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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS Silene.

XVIII. 2-DEOXYECDYSTERONE 20,22-MONOACETONIDE FROM Silene brahuica

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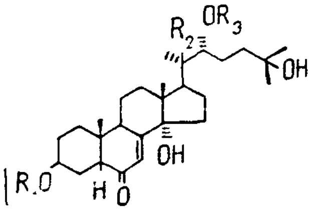
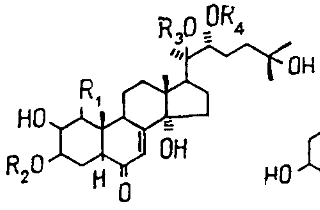
In addition to the known 2-deoxy-α-ecdysone, 2-deoxyecdysterone, 2-deoxy-α-ecdysone-22-O-acetate, ecdysterone, integristerone A, and sileneoside A, B, and C, the new ecdysteroid 2-deoxyecdysterone 20,20-monoacetonide has been isolated from the roots of the plant Silene brahuica Boiss.

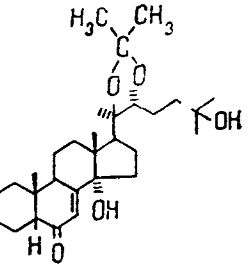
We have previousyl reported the isolation from the epigeal organs of the plant Silene brahuica Boiss., gathered in the valley of the river Chonkemin (Kungai Ala-Tau range, northern Tien-Shan) of a number of phytoecdysteroids [1]. Having studied the roots of this plant, in addition to the known 2-deoxy-α-ecdysone (I), 2-deoxyecdysterone (II), 2-deoxy-α-ecdysone-22-O-acetate (III), ecdysterone (Iv), integristerone A (V), and sileneosides A (VI), B (VII), and C (VIII), we have isolated a new phytoecdysteroid (X) with the composition $C_{30}H_{48}O_6$.



I-III



IV-IX



X

I. $R_1=R_2=R_3=H$
II. $R_1=R_3=H;\ R_2=OH$
III. $R_1=R_2=H;\ R_3=Ac$
IV. $R_1=R_2=R_3=R_4=H$
V. $R_1=OH;\ R_2=R_3=R_4=H$
VI. $R_1=R_2=R_3=H;\ R_4=\alpha$-$D$-Gal
VII. $R_1=R_3=H;\ R_2=R_4=\alpha$-$D$-Gal
VIII. $R_1=OH;\ R_2=R_3=H;\ R_4=$-$\alpha$-$D$-Gal
IX. $R_1=R_2=H;\ R_3=R_4=(CH_3)_2C<$

The mass spectrum of the ecdysteroid (X) contained the peak of the molecular ion, M^+ 504, and also the peak of an ion with m/z 347 (M − 157), and also fragments with m/z 201 and

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TABLE 1. Chemical Shifts of the Protons of 2-Deoxyecdysterone (II), Edcysterone (IV), Ecdysterone 20,22-Monoacetonide (IX), and 2-Deoxyecdysterone 20,22-Monoacetonide (X) (δ, ppm 0 – TMS)

Positions of the protons	Compound									
	H-2	H-3	H-7	H-9	H-22	CH_3-18	CH_3-19	CH_3-21	CH_3-26/27	protons of the isopropylidene group
II	–	4,11	6,22	3,52	3,85	1,22	1,05	1,58	1,38	–
IV	4,02	4,32	6,2	3,57	3.84	1,19	1.06	1,55	1,34	–
IX	4,02	4,32	6,23	3,52	3,96	1,05	1,03	1,55	1,37	1,37; 1,46
X	—	4,12	6,25	3.47	3,95	1,05	1,05	1,56	1,37	1,37; 1,48

102 corresponding to the side chain of an ecdysteroid bearing a 20,22-acetonide grouping [2]. These facts and the characteristics of the PMR spectrum of the ecdysteroid (X) in comparison with the indices for 2-deoxyecdvsterone (II) (Tale 1) permitted the assumption that this substance was 2-deoxyecdysterone 20,22-monoacetonide. It must be mentioned specially that the ecdysteroid with an acetonide group, just like other ecdysone-like compounds of similar structure, was obtained under conditions excluding the use of acetone. The native nature of the product was confirmed by direct qualitative analysis of an extract of the plant.

It is characteristic that in the PMR spectrum of the 20,22-monoacetonide (X), the signal of the 18-methyl group was shifted upfield. An analogous upfield shift of the 18-methyl singlet has also been observed for ecdysterone 20,22-monoacetonide (IX) [3] (Table 1). In both cases, the upfield shift was caused by the influence of the 20,22-isopropylidene group. For an unambiguous confirmation of the structure of the ecdysteroid (X), we obtained this compound by treating a soution of 2-deoxyecdysterone (II) in dry acetone with molybdophosphoric acid. The 2-deoxyecdysterone 20,22-monoacetonide (X) isolated from the plant coincided with respect to its constants and spectral characteristics with the authentic sample obtained synthetically.

EXPERIMENTAL

Mass spectra were taken on a MKh-1310 instrument at an ionizing voltage of 50 V and a temperature of the ionization chamber and evaporator ampul of 100-140°C; PMR spectra were taken on a BS-567 A (100 MHz, Tesla) instrument in C_5D_5N (δ, 0 – TMS). The following solvent systems were used: chloroform–methanol (15:1) (1), 9:1) (2), and (4:1) (3), and chlorofrom–methanol–waer (4:1:0.1) (4) and (70:23:2) (5). For other information, see [4].

Isolation of the Phytoecdvsteroids. The raw material – roots of the plant Silene brahuica Boiss. – was collected in May, 1982 in the valley of the River Chonkemin in the environs of the village Novorossiiska, Kirghiz SSR. The comminuted air-dry roots (5 kg) were exhaustively extracted with 25 liters of methanol. The extract was concentrated to 1 liter and was then diluted with 2.5 liters of water and the methanol was evaporated off. The aqueous solution was shaken several times with chloroform. The ecdysteroids were extracted from the purified solution first with ethyl acetate and then with butanol.

The total phytoecdysteorids (6.7 g) obtained adter the ethyl acetate had been distilled off were chromatographed on a column of silica gel. Elution with system 1 yielded 3 g (0.06%; here and below, the yield calculated on the air-dry raw material is given) of 2-deoxy-α-ecdysone (I), mp 235-236°C (from aqueous ethanol), $[\alpha]_D^{20}$ 92.5 ± 2° (c 1.5; methanol) [5, 6].

Washing the column with system 2 led to the isolation of 1.2 g (0.04%) of 2-deoxyecdysterone (II), mp 254-255°C (from aqueous ethanol) $[\alpha]_D^{20}$ + 81.9 ± 2° (c 1.3; methanol) [5,6].

Elution of the column with system 3 yielded 2 g (0.04) of ecdysterone (IV), mp 239-241°C (from acetone) $[\alpha]_D^{20}$ + 59.5 ± 2° (c 0.40; methanol) [7, 8].

The total ecdysteroids obtained after the butanol had been distilled off (49 g) were chromatographed on a column of silica gel. Elution with system 3 gave an additional 6 g (0.12%) of ecdysterone (IV).

Washing the column with system 4 led to 350 mg (0.007%) of integristerone A (V), mp 245-246°C (from ethyl acetate–methanol); $[\alpha]_D^{20}$ + 35.6 ± 2° (c 0.32; methanol [8, 9].

The further use of the same solvent system gave 175 mg (0.003%) of sileneoside A (VI), mp 253-255°C (from methanol–water), $[\alpha]_D^{20}$ + 92.7 ± 2° (c 0.47; methanol) [8].

Passage to system 5 led to the isolation of 142 mg (0.003%) of sileneoside B (VII), $[\alpha]_D^{20}$ + 110.7 ± 2° (c 0.50; methanol) [10], Then, with the aid of the same system, 130 mg (0.002%) of sileneoside C (VIII) was obtained, with mp 232-234°C (from methanol–ethyl acetate), $[\alpha]_D^{20}$ + 90.2 ± 2° (c 1.02; methanol) [11].

Isolation of 2-Deoxy-α-ecdysone 22-Acetate (III) and 2-Deoxyecdysterone 20,22-Monoacetonide (X). The mother liquors (containing 250 mg of material) obtained on the recrystallization of 2-deoxy-α-ecdysone were rechromatographed on a column of silica gel. Elution by system 1 gave 110 mg (0.002%) of 2-deoxy-α-ecdysone 22-acetate (III), mp 146-148°C (methanol–water), $[\alpha]_D^{20}$ + 50.2 ± 2° (c 0.15; methanol) [12].

The further washing of the column with the same system led to the isolation of 70 mg (0.0014%) of 2-deoxyecdysterone 20,22-monoacetonide (X), $C_{30}H_{48}O_6$, amorphous, $[\alpha]_D^{20}$ + 78.2 ± 2° (c 0.32; methanol; ν_{max}^{KBr} (cm^{-1}): 3400-3500 (OH), 1670 (Δ^7-6-keto grouping).

Mass spectrum, m/z (%): M^+ 504(0.4); 489(0.6); 486(0.6); 471(1.2); 453(1.2); 429(2); 411(19); 405(2); 493(5); 347(100); 329(25), 285(7.2); 234(9); 233(6); 201(8); 143(21); 125(21); 102(40); 99(40); 81(10).

2-Deoxyecdysterone 20,22-Monoacetonide (X) from 2-Deoxyecdysterone (II). A solution of 100 mg of the ecdysteroid (II) in 10 ml of anhydrous acetone was treated with 3 g of molybdophosphoric acid, and the reaction mixture was stirred at room temperature until the solid matter had dissolved completely. After 20 h, the mixture was neutralized with sodium bicarbonate and was then evaporated to half-volume and diluted with water. The neutral solution was extracted with ethyl acetate, and the extract was chromatographed on a column of silica gel.

Elution with system 1 led to 54 mg of 2-deoxyecdysterone 20,22-monoacetonide, $[\alpha]_D^{20}$ + 79.0 ± 2° (c 0.39; methanol). In its constants, R_f value in TLC (system 1), and spectral characteristics, the monoacetonide that had been synthesized proved to be identical with the 2-deoxyecdysterone 20,22-monoacetonide isolated directly from the plant.

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