PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*.

III. *SILENEOSIDE A* -- A NEW GLYCOSIDIC ECDYSTEROID OF *Silene brachuica*

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Ecdysterone (I), viticosterone E, polypodine B, and integristerone A (II) have been isolated from the epigeal part of the plant *Silene brachuica* Boiss. In addition to substances (I) and (II), the phytoecdysteroid sileneoside A has been isolated from the root of this plant. It has been shown that sileneoside A is ecdysterone 22-O-α-D-galactoside.

We are continuing a study of the ecdysteroids of plants of the genus *Silene* (family Caryophyllaceae) [1]. The presence of ecdysterone (I), viticosterone E (II), polypodine B (III), and integristerone A (IV) in the epigeal parts of the *Silene brachuica* Boiss. has been shown. Five ecdysteroids have been detected in the roots of the plant, and these have been denoted in order of increasing polarity as substances A, B, C, D, and E. Components A and C have been identified, respectively, as ecdysterone (I) and integristerone A (IV). The other phytoecdysteroids have proved to be new. In the present communication the structure of product B, which we have called sileneoside A (V) is considered.

In the UV spectrum of compound (V), the α,β-unsaturated ketone grouping that is characteristic for the ecdysteroids is revealed by a maximum at 246 nm (log ε 4.15), and in the IR spectrum it is shown by absorption at 1645 cm⁻¹. The positions of the maxima and the size of the dichromic absorption [Δε = −5.03 (249 nm); Δε = 2.01 (330 nm)] of the CD curve of compound (V) are indicative for 5β-ecdysteroids [2].

The presence in the mass spectrum of substance (V) of the products of the successive dehydration of the molecular ion with m/z 624, 606, 588, and 570, in combination with fragments having m/z 363, 345, 327, 99, 81, and 69, characteristic of ecdysteroids [3, 4], and...
TABLE 1. Chemical Shifts of the Protons of Ecdysterone (I) and of Sileneoside A (V) and its Derivatives (δ, ppm; 0–DMSO)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Positions of the protons</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>H-2,3</td>
</tr>
<tr>
<td>I</td>
<td>3.9–4.2</td>
</tr>
<tr>
<td>V</td>
<td>4.0–4.2</td>
</tr>
<tr>
<td>VI</td>
<td>6.00</td>
</tr>
<tr>
<td>VII</td>
<td>5.0–5.3</td>
</tr>
<tr>
<td>VIII</td>
<td>5.0–5.3</td>
</tr>
</tbody>
</table>

Spectra taken in CD$_3$D$_2$N. The signals of the protons of the methyl groups have a singlet nature; in all cases the H-7 proton appears in the form of a broadened singlet and the remaining signals (with the exception of H-1') are broadened multiplets.

also of fragments with m/z 163 and 145 corresponding to the fragmentation of a hexose permitted the assumption that compound (V) is a glycoside of ecdysterone (I).

The correctness of this hypothesis is confirmed by the presence in the PMR spectrum of sileneoside A of the signals of six protons of a carbohydrate ring in the 4.20–4.60 ppm region, by the resonance signal of the anomeric proton at 5.50 ppm, and also by the good agreement of the chemical shifts of methyl groups (C-18, C-19, C-21, C-26, and C-27) of sileneoside A (V) and ecdysterone (I) (Table 1).

It has been shown by the GLC method [5] that sileneoside A contains one molecule of D-galactose. The presence of ecdysterone as genin was confirmed by its identification in the products of the enzymatic cleavage of the glycoside (V) carried out with the combined enzymes isolated from sweet almond [6].

In dry acetone solution, sileneoside A (V) formed a diacetonide (VI). The molecular weight of the diacetonide (M$^+$ 722) agrees with the presence of one galactose molecule. The mass spectrum of the glycoside (VI) has the strong (50%) peak of an ion with m/z 403 (C$_{22}$H$_{32}$O$_{12}$), which is characteristic for ecdysterone acetonide [3, 4]. This fragment indicates that the sugar is not bound to the steroid part of the molecule but is present in the side chain of ecdysterone and may be located at C-22 or C-25.

The position of the D-galactose residue was definitively elucidated in the following way.

Acetylation of sileneoside A (V) with acetic anhydride in pyridine gave a hexa-acetate (VII) (M$^+$ 894) and a hepta-acetate (VIII) (M$^+$ 936).

It can be seen from Table 1 that the characteristics of the PMR spectra of the acetates (VII) and (VIII) are extremely close, with the exception of the chemical shifts of the C-26 and C-27 protons. The downfield shifts of the signals of the C-26 and C-27 methyl groups of the hepta-acetate (VII) (1.36/1.47 ppm) as compared with the corresponding indices for the initial glycoside (V) (1.24/1.30 ppm) and the hexa-acetate (VII) (1.31/1.31 ppm) show the presence of an acetyl group at C-25 in the molecule of compound (VIII). Consequently, the possibility of the attachment of the sugar residue at this hydroxyl is excluded.

In the PMR spectrum of sileneoside A (V) there is a one-proton multiplet at 3.59 ppm belonging by the nature of the signal and the size of the chemical shift to the proton geminal to the hydroxy group at C-22 (see the table in [7]). This assignment is confirmed by other facts. Thus, in the double-resonance spectrum of the galactoside (V) the multiplicity