A phytoecdysteroid, sileneoside D, has been isolated from the roots of *Silene brahuica* Boiss. and it has been shown to be ecdysterone 3-O-α-D-galactopyranoside.

We have previously described the structures of sileneosides A, B, and C [1, a-c], isolated from *Silene brahuica* Boiss. (family Caryophyllaceae). In this communication we consider the structure of a new ecdysteroid of glycosidic nature — sileneoside D (I) — also isolated from this plant.

It was shown by GLC [2] that glycoside (I) contained one D-galactose residue. In the products of the enzymatic cleavage of sileneoside D (I) performed by enzymes obtained from almond [3], ecdysterone (II) was identified as the aglycone.

The acetylation of the ecdysterone galactoside (I) with acetic anhydride in pyridine gave a heptaacetate (III) (M+ 936).

In the P~N~R~ spectrum of the heptaacetate (III), the signal of the H-22 proton and the signals of the 26/27-methyl groups had undergone paramagnetic shifts (Table 1) due to the acetylation of the corresponding hydroxy groups of the side chain. These results, together with the peaks of ions with m/z 622 [4] and 735 observed in the mass spectrum of the acetate (III) gave grounds for considering that the sugar was attached to the steroid moiety of the molecule.

In the 13C NMR spectra of ecdysterone (II) [5] and of sileneoside D (I), the signals of the carbonyl carbon atoms were characterized by the following values of the chemical shifts (ppm; the figures for sileneoside D are given in parentheses): 68.0 (68.0) C-2; 68.0 (79.0) C-3; 84.2 (84.1) C-14; 76.9 (76.8) C-20; 77.5 (77.5) C-22; and 76.9 (69.6) C-25. Thus, in the 13C NMR spectrum of galactoside (I) only the signal relating to the C-2 or C-3 carbon atom had undergone a paramagnetic shift by +11.0 ppm due to glycosylation [1 c, 6].

The site of attachment of the D-galactose residue was established in the following way. In the P~M~R~ spectrum of the residue of the heptaacetate (III), the signal of the H-2 proton and the signals of the 26/27-methyl groups had undergone paramagnetic shifts (Table 1) due to the acetylation of the corresponding hydroxy groups of the side chain. These results, together with the peaks of ions with m/z 622 [4] and 735 observed in the mass spectrum of the acetate (III) gave grounds for considering that the sugar was attached to the steroid moiety of the molecule.

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(C-2'); 71.6 (C-3'); 70.9 (C-4'); 73.3 (C-5') and 62.5 (C-6'). These figures indicate the pyranose form of the D-galactose residue [8].

The anomeric proton, H-1', of silenoside D (I) resonated at 5.48 ppm with J = 3.9 Hz (Table 1). These indices [9], and also the molecular rotation differences [10] between sileneoside D (I) and ecdysterone (II) shows the α configuration of the glycosidic center.

Thus, sileneoside D is ecdysterone 3-O-α-D-galactopyranoside.

EXPERIMENTAL

PMR spectra were taken on a JNM-100 instrument (C₆D₅N, ppm, 0 – HDMDS), and ¹³C NMR spectra on a CFT-20 instrument (Varian) (C₆D₅N, 0 – TMS). For other information, see [1a].

Silenoside D (I). The mother liquors that had accumulated in the isolation of sileneoside A [1a] from 10 kg of Silene brahica were rechromatographed repeatedly on a column of silica gel in the chloroform–methanol (4:1) system. After recrystallization from methanol–acetone, 136 mg (yield 0.0013% calculated on the air-dry raw material) of sileneoside D (I) was obtained with C₃₃H₄₀O₁₂, mp 240-242°C, [α]D²⁰ +91.2 ± 2° (c 1.01; methanol). λmaxC₂H₅OH: 247 nm (log δ 4.15). νmaxKBr (cm⁻¹): 3380-3430 (OH), 1648 (Δ²⁺-keto group). CD (c 0.10; methanol): Δc = 5.5 (250 nm), Δc = +42.2 (327 nm).

Mass spectrum, m/z (%): 624 (M⁺ - H₂O 0.5); 606 (0.8), 588 (5), 570 (1), 514 (0.8), 507 (0.7), 490 (0.9), 473 (0.6), 462 (1), 444 (1), 426 (11), 411 (2), 408 (3), 393 (1), 375 (1.0), 363 (5), 345 (55), 327 (13), 309 (10), 300 (11), 284 (11), 145 (10), 143 (12), 135 (11), 99 (100), 81 (55), 69 (53).