified as 5α-ecdysterone (V). Authentic 5α-ecdysterone was obtained by the alkaline isomerization of ecdysterone [3].

Thus, compound (VI) was 5α-ecdysterone 22-O-benzoate.

EXPERIMENTAL

PMR spectra were taken on JNM-4H-100/100 MHz (JEOL) and BS-567A (100 MHz, Tesla) spectrometers in C_5D_5N (δ, 0 — TMS). For other information, see [1].

5α-Ecdysterone 22-O-Benzoate (VI). The mother solutions obtained on the isolation and recrystallization of ecdysterone 22-O-benzoate (III) were combined and chromatographed on a column of silica gel. Elution was performed with the chloroform–ethanol (9:1) system. This led to the isolation of 15 mg of the ecdysteroid (VI), $C_{34}H_{48}O_8$, mp 262-264°C (from a mixture of methanol and water), $[\alpha]_D^{20}$ +45.8 ± 2°, ν_{max}^{KBr}, cm^{-1}: 3420-3470 (OH), 1660 (Δ^7-6-keto groupings); 1720, 1710, 1280 (ester); 1610, 1580, 723 (benzene ring).

TABLE 1. Chemical Shifts of the Protons of Compounds (II), (III), (V) and (VI)*

Compound	Positions of the protons								Aromatic protons
	H-2,3	H-7	H-9	H-22	CH_3-18	CH_3-19	CH_3-21	CH_3-26/27	
II	4,0—4,3	6,21	3,57	3,84	1,19	1,06	1,55	1,34	—
III	4,0—4,3	6.22	3,60	5,76	1,21	1,10	1,78	1,32	7,40 (3H) 8,27 (2H)
V	4,36; 3,9	6,22	3,62	3.9	1.22	1,43	1,60	1,40	—
V (according to the literature [3, 4])	—	—	—	—	1,21	1,41	1.59	1,39	—
VI	4,37; 3,89	6,21	3,60	5.77	1,21	1,44	1.79	1,34	7,40 (3H) 8,26 (2H)

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*The signals of the protons of the methyl groups had a singlet nature; in the spectrum compound (V), H-7 appeared in the form of a doublet with ^4J = 2 Hz, while in the other cases it formed a broadened singlet; the H-2, H-3, H-9, and H-22 signals were multiplets.

Mass spectrum, m/z (%): 566 (M–H_2O; 0.1), 548(0.2), 530(0.3), 515(0.2), 512(0.2), 462 (0.7), 444 (1), 426(6), 411(2), 408(6), 393(2), 363(2), 345(6), 329(2), 327(2), 301(8), 300 (9), 250(7), 122(44), 105(100), 99(22), 81(23), 77(50), 69(24), 55(24), 51(20).

Alkaline Hydrolysis of 5α-Ecdysterone 22-O-Benzoate (VI). To 5 mg of the ecdysteroid (VI) in 5 ml of methanol was added 3 ml of a 1% aqueous solution of potassium bicarbonate. The reaction mixture was left in an atmosphere of nitrogen at 40°C for 5 days and was then diluted with water, neutralized, and extracted with ethyl acetate. The solvent was distilled off to dryness, and the residue was recrystallized from methanol to give 1.5 mg of the ecdysteroid (V) with mp 276-278°C, identified from its IR spectrum and R_f value in TLC (ethyl acetate–ethanol (9:1) system) with an authentic sample of 5α-ecdysterone (for preparation, see below).

Benzoic acid was isolated from the aqueous solution after acidification with dilute hydrochloric acid (1:1) and extraction with ethyl adetate.

Isomerization of Ecdysterone (II) into 5α-Ecdysterone (V). A solution of 225 mg of ecdysterone (II) in 25 ml of 90% methanol containing 0.6% of potassium bicarbonate was boiled in an atmosphere of nitrogen for 30 min. After cooling, the reaction products were neutralized with acetic acid, the methanol was evaporated off to half-volume, water was added, and the mixture was extracted with butanol. The butanolic extract was distilled off to dryness and the residue was chromatographed on a column of alumina. Elution with the chloroform–methanol (9:1) system yielded 20 mg of 5α-ecdysterone (V), $C_{27}H_{44}O_7$, mp 276-278°C (methanol), $[\alpha]_D^{20}$ +54.6 ± 2° (c 0.34; methanol). Literature figures for substance (V) [3]: mp 278°C $[\alpha]_D$ +55.5°. When the washing of the column was continued with the same solvent system, the initial ecdysterone was isolated.

CONCLUSIONS

The new ecdysteroid 5α-ecdysterone 22-O-benzoate has been isolated from the epigeal organs of the plant *Silene scabrifolio* Kom.

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PHYTOECDYSTEROIDS OF *Rhaponticum carthamoides*

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From the roots with rhizomes of the plant *Rhaponticum carthamoides* Willd) Iljin Compositae), in addition to integristerone A, ecdysterone, polypodin B, 2-deoxyecdysterone, and 24(28)-dehydromakisterone A, we have isolated the new compounds ecdysteron3-2,3-monoacetonide (I), ecdysterone 20,22-monoacetonide (II)) and rhapisterone (III): I – $C_{30}H_{48}O_7$, mp 232-233° (ethyl acetate–methanol) $[\alpha]_D^{20}$ +56.4 ± 2° (c 0.9; methanol); II – $C_{30}H_{48}O_7$, mp 227-229° (ethyl acetate–methanol), $[\alpha]_D^{20}$ +60.1 ± 2° (c 1.3; methanol); III – $C_{29}H_{48}O_7$, mp, 241-242° (ethyl acetate–methanol), $[\alpha]_D^{20}$ +30 ± 2° (c 0.1; dioxane). The structure of (III) was established on the basis of spectral characteristics as 2β,3β,14α,20R,22R,23ξ-5β-stigmast-7-en-6-one. Details of the PMR, mass, and IR spectra of all the compounds and of the CD of rhapisterone are given.

Even in our first publications on plant ecdysone-like compounds we showed that *Rhaponticum carthamoides* (Willd) Iljin is a rich source of a universal arthropod molting hormone–

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