cm. Methanol was used as solvent. For amination, two drops of freshly distilled piperidine or morpholine was added to 3 ml of a methanolic solution of the lactone.

SUMMARY

1. It has been established that the presence of an α-oriented hydroxy group at C_8 in guaianolides promotes the stereospecificity of the amination of an exomethylene bond conjugated with a γ-lactone grouping.

2. It has been shown that the addition of morphiline and piperidine to the exomethylene bond of the lactone ring of a guaianolide containing an α-orientated hydroxy group at C_8 takes place with the preferential formation of the 11S isomer.

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CYCLIZATION AND REARRANGEMENT OF DITERPENOIDS. III. SYNTHESIS OF ISOAGATHOLACTONE AND METHYL SPONGIA-13(16),14-DIEN-19-OATE

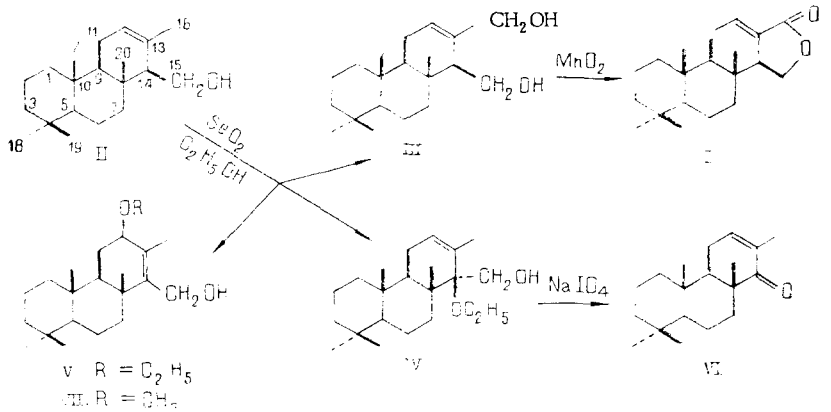
P. F. Vlad and N. D. Ungur

UDC 547.596/599+547.7/8

The synthesis of isoagatholactone has been effected by the successive oxidation of (14R)-isoagath-12-en-15-ol with selenium dioxide and manganese dioxide. Methyl spongia-13(16),14-dien-19-oate has been obtained by the cyclization of methyl lambertianate with 100% sulfuric or fluorosulfonic acid.

Isoagatholactone (I) [1] is the first representative of a group of tricyclic isoagathane diterpenoids detected in a natural source. At the present time, monotypical syntheses of this compound [2], of its racemic form [3], and of its antipode [4] have been performed. However, they have involved several stages and have given low yields of the lactones.

The synthesis of isoagatholactone (I) from (14R)-isoagath-12-en-15-ol (II) — its probably biogenic precursor — including as the main stage the oxidation of the C_{16}-methyl group of the alcohol (II), would be shorter and more effective. As is well known [5], the alcohol (II) is one of the products of the cyclization of a whole series of labdane diterpenoids.



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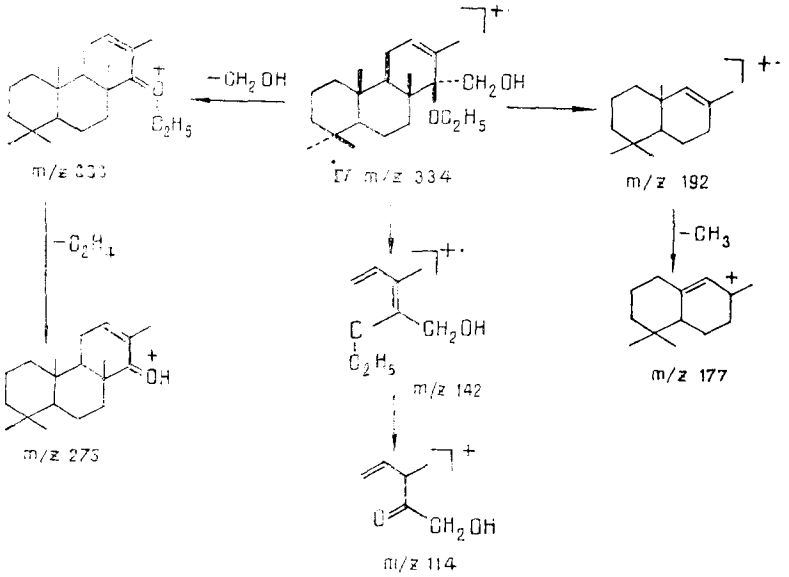
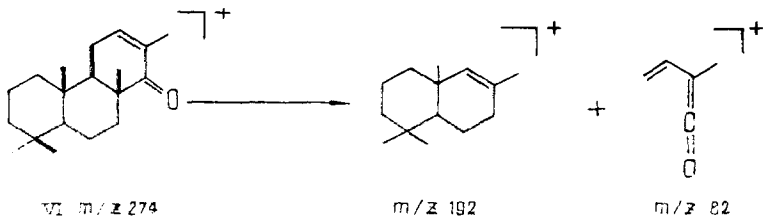
We have succeeded in performing such a synthesis of isoagatholactone (I) in two stages. The oxidation of the alcohol (II) with selenium dioxide in ethanol formed a mixture of (14R)-isoagath-12-ene-15,16-diol (III), 14-ethoxyisoagath-12-en-15-ol (IV), and 12-ethoxyisoagath-13-3n-15-ol (V), which was separated by chromatography. The diol (III) was identified by comparing its physicochemical characteristics with those given by Cimino et al. [1]. Its oxidation with manganese dioxide [2, 4] has given isoagatholactone (I).

The structure of the hydroxy ether (IV) followed from its spectral characteristics. Its IR spectrum contained maximum characteristic for hydroxy and ether groups and of a trisubstituted double bond, and the PMR spectrum contained the signal of four methyls at quaternary carbon atoms and one at a double bond, of a vinyl proton, and of the AB system of the C_{15}-hydroxymethyl group upon which the two proton signal of a methylene group linked to oxide oxygen was superposed. The signal of the methyl radical of the ether group was superposed on the signals of the other methyls and was not observed in the spectrum. However, judging from the integral curve the substance contained six methyl groups. Since the introduction of a hydroxyethyl group into the molecule of the alcohol (II) led to the descreening of its methyl group at C_8, the ether group must have the β configuration. The structure of the hydroxy ether (IV) was confirmed by its mass spectrum, which contained the peaks of ions with m/z 334, 303, 275, 192, 177, 142, 114, and 69, a possible pathway for the formation of which is shown in scheme 1.



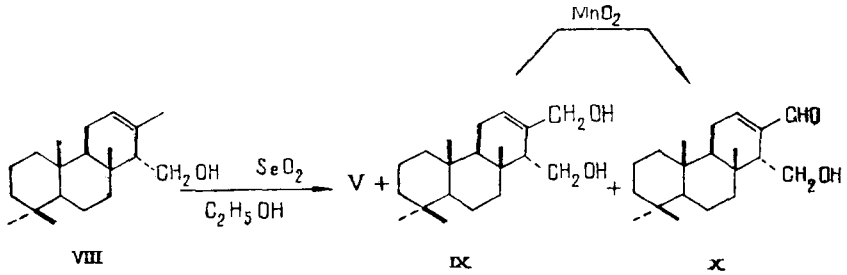
Compound (IV) reacted with sodium periodate, giving the ketone (VI). According to its IR spectrum, compound (VI) contained a keto group conjugated with a double bond and, according to its PMR spectrum, there were four methyl groups at quaternary carbon atoms and one at a double bond in its molecule. The structure of the ketone (VI) was confirmed by its mass spectrum, which contained the intense peak of an ion with m/z 82 formed as the result of the retrodiene breakdown of the molecular ion, as shown in scheme 2.



Compound (V) is isomeric with the hydroxy ether (IV). Judging from their IR and PMR spectra they contain the same functional groups, and the difference between them amounts to the fact that in the hydroxy ether (V) the double bond is tetrasubstituted and occupies the C_{13}—C_{14} position and the hydroxyethyl group is present at C_{12}.

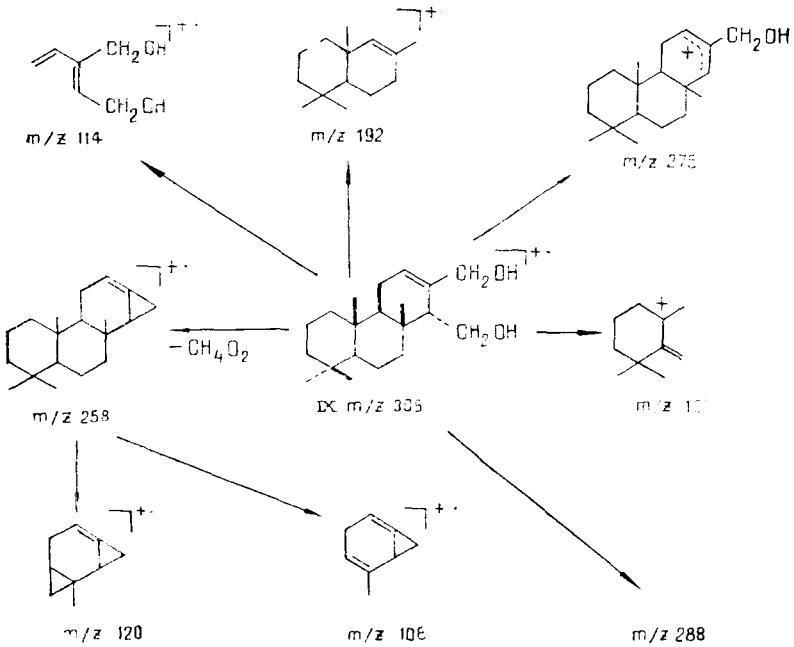
If the oxidation of the alcohol (II) with selenium dioxide was performed in methanol, in addition to the diol (III) only 12-methoxyisoagath-13-en-15-ol (VII) was formed. Its spectral characteristics were similar to those for compound (V).

It must be mentioned that an attempt to oxidize the alcohol (II) to the diol (III) with selenium dioxide had been made previously [4] but proved unsuccessful. The authors concerned [4] explained their lack of success by the fact that the C_{16}-methyl group of the alcohol (II) is spatially screened by the hydroxymethyl group. We have established that this is not the case, and that the course of the reaction is substantially affected by the purity of the oxidant. The reaction takes place well with selenium dioxide that has been freshly sublimed in vacuum.



VIII IX X

When the epimer of the alcohol (II) at C_{14} – (14S)-isoagath-12-en-15-ol (VIII), which is also one of the products of the acid cyclization of labdanoids [5] – was oxidized with selenium dioxide, the main reaction product proved to be (14S)-isoagath-12-ene-15,16-diol (IX). In addition to this, a small amount of the hydroxy ether (V) and of (14S)-15-hydroxyisoagath-12-en-16-al (X) was obtained. The structure of the diol (IX) followed from its spectral characteristics, which were close to those for its epimer (III) (see the Experimental part). In particular, the most informative direction of its mass-spectrometric fragmentation is shown in scheme 3.



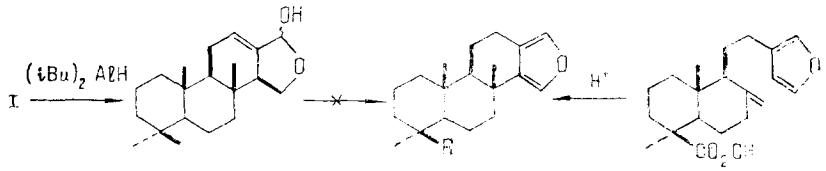
The structure of the hydroxy aldehyde (X) also followed from its spectral characteristics and was confirmed by its formation as the result of the oxidation of the diol (IX) with manganese dioxide. In contrast to the diol (III), here the epimer of the isoagatholactone (I) at C_{14} was not formed since, because the great remoteness of the aldehyde and hydroxymethyl groups, the aldehyde (X) cannot exist in the form of cyclic semiacetal.

A substance close in structure to isoagatholactone (I) is spongia-13(16),14-diene (XI), which has recently been isolated [6] together with compounds related to (XII) and (XIII) from marine sponges in which isoagatholacetone (I) had also been detected previously. Apparently, all these diterpenoids are formed from one and the same biogenetic precursor.

As is well known [7], on reduction with diisobutylaluminum hydride, γ-lactones are converted into the corresponding furans. However, an attempt to synthesize spongia-13(6),14-diene (XI) by reducing isoagatholactone (I) with this reagent was unsuccessful. When the reaction was performed in tetrahydrofuran at –40°C [8] isoagatholacetone gave a complex mixture of substances in which spongia-13(16),14-diene (XI) did not appear, and under milder condi-

tions (toluene, −70°C [9]) (14R)-15,16-epoxyisoagatho-12-en-16-ol (XIV) was obtained. The dehydration of the latter with p-toluenesulfonic or phosphoric acid also led to a complex mixture of substances not containing spongia-13(16),14-diene. The structure of the lactone (XIV) was shown spectrally. Its IR spectrum contained maxima characteristic for a hydroxy group and an oxide ring. Its PMR spectrum contained the signals of four methyls at quaternary carbon atoms, of a vinyl proton, of a methylene group bound to ethereal oxygen, and of a proton at a carbon atom bearing a semiacetal hydroxy.

We synthesized methyl spongia-13(16),14-diene-19-oate (XV) by cyclizing methyl lambertianate (XVI) [10] with 100% sulfuric acid in nitromethane—toluene (1:1) [11] or with fluorosulfonic acid—nitropropane. Its physicochemical characteristics coincided with those given in the literature [6]



XIV

XI. R = CH_3
XII. R = CHO
XIII. R = CO_2H
XV. R = CO_2CH_3

XVI

The synthesis performed is simultaneously a synthesis of compounds (XI-XII), since they have been obtained previously from the ester (XV) [6].

EXPERIMENTAL

Melting points were determined on a Boëtius heated stage. Specific rotations were measured in a chloroform on a Polamat S polarimeter. IR spectra were recorded in CCl_4 on a Specord 741R spectrometer, PMR spectra in CCl_4 on a Tesla BS467 instrument with TMS as internal standard, and mass spectra on a MKh-1320 spectrometer with a system for the direct introduction of the sample into the ion source at an ionizing energy of 70 eV. GLC analysis was performed on Tsvet-106 chromatograph with a 1 m × 3.5 mm glass column filled with 5% of SE-30 on Chromaton N-AW-DMCS (0.16-0.20 mm) at a rate of flow of helium of 45 ml/min, a column temperature of 210°C and a evaporator temperature of 230°C with a FID.

Solutions of the substances in organic solvents were dried with anhydrous sodium sulfate. The petroleum ether used had bp 44-60°C. Silica gel L40/100 μ was employed for column chromatography, and LS 5/40 μ (Czechoslovakia) for TLC. The plates for TLC were dried for 3 days at room temperature. Spots were revealed with concentrated sulfuric acid followed by heating the plates with the flame of a gas burner.

Oxidation of (14R)-Isoagath-12-en-15-ol (II) with Selenium Dioxide. A. A solution of 145 mg of the alcohol (II) in 1.5 ml of ethanol was treated with 24 mg of selenium dioxide, and the mixture was boiled under reflux for 60 h and was then diluted with water and extracted with ether; the extract was washed with saturated $(NH_4)_2S$ solution and with water, and was dried, and the solvent was distilled off in vacuum. The residue (157 mg) was chromatographed on a column containing 3.2 g of silica gel. Gradient elution with petroleum ethyl—ethyl acetate gave four fractions: 1) 10 mg of the initial alcohol (II); 2) 28.5 mg (18.3%) of a crystalline compound (IV) with mp 148-149°C (from CH_3CN); $[\alpha]_D^{24}$ +71.2° (c 1.1). Found, %: C 78.83; H 11.42. $C_{22}H_{38}O_2$. Calculated, %: C 78.99; H 11.45. IR spectrum (cm^{-1}): 1120 (OCH_2-H_5); 1075, 3430 (band), 3615 (OH); 1672 (trisubstituted double bond). PMR spectrum (δ, ppm): singlets of 3 H each at 0.77 (C_{10}—CH_3), 0.81 and 0.88 (C_4—CH_3), 0.92 (C_8—CH_3), and 1.75 (C_{13}—CH_3); 2.51 (br.s, 1 H, OH); 3.26 (d, H_B, J = 12 Hz); 3.65 (d, H_A, J = 12 Hz) (C_{15}—CH_2); 3.26-4.05 (m, 2 H, O—CH_2); 5.45 (br.s., 1 H, C_{12}—H). Mass spectrum, m/z (%): 334 (M^+, 9), 319 (10), 303 (41), 275 (23), 257 (4), 192 (10), 177 (13), 137 (11), 123 (13), 114 (100%), 69 (27). 3) 48.3 mg (31%) of compound (V), a viscous colorless liquid, $[\alpha]_D$ −36.1 (c. 2.5). Found, %: C 78.79; H 11.38. $C_{22}H_{38}O_2$. Calculated, %: C 78.99; H 11.45. IR spectrum (cm^{-1}): 1080, 1115 (OC_2H_5); 1000, 3445 (band), 3615 (OH). PMR spectrum (δ, ppm): 0.86 (s, 9 H, C_4— and C_{10}—CH_3); 1.08 (s, 3 H, C_8—CH_3); 1.20 (t, 3 H, J = 7 Hz, CH_3CH_2O); 1.77 (s, 3 H, C_{13}—CH_3); 3.13-3.80 (m, 3 H, C_{12}—H and C_{12}—OCH_2CH_3); 3.98 (br.s, 2 H, C_{15}—CH_2). Mass spectrum, m/z (%): 334 (M^+, 16), 319 (23, M − CH_3), 303 (100, M − CH_2OH), 275 (4), 259 (6), 191 (6), 177 (6), 159 (7), 137 (10), 119 (24), 69 (27). 4) 68.4 mg (48%) of the crystalline diol (III), mp 161-162.5°C (from petroleum ether); $[\alpha]_D^{20}$ −18.6° (c 2.3). IR spectrum (cm^{-1}):

984, 1037, 3411 (band), 3604, 3613 (OH); 1660 (>C=C<H) . PMR spectrum (δ, ppm): 0.73 (s, 3 H, C_{10}—CH_3); 0.82 (s, 3 H, C_4—CH_3); 0.87 (s, 6 H, C_4—C_8—CH_3); 3.25 (br.s, 2 H, OH groups); 3.91 (d, H_B, J = 13 Hz); 4.33 (d, H_A, J = 13 Hz) (C_{16}—CH_2); 3.71 (d, 2 H, J = 8 Hz, H_{15}—CH_2); 5.75 (br.s, 1 H, C_{12}—H). Mass spectrum, m/z (%): 306 (M^+, 8), 288 (18), 275 (12), 158 (41), 192 (100), 177 (93), 163 (11), 149 (37), 137 (37), 123 (59). According to the literature [1]: mp 159-161°C, $[\alpha]_D$ −16.5°.

B. A solution of 290 mg of the alcohol (II) in 3.5 ml of methanol was treated with 50 mg of selenium dioxide, and the mixture was boiled under reflux for 49 h. It was worked up as described above, and the product (284 mg) was chromatographed on a column containing 6 g of silica gel. Petroleum ether—ethyl acetate (9:1) eluted 172 mg of the initial alcohol (II), and the same solvents in a ratio of 17:3 eluted 47.3 mg of the liquid 12-methoxyisoagath-13-en-15-ol (VII), $[\alpha]_D^{23}$ −27.8° (C 1.2). Found, %: C 78.64; H 11.31. $C_{21}H_{36}O_2$. Calculated, %: C 78.70; H 11.32. IR spectrum (cm^{-1}): 1120, 2815 (OCH_3); 1070, 3345 (band), 3610 (OH). PMR spectrum (δ, ppm): 0.87 (s, 9 H, C_4— and C_{10}—CH_3); 0.90 (s, 6 H, C_8—CH_3); 1.70 (s, 3 H, C_{13}—CH_3); 3.25 (s, 3 H, OCH_3); 3.55 (m, 1 H, C_{12}—H); 3.93 (br.s, 2 H, C_{15}—CH_2). Mass spectrum, m/z (%): 320 (M^+, 15), 305 (16, M − CH_3), 289 (73, M − CH_2OH). Petroleum ether—ethyl acetate (4:1) eluted 50.8 mg of the diol (III) with mp 160.5-162°C, identical with the product obtained above.

Oxidation of 14-Ethoxyisoagath-12-en-15-ol (IV) with Sodium Periodate. A solution of 45 mg of the hydroxy ether (IV) in 2 ml of ethanol was treated with 1 ml of saturated K_2CO_3 solution and a solution of 280 mg of $NaIO_4$ in 1.5 ml of water. The mixture was boiled under reflux for 5 h cooled, diluted with 10 ml of water, and extracted with ether. The extract was washed with water and dried, and the solvent was distilled off. The residue was chromatographed on a column containing 1 g of silica gel. Petroleum ether—ethyl acetate (19:1) eluted 16.2 mg of 14-norisoagath-12-en-14-one (VI), mp 98-99.5°C (from CH_3CN), $[\alpha]_D^{22}$ −30.8° (c 1.2). Found, %: C 83.18; H 11.09. $C_{19}H_{30}O$. Calculated, %: C 83.15; H 11.02. IR spectrum (cm^{-1}): 1667 (conjugated ketone). PMR spectrum (δ, ppm): 0.85 (s, 3 H, C_{10}—CH_3); 0.88 (s, 3 H, C_4—CH_3); 0.98 (s, 6 H, C_4— and C_8—CH_3); 1.68 (d, 3 H, J = 2 Hz, C_{13}—CH_3); 6.42 (br.s, 1 H, C_{12}—H). Mass spectrum, m/z (%): 274 (M^+, 100), 259 (19), 241 (5), 231 (9), 192 (4), 177 (16), 163 (11), 144 (27), 136 (41), 123 (50), 109 (35), 82 (66). A mixture of the same solvents in a ratio of 9:1 eluted 22.4 mg of the initial hydroxy ether (IV).

Isoagatholactone (I). A solution of 125 mg of the diol (III) in 30 ml of CH_2Cl_2 was treated with 7 g of manganese dioxide [12] and the mixture was stirred for 36 h. Then it was filtered and the solvent was distilled off. This gave 118 mg (95.6%) of isoagatholactone (I) mp 152.5-154°C (from CH_3OH), $[\alpha]_D^{22}$ +7.8° (c 1.8). IR spectrum ($CHCl_3$, cm^{-1}): 1680, 1745 (γ-lactone the carbonyl of which is conjugated with a double bond). PMR spectrum ($CDCl_3$, δ, ppm): 0.78 (s, 3 H, C_{10}—CH_3); 0.83 (s, 3 H) and 0.88 (s, 3 H) (C_4—CH_3); 0.93 (s, 3 H, C_8—CH_3); 4.16 (dt, 2 H, J_1 = 9 Hz, J_2 = 21 Hz, C_{15}—CH_2); 6.85 (dd, 1 H, J_1 = 3 Hz, J_2 = 7 Hz, C_{12}—H). Mass spectrum, m/z (%): 302 (M^+, 12), 287 (7), 259 (2), 192 (100), 177 (48), 149 (19), 137 (27), 128 (28). According to the literature [1]; mp 152-155°C, $[\alpha]_D$ +6.3°.

Isogatholactol (XIV). With stirring at −70°C, 0.19 ml of a 27.4% solution of diisobutylaluminum hydride in hexane was added to a solution of 68 mg of the lactone (I) in 1.7 ml of dry toluene. The mixture was stirred at the same temperature for another 9 h and then was acidified with 10% H_2SO_4 and extracted with wther. The extract was washed with water, with saturated sodium bicarbonate solution, and again with water, and was dried, and the solvent was distilled off. The residue (61 mg) was chromatographed on a column containing 1.8 g of silica gel. Petroleum ether—ethyl acetate (19:1) eluted 25.4 mg of the initial isoagatholactone (I), and a mixture of the same solvents in a ratio of 17:3 eluted 23 mg of isoagatholactol (XIV) with mp 147-149°C (from petroleum ether), $[\alpha]_D^{22}$ +43.6° (1.4). Found, %: C 78.74; H 10.62. $C_{20}H_{32}O_2$. Calculated, %: C 78.90; H 10.59. IR spectrum ($CHCl_3$, cm^{-1}): 3440 (band), 3600 (OH). PMR spectrum (δ, ppm): singlets of 3 H each at 0.82 (C_{10}—CH_3), 0.88 and 0.90 (C_4—CH_3), and 1.21 (C_8—CH_3); 3.67 (m, 3 H, C_{15}—CH_2 and C_{16}—H); 5.75 (br.s, 1 H C_{12}—H). Mass spectrum, m/z (%): 304 (M^+, 29), 289 (23), 274 (24), 259 (10), 237 (13), 192 (100), 177 (60). Ether eluted from the column 12 mg of the diol (III) with mp 161-162°C.

Oxidation of (14S)-Isoagath-12-en-15-ol (VIII) with Selenium Dioxide. A solution of 580 mg of the alcohol (VIII) in 6 ml of ethanol was treated with 96 mg of selenium dioxide, and the mixture was boiled under reflux for 96 h. Then it was worked up as described above. The product (591 mg) was chromatographed on a column containing 13.5 g of silica gel. Petroleum ether—ethyl acetate (19:1) eluted 353.8 mg of the initial alcohol (VIII). A mixture of the

same solvents in a ratio of 13:1 eluted 17.2 mg of the hydroxy ether (IV), 10.7 mg of a mixture of it with the hydroxy aldehyde (X), and then 23.5 mg of (14S)-15-hydroxyisoagath-12-en-16-al (X) with mp 95-97°C (from CH CH). $[\alpha]_D^{22}$ −35.5° (c 1.2). Found, %: C 78.85; H 10.49. $C_{20}H_{32}O_2$. Calculated, %: C 78.90; H 10.59. IR spectrum (cm^{-1}): 1133, 3450 (band), 1610 (OH); 1633, 1673, 2720 (conjugated aldehyde). PMR spectrum ($CDCl_3$, δ, ppm): 0.82 (s, 6 H, C_4— and C_{10}—CH_3); 0.87 (s, 3 H, C_4—CH_3); 0.93 (s, 3 H, C_8—CH_3); 3.46 (dd, 1 H, J_1 = 5 Hz, J_2 = 10 Hz), and 3.82 (dd, 1 H, J_1 = 6 Hz, H_2 = 10 Hz) (the AB part of a ABX system, C_{15}—CH_2); 6.83 (t, 1 H, J = 4 Hz, C_{12}—H); 9.40 (s, 1 H, CHO). Mass spectrum, m/z (%): 304 (M^+, 14), 274 (100), 259 (36), 192 (21), 177 (33), 149 (23), 137 (25), 121 (79). A mixture of the same solvents in a ratio of 4:1 eluted from the column 179.6 mg of (14S)-isoagath-12-ene-15,16-diol (IX), mp 119-120.5°C (from petroleum ether), $[\alpha]_D^{22}$ +97.3° (c 1.8). Found, %: C 78.52; H 11.20. $C_{20}H_{34}O_2$. Calculated, %: C 78.38; H 11.18. IR spectrum ($CHCl_3$, cm^{-1}): 827, 1667 ($>C=C<^{H}$); 995, 1018, 3350 (band), 3610 (OH). PMR spectrum ($CDCl_3$, δ, ppm): 0.82 (s, 8 H, C_{10}—CH_3); 0.87 (s, 9 H, C_4— and C_8—CH_3); 3.39-4.08 (m, 6 H, C_{15}— and C_{16}—CH_2 groups and two OH groups); 5.75 (t, J = 3 Hz, 1 H, C_{12}—H). Mass spectrum, m/z (%): 306 (M^+, 17), 288 (23), 275 (20), 258 (97), 243 (29), 192 (29), 177 (56), 137 (49), 120 (100), 114 (9), 106 (97).

Oxidation of (14S)-Isoagath-12-ene-15,16-diol (IX) with Manganese Dioxide. A solution of 173 mg of the diol (IX) in 30 ml of CH_2Cl_2 was treated with 7 g of manganese dioxide (XII) and the mixture was stirred at room temperature for 58 h. Then it was worked up as described above, and the product (167.3 mg) was chromatographed on a column containing 3.5 g of silica gel. Petroleum ether—ethyl acetate (9:1) eluted 53.1 mg of a mixture of five substances which was not investigated further. A mixture of the same solvents in a ratio of 17:3 eluted 98.4 mg of the hydroxy aldehyde (X), mp 96-97.5°C, identical with the product obtained above.

Preparation of Methyl Spongin-13(16),14-dien-19-oate (XV). A. With stirring at −42 to −40°C, 470 mg of methyl lambertianate (XVI) in 3.5 ml of nitromethane—toluene (1:1) was added to a solution of 700 mg of 100% sulfuric acid in 4 ml of nitromethane—toluene (1:1). The mixture was stirred at the same temperature for another 25 min and was then poured into a saturated solution of sodium carbonate containing ice. The reaction product was extracted with ether. The extract was washed with water and was dried, and the solvent was distilled off. The residue (468.5 mg) was chromatographed on a column containing 8.5 g of silica gel. Petroleum ether—ethyl acetate (199:1) eluted 151 mg of (32.1%) of the ester (XV), mp 126-129.5°C (from CH_3CN), $[\alpha]_D^{23}$ −8.4 (c 1.9). IR spectrum (cm^{-1}): 890, 1040 (furan ring); 1716 (CO_2CH_3). PMR spectrum (δ, ppm): 0.73 (s, 3 H, C_{10}—CH_3); 1.16 (s, 3 H, C_8—CH_3); 1.19 (s, 3 H, C_4—CH_3); 3.60 (s, 3 H, CO_2CH_3); 5.92 (d, 1 H, J = 2 Hz, C_{15}—H); 7.05 (d, 1 H, J = 2 Hz, C_{16}—H). Mass spectrum, m/z (%): 330 (M^+, 86), 315 (100), 283 (10), 271 (12), 255 (34), 181 (28), 147 (62), 121 (42). According to the literature [6]: mp 138-140°C.

A mixture of the same solvents (19:1) and ether eluted 316 mg of a mixture of polar substances which was not investigated further.

B. With stirring at −70 to −72°C, 348 mg of fluorosulfonic acid in 1.5 ml of 1-nitropropane was added to a solution of 890 mg of methyl lambertianate (XVI) in 5 ml of 1-nitropropane. The mixture was stirred at the same temperature for another 30 min, and then a solution of 3 ml of triethylamine in 5 ml of petroleum ether was added. The resulting mixture was warmed to room temperature and was then diluted with 15 ml of water and extracted with petroleum ether. The extract was washed with water, and the solvent was distilled off. The residue (881 mg) was chromatographed on a column containing 25 g of silica gel. Petroleum ether—ethyl acetate (49:1) eluted 323.4 mg of the ester (XV) (36.3%), mp 125-128.5°C (from CH_3CN), identical with the product obtained by the method described in paragraph A. A mixture of the same solvents in a ratio of 19:1 and ethyl ether eluted 486.5 mg of a mixture of more polar substances which was not investigated further.

SUMMARY

The synthesis of isoagatholactone and of methyl spongia-13(16),14-dien-19-olate has been effected.

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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

XVII. CYCLOASGENIN B FROM *Astragalus tashkendicus*

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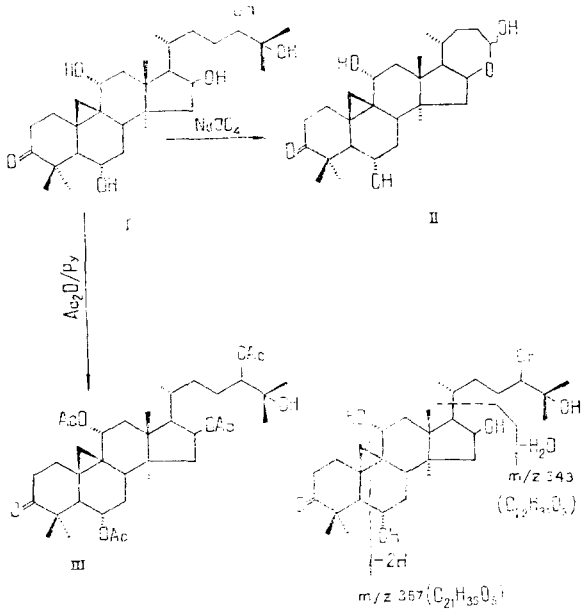
The roots of *Astragalus tashkendicus* Bge. have yielded a new triterpenoid — cycloasgenin B — the structure of which has been established on the basis of chemical transformations and spectral characteristics as (24R)-6α,11α,16β,24,25-pentahydroxycycloartan-3-one.

We are continuing the study of the methylsteroids of *Astragalus taskhendicus* Bge. (*Leguminosae*). The present paper is devoted to a proof of the structure of substance B [1], which we have called cycloasgenin B (I, scheme) [2]



The elementary composition of the genin (I), $C_{30}H_{50}O_6$, and the presence of its PMR spectrum of two one-proton doublets at 0.59 and 1.75 ppm interacting with one another in the manner of an AB system and also of the signals of seven methyl groups, permitted us to assign the compound under consideration to the methylsteroids of the cycloartane series [3].

The IR spectrum of cycloasgenin B showed carbonyl absorption at 1697 cm^{-1}, which is characteristic for a six-membered cyclic ketone. This was also shown by a signal of 21.96 ppm in the ^{13}C NMR spectrum.

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