Identification of the Methylated Monosaccharides. The methanolysis of 5 mg of each of the methyl ethers (IV) and (V) in 2 ml of absolute methanol containing 5% of hydrogen chloride was carried out for 4 h.

It was shown with the aid of GLC [6] that the methanolysis products of the two methyl ethers were identical and included two components, identified as 2,3,4,6-tetra-O-methyl-D-glucopyranose (T_{rel}: 1.00, 1.22) and 2,3,4-tri-O-methyl-D-xylopyranose (T_{rel}: 0.40, 0.44).

SUMMARY

A new cycloartane bisdesmoside – cycloorbicoside G has been isolated from the epigeal part of the plant Astragalus orbiculatus Ledeb. (Leguminosae) and has been found to be (23R, 24S)-16β,23;16α,24-diepoxycycloartane-3β,7β,25-triol 25-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside.

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STEROIDS OF THE SPIROSTAN AND FUROSTAN SERIES OF PLANTS OF THE Allium GENUS.

XXIII. STRUCTURE OF CEPAGENIN AND OF ALLIOSPIROSIDES C AND D FROM Allium cepa

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UDC 547.918:547.926

Two new steroid glycosides of the spirostan series have been isolated from the fruit of Allium cepa L. (family Liliaceae): alliospirosides C and D. On the basis of chemical transformations and spectral characteristics it has been established that the aglycon of both glycosides is a new steroid sapogenin – cepagenin – having the structure of (24S,25R)-spirost-5-ene-1β,3β,24-triol. Alliospirosides C and D are cepagenin 1-O-[O-α-L-rhamnopyranosyl-(1→2)α-L-arabinopyranoside] and 1-O-[O-α-L-rhamnopyranosyl-(1→2)-O-β-D-galactopyranoside], respectively.

Continuing the fractionation of the total extractive substances from the fruit of the garden onion Allium cepa L. (family Liliaceae) [1], we have isolated two new glycosides which have been called alliospirosides C (II) and D (III). The present publication is devoted to the proof of the structures of these glycosides.

Both compounds (II) and (III) appeared in the form of violet spots when chromatograms (TLC) were treated with vanillin–phosphoric acid. The set of lines in the IR spectra of glycosides (II) and (III) in the "fingerprint" region differed substantially from the pattern characteristic for an unsubstituted spiroketal grouping [2, 3]. Nevertheless, the possibility could not be excluded of assigning alliospirosides C and D to derivatives of

Institute of the Chemistry of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 843-849, November-December, 1987. Original article submitted April 20, 1987.

 0009-3130/87/2306-0700$12.50

TABLE 1. Chemical Shifts of the Carbon Atoms of Cepagenin (I) and of Alliospirosides C (II) and D (III) (C_5D_5N, δ, ppm, 0 – TMS)

Carbon atom of the aglycon	Compound			Carbon atom of the sugar residue	Compound	
	I	II	III		II	III
1	78,24	83,94	84,67	L-Rhamnose		
2	43,97	37,54	36,12			
3	68,26	68,36	68,39	1	101,76	101,80
4	43,54	43,95	43,97	2	72,67	72,71
5	140,42	139,69	139,74	3	72,67	72,71
6	124,50	124,89	125,06	4	74,39	74,49
7	32,47	32,15	32,21	5	69,54	69,48
8	33,15	33,31	33,30	6	19,11	19,18
9	51,46	50,61	50,84			
10	43,73	43,08	43,05	L-Arabi-		
11	24,36	24,19	24,23	nose		
12	40,72	40,36	40,40			
13	40,39	40,48	40,60	1	100,63	
14	57,12	57,02	57,32	2	75,39	
15	32,54	32,51	32,56	3	75,97	
16	1,68	81,74	81,76	4	70,19	
17	62,62	62,65	62,73	5	67,44	
18	16,76	16,83	17,02			
19	14,07	15,06	15,04	D-Galac-		
20	42,76	42,71	42,77	tose		
21	15,00	15,18	15,21			
22	111,60	111,63	111,70	1		100,97
23	36,13	36,15	36,00	2		76,96
24	66,69	66,69	66,77	3		75,21
25	35,96	35,97	36,00	4		70,56
26	64,72	64,72	64,76	5		76,46
27	9,90	9,76	9,96	6		62,13

the spirostan series. It is known that when functional groups are present in ring F of a spirostanol the staining of the reaction products with the above mentioned revealing agent [4, 5] and the nature of the absorption in the 800-1000 cm^{-1} region of the IR spectrum [5, 6] change.

Under the conditions of complete acid hydrolysis, the genin moiety of glycosides (II) and (III) underwent decomposition. At the same time, Smith degradation [7] of each of the glycosides under discussion led to the same aglycon, which has been called cepagenin (I).

The first indication of the fact that genin (I) belonged to the spirostan series was the nature of its mass spectrometric fragmentation. The elementary composition of the molecular ion M^+ 446 ($C_{27}H_{42}O_5$), and also the presence of the peaks of ions with m/z 387, 361, 358, 316, 301, 287, 155, and 131 permitted the assumption of cepagenin was a spirostenetriol [4, 5, 8, 9]. The two hydroxy groups and the double bond in compound (I) were most probably located in the steroid part of the molecule, while the third hydroxylic function was in ring F at C-25, as was shown by the peaks of ions with m/z 387, 155, and 131.

In the ^{13}C NMR spectrum of the aglycon (I) taken under the conditions of the retention of $^{13}C-^{1}H$ spin-spin interaction (GD spectrum), a number of signals were located in characteristic regions (Table 1). A singlet at 140.42 and a doublet at 124.50 ppm showed the presence in the cepagenin molecule of a trisubstituted double bond. In the region of resonance of carbon atoms linked to two oxygen atoms there was a singlet with a chemical shift (CS) of 111.60 ppm. Five signals corresponded to the resonance of carbon atoms, each bearing one oxygen atom: doublets with CSs of 81.68, 78.24, 68.26, and 66.69 ppm and a triplet with CS 64.72 ppm. Finally, four quartets with CSs of 16.76, 15.00, 14.07, and 9.90 ppm indicated the presence in the cepagenin molecule of four methyl groups.

At this stage of the analysis of the spectrum the hypothesis put forward above that the aglycon (I) was a spriostenetriol became indisputable [10]. Furthermore, the conclusion of the secondary nature of all three hydroxy groups were justified.

The PMR spectrum of cepagenin was interpreted with the aid of the method of selective double homonuclear resonance in the ordinary and difference variants (Table 2). Some of the signals characteristic for the genins of the spirostan series could be assigned simply in a consideration of the general spectrum. The protons of two tertiary methyl groups (singlets with CSs of 0.86 and 1.29 ppm) and of two secondary methyl groups (doublets with CSs of 1.10 and 1.27 ppm) resonated in the strong field. The values of the CSs of the double signals showed that the CH_3-27 group was oriented axially [5]. Doublets of doublets at 3.53 and 4.02 ppm corresponded to the resonance of the two hydrogen atoms at C-26. The CSs of

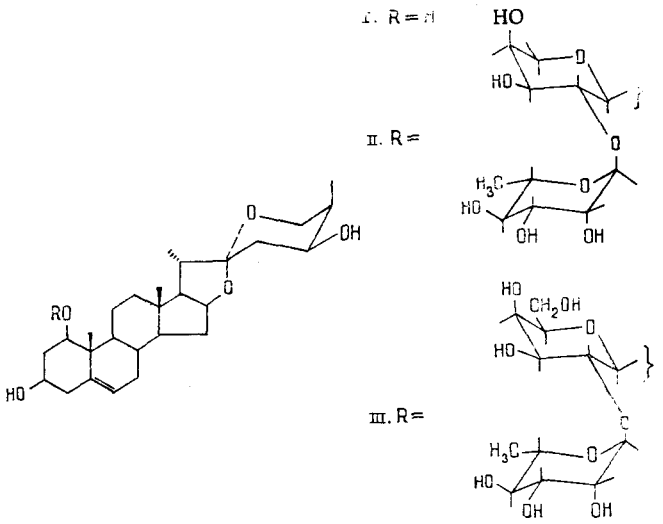
TABLE 2. Chemical Shifts (δ, ppm) and SSCCs (J, Hz) of the Protons of Cepagenin (I) and of Alliospirostides C (II) and D (III) (C_5D_5N; 0 – TMS).

Proton of the aglycon	Compound I		II	III	Proton of the sugar residues	Sugar residues in the glycosides			
						L-arabinose in (II)		L-rhamnose in (II)	
CH_3-18	0,85 s		0,77 s	0,77 s					
CH_3-19	1,29 s		1,33 s	1,29 s	1	4,62 d	$J_{1,2}=7,5$	6,21 q	$J_{1,2}=1,7$
CH_3-21	1,10 d	$J_{21,20}=7,0$	1,04 d	1,11 d	2	4,48 dd	$J_{2,3}=8,1$	4,64 dd	$J_{2,3}=3,1$
CH_3-27	1,27 d	$J_{27,25}=7,0$	1,23 d	1,27 d	3	4,07 dd	$J_{3,4}=3,5$	4,53 dd	$J_{3,4}=9,2$
1a	3,77 dd	$J_{1a,2a}=11,5$	3,72 dd	3,70 m	4	4,10 ddd	$J_{4,5a}=1,0$	4,22 t	$J_{4,5}=9,2$
		$J_{1a,2e}=4,5$			5a	3,62 dd	$J_{5a,5e}=11,5$	4,75 dq	$J_{5,6}=6,1$
2a	2,21 q	$J_{2a,2e}=11,5$			5e	4,20 dd	$J_{5e,4}=2,0$		
		$J_{2a,3a}=11,5$			CH_3-6			1,66 d	
2e	2,53 m	$J_{2e,3a}=6,0$							
3a	3,92 m	$J_{3a,4a}=12,0$	3,78 m	3,64 m		D-galactose in (III)		L-rhamnose in (III)	
		$J_{3a,4e}=5,0$			1	4,64 d	$J_{1,2}=8,0$	6,21 d	$J_{1,2}=1,7$
4a	2,65 t	$J_{4a,4e}=12,0$			2	4,48 dd	$J_{2,3}=9,0$	4,62 dd	$J_{2,3}=3,5$
4e	2,53 dd				3	4,07 dd	$J_{3,4}=3,5$	4,50 dd	$J_{3,4}=9,2$
6	5,57 br.d	$J_{6,7}=5,5$	5,52 br.d	5,50 br.d	4	4,37 dd	$J_{4,5}=1,0$	4,18 t	$J_{4,5}=9,2$
16	4,49 dt	$J_{16,17}=8,0$	4,43 m	4,43 m	5	3,84 dt	$J_{5,6'}=6,5$	4,76 dq	$J_{5,6}=6,0$
		$J_{16,15}=8,0$			6	4,33 dd	$J_{6,5}=5,6$		
		$J_{16,15'}=6,2$			6′	4,23 dd	$J_{6,6'}=10,5$		
23a	2,11 dd	$J_{23a,23e}=13,0$			CH_3-6			1,63 d	
		$J_{23a,24a}=11,0$							
23e	2,02 dd	$J_{23e,24a}=5,5$							
24a	4,60 dt	$J_{24a,25e}=5,5$	4,53 m	4,50 m					
26e	3,53 dd	$J_{26a,26e}=11,1$	3,49 dd	3,47 dd					
		$J_{26e,25e}=1,6$							
26a	4,02 dd	$J_{26a,25e}=2,4$	3,93 dd	3,95 dd					

these signals with Δδ 0.49 ppm and their multiplicities also showed the axial orientation of the CH_3-27 group. A doublet of triplets at 4.49 ppm was due to the resonance of H-16. A vinyl proton resonated at 5.57 ppm (doublet with broadened components).

In the low-field part of the PMR spectrum of aglycon (I), in addition to the signals described above there were also three multiplets: a doublet of doublets with a CS of 3.77, a multiplet at 3.92, and a doublet of triplets at 4.60 ppm. In the light of the mass spectrum and the ^{13}C NMR spectrum of cepagenin, it must be considered that these signals corresponded to protons geminal to hydroxy groups.

Analysis of the multiplicities of the signals under consideration and the results of double-resonance experiments showed that the proton having a CS of 3.77 ppm was coupled by spin-spin interaction with two, the proton having a CS of 3.92 ppm with four, and the proton having a CS of 4.60 ppm with three, other protons. The quartet at 2.21 ppm and the multiplet at 2.58 ppm corresponded to protons forming a methylene group. These protons were linked to one another by a geminal spin-sping coupling constant (SSCC) of 11.5 Hz. They interacted with the methine protons resonating at 3.77 and 3.92 ppm. A doublet of doublets with a CS of 2.58 ppm (superposed as one of the signals described above) and a triplet with a CS of 2.65 ppm likewise had a common geminal SSCC of 12.0 Hz). The methylene protons with the CSs mentioned were coupled by spin-spin interaction to only one proton geminal to a hydroxy group, the signal of which was located at 3.92 ppm.



Consequently, the cepagenin molecules contain a $-CH(OH)-CH_2-CH(OH)-CH_2-$ grouping. Such a sequence can be realized only in ring A of cepagenin. The SSCCs of the protons geminal to hydroxy groups indicated an axial orientation of these protons, i.e., both OH groups have the equatorial orientations.

The conclusions drawn above gave grounds for comparing the aglycon (I) with (25S)-ruscogenin, which we had isolated from the same material and which is (25S)-spirost-5-ene-1β,3β-diol [1].

To assign the signals in the ^{13}C NMR spectrum of cepagenin we used the methods of complete suppression of $^{13}C-^{1}H$ spin-spin coupling and of selective $^{13}C_i-\{^{1}H_i\}$ double heteronuclear resonance, and a comparison with the spectrum of (25S)-ruscogenin (see Table 1) [1].

In a comparison of the parameters of the spectra under discussion, it was seen that the CSs of the C-1–C-21 atoms scarcely differed. This indicated that in the cepagenin molecule the equatorial hydroxy groups were localized at C-1 and C-3, and the double bond was between C-5 and C-6. Differences in the CS values of the C-22–C-27 atoms (the CS of the C-24 atom underwent the greatest change) showed that the third hydroxy group of the aglycon (I) was located at C-27.

It followed from this that the signal at 4.60 ppm in the PMR spectrum of compound (I) was that of a proton geminal to the OH group at C-24. This was in harmony with the facts given previously on the spin-spin coupling of this proton with three other protons.

The SSCC of the doublet of triplets with a CS of 4.60 ppm (see Table 2) showed that H-24 had the axial, and H-25 the equatorial, orientation. Consequently the hydroxy group

at C-24 was arranged equatorially and the CH_3-27 group axially. Thus, the C-24 and C-25 chiral centers had the S- and R-configurations, respectively.

All that has been said above permitted cepagenin to be assigned the structure of (24S, 25R)- spirost-5-ene 1β,3β,24-triol.

Analysis of the products of the methanolysis of allium spirosides C and D by GLC [11] showed that the carbohydrate moiety of glycoside (II) consisted of L-arabinose and L-rhamnose residues in a ratio of 1:1. Glycoside (III) contained one residue each of D-galactose and L-rhamnose.

In the recording and interpretation of the PMR and ^{13}C NMR spectra of biosides (II) and (III) we used the methods given in the discussion of the corresponding spectra of cepagenin.

The values of the SSCCs of the protons of the carbohydrate residues of alliospiroside C given in Table 2 confirmed that the molecule of glycoside (II) contained a L-rhamnopyranose and a L-arabinopyranose residue [12]. The values of the SSCCs of the anomeric protons showed that the L-rhamnose had the α-configuration of the glycosidic center with the $^1C_4$-conformation of the ring ($J_{1,2}$ = 1.7 Hz), and the L-arabinose residue the α-configuration of the anomeric center with the $^4C_1$ conformation of the ring ($J_{1,2}$ = 7.5 Hz).

The position of attachment of the sugars was established through the observation of nuclear Overhauser effects (NOEs). The preirradiation of the H-1 atom of the L-arabinose residue caused an appreciable enhancement of the signals (5-10% of the difference NOE spectrum) of the H-3 and H-5_a atoms of L-arabinose and H-1 and H-2_e atoms of cepagenin. It followed from this that the L-arabinose was linked by an α-glycosidic bond to the hydroxy group at C-1 of genin (I).

Preirradiation of the H-1 atom of the L-rhamnose residue caused an enhancement of only two signals: H-2 of the L-rhamnose residue and H-2 of the L-arabinose residue. This enabled us to state that the L-rhamnose residue was attached to the hydroxy group at C-2 of the L-arabinose residue through an α-glycosidic bond.

The following conclusions follow from the values of the SSCCs of the signals of the protons of alliospiroside D: the molecule of glycoside (III) contained L-rhamnopyranose and D-galactopyranose residues; the glycosidic bond of the L-rhamnose residue had the α-configuration ($J_{1,2}$ = 1.7 Hz; $^1C_4$-conformation of the ring); and the glycosidic bond the D-galactose residue has the β-configuration ($J_{1,2}$ = 8.0 Hz; $^4C_1$ conformation of the ring).

A comparison of the value of the chemical shifts of the carbon atoms of cepagenin and its biosides (II, III) (see Table 1) showed that on passing from the aglycon (I) to the glycosides (II) and (III) the C-1 signal underwent considerable paramagnetic shifts (Δδ = 5.70 and 6.43 ppm, respectively). For the C-2 signals there were substantial diamagnetic shifts (Δδ 6.43 and 7.85 ppm, respectively).

When the ^{13}C NMR spectra of alliospirosides C and A, and also D and B [1], were compared it was seen that they differed only by the values of the CSs of the carbon atoms forming ring F of the aglycons. Thus, there was no doubt that in both glycosides (II) and (III) the carbohydrate chains were attached to the hydroxy group at C-1 of the cepagenin residue. In addition to this, the glycosylation of the α-L-rhamnopyranose OH group at C-2 by the α-L-arabinopyranose residue in the case of bioside (II) was confirmed. It became obvious that for compound (III) the terminal α-L-rhamnopyranose residue was attached to the hydroxy group at C-2 of the β-D-galactopyranose residue.

Consequently, alliospiroside C is (24S,25R)-spirost-5-ene-1β,3β,24-triol 1-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside]. Alliopsiroside D has the structure of (24S, 25R)-spirost-5-ene-1β,3β,24-triol 1-O-[O-α-L-rhamnopyranosyl-(1→2)-O-β-D-galactopyranoside].

EXPERIMENTAL

General Observations. Silufol plates (Czechoslovakia) and also type L silica gel (with a particle size <63 μ) containing 10% of gypsum were used for thin layer chromatography; silica gels of types KSK and L (particle size 63-100 μ) were used for column chromatography. The following solvent systems were employed: 1) chloroform–methanol–water [a) (65:15:2; b) (65:22:4)], 2) ethyl acetate–methanol–water (65:12:3); and 3) chloroform–methanol [a) (10:1), b)(20:1)].

The PMR and ^{13}C NMR spectra were taken on Bruker WM-250 and AM-300 instruments, respectively, at 30°C. The solvent was C_5D_5N.

Gas-liquid chromatography was performed on a Biokhrom-1 chromatograph. The monosaccharides were chromatographed in the form of the trimethylsilyl ethers of the corresponding methyl glycosides [11] in a glass capillary column (0.25 mm × 50 m) coated with the phase OV-101. The thermostat temperature was 160°C, and the carrier gas, helium, had a rate of 4 ml/min. Other details are given in [1].

Isolation of Alliospirosides C and D. The enriched fractions collected on the accumulation of alliospirosides A and B from 35 kg of Allium cepa fruit [1] were subjected to repeated rechromatography on silica gel columns in solvent systems 1a, 1b, and 2. After recrystallization, 17.2 g of alliospiroside C and 2.5 g of alliospiroside D were obtained. The yields calculated on the weight of the air-dry raw material amounted to 0.049 and 0.007%, respectively.

Alliospiroside C – $C_{38}H_{60}O_{13}$, mp 223-225°C (from aqueous methanol), $[\alpha]_D^{22}$ −105.7 ± 2° (c 0.94; pyridine); ν_{max}^{KBr} (cm^{-1}): 825, 845, 870, 880, 908, 920, 965, 1000, 3200-3600.

Alliospiroside D – $C_{39}H_{62}O_{14}$, mp 242-243°C (methanol); $[\alpha]_D^{22}$ −89.9 ± 2° (c 0.75; pyridine). ν_{max}^{KBr} (cm^{-1}): 830, 850, 870, 880, 910, 925, 965, 990, 1000, 3200-3600.

Cepagenin (I) from (II). A solution of 800 mg of glycoside (II) in 100 ml of 50% aqueous methanol was treated with 2.7 g of $NaIO_4$, and the mixture was stirred at room temperature for 3 h. The unchanged oxidant was decomposed with ethylene glycol, and then 50 ml of water were added, the methanol was distilled off, and the aqueous solution was extracted with butanol. The combined butanolic extracts were washed with water and the butanol was distilled off, and the residue was treated with 160 ml of 50% aqueous methanol and 2.25 g of $NaBH_4$. The reaction mixture was left in the dark at room temperature for 48 h. Then sulfuric acid was added to give a total concentration of 1%. Hydrolysis was carried out at room temperature for 2 days. After this, an equal volume of water was added, the methanol was evaporated off, and the aqueous solution was extracted with butanol. The butanol extracts were washed with water and evaporated to dryness. The residue was subjected to column chromatography in solvent system 3b. The fractions containing the individual aglycon were recyrstallized from ethanol, giving 195 mg of cepagenin, $C_{27}H_{42}O_5$, mp 268-270°C, $[\alpha]_D^{22}$ −82.6 ± 2° (c 0.99; pyridine); ν_{max}^{KBr} (cm^{-1}): 808, 840, 876, 908, 940, 965, 982, 1000, 3200-3500. Mass spectrum, m/z (%): M^+ 446 (1), 428 (100), 410 (21), 395 (7), 387 (8), 361 (2), 358 (3), 340 (14), 316 (4), 301 (8), 287 (5), 155 (82), 131 (9), 122 (10).

Cepagenin (I) from (III). Glycoside (III) (75 mg) was dissolved in 15 ml of 50% aqueous methanol and the reaction was performed as described for allioside C (II). After the reaction mixture had been worked up, 15 mg of genin with mp 267-269°C were isolated and shown to be identical with cepagenin by TLC (system 3a) and from the absence of a depression of a mixed melting point.

Methanolysis of Alliospirosides C (II) and D (III). A solution of 11.2 mg of compound (II) in 4 ml of absolute methanol containing 5% of hydrogen choride was boiled for 14 h. After cooling and the addition of an equal volume of water, the precipitate that had deposited was filtered off. The filtrate was neutralized with silver carbonate, the silver chloride that deposited was separated off, and the solution was evaporated to dryness. L-Arabinose and L-rhamnose were identified by GLC in a ratio of 1.00:0.90.

Compound (III) (10.0 mg) was subjected to methanolysis similarly. It was found by GLC that alliospiroside D contained L-rhamnose and D-galactose residues in a ratio of 1.00:0.95.

SUMMARY

Two new glycosides have been isolated from the fruit of Allium cepa L. (family Liliaceae): alliospirosides C and D. Their aglycon is a previously undescribed genin of the spirostan series – cepagenin –, which has the structure of (24S,25R)-spirost-5-ene-1β,3β,24-triol. Alliospirosides C and D are (24S,25R)-spirost-5-ene-1β-3β,24-triol 1-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside] and 1-O-[O-α-L-rhamnopyranosyl-(1→2)-β-galactopyranoside], respectively.

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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS Silene.

XIV. ECDYSTERONE 20-O-BENZOATE FROM Silene tatarica

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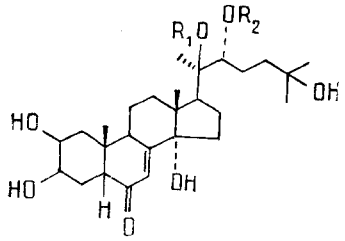
UDC 547.926

A new ecdysteroid, which has proved to be ecdysterone 20-O-benzoate, has been isolated from the whole plant Silene tatatica (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. $R_1 = COC_6H_5$; $R_2 = H$
II. $R_1 = R_2 = H$
III. $R_1 = H$; $R_2 = COC_6H_5$

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

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

The presence in the PMR spectrum of the signals of five aromatic protons at 7.35 ppm (3 H) and 8.20 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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Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 850-852, November-December, 1987. Original article submitted April 22, 1987.

 0009-3130/87/2306-0706$12.50