SUMMARY

1. The isomerization equilibrium of nine p-menthadienes has been studied in the gas phase at 250°C and their equilibrium ratios have been determined.

2. A procedure has been developed for the quantitative GLC analysis of isomeric mixtures of p-menthadienes.

LITERATURE CITED

1. G. A. Rudakov, The Chemistry and Technology of Camphor [in Russian], Moscow–Leningrad (1961), p. 42.
2. H. Pines and H. E. Eschinazi, J. Am. Chem. Soc., 77, 6314 (1955); G. L. K. Hunter and W. B. Brogden, J. Org. Chem., 28, 1679 (1963).
3. I. I. Bardyshev, L. A. Popova, and E. F. Buinova, Izv. Akad. Nauk BSSR, Ser. Khim., No. 4, 112 (1976).
4. S. Bank, C. A. Rorve, A. Schriesheim, and L. A. Naslund, J. Org. Chem., 33, 221 (1968).
5. R. B. Bates, E. S. Caldwell, and H. P. Klein, J. Org. Chem., 34, 2615 (1969).
6. V. G. Berezkin, Analytical Reaction Gas Chromatography [in Russian], Moscow (1966), p. 18.
7. S. Geger, W. Ziger, S. Helm, and R. Mayer, Z. Chem., 5, 309 (1968).
8. I. I. Bardyshev and V. I. Kulikov, Zh. Anal. Khim., 23, 1081 (1968).
9. S. V. Petrova-Kuminskaya, O. M. Baranov, G. N. Roganov, and G. Ya. Kabo, Neftekhimiya, 23, 489 (1983).
10. I. A. Yursha and G. Ya. Kabo, Dokl. Akad. Nauk BSSR, 21, 1100 (1977).
11. B. M. Mitzner, E. T. Theimer, and S. K. Freeman, Appl. Spectrosc., 19, No. 6, 169 (1965).

ISOLATION OF NATIVE AGLYCONES FROM TRITERPENE GLYCOSIDES OF THE PACIFIC OCEAN HOLOTHURIAN *Cucumaria japonica*

V. F. Sharypov, A. I. Kalinovskii,
V. A. Stonik, S. A. Avilov, and G. B. Elyakov

UDC 547.996:593.96

New native aglycones — 3β-hydroxyholosta-7,25-dien-16-one and holosta-7,25-dien-3β-ol — have been isolated from the glycosidic fraction of the holothurian *Cucumaria japonica*. It has been shown that holostane derivatives with a 16-keto group can be transformed on reduction with sodium tetrahydroborate into previously unknown compounds with an 18 → 16-lactone fragment.

As is well known, the aglycones of holothurian glycosides are unstable under the conditions of cleavage of glycosidic bonds. Therefore, proposals concerning the true structure of the triterpene moiety are made in many cases after the determination of the structure of the corresponding artefactual genins and the study of the ^{13}C NMR spectra of the initial glycosides. Thus, the structure of 3β-hydroxyholosta-7,25-dien-16-one (I) has been proposed for the main aglycone of the glycosides of the industrially caught Pacific Ocean holothurian *Cucumaria japonica* [1]. The native aglycone of glycosides of the Far Eastern trepang *Stichopus japonicus* is an isomeric compound — 3β-hydroxyholosta-9(11), 25-dien-16-one (II) [2].

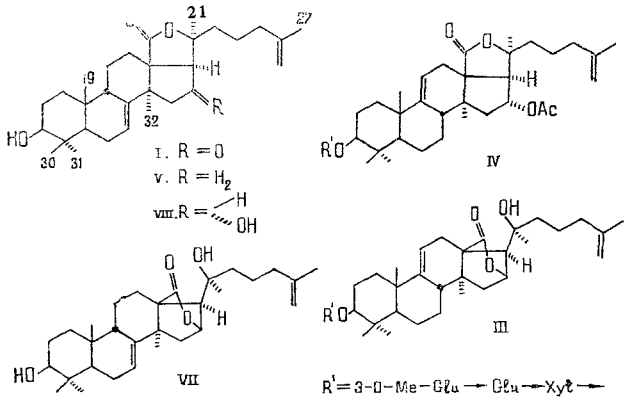
Recently, to cleave the glycosides of *Bohadshia argus* we used the method of two-stage Smith degradation, as the result of which only native genins were obtained [3]. However, in the determination of the structure of holotoxin A_1 from *S. japonicus* [4] under the

Pacific Ocean Institute of Bioorganic Chemistry, Far-Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 55-59, January-February, 1985. Original article submitted February 27, 1984.

0009-3130/85/2101-0051$09.50

conditions of Smith degradation we observed transformations that are characteristic for (II) due to the presence of the 16-keto group. We established the directions of these processes and, after eliminating them, we obtained close native aglycones from the glycosides of *C. japonica*.

The treatment of holotoxin A_1 with sodium periodate and then with sodium tetrahydroborate and, finally, with 0.5% hydrochloric acid (Smith degradation) led to two progenins, which were isolated in the form of the corresponding peracetates (III and IV). Analysis of ^1H and ^{13}C NMR spectra showed that the two progenins had the same carbohydrate chain and their aglycones differed from the native aglycone (II). Thus, aglycones (III) and (IV) did not contain a 16-keto group, and instead of an 18 → 20-lactone ring (III) had a new 18 → 16-lactone. It is obvious that under the conditions of the Smith degradation of holotoxin A_1 the keto group in (II) underwent reduction with the formation of 16α- and 16β-hydroxy derivatives and then the latter underwent "recyclization" of the lactone at the 16β-hydroxy group that had appeared. The structures of genins (III) and (IV) were confirmed by their spectral characteristics.



In the weak-field region of the ^{13}C NMR spectrum of (III) there were characteristic signals at (ppm) 145.1 (s, C-25), 110.4 (t, C-26), 148.1 (s, C-9), and 113.0 (d, C-11) indicating the 25(26) and 9(11) positions of the double bond [2]. At the same time, it lacked signals at 83.2 ppm (s, C-20, 18 → 20-lactone) and 212 ppm (s, C-16, keto group) that were recorded in the spectrum of the initial glycoside. In addition to these, signals were observed at (ppm) 72.0 (s, C-20), 79.2 (d, C-16), and 177.6 (s, C-18).

In the ^1H NMR spectrum of (III), which is typical for holostane derivatives, the CH_3-21 signal in the 1.4 ppm region had shifted to 1.21 ppm, which shows the presence of a tertiary hydroxy group at C-20. The assignment of the signals in the spectrum of the aglycone moiety of (III) (Table 1) was made with the aid of differential decoupling and the recording of the signals of the nuclear Overhauser effect (NOE). Thus, the appearance of a NOE signal at 2.33 ppm (12α-H) was recorded when the CH_3-21 and CH_3-32 signals were irradiated.

The ^{13}C NMR spectrum of (IV) revealed the presence of 25(26)- and 9(11)- double bonds (145.1 s, 110.4 t, 151.2 s, and 110.1 d), of an 18 → 20-lactone (176.4 s, 83.2 s) and showed the absence of a 16-keto group. A signal at 4.45 ppm (C<u>H</u>—OAc) appearing in the ^1H NMR spectrum of (IV) but not in the spectrum of the peracetate of holotoxin A_1 confirmed the reduction of the keto group to the corresponding hydroxy derivative. If the assumption concerning the conformation of ring D [5] is correct, it follows from the spin—spin coupling constant (SSCC) (Table 2) that the 16-OAc substituent in (IV) has the α-configuration.

It was previously possible to exclude the processes of transformation of (II) that had been found by performing the short-time treatment of holotoxin A_1 with tetrahydroborate in absolute ethanol [4]. A similar double Smith degradation enabled us to obtain the native aglycones (I and V) from the glycosidic fraction of *C. japonica*.

The results of a study of the spectral properties of (I) confirmed the hypothesis that the main native aglycone had the structure of 3β-hydroxyholosta-7,25-dien-16-one. In the mass spectrum of (I) the peak of the molecular ion with m/z 468 ($C_{30}H_{44}O_4$) was observed. The IR spectrum contained a broad absorption band of the carbonyl groups of a lactone and a ketone in the 1750-1760 cm^{-1} region [6, 7]. The presence of a keto group at C-16 followed from the multiplicity of the 2H-15 and H-17 signals in the ^1H NMR spectrum. The former appeared as multiplets with centers at 2.27 and 2.48 ppm [17], and the 17α-H signal as a

TABLE 1. ^{1}H NMR Spectra of the Aglycone Moieties of the Peracetates of the Progenins (III) and (IV) and of the Genins (I) and (V-VIII) (250 MHz, $CDCl_3$, δ, ppm, TMS — 0)

Positions of the protons	III	IV	I	V	VI	VII	VIII
CH_3-19	0,99 s	1,15 s	1,08 s	1,04 s	1,04 s	0,92 s	1,03 s
CH_3-21	1,21 s	1,44 s	1,44 s	1,42 s	1,42 s	1,24 s	1,47 s
CH_3-27	1,71 s	1,69 s	1,72 t	1,72 t	1,76 t	1,72 t	1,73 t
CH_3-30	0,74 s	0,78 s	0,90 s	0,89 s	0,88 s	0,86 s	0,88 s
CH_3-31	0,89 s	0,91 s	1,03 s	1,03 s	1,02 s	1,01 s	1,03 s
CH_3-32	1,06 s	1,00 s	1,17 d	1,13 s	1,13 s	1,36 s	1,36 d
H-3α	3,05 dd	3,05 dd	3,22 m	3,22 m	3,20 m	3,20 m	3,21 m
H-7	—	—	5,56 m	5,56 m	5,55 m	5,50 m	5,53 m
H-9β	—	—	3,45 dm	3,21 m	3,21 m	2,77 dm	3,17 dm
H-11	5,38 m	5,19 m	—	—	—	—	—
H-12α	2,33 B dm	2,58 A dm	—	—	—	—	—
H-12β	2,48 A dm	2,42 B dm	—	—	—	—	—
H-15α	1,62 Bdd	1,78 Ad	2,48 Add	—	—	1,95 B dd	1,83 Bdd
H-15β	1,78 Ad	1,66 Bdd	2,27 Bdt	—	—	2,09 A dd	1,88 Add
H-16	4,82 d	5,45 dd	—	—	—	4,81 dd	4,55 m
H-17α	2,31 s	2,52 d	2,52 s	—	—	2,37 s	2,33 d
H-26	4,68 m	4,66 m	4,68 m	4,68 m	4,74 m	4,68 m	4,68 m
H'-26	4,74 m	4,71 m	4,71 m	4,73 m	4,82 m	4,73 m	4,73 m

TABLE 2. SSCCs of the Protons in the ^{1}H NMR Spectra, Hz

J	III	IV	I	VII	VIII	16-OH*	
						α	β
15α, 15β	13,5	15,1	15,8	13,6	14,2	—	—
15α, 16	2,7	0	—	2,7	1,7	1,4	9,4
15β, 16	0	7,1	—	0,8	7,1	6,5	5,7
16, 17α	0	2,6	—	0	3,6	3,0	7,7
15β, 32	—	—	1,4	—	0,8	—	—

*Calculated from an equation given in [11]. The values of the dihedral angles were taken from the results of an x-ray structural analysis of 23(S)-acetoxyholost-7-en-3β-ol.

broadened singlet at 2.52 ppm ($J_{17,15\alpha}$ = 1.2 Hz, $J_{17,15\beta}$ = 1.1 Hz). A signal at 1.44 ppm (CH_3-21) indicated the presence of an 18 → 20-lactone, and signals at (ppm) 4.71, 4.68 (2H-26), and 1.72 (3H, CH_3-27) confirmed the position of the 25(26)- double bond. The position of the signal of an olefinic proton in the cyclic moiety at 5.56 ppm permitted a 9β-H-7(8)-ene fragment to be identified [8, 9].

We assigned a signal at 1.17 ppm in the ^{1}H NMR spectrum of (I) to CH_3-32 in view of the detection of an SSCC with 15α-H (J = 1.4 Hz) and the recording of NOE signals of 17α-H (3%) and of 15α-H when it was irradiated. In this experiment, no analogous signals of 15β-H and 9β-H were observed. On the contrary, NOE signals were obtained at 3.45 ppm (9β-H) and 0.90 (CH_3-30) when CH_3-19 (1.08 ppm) was irradiated. In its turn, when 9β-H was irradiated only the CH_3-19 (1.08 ppm) signal was obtained. These observations confirmed the 9β-H configuration in (I).

The minor aglycone (V) was close in many of its spectra characteristics to (I). However, the peak of its molecular ion was observed a m/z 454 ($C_{30}H_{46}O_3$) and a shift of 14 units in comparison with the mass spectrum of (I) suggested the absence of a keto group from (V). In fact, the ^{1}H NMR spectrum of (V) did not contain in the weak field the signals of C-15 methylene and C-17 methine groups that were characteristic for (I). But this spectrum showed almost complete coincidence of the signals with the spectrum of the model 23(S)-acetoxyholost-7,25-dien-3β-ol (VI) (see Table 1). It follows from this that (V) had the same cyclic system and positions of the double bonds as in (VI).

The position of the 7(8)- double bond in (V) was confirmed by a spin system of the XABPT type for H-5, H-6α, H-6β, H-7, and H-9, revealed with the aid of differential

TABLE 3. NMR Spectrum of Genin (V)* (C_6D_6)

Proton absorption	ppm †		Hz	SSCC	Hz
CH_3-19	1,10	H-7	1409,0	6α, 7	6,9
CH_3-21	1,23	H-5	242 0	6α, 9	1,2
CH_3-27	1 64	H-6α	499.9	6α, 6β	16,8
CH_3-30	0,90	H-6β	517,8	6β, 7	1,9
CH_3-31	0,92	H-9β	897,0	7,9	2,6
CH_3-32	1.11			5,6α	3.4
H-3	3,11			5,6β	11,9
H-26	4 78			5,7	0
H'-26	4,83			5,9	0
				6β,9	3,5

*Values of the chemical shifts in H—5, H—6α, H—6β, H—7, H—9, and KCCB were calculated according to the agreement of the calculated spectrum with the experimental to the accuracy of ±0.2Hz (ASPECT-2000 computer).

†Signal referral for methyl groups is non-homogeneous.

spectroscopy (Table 3). For a 9(11)- double bond the spin system would have the ABPT form. The assignment of the signals of the protons in the ^{1}H NMR spectrum of (V) was confirmed by double-resonance experiments. As for (I), the 9β-H configuration was also confirmed.

The native aglycone (I) was also capable of the transformations described above. The treatment of (I) with sodium tetrahydroborate in aqueous dioxane led to new derivatives (VII) and (VIII) which proved to be isomeric with the $\Delta^{9(11)}$ genins in (III) and (IV).

In its mass spectrum, derivative (VII) had a low-intensity peak of the molecular ion with m/z 470. In its IR spectrum, the carbonyl group of the lactone appeared at 1770 cm^{-1}, and not at 1750-1760 cm^{-1} as in (I). The position of the CH_3-21 in the ^{1}H NMR spectrum of (VII) at 1.24 ppm showed the presence of a tertiary hydroxyl at C-20. The formation of an 18 → 16-lactone was confirmed by the position of the signal of the newly appearing proton (H-16) at 4.81 ppm, and also by the upfield shift of the 9β-H and CH_3-19 signals (Table 1).

By recording the NOE signals on the irradiation of the methyl groups, the 9β-H, 3α-H, and 17α-H configurations in (VII) were confirmed. Thus, irradiation at 1.36 ppm (CH_3-32) revealed H-7, H-17, and 15α-H signals; irradiation at 1.24 ppm (CH_3-21), H-17 and H-16 signals; irradiation at 0.92 ppm (CH_3-19), H-9 and CH_3-30 signals; and irradiation at 1.01 ppm (CH_3-31), H-3 and CH_3-30 signals. The assignment of the signal at 1.36 ppm to CH_3-32 was confirmed by irradiation at 5.50 ppm (H-7).

Compound (VIII) had a ^{1}H NMR spectrum similar to that of the initial aglycone (I). However, in the spectrum of (VIII) a signal appeared at 4.55 ppm (H-16), and the singlet at 2.52 ppm (17α-H) was converted into a doublet at 2.33 ppm. The CH_3-32 signal was shifted downfield from 1.17 to 1.36 ppm (d, $J_{15\beta,32}$ = 0.8 Hz) because of 1,3-diaxial interaction with the 16α-hydroxy group [10]. The same configuration at C-16 was also indicated by a comparison of the SSCCs of the 16β-H with the neighboring protons calculated theoretically from the formula [11] for both epimers (Table 2) on the basis of the results of an x-ray structural analysis of 23(S)-acetoxyholost-7-en-3β-ol [12].

The acetylation of (VII) and (VIII) gave the monoacetate (VIIa) and the diacetate (VIIIa), respectively. The diacetate (VIIIa) is an isomer of the previously known diacetate of holost-7, 24-diene-3β, 16β-diol [5]. As was to be expected, the ^{1}H NMR spectra of the cyclic moieties of both isomers practically coincided, with the exception of the H-16 and CH_3-32 signals, which were located in the case of the latter at 5.67 and 1.17 ppm, respectively, as compared with 5.45 and 1.26 ppm in the spectrum of (VIIIa).

The SSCCs in the ^{1}H NMR spectra of the recyclized products (III) and (VII) apparently reflect a change in the conformation of ring D, which, in particular, also explains the shift of the CH_3-32 signal in the spectrum of (VII) to a value of 1.36 ppm that is characteristic only for the 16α-hydroxy derivative (VIII).

Thus, the native aglycones (I) and (V) have been obtained from the glycosidic fraction of *C. japonica* and it has been shown that a holostane derivatives with a 16-keto group may be transformed on reduction with tetrahydroborate into previously unknown compounds with an 18 → 16-lactone fragment.

EXPERIMENTAL

The glycosidic fractions and holotoxin A_1 were obtained as described previously [2, 4]. Smith degradation was carried out as in [3] or by the modification described in [4]. Acetylation was performed with acetic anhydride in pyridine.

Acetates of the progenins: amorphous III — $[\alpha]_D^{20}$ — 21° (*c* 1.0; $CHCl_3$), IV — $[\alpha]_D^{20}$ —44° (*c* 1.0; $CHCl_3$). ^1H NMR (Bruker WM-250), see Tables 1 and 2.

3 -Hydroxyholosta-7, 25-dien-16-one (I) (6 mg): mp 225-227°C, $[\alpha]_D^{20}$ — 160° (*c* 0.5; $CHCl_3$). IR spectrum, cm^{-1}: 1750-1760, 3460 (OH). Mass spectrum, *m/z* (%): 468 (M^+, 42), 453(20), 450(10), 435(30), 423(15), 382(9), 381(9), 274(30), 259(35), 241(22), 228(27), 213(32), 109(100), 95(42), 81(40), 69(78), 55(70), 43(62), 41(75).

Holosta-7,25-dien-3β-ol (V) (2 mg): mp 188-190°C, $[\alpha]_D^{20}$ —36° (*c* 0.15; $CHCl_3$). Mass spectrum (%): 454(M^+, 70), 439(53), 421(65), 395(32), 393(10), 377(20), 325(20), 267(26), 159(32), 145(32), 127(40), 109(93), 105(40), 95(65), 81(59), 69(100), 55(93), 43(80), 41(80). Metastable ions: 425, 404.

The reduction of (I) (5 mg) was carried out with sodium tetrahydroborate in dioxane—water (4:1) at 20°C for 4 h. As a result, 1.5 mg of (VII) and 1.5 mg of (VIII) was obtained.

Derivative (VII): mp 235-238°C, $[\alpha]_D^{20}$ —97° (*c* 0.15, $CHCl_3$). IR spectrum: 1770 cm^{-1}. Mass spectrum, (%): 470(0,5), 452(5), 407(10), 302(26), 284(10), 162(24), 145(10), 140(23), 123(15), 122(100), 109(20), 96(27), 95(18), 81(15), 69(36), 55(21), 43(35), 41(23). ^1H NMR of (VIIa) (ppm): 5.54 (m, H-7); 4.81 (d, H-16); 4.68, 4.73 (m, 2H-26); 4.48 (m, H-3); 2.78 (m, H-9); 2.37 (s, H-17); 1.72 (s, CH_3-27); 1.36 (s, CH_3-32); 1.23 (s, CH_3-21); 0.94 (s, CH_3-31); 0.93 (s, CH_3-19); 0.89 (s, CH_3-30); 2.06 (s, CH_3COO).

Derivative (VIII): mp 249-252°C, $[\alpha]_D^{20}$ —104° (*c* 0.15; $CHCl_3$) . IR: 1750 cm^{-1}. Mass spectrum (%): 470(M^+, 62), 455(40), 437(48), 419(17), 411(8), 393(13), 391(5), 382(8), 381(8), 283(12), 265(17), 241(8), 239(8), 213(10), 109(100), 95(48), 93(25), 81(31), 69(73), 55(59), 43(59), 41(50). Metastable ions: 442, 420. ^1H NMR of (VIIIa) (ppm); 5.52 (m, H-7); 5.45 (m, H-16); 4.65, 4.73 (m, 2H-26); 4.48 (m, H-3); 3.20 (m, H-9); 2.50 (d, H-17); 2.06 (s, CH_3COO); 2.04 (s, CH_3COO); 1.72 (s, CH_3-27); 1.47 (s, CH_3-21); 1.26 (s, CH_3-32); 1.06 (s, CH_3-19); 0.96 (s, CH_3-31); 0.91 (s, CH_3-30).

SUMMARY

New native aglycones — 3β-hydroxyholosta-7,25-dien-16-one (I) and holosta-7,25-dien-3β-ol (V) — have been obtained from the glycosidic fraction of the holothurian *Cucumaria japonica*. It has been shown that holostane derivatives with a 16-keto group can be transformed on reduction with sodium tetrahydroborate into previously unknown compounds with an 18 → 16-lactone fragment.

LITERATURE CITED

1. G. B. Elyakov, V. A. Stonik, Sh. Sh. Afiyatullov, V. F. Kalinovskii, V. F. Sharypov, and L. Ya. Korotkikh, Dokl. Akad. Nauk SSSR, 259, 1367 (1981).
2. A. I. Kalinovskii, V. F. Sharypov, V. A. Stonik, and G. B. Elyakov, Bioorg. Khim., 6, 951 (1980).
3. V. A. Stonik, V. F. Sharypov, A. I. Kalinovskii, and T. A. Kuznetsova, Khim. Prir. Soedin., 790 (1982).
4. G. B. Elyakov, I. I. Mal'tsev, A. I. Kalinovskii, and V. A. Stonik, Bioorg. Khim., 9, 280 (1983).
5. Sh. Sh. Afiyatullov, V. A. Stonik, A. I. Kalinovskii, and G. B. Elyakov, Khim. Prir. Soedin., 59 (1983).

6. I. Kitagawa, T. Sugawara, I. Yosioka, and K. Kuriyama, Tetrahedron Lett., 963 (1975).
7. W. L. Tan, C. Djerassi, J. Fayos, and J. Clardy, J. Org. Chem., 40, 466 (1975).
8. J. P. Kutney, N. D. Westcott, F. H. Allen, N. W. Isaacs, O. Kennard, and W. D. S. Motherwell, Tetrahedron Lett., 3463 (1971).
9. A. I. Kalinovskii, V. F. Sharypov, Sh. Sh. Afiyatullov, T. A. Kuznetsova, V. A. Stonik, and G. B. Elyakov, Bioorg. Khim., 9, 1558 (1983).
10. D. Lavie, B. S. Benjamino, and Y. Shvo, Tetrahedron, 20, 2585 (1964).
11. C. A. C. Haasnoot, H. P. M. de Leeuw, F. A. M. de Leeuw, and C. Altona, Org. Magn. Reson., 15, 43 (1981).
12. S. G. Il'in, V. F. Sharypov, V. A. Stonik, G. V. Malinovskaya, N. I. Uvarova, G. B. Elyakov, M. Yu. Antinov, and Yu. T. Struchkov, in: IIIrd All-Union Conference on Organic Crystal Chemistry. Abstracts of Lectures [in Russian], Gor'kii, (1981), p. 145.

PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*.

VIII. 2-DEOXYECDYSTERONE 3-ACETATE FROM *Silene praemixta*

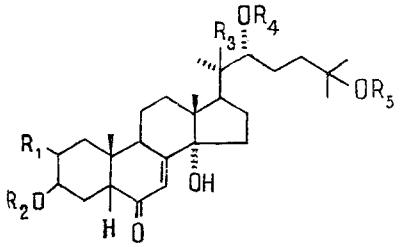
Z. Saatov, M. B. Gorovits,
N. D. Abdullaev, B. Z. Usmanov, and
N. K. Abubakirov

UDC 547.926+591.147:595.2

A phytoecdysteroid, 2-deoxyecdysterone 3-acetate, has been isolated from the epigeal organs of *Silene praemixta* M. pop.

We have previously detected in the plant *Silene praemixta* M. Pop (family Caryophyllaceae) ecdysterone, 2-deoxy-α-ecdysone, 2-deoxyecdysterone, silenosterone, and premixisterone [1].

Rechromatography on a column of silica gel of the mother liquors obtained in the isolation of the substances mentioned led to the isolation of viticosterone E (IV) [2, 3], α-ecdysone (V) [4, 5], and a new phytoecdysteroid (II) with the composition $C_{29}H_{46}O_7$. In the IR spectrum of compound (II), in addition to the absorption due to hydroxy groups (3450 cm^{-1}) and an α,β-unsaturated keto grouping (1655 cm^{-1}), there were absorption bands at 1740 and 1255 cm^{-1} showing the presence of an ester residue. This was also indicated by the presence of a three-proton singlet at 2.00 ppm in the PMR spectrum of the ecdysteroid (II).



I. $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$
II. $R_1 = R_4 = R_5 = H$; $R_3 = OH$; $R_2 = Ac$
III. $R_1 = R_5 = H$; $R_3 = OH$, $R_2 = R_4 = Ac$
IV. $R_2 = R_4 = H$; $R_1 = R_3 = OH$, $R_5 = Ac$
V. $R_2 = R_3 = R_4 = R_5 = H$; $R_1 = OH$

A peak with m/z 389 (cleavage of the C-20–C-22 bond) and its derivatives with m/z 371, 329, and 311 permitted the assumption that compound (II) belonged to the 2-deoxyecdysteroid group and had an acetyl residue in the steroid nucleus [6].

The characteristics of the PMR spectra of the ecdysteroid (II) and of 2-deoxyecdysterone (I) were close, with the exception of the chemical shifts of the resonance lines of the protons at C-3 and C-19. In the PMR spectra of compounds (II) and (I) (the corresponding values are given in parentheses), signals at 5.03 (4.14) ppm and 1.02 (1.07) ppm corresponded to

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 60-62, January-February, 1985. Original article submitted April 12, 1984.

 0009-3130/85/2101-0056$09.50