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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*.

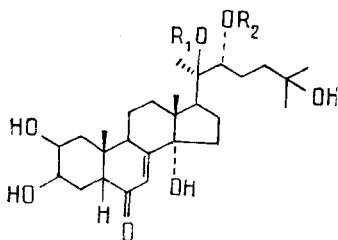
XIV. ECDYSTERONE 20-O-BENZOATE FROM *Silene tatarica*

U. A. Baltaev, V. N. Darmograi, and N. K. Abubakirov

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A new ecdysteroid, which has proved to be ecdysterone 20-O-benzoate, has been isolated from the whole plant *Silene tatarica* (L.) Pers.

Continuing a study of plants of the family Caryophyllaceae for the presence of phytoecdysteroids, we have investigated *Silene tatarica* (L.) Pers. It was first determined by TLC that the plant contained at least eight ecdysone-like substances. In the present paper we consider the establishment of the structure of one of the weakly polar ecdysteroids of *S. tatarica*.



- I.  $R_1 = \text{COC}_6\text{H}_5$ ;  $R_2 = \text{H}$
- II.  $R_1 = R_2 = \text{H}$
- III.  $R_1 = \text{H}$ ;  $R_2 = \text{COC}_6\text{H}_5$

In the IR spectrum of ecdysteroid (I), in addition to the absorption band of hydroxy groups ( $3400\text{-}3480\text{ cm}^{-1}$ ) and of a keto group conjugated with double bond ( $1665\text{ cm}^{-1}$ ), we observed the bands of an ester group ( $1710$  and  $1287\text{ cm}^{-1}$ ) and of an aromatic ring ( $1610$ ,  $1590$ , and  $720\text{ cm}^{-1}$ ).

In the UV spectrum of (I) an intense maximum appeared at  $232\text{ nm}$  ( $\log \epsilon 4.08$ ). As compared with the spectra of known ecdysteroids, this maximum was shifted in the shortwave direction by  $10\text{-}12\text{ nm}$ .

The presence in the PMR spectrum of the signals of five aromatic protons at  $7.35\text{ ppm}$  (3 H) and  $8.20\text{ ppm}$  (2 H) and also the appearance in the mass spectrum of intense peaks of ions with  $m/z$  122, 105, and 77, in combination with the features of the IR and UV spectra, made it possible for us to consider that we were dealing with an ecdysteroid containing a benzene radical in its molecule.

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The mass spectrum of ecdysteroid (I) lacked the molecular ion, and in the region of high mass numbers, in contrast to that of ecdysterone 20-O-benzoate (III) [1], the peak of an ion with  $m/z$  485, formed after the splitting out of the side chain (C-20-C-22 cleavage), was observed.

Cleavage of the C-17-C-20 bond of ecdysteroid (I) was characterized by an ion with  $m/z$  301, which is characteristic of the steroid moiety of ecdysterone (II). In contrast to ecdysterone (II) and ecdysterone 20-O-benzoate, in which an ion with  $m/z$  363 corresponds to the cleavage of the C-20-C-22 bond, this ion was absent from the spectrum of ecdysteroid (I). In place of it there was an ion with  $m/z$  468. It followed from this that the hydroxy group at C-20 was substituted by a benzoic acid residue. In addition to the facts given, the downfield shift of the signal of the C-21 methyl group (1.65 ppm) as compared with ecdysterone (1.44 ppm) convincingly confirmed the correctness of our hypothesis.

In the region where olefinic protons usually resonate, the PMR spectrum of our compound contained a one-proton broadened singlet at 6.10 ppm, which is characteristic for the protons at C-7 of ecdysteroids. Furthermore, the spectrum contained the signal of a proton geminal to a hydroxy group at C-22 (3.66 ppm).

The simultaneous presence of OH groups at C-22 and C-25 in ecdysteroids usually leads, after their dehydration and the cleavage of the C-20-C-22 bond, to a cyclic fragment giving a peak at  $m/z$  99 in the mass spectrum [2]. This peak was absent from the spectrum of compound (I). At the same time, peaks appeared of ions with  $m/z$  122, 105, and 77, corresponding to the mass spectrometric breakdown of the benzene residue. The presence in the PMR spectrum of a six-proton signal at 1.22 ppm showed the similarity of the side chain of ecdysteroid (I) to that of ecdysterone.

The alkaline hydrolysis of ecdysteroid (I) yielded ecdysterone and benzoic acid.

Thus, compound (I) had the structure of ecdysterone 20-O-benzoate.

#### EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrophotometer (KBr). Mass spectra were taken on a MKh-1310 instrument fitted with a system for direct introduction of the substance into the ion source, at an ionizing voltage of 50 V, a collector current of 60  $\mu$ A, and a temperature of the evaporator bulb and of the ionizing chamber of 170°C. The PMR spectrum was taken on a JNM-C60-H (60 MHz, Jeol) instrument.

Isolation of Ecdysterone 20-O-Benzoate (I). Air-dry whole *Silene tatarica* plants (3 kg), collected in 1984 in the environs of Ryazan' were extracted with ethanol. The total extract was concentrated to 200 ml and was diluted with 2 volumes of water. To eliminate hydrophobic compounds, the aqueous ethanolic extract was treated with hexane, and then the ecdysteroids were extracted with butanol. After the solvent had been distilled off, 60 g of combined extractive substances were obtained.

This total material was transferred to a column of silica gel and elution was performed with chloroform-methanol (4:1).

In the first fractions unknown weakly polar substances, and, among them, the new phytoecdysteroid were eluted. These fractions were combined and rechromatographed. This gave 72 g of ecdysterone 20-O-benzoate, the yield, on the weight of the air-dry raw material being 0.0026%.

Ecdysterone 20-O-benzoate (I),  $C_{34}H_{48}O_8$ , mp 232-233°C (ethyl acetate-methanol),  $[\alpha]_D^{20} +34.4 \pm 2^\circ$  (c 0.9; methanol);  $\nu_{\max}^{KBr}$ ,  $cm^{-1}$ : 3400-3480 (OH), 1665 ( $\Delta^7$ -6-keto group), 1710 and 1287 (ester), 1610, 1590, and 720 (benzene ring). Mass spectrum,  $m/z$  (%): 485 (5), 470 (1), 468 (1), 452 (2), 444 (5), 439 (15), 426 (35), 411 (10), 408 (5), 393 (5), 353 (5), 301(5), 122(100), 105(90), 77(40). PMR spectrum ( $C_6D_6N$ ,  $\delta$ , 0-HMDS, ppm): 0.197 (3 H, s, H-19), 1.08 (3 H, s, H-18), 1.22 (6 H, s, H-26 and H-27), 1.65 (3 H, s, H-21), 3.45 (1 H, m, H-9), 3.66 (1 H, m, H-22), 4.10 (2 H, m, H-2 and H-3), 6.12 (1 H, broadened singlet, H-7).

Alkaline Hydrolysis of Ecdysterone 20-O-Benzoate (I). A solution of 30 mg of the ecdysteroid (I) in 3 ml of methanol was treated with 20 mg of potassium bicarbonate in 2 ml of water. The reaction mixture was left at 20-22°C for 7 days and was then kept in a thermostat at 38°C for 36 h. The reaction products were diluted with water (25 ml), neutralized,

and extracted with ethyl acetate. After the solvent had been distilled off, the residue was recrystallized from methanol-ethyl acetate. This gave 7 mg of ecdysterone with mp 236-237°C, identified by TLC and also by mass spectrometry.

The aqueous solution, after acidification and extraction with ethyl acetate, gave 2 mg of benzoic acid with mp 120-121°C.

#### SUMMARY

A new ecdysteroid which has proved to be ecdysterone 20-O-benzoate has been isolated from whole Silene tatarica (L.) Pers. plants.

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#### PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS Silene.

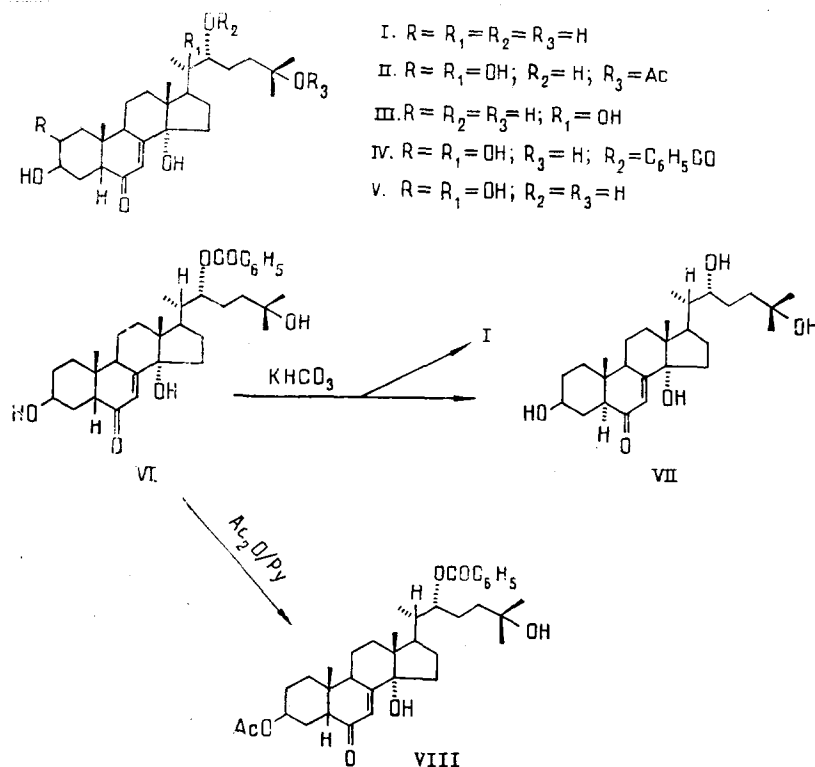
#### XV. 2-DEOXY- $\alpha$ -ECDYSONE 22-O-BENZOATE FROM Silene wallichiana

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UDC 547.926

A new phytoecdysteroid, 2-deoxy- $\alpha$ -ecdysone 22-O-benzoate, has been isolated from the epigeal organs of Silene wallichiana Klotzch.

Continuing an investigation of the ecdysone-like substances of plants of the genus Silene (family Caryophyllaceae) [1], we have studied the phytoecdysteroids of the epigeal part



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