gem-dimethyl group); 1076, 3100-3600 (band with a maximum at 3450) (OH); 1240, 1727 (OAc). PMR spectrum (ppm): 0.77 (3H, s, CH_3 at C-10), 0.83 (3H, s), 0.85 (3H, s) [$C(CH_3)_2$]; 1.42 (3H, s, CH_3 at C-8); 1.88 (3H, s, $CH_3\overset{\overset{O}{\|}}{C}O$), 3.45 (2H, t, J = 6 Hz, CH_2O). Found, %: C 73.10; H 11.09. $C_{18}H_{32}O_3$. Calculated, %: C 72.93; H 10.88.

b) At −65 to −70°C, a mixture of ozone and oxygen was passed through a solution of 100 mg of the oxide (I) in 10 ml of methanol until the ozone broke through. The ozone was displaced by nitrogen and the mixture was allowed to assume room temperature. Then 55 mg of KBH_4 was added to it and the resulting mixture was boiled under reflux for 2 h. After working up in the usual way, 81 mg of a neutral fraction and 15 mg of an acid fraction were obtained. Recrystallization of the neutral fraction from a mixture of petroleum ether and diethyl ether gave 60 mg (53%) of 8α-acetoxybicyclohomofarnesan-12-ol (VII), with mp 83-84°C.

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SYNTHESIS OF (+)-DRIM-8-EN-11-OIC ACID

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A four-stage synthesis of (+)-drim-8-en-11-oic acid (IX) from norambreinolide (II) has been developed. The latter was converted by boiling with ethanolic sulfuric acid into a mixture of the methyl esters of bicyclohomofarnes-7- and -8-enoic acids which, on reaction with methyllithium, gave a mixture of 12-methyl-14,15,16-trinorlabd-7- and -8-en-12-ols. The alcohol with the Δ^8 double bond was dehydrated with p-toluenesulfonic acid to 11-methyl-14,15,16-trinorlabd-8,11-diene, the ozonization of which yielded (+)-drim-8-en-11-oic acid.

No few methods of synthesizing drimane sesquiterpenoids, among which there are valuable biologically active substances with various actions, have been described [1, 2]. The majority of these methods are multistage and inefficient; in addition, many of them lead to racemic products. The further search for convenient methods of obtaining the sesquiterpenoids therefore remains an urgent problem. Convenient starting compounds for the synthesis of drimane sesquiterpenoids are labdane diterpenoids, some of which are fairly readily available substances.

The aim of the present work was the synthesis of drim-8-en-11-oic acid (IX) from norambreinolide (II) — a product of the breakdown of sclareol (I) obtained industrially.

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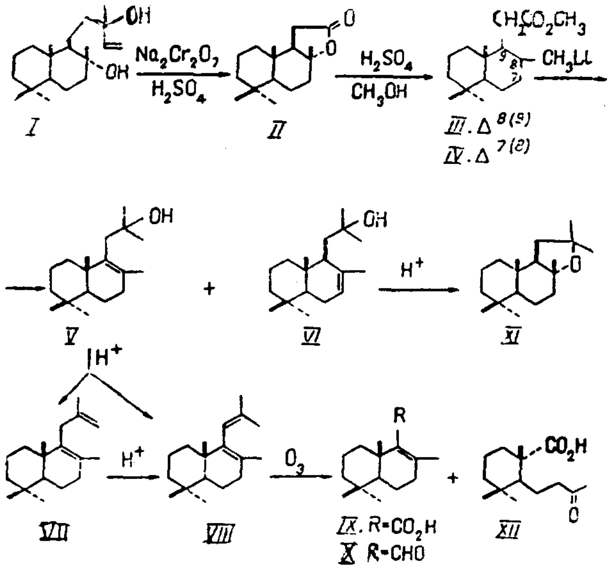
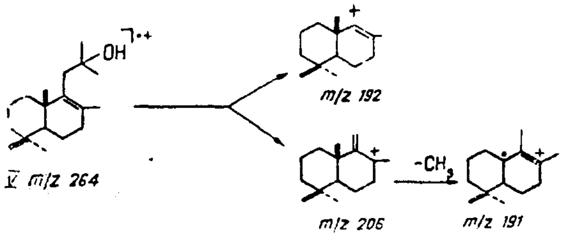


By a known method [4], a mixture of the methyl esters (III) and (IV) in a ratio of 2:1 was obtained from norambreinolide (II). An attempt to isomerize the ester (IV) into the thermodynamically more stable ester (III) by boiling with p-toluenesulfonic acid in benzene was unsuccessful. Therefore, the mixture of esters (III) and (IV) was subsequently converted with 90% yield into a mixture of the unsaturated alcohols (V) and (VI), which were separated by column chromatography on silica gel.

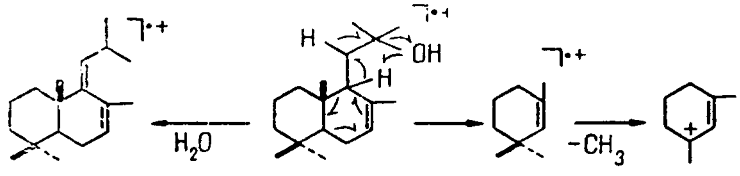
The least polar fraction eluted from the column consisted of a crystalline substance with the composition $C_{18}H_{32}O$, the structure of which was shown on the basis of spectral characteristics. Its IR spectrum contained maxima characteristic for a tertiary hydroxy group (1120, 3520, and 3600 cm^{-1}) and for a gem-dimethyl group (1370, 1380 cm^{-1}). The PMR spectrum showed the singlet signals of three methyl groups at quaternary carbon atoms, of one at an olefinic carbon atom (1.58 ppm), and of two at a carbinol carbon atom (1.22 and 1.26 ppm), and the multiplet signal of a methylene group (2.34 ppm). In the mass spectrum of this compound the maximum peak was that of an ion with m/z 191. It also contained strong peaks with m/z 206 (54%) and 192 (19%), the presence of which confirmed the structure of the compound under investigation and, especially, its side chain. A possible route of their formation is shown in the scheme given below.



The presence of peaks of ions with m/z 137, 123, and 129 agreed with a bicyclic structure for the substance under investigation. The combination of facts given above led to the structure of 12-methyl-14,15,16-trinorlabd-8-en-12-ol (V) for the alcohol under investigation.

The more polar liquid chromatographic fraction was an individual substance according to TLC which was unstable and underwent partial change even in the process of determining its physical and spectral characteristics. According to the results of mass spectrometry and elementary analysis, this substance had the same composition as the unsaturated alcohol (V). Its IR spectrum contained maxima characteristic for a tertiary hydroxy group (1125, 3490, 3610 cm^{-1}) and a gem-dimethyl group (1360 and 1380 cm^{-1}) and for a trisubstituted double bond (860, 1660, 3020 cm^{-1}). In its PMR spectrum there were the signals of three methyl groups at quaternary carbon atoms, of two at a carbinol carbon atom (1.22 ppm), and of one at a double bond (1.71 ppm), and the signal of one vinyl proton at 5.43 ppm. The mass spectrum of this compound differed substantially from that of the alcohol (V). Thus, the molecular ion with m/z

264 had a very low value (2%). An intense peak was that of an ion with m/z 246, formed as the result of the dehydration of the initial substance. Since the dehydration of alcohols under the action of electron impact takes place mainly in the manner of 1,3- and 1,4-eliminations [6], the presence of a proton on the tertiary carbon atom at C-9 would favor this process. The mass spectrum of the compound under investigation also had the peaks of ions with m/z 123, 124, and 109 formed in a retro-Diels-Alder cleavage of ring B, the pathway of the formation of which shown in the scheme given below.



m/z 246 VI m/z 264 m/z 124 m/z 100

The facts mentioned agree with the structure of 12-methyl-14,15,16-trinorlabd-7-en-12-ol (VI) for the compound under investigation. The dehydration of alcohol (V) by boiling with p-toluenesulfonic acid in benzene for 30 min formed a mixture of isomeric hydrocarbons (VII) and (VIII), which were separated by chromatography on a column of silica gel impregnated with silver nitrate. A hydrocarbon containing, according to IR spectroscopy, a trisubstituted double bond (845, 1650 cm^{-1}) as the only functional group was eluted from the column first. Its PMR spectrum contained singlet signals of three methyl group at quaternary carbon atoms and of three methyl groups at double bonds, and a singlet signal of a vinyl proton at C-11 (5.58 ppm). The facts mentioned agree with the structure of 12-methyl-14,15,16-trinorlabda-8,11-diene (VIII) for this substance.

A hydrocarbon with the structure (VII) was the second substance eluted from the column. Its structure followed from its IR spectrum which contained strong bands of an exomethylene double bond (890, 1640, 3080 cm^{-1}) and of a gem-dimethyl group (1370, 1390 cm^{-1}). In its PMR spectrum there were three-proton singlet signals of three methyl groups at quaternary carbon atoms and of two methyl groups at double bonds (1.48 and 1.73 ppm), and the singlet signals of two vinyl protons at 4.59 and 4.73 ppm.

Under the action of an acid, the hydrocarbon (VII) isomerized into hydrocarbon (VIII). Thterefore if the dehydration of alcohol (V) was performed with a larger amount of p-TSA and for a longer time, the sole dehydration product would be hydrocarbon (VIII).

The dehydration of alcohol (VI) under the same conditions as for alcohol (V) led mainly to the known oxide compound (XI) which we have obtained previously [7]. The ozonation of hydrocarbon (VIII) in ethyl acetate in the presence of pyridine led to a mixture of neutral and acidic products in a ratio of 1:2. The products present as components of the neutral fraction were unstable, and on standing or in chromatography they were partially converted into products into products that were present in the acid fraction. This shows that the neutral fraction apparently contained aldehydes. The acid fraction of the product of the ozonization of hydrocarbon (VIII) consisted of two substances, which were separated by column chromatography on silica gel. The less polar of them, with the composition $C_{15}H_{24}O_2$, mp 137-138°C, contained in its molecule, judging from its IR spectrum, an α,β-unsaturated carboxy group (1640, 1680 cm^{-1}). In its PMR spectrum there were three-proton singlet signals of methyl groups attached to quaternary carbon atoms at 0.86 and 0.89 ppm [$C(4)-(CH_3)_2$] and 1.23 ppm [$C(10)-CH_3$], the signal of a methyl group on a double bond at 1.73 ppm [$C(8)-CH_3$], and a one-proton signal of an acidic proton at 10.53 ppm. THe facts given, taken together, led to the structure drim-8-en-11-oic acid (IX) for the compound under investigation. It must be mentioned that racemic drim-8-en-11-oic acid (IX) has been obtained by the cyclization of farnesylic acid [8, 9].

The second component of the acid fraction of the product of the ozonolysis of hydrocarbon (VIII) possessed structure (XII), whcih followed from its IR and PMR spectra. In its IR spectrum there were maxima characteristics for carboxy and methyl ketone groups (1160, 1270, 1680, 1770 cm^{-1}), and its PMR spectrum contained three-proton singlet signals of three methyl groups at quaternary carbon atoms and of a methyl ketone group at 2.01 ppm, a two-proton multiplet of a methylene group adjacent to a carbonyl group (2.36 ppm), and the signal of a carboxy group (11.55 ppm).

The compound under investigation was formed as the result of the ozonolytic cleavage of the hydrocarbon at both double bondes, at C-8 and C-11. A compound with the structure (XII) has been mentioned in the literature [10], but its constants were not given.

With a change in the conditions of ozonolysis, the qualitative composition of the product of the ozonolysis of the hydrocarbon (VIII) also changed. Ozonolysis in methanol—methylene chloride (2:1) in the presence of pyridine led to a neutral fraction (44%) consisting of the very unstable aldehyde (X) which was readily oxidized in the air to the acid (IX). The acid fraction (55%) mainly contained the acid (XII). The acid (XII) was the main product of ozonolysis if this was carried out in ethyl acetate in the presence of 0.1% of pyridine.

Thus, we have developed a four-stage synthesis of optically active drim-8-en-11-oic acid (IX) with 16% yield from the readily available norambreinolide (II).

EXPERIMENTAL

Melting points were determined on a Boëtius instrument. Specific rotations were measured in chloroform on a type CM polarimeter. IR spectra were recorded in carbon tetrachloride on a Specord 71-IR spectrophotometer. PMR spectra were recorded in carbon tetrachloride on a Tesla BS-467 instrument (60 MHz) with TMS as internal standard (the signals are given in the δ scale). Mass spectra were obtained on a MKh-1310 instrument with a system for direct introduction to the ion source. For column chromatography we used type L silica gel (Czechoslovakia) with a grain size of 40-100 μm, and also the same silica gel impregnated with silver nitrate (SGSN). For thin-layer chromatography (TRLC) we used silica gel LS 5/40 μm containing 13% of gypsum and also the same silica gel impregnated with silver nitrate on glass plates, which were sprayed with concentrated sulfuric acid and with a 4% aqueous solution of $KMnO_4$, respectively.

Preparation of the Methyl Esters (III) and (IV). A solution of 20 g (80 mmole) of norambreinolide (II) in 380 ml of absolute methanol was charged into a round-bottomed flask fitted with a reflux condenser, and 14 ml of concentrated sulfuric acid was carefully added. The reaction mixture was boiled under reflux for 96 h, in agreement with [4], and then part of tthe methanol was distilled off in vacuum and the residue was dissolved in ether; this solution was washed with water, with saturated sodium bicarbonate solution, and with water again and was dried and evaporated. This gave 21.1 g of a liquid mixture of the esters (III) and (IV). Its IR spectrum was identical with the spectrum of a sample of the esters (III) and (IV) [11].

Preparation of a Mixture of 12-Methyl-14,15,16-trinorlabd-8-en-12-ol (V) and 12-Methyl-14,15,16-trinorlabd-7-en-12-ol (VI). In an atmosphere of nitrogen, with stirring and the maintenance of a temperature of 0°C, a solution of 925 mg (3.5 mmole) of the mixture of isomeric esters (III) and (IV) in 30 ml of absolute diethyl ether was added to 11 ml of a 0.97 N solution of methyllithium in 30 ml of absolute diethyl ether. Then the temperature of the reaction mixture was gradually, over half an hour, raised to 25°C and it was stirred at this temperature for another 1 h. The resulting solution was acidified with 10% sulfuric acid, and the ethereal layer was separated off and was washed with water, saturated sodium bicarbonate solution,and water again to neutrality, and was dried and evaporated in vacuum. This gave 855 mg of a product (90%) which was chromatographed on a column containing 80 g of silica gel.

Petroleum ether—diethyl ether (19:1) eluted 0.33 g of the alcohol (V), mp 73-73.5°C (from petroleum ether) $[\alpha]_D^{20}$ + 36° (c 5.1; $CHCl_3$). IR spectrum (cm^{-1}): 1120, 3520, 3600 (OH); 1370, 1380 $[C(CH_3)_2]$. PMR spectrum (ppm): 0.84 (3H, s), 0.86 (3H, s) $[(CH_3)_2$ at C-4], 0.99 (3H, s, CH_3 at C-10), 1.22 (3H, s), 1.25 (3H, s) $[(CH_3)_2$ at C-12], 1.58 (3H, s, CH_3 at C-8), 2.34 (2H, m, CH_2-11). Mass spectrum m/z (%): 264 (M^+, 6), 249(2), 231(3), 207(9), 206(54), 201(3), 192(19), 191(100), 190(4), 175(6), 162(17), 151(4), 150(16), 149(11), 147(5), 144(3), 136(12), 135(12), 134(19), 133(3), 132(6), 123(4), 122(9), 121(10), 120(35), 119(4), 118(16), 110(4), 109(18), 108(6), 107(16), 96(7), 95(6), 94(5), 93(3), 83(3), 82(8), 80(12), 79(3), 76(6), 69(11), 67(12), 59(4), 58(7), 56(6), 55(4), 54(8), 53(4), 43(3), 42(9), 40(7). Found, %: C 81.89; H 12.32. $C_{18}H_{32}O$. Calculated, %: C 81.75; H 12.20.

The same solvent then eluted from the column 0.34 g of a mixture of the alcohols (V) and (VI), and petroleum ether—diethyl ether (47:3) eluted 0.14 g of the liquid alcohol (VI), $[\alpha]_D^{20}$ −22° (c 5.6; $CHCl_3$). IR spectrum (cm^{-1}): 850, 1660, 3020, $\left(>C=C<^{H}\right)$, 1360, 1380 $[C(CH_3)_2]$. 1125, 3490, 3610 (OH), PMR spectrum (ppm): 0.71 (3H, s), 0.84 (3H, s) $[(CH_3)_2$ at C-4], 0.85 (3H, s, CH_3 at C-10), 1.22 [6H, s, $(CH_3)_2$ at C-12], 1.71 (3H, s, CH_3 at C-8), 1.52 (2H, d, J = 5 Hz, CH_2-11), 5.43 (1H, br.s, H-7). Mass spectrum, m/z (%): 264 (M^+, 2), 242(16), 241(82), 231(11), 205(4), 204(3), 203(10), 192(3), 191(23), 190(27), 189(13), 177(4), 176(5), 175(25), 163(7), 162(4), 161(10), 150(6), 149(6), 148(4), 147(8), 137(9), 136(8), 135 (11), 134(4), 133(13), 125(13), 124(31), 123(18), 122(34), 121(22), 120(10), 119(30), 111(4), 110(10), 109(95), 108(8), 107(31), 106(8), 105(27), 97(6), 96(6), 95(23), 94(6), 93(23), 92(5), 91(27), 85(5), 83(24), 82(100), 81(38), 80(7), 79(23), 77(14), 71(8), 70(5), 69(41), 68(6), 67(27), 65(4), 59(7), 58(95), 56(23), 50(44). Found, %: C 81.75; H 12.09. $C_{18}H_{32}O$. Calculated, %: C 81.75; H 12.20.

Dehydration of the Alcohol (V). A. A solution of 100 mg (0.38 mmole) of the alcohol (V) in 10 ml of dry benzene was treated with 3 mg (0.0017 mmole) of p-toluenesulfonic acid (p-TSA), and the solution was boiled in a Dean-Stark apparatus for 1 h. The reaction mixture was cooled and, after the addition of an equal volume of ether, it was washed with water, with sodium bicarbonate solution, and with water again and was dried, filtered, and evaporated in vacuum. The residue (95 mg), consisting, according to TLC on $SiO_2 \cdot AgNO_3$ of an individual substance, was chromatographed on a column containing 2 g of silica gel. Petroleum ether eluted 84 mg of the hydrocarbon (VIII), n_D^{20} = 1.5100, $[\alpha]_D^{20}$ + 167° (c 12; $CHCl_3$), spectrum (cm^{-1}); 845, 1650 $\left(>C=C<^{H}\right)$, 1366, 1380 $[C(CH_3)_2]$. PMR spectrum (ppm): 0.84 (3H, s), 0.89 (6H, s) $[(CH_3)_2$ at, C-4 and CH_3 at C-10], 1.45 [6H, s, $(CH_3)_2$ at C-12], 1.74 (3H, d, J = 1 Hz, CH_3 at C-8), 5.58 (1H, br.s., H-11). Found, %: C 87.68; H 12.24. $C_{18}H_{30}$. Calculated, %: C 87.73; H 12.27.

B. Under the conditions described in experiment A, 100 mg (0.38 mmole) of the alcohol (V) was dehydrated by boiling in 10 ml of benzene with 1 mg of p-TSA for 30 min. This gave 98 mg of a product, which was chromatographed on a column containing 3 g of silica gel impregnated with silver nitrate. Petroleum ether eluted successively 50 mg of the hydrocarbon (VIII), 26 mg of the hydrocarbons (VIII) and (VII), and 15 mg of hydrocarbon (VII), $[\alpha]_D^{20}$ + 82.2° (c 3.7; $CHCl_3$). IR spectrum (cm^{-1}): 890, 1640, 3680 ($>C=CH_2$), 1370, 1390 $[C(CH_3)_2]$. PMR spectrum (ppm): 0.84 (3H, s), 0.89 (3H, s) $[(CH_3)_2$ at C-4], 0.94 (3H, s, CH_3 at C-10), 1.48 (3H, s, CH_3 at C-13), 1.73 (3H, s, CH_2 at C-8), 2.61 (2H, br.s, CH_2-11), 4.59 (s) and 4.73 (s) (2H, $>C=CH_2$).

Dehydration of the Alcohol (VI). A solution of 100 mg (0.38 mmole) of the alcohol (VI) in 10 ml of dry benzene was treated with 3 mg (0.17 mmole) of p-toluenesulfonic acid, and the resulting solution was boiled in an Dean-Stark apparatus until the reaction was complete (30 min; monitoring by TLC). The reaction mixture was cooled and, after the addition of an additional volume of ether, it was washed with water, with sodium bicarbonate solution, and again with water, and it was dried, filtered, and evaporated in vacuum. The residue (96 mg) was chromatographed on 2 g of silica gel. Petroleum ether eluted 46 mg of a mixture of 4 hydrocarbons (monitoring by TLC on SGSN). Then petroleum ether–ethyl acetate (19:1) eluted from the column 42 mg of the oxide (XI) with mp 68-69°C from CH_3CN, which gave no depression of the melting point with an authentic sample of the oxide (XI). Their IR spectra and R_f values in TLC on silica gel were identical [7].

Ozonation of the Hydrocarbon (VIII). At −45 to −55°C, a current of ozonized oxygen (the productiviyt of the ozonizer being 1.8 g of O_3 per hour) was passed through a solution of 1.07 g (4.37 mmole) of the hydrocarbon (VIII) in 110 ml of ethyl acetate and 1 ml of pyridine until the initial substance had disappeared (monitoring by TLC). The reaction mixture was allowed to warm up to room temperature and was washed with 10% sulfuric acid solution and with water, and then with 2% KOH solution and again with water to neutrality, and was dried and the ether was distilled off. This gave 366 mg of a neutral fraction. The aqueous layer was acidified with 10% sulfuric acid and the acid liberated was extracted with the ether. The extract was washed with water, dried, and filtered and the solvent was evaporated off, leaving 630 mg of an acid fraction which was chromatographed on a column containing 20 g of silica gel.

Benzene–ethyl acetate (9:1) eluted 295 mg (28.8%) of crystalline drim-8-en-11-oic acid (IX), mp 137-138°C (from petroleum ether), $[\alpha]_D^{20}$ + 84° (c 4.0; $CHCl_3$). IR spectrum (cm^{-1}): 1640, 1680 ($>C=C-CO_2H$). PMR spectrum (ppm): 0.86 (3H, s), 0.89 (3H, s) $[(CH_3)_2$ at C-4], 1.23 (3H, s, CH_3 at C-10), 1.73 (3H, s, CH_3 at C-8), 10.53 (1H, s, CO_2–H). Mass spectrum m/z (%): 236 (M^+, 12), 235(64), 222(2), 221(14), 220(91), 218(3), 219(7.3), 206(3), 207(3), 203(14), 202(100), 193(3), 192(14), 191(7), 190(46), 189(11), 188(3), 179(7), 178(6), 175(5), 174(28), 167(4), 166(10), 165(19), 163(4), 162(18), 161(13), 152(18), 151(17), 150(92), 146(23), 140 (10), 138(91), 134(23), 133(10), 132(17), 130(10), 127(5), 125(14), 124(91), 123(13), 122(91), 121(13), 120(50),119(7), 118(28), 117(5), 116(10), 115(5), 114(10), 113(23), 110(14), 109(37), 108(50), 107(14), 106(59), 105(10), 104(50). Found, %: C 76.57; H 10.09. $C_{15}H_{24}O_2$. Calculated, %: C 76.22; H 10.23.

Then the same solvent eluted from the column 334 mg (32%) of the keto acid (X), mp 48-49°C, $[\alpha]_D^{20}$ + 15.6° (c 13.3; $CHCl_3$). IR spectrum (cm^{-1}): 1630, 1720, 1270 ($CH_3C{=}O$, Co_2H), 1160 ($CH_3C{=}O$). PMR spectrum (ppm): 0.87 (3H, s), 0.90 (3H, s) [$(CH_3)_2$ at C-5], 1.18 (3H, c, CH_3 at C-1), 2.01 (3H, s, $CH_3{-}\underset{|}{C}{=}O$), 2.36 (2H, m, $-CH_2-CO-$), 11.55 (1H, s, $-CO_2H$). Found, %: C 70.04; H 10.15. $C_{14}H_{24}O_3$. Calculated, %: C 69.96; H 10.06.

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TWO NEW TRITERPENE GLYCOSIDES FROM THE HOLOTHURIAN *Duasmodactyla kurilensis*

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UDC 547.996:593.96

Two new glycosides have been isolated from the total triterpene glycosides of the holothurian *Duasmodactyla kurilensis*: kurilosides A (III) and C (IV). It has been established that (III) is 16α-acetoxy-3β-{[O-β-D-glucopyranosyl-(1 → 4)-O-β-D-quinovopyranosyl-(1 → 2)]-[O-(3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-O-(6-O-(sodium sulfato)-β-D-glucopyranosyl)-(1 → 4)]-β-D-xylopyranosyloxy}-4,4,14-trimethylpregen-9(11)-en-20-one, while the minor glycoside (IV) is 16α-acetoxy-3β-{O-β-D-quinovopyranosyl-(1 → 2)-[O-(3-O-methyl-β-D-glucopyranosyl-(1 → 3)-O-(6-O-(sodium sulfato)-β-D-glucopyranosyl)-(1 → 4)]-β-D-xylopyranosyloxy}-4,4,14-trimethylpregn-9(11)-en-20-one.

Previously, having started a study of triterpene glycosides from the Far Eastern holothurian *Duasmodactvla kurilensis* Levin (Phyllophoridae, Dentrochirots), we reported the isolation of two new genins – kurilogenin (I) and nemogenin (II) [1, 2]. Continuing our investigation, we have isolated glycosides which we have called kurilosides A (III) and C (IV) and have determined their structures.

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