EXPERIMENTAL

The IR spectra of the substances were measured on a UR-20 instrument, PMR spectra on a Varian HA-100D instrument in $CDCl_3$ and CF_3COOH, and mass spectra on a Varian instrument.

Reaction of Oleanolic Acid with Trifluoroacetic Acid (TFA). A solution of 0.5 g of oleanolic acid (I) in 10 ml of TFA was left at room temperature for two days. Then the reaction mixture was poured into 100 ml of water and the resulting precipitate was filtered off, washed with water to neutrality, and dried at 60°C for 6 h.

The mixture of reaction products (0.525 g) was chromatographed on a column (diameter 2 cm) of 40/100 μm silica gel (10.0 g). Elution was performed with chloroform, 3-ml fractions being collected. Fractions 4 and 5 contained traces of an oily product consisting of two substances with M^+ 508 and 506. Fractions 7 and 8 yielded compound (III) — $C_{32}H_{47}F_3O_4$, mp 300-303°C (from ethanol), M^+ 552.

From fractions 17, 18, and 19 was isolated compound (II) — $C_{32}H_{47}F_3O_4$, mp 235-248°C (from aqueous ethanol), M^+ 552.

SUMMARY

Under the action of trifluoroacetic acid, oleanolic acid forms a γ-lactone at the COOH group and C-13 and also 3-trifluoroacetoxyolean-13(18)-en-28-oic acid, which indicates an unambiguous route of the stabilization of the intermediate carbocation with the charge at C-13. The hydroxy group at C-3 is esterified by the trifluoroacetic acid.

LITERATURE CITED

1. C. H. Brieskorn and L. Capuano, Chem. Ber., 86, 866 (1963).
2. C. H. Brieskorn and H. Herrig, Arch. Pharmaz., 292, 485 (1959).
3. É. T. Oganesyan, Khim. Prir. Soedin., 647 (1980).
4. A. A. Savina, Yu. E. Sklyar, V. I. Sheichenko, I. A. Kir'yanova, and D. A. Fesenko, Khim. Prir. Soedin., 630 (1979).
5. H. Budzikiewicz, J. M. Wilson, and C. Djerassi, J. Am. Chem. Soc., 85, 3688 (1963).

PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*

X. SILENEOSIDE E — 2-DEOXY-α-ECDYSONE 3-O-β-D-GLUCOPYRANOSIDE — FROM *Silene brahuica*

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A new ecdysteroid has been isolated from the epigeal organs of *Silene brahuica* Boiss. — 2-deoxy-α-ecdysone 3-O-β-D-glucopyranoside (I), $C_{33}H_{54}O_{10}$, mp 195-196°C, $[\alpha]_D^{20}$ + 44.4° (methanol). The enzymatic hydrolysis of (I) led to 2-deoxy-α-ecdysone. Details of the IR, UV, mass, and ^1H and ^{13}C NMR spectra of all the compounds are given.

We are continuing a study of the ecdysteroids of plants of the genus *Silene* (family Caryophyllaceae) [1, 2]. From the epigeal organs of the plant *S. brahuica* Boiss. collected in the valley of the R. Chomkemin (Kungei-Alatau range, northern Tien-Shan), in addition to the known 2-deoxy-α-ecdysone (I), 2-deoxyecdysterone (II), and ecdysterone (III), we have isolated a new ecdysteroid — sileneoside E (IV).

Compound (IV) proved to be a glycoside and, according to GLC [3] contained one D-glucose residue. In the products of the enzymatic hydrolysis of sileneoside E performed with the gastric juice of the snail *Helix plectotropis* 2-deoxy-α-ecdysone (I) was detected as the aglycon.

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TABLE 1. Chemical Shifts of the Protons of 2-Deoxy-α-ecdysone (I) and of Sileneoside E (IV) (δ, ppm, 0 is TMS)

Compound	Positions of the protons								
	H-3	H-7	H-9	H-22	H-1′	CH_3-18	CH_3-19	CH_3-21	CH_3-26/27
I	4,14 br.m $W_{1/2} \approxeq 10$ Hz	6,22 br.d $J \simeq 2$ Hz	3,52 m	4,08 br.d $^3J \simeq 9,2$ Hz	—	0,75 s	1,07 s	1,31, d. $^3J = 6,6$ Hz	1,40, s
IV	3,86 br.m $W_{1/2} \simeq 10$ Hz	6 19 br.d $J \simeq 2$ Hz	3,48 m	~4,1*	4,90 d $^3J = 7,5$ Hz	0,72 s	0,88 s	1,29, d. $^3J = 6,5$ Hz	1,40 s

*Overlapped by the signals of the carbohydrate residue. Symbols: s) singlet; d) doublet; br.d) broadened doublet; br.m) broadened multiplet.

It can be seen from a comparison of the chemical shifts of the protons in the PMR spectra of 2-deoxy-α-ecdysone (I) and of sileneoside E (IV) (Table 1) that the values of the signals differ to the greatest extent for the H-3 atom ($\Delta\delta = -0.28$ ppm) and the CH_3-19 group ($\Delta\delta = -0.19$ ppm). This leads to the assumption that the D-glucose residue is attached to the hydroxy group at C-3.

It can be seen from Table 2, which contains the results of a comparative study of the ^{13}C NMR spectra of 2-deoxy-α-ecdysone (I) and sileneoside E (IV), that in the spectra of those compounds the values of the chemical shifts of the carbinol atoms of the side chain, C-22 and C-25, are mutually identical, while the C-3 signal has undergone a paramagnetic shift by +14.4 ppm in the case of glycoside (IV). This fact also indicates that the D-glucose residue is substituted in the hydroxy group at C-3.

The values of the chemical shifts of the carbon atoms of the carbohydrate residue of (IV) (Table 2) are typical for the pyranose ring of D-glucose [4, 5].

The anomeric proton of sileneoside E resonates at 4.90 ppm in the form of a doublet with J = 7.5 Hz (Table 1) and the corresponding C-1' carbon atom at 103.3 ppm (Table 2). In combination, these facts show the β configuration of the glycosidic center.

Consequently, sileneoside E (IV) is 2-deoxy-α-ecdysone 3-O-β-D-glucopyranoside.

It must be mentioned that the plant *Silene brahuica* from different growth sites not infrequently differs in the qualitative composition of its ecdysteroids. Previously, from the epigeal part of this plant collected in the Tashkent province, we isolated ecdysterone, viticosterone E, polypodin B, and integristerone A [1]. Ecdysteroid glycosides — sileneosides A, B, C, and D — were detected only in the roots [1].

EXPERIMENTAL

As the systems for eluting columns we used mixtures of chloroform and methanol in ratios of 1) (15:1), 2) (9:1), and 3) (4:1), and chloroform—ethanol—water (65:35:1).

PMR spectra were taken on a Varian SC-300 instrument (C_5D_5N, 0 is TMS) and ^{13}C NMR spectra on a Varian CFT-20 instrument (C_5D_5N, 0 is TMS). For other information, see [7].

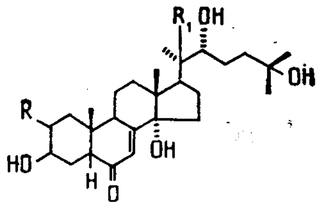
Isolation of the Phytoecdysteroids. The raw material was the epigeal part of the plant *Silene brahuica* Boiss. collected in May, 1982, in the valley of the R. Chonkemin in the environs of the village of Novorossiika, KirgSSR. The dried and comminuted plant (10 kg) was exhaustively extracted with ethanol (80 liters). The extract was concentrated, the residue was diluted with water, and the resulting precipitate was separated off. The ethanol was evaporated and the aqueous residue was extracted first with petroleum ether and then with butanol. The black resinous mass obtained after the butanol had been distilled off was chromatographed on a column of silica gel. Elution with system 1 gave 15 g (0.15%) (here and below the yields given are calculated on the air-dry raw material) of 2-deoxy-α-ecdysone (I), mp 235-236°C (from aqueous ethanol, $[\alpha]_D^{20}$ +93.3 ± 3° (c 1.5; methanol) [8].

By eluting the column with system 2 we isolated 3 g (0.03%) of 2-deoxyecdysterone (II), mp 254-255°C (from aqueous ethanol), $[\alpha]_D^{20}$ +82.0 ± 3° (c 1.3; methanol) [8].

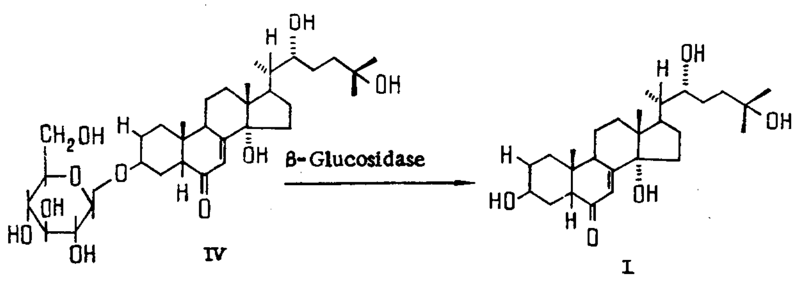
TABLE 2. Values of the Chemical Shifts of the ^{13}C Signals (δ, ppm, C_5D_5N, TMS) of 2-Deoxy-α-ecdysone (I) and of Sileneoside E (IV)

C Atom	I	IV	C Atom	I	IV
1	29,3 (a)	29,5 (a)	18	15,8	15.8
2	28,7 (a)	27,5	19	24,1	24,0
3	64,2	78,6	20	42,7	43.0
4	32,7	29,6 (a)	21	13,4	13,6
5	51,3	51,5	22	74,0	74,0
6	203,8	203,9	23	25,2 (b)	25,6 (b)
7	121,1	121,3	24	42.0	42,5
8	166,4	165,9	25	70,0	69,7
9	34,4	34,5	26	29,9 (c)	30,2 (c)
10	36,8	36,7	27	29,6 (c)	30,0 (c)
11	21,4	21,5	1′	—	103,3
12	31,5	31,7	2′	—	75,2
13	47,9	48,1	3′	—	78,6 (d)
14	84,1	84,0	4′	—	71,8
15	31,5	31,7	5′	—	78,2 (d)
16	26,5 (b)	26,7 (b)	6′	—	62,9
17	48,1	48,3			

Note. The assignment of the signals was made from the results of a comparative study of the ^{13}C NMR spectra taken under conditions of complete and partial suppression of spin-spin coupling with protons and of an analysis of the values of the chemical shifts of the carbon atoms in the light of the characteristics of α-ecdysone, ecdysterone [2]. The chemical shifts of the signals the assignments of which may be interchanged within a column are shown by identical pairs of letters in parentheses.



I. R = R₁ = H
II. R = H; R₁ = OH
III. R = R₁ = OH



Continuing the elution of the column with the same system, we obtained 5 g (0.05%) of ecdysterone (III), mp 241-242°C (from acetone), $[\alpha]_D^{20}$ +60.7 ± 2° (c 1.02; methanol).

The use of systems 3 and 4 led to fractions containing a mixture of ecdysterone (III) and sileneoside E (IV). The rechromatography of the eluates using system 4 gave 250 mg (0.0025%) of sileneoside E (IV), $C_{33}H_{54}O_{10}$, mp 195-196°C (from acetone), $[\alpha]_D^{20}$ +44.4 ± 2°

(c 0.80; methanol). $\lambda_{max}^{C_2H_5O}$ 245 nm (log ε 4.0). ν_{max}^{KBr} (cm^{-1}): 3380-3430 (OH); 1655 (Δ^7-6-keto grouping, CD (c 0.12; ethanol); Δε = −1.28 (253 nm); Δε = +1.35 (330 nm).

Mass spectrum, m/z (%): 446 (M^+ − 164; 0.2), 430 (1), 412 (5), 403 (1.5), 398 (2), 395 (2), 379 (2), 361 (4), 343 (3), 332 (4), 314 (4), 311 (4), 299 (7), 285 (8), 284 (15), 264 (7), 251 (8), 234 (6), 233 (6), 185 (7), 149 (100), 135 (11), 129 (1), 99 (15), 81 (27), 69 (30).

Enzymatic Hydrolysis of Sileneoside E (IV). A solution of 20 mg of sileneoside E (IV) in 2 ml of water was treated with 2 ml of the complex enzyme of the snail *Helix plectotropis* and the mixture was left at 36°C for six days. Then another 10 ml of water was added to it and it was extracted with ethyl acetate. After evaporation of the solvent and recrystallization of the residue from aqueous methanol, 12 mg of 2-deoxy-α-ecdysone (I) was obtained with mp 235-236°C (from aqueous ethanol), $[\alpha]_D^{20}$ + 93.3 ± 3° (c 1.5; methanol), identical with an authentic sample with respect both to its R_f value in TLC (system 1) and its IR spectrum.

SUMMARY

A new ecdysteroid, sileneoside E, has been isolated from the epigeal part of *Silene brahuica* Boiss. and has been shown to be 2-deoxy-α-ecdysone 3-O-β-D-glucopyranoside.

LITERATURE CITED

1. Z. Saatov, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov Khim. Prir. Soedin., 741 (1984).
2. Z. Saatov, M. B. Gorovits, N. D. Abdullaev, B. Z. Usmanov, and N. K. Abubakirov, Khim. Prir. Soedin., 60 (1985).
3. T. T. Gorovits, Khim. Prir. Soedin., 263 (1970).
4. R. C. Beier and B. P. Mundy, Canad. J. Chem., 58, 2800 (1980).
5. A. S. Shamkov and O. S. Chizhov, Biorg. Khim., 2, 437 (1976).
6. H. Hikino, T. Okuyama, C. Komno, and T. Takemoto, Chem. Pharm. Bull., 23, 125 (1975).
7. Z. Saatov, M. B. Gorovits, N. D. Abdullaev, B. Z. Usmanov, and N. K. Abubakirov, Khim. Prir. Soedin., 738 (1981).
8. Z. Saatov, B. Z. Usmanov, and N. K. Abubakirov, Khim. Prir. Soedin., 793 (1979).

WITHASTEROIDS OF *PHYSALIS*

VI. ^{1}H AND ^{13}C NMR SPECTRA OF WITHASTEROIDS IXOCARPALACTONE A AND IXOCARPANOLIDE

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The ^{1}H and ^{13}C NMR spectra of two withasteroids isolated from *Physalis ixocarpa* Brot. have been studied in detail. Their spectral characteristics are discussed. A comparison of the results obtained has led to the identification of a withasteroid with the composition $C_{28}H_{40}O_8$, mp 291-292°C (from methanol) as ixocarpalactone A, in spite of some difference in its physical constants. The other compound, with mp 252-253°C (from methanol), had the composition $C_{28}H_{40}O_6$, $[\alpha]_D^{20}$ +27 ± 4°, is new and has been called ixocarpanolide. The structure of 5α,20R-dihydroxy-1-oxo-6α,7α-epoxy-22R-witha-2-enolide has been proposed for it.

It is known that the qualitative and quantitative presence of withasteroids changes according to the chemotype of the plant. This has been shown, in particular, for the case of *Withania somnifera* [1]. *Physalis ixocarpa* Brot. (tomatillo ground-cherry) has been studied by two groups of workers. Physalin B was isolated from a *Physalis* growing in India [2], and ixocarpalactones A and B from a plant growing in Israel [3]. We were interested in what

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