6. I. Kitagawa, T. Sugawara, I. Yosioka, and K. Kuriyama, Tetrahedron Lett., 963 (1975).
7. W. L. Tan, C. Djerassi, J. Fayos, and J. Clardy, J. Org. Chem., 40, 466 (1975).
8. J. P. Kutney, N. D. Westcott, F. H. Allen, N. W. Isaacs, O. Kennard, and W. D. S. Motherwell, Tetrahedron Lett., 3463 (1971).
9. A. I. Kalinovskii, V. F. Sharypov, Sh. Sh. Afiyatullov, T. A. Kuznetsova, V. A. Stonik, and G. B. Elyakov, Bioorg. Khim., 9, 1558 (1983).
10. D. Lavie, B. S. Benjamino, and Y. Shvo, Tetrahedron, 20, 2585 (1964).
11. C. A. C. Haasnoot, H. P. M. de Leeuw, F. A. M. de Leeuw, and C. Altona, Org. Magn. Reson., 15, 43 (1981).
12. S. G. Il'in, V. F. Sharypov, V. A. Stonik, G. V. Malinovskaya, N. I. Uvarova, G. B. Elyakov, M. Yu. Antinov, and Yu. T. Struchkov, in: IIIrd All-Union Conference on Organic Crystal Chemistry. Abstracts of Lectures [in Russian], Gor'kii, (1981), p. 145.

PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*.

VIII. 2-DEOXYECDYSTERONE 3-ACETATE FROM *Silene praemixta*

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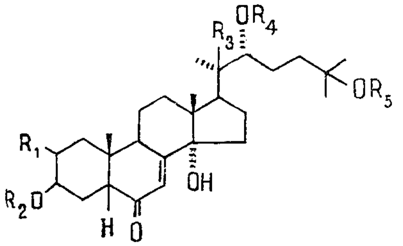
A phytoecdysteroid, 2-deoxyecdysterone 3-acetate, has been isolated from the epigeal organs of *Silene praemixta* M. pop.

We have previously detected in the plant *Silene praemixta* M. Pop (family Caryophyllaceae) ecdysterone, 2-deoxy-α-ecdysone, 2-deoxyecdysterone, silenosterone, and premixisterone [1].

Rechromatography on a column of silica gel of the mother liquors obtained in the isolation of the substances mentioned led to the isolation of viticosterone E (IV) [2, 3], α-ecdysone (V) [4, 5], and a new phytoecdysteroid (II) with the composition $C_{29}H_{46}O_7$. In the IR spectrum of compound (II), in addition to the absorption due to hydroxy groups (3450 cm^{-1}) and an α,β-unsaturated keto grouping (1655 cm^{-1}), there were absorption bands at 1740 and 1255 cm^{-1} showing the presence of an ester residue. This was also indicated by the presence of a three-proton singlet at 2.00 ppm in the PMR spectrum of the ecdysteroid (II).



I. $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$
II. $R_1 = R_4 = R_5 = H$; $R_3 = OH$; $R_2 = Ac$
III. $R_1 = R_5 = H$; $R_3 = OH$, $R_2 = R_4 = Ac$
IV. $R_2 = R_4 = H$; $R_1 = R_3 = OH$, $R_5 = Ac$
V. $R_2 = R_3 = R_4 = R_5 = H$; $R_1 = OH$

A peak with m/z 389 (cleavage of the C-20—C-22 bond) and its derivatives with m/z 371, 329, and 311 permitted the assumption that compound (II) belonged to the 2-deoxyecdysteroid group and had an acetyl residue in the steroid nucleus [6].

The characteristics of the PMR spectra of the ecdysteroid (II) and of 2-deoxyecdysterone (I) were close, with the exception of the chemical shifts of the resonance lines of the protons at C-3 and C-19. In the PMR spectra of compounds (II) and (I) (the corresponding values are given in parentheses), signals at 5.03 (4.14) ppm and 1.02 (1.07) ppm corresponded to

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TABLE 1. Chemical Shifts of the ^{13}C NMR Signals (ppm, δ scale, TMS) of 2-Deoxyecdysterone (I) and of 2-Deoxyecdysterone 3-Acetate (II)

C atom	I	II	Δδ*	C atom	I	II	C atom	I	II
1	28 8	29,5	+0,7	11	21,4	21,5	21	21.4	21.5
2	29,3	25,6	−3,7	12	31,3	31,5	22	77,5	77 5
3	64,1	68,3	+4,2	13	48.4	48,5	23	27,2	27.4
4	32,9	29,7	−3,2	14	84,5	84,3	24	42,2	42.6
5	51,5	52,1	+0,6	15	32,1	32,2	25	69,8	69,5
6	203,5	201,8	−1,7	16	21,4	21,5	26	29,8	30,0
7	121,3	121 2		17	50,0	50,1	27	29,8	30,0
8	166,4	166,5		18	17,7	17,8	OC=O	—	170,0
9	34,2	34,2		19	24,2	24,1	CH_3	—	21,1
10	36,8	36,6		20	76,9	76,8			

* $\Delta\delta = \delta_I - \delta_{II}$.

these protons. Consequently, the signal of the C-3 proton had undergone a downfield shift by 0.89 ppm. This could take place under the influence an acetyl group located on the same carbon atom.

We also investigated the ^{13}C NMR spectra of 2-deoxyecdysterone (I) and the ecdysteroid (II).

It can be seen from Table 1 that the values of the chemical shifts of the carbon atoms of compounds (I) and (II) are identical, with the exception of the C-1—C-6 group of atoms.

On passing from compound (I) to (II), the signal of the C-3 carbon atom undergoes a paramagnetic shift by +4.2 ppm, while the resonance lines of the C-2, C-4, and C-6 atoms shift upfield by −3.7, −3.2, and −1.7 ppm, respectively. The chemical shifts of the C-1 and C-5 carbon atoms, experiencing the γ-influence of the substituent at C-3, also change. These facts are in harmony with the assumption expressed above that the acetyl group in ecdysteroid (II) is located at C-3 [7-9].

For confirmation, we subjected 2-deoxyecdysterone (I) to selective acetylation with acetic anhydride in pyridine. From the reaction mixture we isolated the known 2-deoxyecdysterone 3,22-diacetate (III) [1] and a substance identified as compound (II).

Thus, ecdysteroid (II) is 2-deoxyecdysterone 3-acetate.

EXPERIMENTAL

PMR spectra were obtained on a spectrometer with a working frequency of 300 MHz in C_5D_5N (δ, 0 — TMS) and ^{13}C NMR spectra on a SFT-20 instrument (Varian) in C_5D_5N (0 — TMS). The assignment of the signals of the carbon atoms was made by a comparative study of the spectra recorded under the conditions of complete and partial decoupling from protons, and on the basis of literature information for ecdysterone [7, 8]. For further details, see [1].

Isolation of the Ecdysteroids. The mother liquors obtained in the isolation and recrystallization of the ecdysteroids obtained previously that were isolated from 6 kg of *Silene praemixta* [1] were combined and chromatographed on a column of silica gel. Elution was performed with the chloroform—methanol (25:1) system, which gave 120 mg of 2-deoxyecdysterone 3-acetate (II) (0.002% on the weight of the air-dry raw material).

The subsequent washing of the column with the chloroform—ethanol (15:1) system yielded 100 mg (0.0017%) of viticosterone E (IV), $C_{29}H_{46}O_8$, mp 194-196°C (from acetone), $[\alpha]_D^{20} + 58.6 \pm 2°$ (*c* 0, 52 ; methanol).

The use of chloroform—methanol (9:1) for the elution of the column led to 1.5 g (0.025%) of the ecdysteroid (V), $C_{27}H_{44}O_6$, mp 236-238°C (methanol—water), $[\alpha]_D^{20} + 63.6 \pm 2°$ (*c* 0.83 ; methanol), identified as α-ecdysone [5].

2-Deoxyecdysterone 3-acetate (II), $C_{29}H_{46}O_7$, mp 150-152°C (methanol—benzene), $[\alpha]_D^{20} + 72.1 \pm 2°$ (*c* 0.70; methanol), $\lambda_{max}^{C_2H_5OH}$: 246 nm (log ε 4.01); ν_{max}^{KBr}, cm^{-1}: 3450 (OH), 1655 (Δ^7-6-keto grouping), 1740, 1255 (ester group); CD (c 0.10; methanol); Δε = −1.93 (253 nm); Δε = +1.43 (327 nm).

Mass spectrum, m/z (%): 470 $(M-2H_2O)^+$ (1), 455(8), 389(100), 372(96), 371(96), 357(23), 355(22), 329(98), 328(85), 327(24), 300(95), 143(96), 125(96), 99(97), 81(96), 69(96).

PMR spectrum, (δ, ppm); 1.02 (3 H at C-19, s); 1.23 (3 H at C-18, s); 1.39 (6 H at C-26 and C-27, s); 1.62 (3 H at C-21, s); 2.00 (3 H, $OCOCH_3$, s); 3.46 (1 H at C-9, m, $W_1/_2 \simeq 23$ Hz); 3.91 (1 H at C-22, doublet with broadened components, $^3J = 9.2$ and ~1 Hz); 5.03 (1 H at C-3, m, $W_1/_2 \simeq 8$ Hz); 6.23 (1 H at C-7, d, $^4J = 2.4$ Hz).

Acetylation of 2-Deoxyecdysterone (I). At room temperature, 200 mg of the ecdysteroid (I) in 10 ml of pyridine was acetylated with 0.1 ml of acetic anhydride for 2 days. The reaction mixture was diluted with water and was extracted first with chloroform and then with ethyl acetate. The chloroform extract was evaporated to dryness and the residue was chromatographed on a column of silica gel. Elution with chloroform–methanol (15:1) yielded 10 mg of 2-deoxyecdysterone 3,22-diacetate (III), $C_{31}H_{48}O_8$, mp 185–186°C (from methanol), $[\alpha]_D^{20} + 79.3 \pm 2°$ (c 0.50 ; methanol), identified by comparison with an authentic sample [1].

Continuing the washing of the column with the same mixture of solvent led to the isolation of 15 mg of a compound with mp 149–152°C (methanol–benzene), $[\alpha]_D^{20} +70.6 \pm 2°$ (c 0,60; methanol), which was identified by direct comparison on TLC and by spectral characteristics as 2-deoxyecdysterone 3-acetate (II).

An ethyl acetate fraction yielded 142 mg of the initial 2-deoxyecdysterone.

SUMMARY

From *Silene praemixta* M. Pop (family Caryophyllaceae), in addition to ecdysteroids isolated previously — ecdysterone, 2-deoxy-α-ecdysone, 2-deoxyecdysterone, silenosterone, and premixisterone — we have additionally isolated α-ecdysone, viticosterone E, and a new ecdysteroid. The latter has the structure of 2-deoxyecdysterone 3-acetate.

LITERATURE CITED

1. Z. Saatov, B. Z. Usmanov, and N. K. Abubakirov, Khim. Prir. Soedin., 793, 797 (1979).
2. H. Rimpler, Tetrahedron Lett., 329 (1969).
3. Z. Saatov, M. B. Gorovits, N. D. Abdullaev, B. Z. Usmanov, and N. K. Abubakirov, Khim. Prir. Soedin., 738 (1981).
4. P. Karlson, H. Hoffmeister, W. Hoppe, and R. Huber, Ann. Chem., 662, 1 (1963).
5. I. L. Novosel'skaya, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 668 (1981)
6. Ya. V. Rashkes and N. K. Abubakirov, Khim. Prir. Soedin., 518 (1980).
7. I. Krepinsky, I. A. Findlay, B. Danielli, G. Palmisano, P. Beynan, and S. Murakami, Org. Magn. Res., 10, 255 (1977).
8. H. Hikino, T. Okuyama, C. Konno, and T. Takemoto, Chem. Pharm. Bull., 23, 125 (1975).
9. E. Breitmaier and W. Voelter, ^{13}C NMR Spectroscopy, Verlag Chemie, Weinheim and New York (1978), p. 208.