SYNTHESIS OF ISOAGATHANE ALDEHYDES REPRESENTING METABOLITES OF THE SPONGE *Spongia officinalis*

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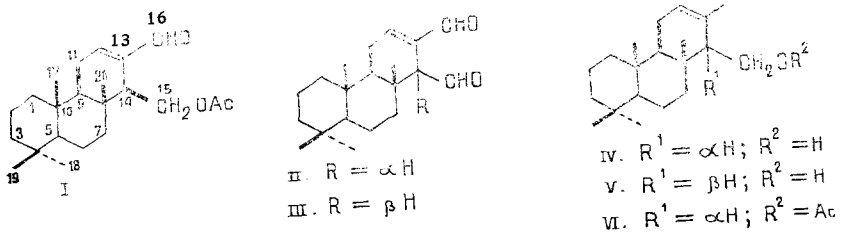
UDC 547.596/599

The synthesis has been performed of (14R)-15-acetoxyisoagath-12-en-16-al and of (14R)- and (14S)-isoagath-12-ene-15,16-dials, which are metabolites of the marine sponge *Spongia officinalis*, and also of a number of substances related to them starting from (14R)- and (14S)-isoagath-12-en-15-ols.

Marine organisms form a rich and still the only natural source of isoagathane diterpenoids. In particular, a series of such compounds has recently been isolated from the marine sponge *Spongia officinalis* [1] among which the aldehydes (I-III) predominate and to which are assigned the role of precursors of the spongian diterpenoids.

In the present paper we describe the synthesis of these aldehydes and also of substances related to them from (14R)- and (14S)-isoagath-12-en-15-ols (IV and V) — the products of the electrophilic cyclization of labdane diterpenoids [2].



Scheme 1

Oxidation of the acetate of (14R)-isoagath-12-en-15-ol (VI) with selenium dioxide in ethanol formed a complex mixture of substances, from which by careful column chromatography on silica gel it was possible to isolate, in order of increasing polarity, compounds (VII), (VIII), (I), (IX), and (X).

The structure of the ethoxy acetate (VII) was shown by spectral methods. According to IR and PMR spectra, its molecule contained a primary acetoxy and a secondary ethoxy group, a tetrasubstituted double bond, four quaternary methyls, and a methyl at a double bond. These facts led to structure (VII) for the ethoxy acetate under investigations, and this was definitively confirmed by its synthesis by the acetylation of the known 12-ethozyisoagath-13-ene-15-ol (XI) [3].

The substance next in polarity proved, judging from its IR and PMR spectra, to be an unsaturated keto acetate the keto group of which was conjugated with a tetrasubstituted double bond. It contained a primary allyl acetoxy group, a methyl at a double bond, and four methyl groups at quaternary carbon atoms. On the basis of these facts, the substance under investigation was ascribed structure (VIII).

The acetoxy aldehyde (I) was identified by a comparison of its physicochemical characteristics with those given in the literature [1].

Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 45-51, January-February, 1985. Original article submitted March 20, 1984.

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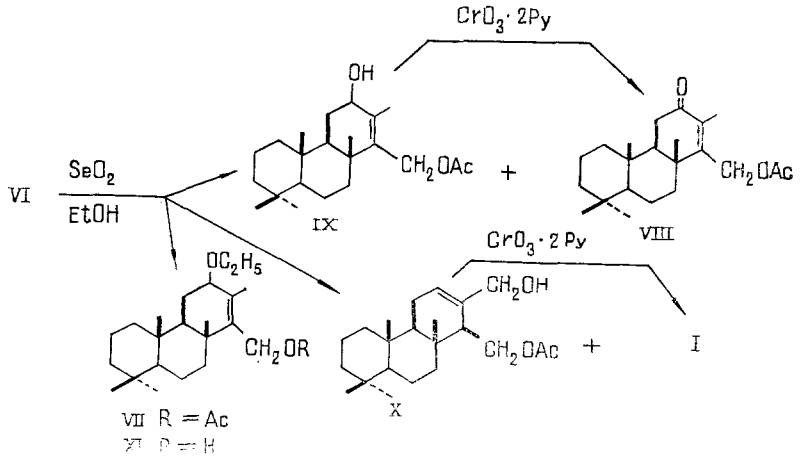
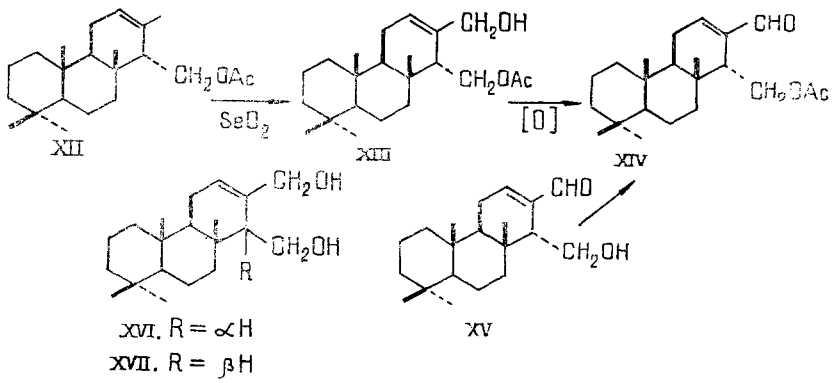


Scheme 2

The two most polar products of the oxidation of the acetate (VI) with selenium dioxide consisted of isomeric unsaturated hydroxy acetates. According to its PMR spectrum, the less polar of them contained a tetrasubstituted double bond, a secondary pseudoaxial hydroxy group (the width of the signal of the carbinol proton at its half-height amounted to 5 Hz [4]), four quaternary methyls, and a methyl at a double bond. These results are in harmony with the structure (IX) for the hydroxy acetate under discussion. It was confirmed by the results of mass spectrometry and by the formation of the keto acetate (VIII) when this compound was oxidized with the complex of chromium trioxide and pyridine [5].

The more polar hydroxy acetate differed from its isomer (IX) by the fact that its molecule had a trisubstituted double bond and a primary hydroxy group. Its structure is consequently given by formula (X). When this was oxidized with the complex of chromium trioxide and pyridine, the acetoxy aldehyde (I) was obtained.

In contrast to the unsaturated acetate (VI), the oxidation of its epimer at C_{14} (XII) with selenium dioxide took place unambiguously, although fairly slowly, and led to (14S)-15-acetoxyisoagath-12-en-16-ol (XIII). The structure of the latter followed from its spectral characteristics, which indicated that in its molecule the methyl group at the double bond of the initial acetate had been replaced by a hydroxymethyl group. On oxidation with the complex of chromium trioxide and pyridine, the hydroxy acetate (XIII) gave (14S)-15-acetoxyisoagath-12-en-16-al (XIV), the epimer of the acetoxyaldehyde (I) at C_{14}. This compound was also formed on the acetylation of the known [3] hydroxy aldehyde (XV) with acetic anhydride in pyridine, which definitively confirmed its structure and that of the acetylated glycol (XIII).



Scheme 3

The dialdehyde (II) described in [1] was obtained with good yield by the oxidation of the glycol (XVI) with oxalyl chloride and dimethyl sulfoxide [6]. Its physical constants and spectral characteristics agreed well with those given in the literature. The epimer of this dialdehyde at C_{14} (III), which has also been detected in *Spongia officinalis* [1], is formed in almost quantitative yields by the oxidation of the aldehyde (XV) or the glycol (XVII) [3] by the complex of chromium trioxide with pyridine.

EXPERIMENTAL

For general experimental matter, see [3].

(14R)-15-Acetoxyisoagath-12-ene (VI). A solution of 1.50 g of (14R)-isoagath-12-en-15-ol (IV) [2] in 10 ml of dry pyridine was treated with 1 ml of acetic anhydride, and the mixture was left at room temperature for 5 h, after which it was diluted with water (15 ml) and was extracted three times with ether. The ethereal extract was washed with 10% hydrochloric acid solution, with water, with saturated $NaHCO_3$ solution, and again with water and was dried, and the solvent was distilled off in vacuum. This gave 1.62 g (yield 94.7%) of (14R)-15-acetoxyisoagath-12-ene, $C_{22}H_{36}O_2$ (VI): mp 43.5-45°C (from CH_3CN); $[\alpha]_D^{19}-32.9^\circ$ (*c* 1.1).

IR spectrum (cm^{-1}): 1227, 1730 (OAc). PMR spectrum* ($CDCl_3$, δ, ppm): 0.78 (s, 3 H, C_{10}—CH_3); 0.81 (s, 3 H) and 0.85 [s, 3 H, C_4—$(CH_3)_2$]; 0.88 (s, 3 H, C_8—CH_3); 1.63 (s, 3 H, C_{13}—CH_3); 2.00 (s, 3 H, OAc); 3.99 (dd, H_B, J_{AB} = 12 Hz, J_{BX} = 6.7 Hz); 4.22 (dd, H_A, J_{AB} = 12 Hz, J_{AX} = 3.2 Hz) (AB part of an ABX system; CH_2OAc); 5.41 (br.s, 1 H, C_{12}—H).

Oxidation (14R)-15-Acetoxyisoagath-12-ene (VI) with Selenium Dioxide. A solution of 2.50 g of (14R)-15-acetoxyisoagath-12-ene (VI) in 15 ml of ethanol was treated with 1.67 g of selenium dioxide, and the mixture was boiled for 23 h under reflux. Then it was cooled, diluted with water (20 ml), and extracted three times with ether. The ethereal extract was washed with saturated $(NH_4)_2S$ solution and with water and was dried, and the solvent was distilled off. The residue was chromatographed on a column containing 55 g of silica gel. The results of the separation are given in Table 1.

15-Acetoxy-12-ethoxyisoagath-13-ene (VII). A. Fraction 3 consisted of pure 15-acetoxy-12-ethoxyisoagath-13-ene (VII) in the form of a viscous liquid, $C_{24}H_{40}O_3$ $[\alpha]_D^{22}-44.1^\circ$ (*c* 3.9). IR spectrum (cm^{-1}): 1073 (—COC_2H_5), 1233, 1730 (OAc). PMR spectrum (δ, ppm) 0.80 (s, 3 H, C_{10}—CH_3); 0.87 [s, 6 H, C_4—$(CH_3)_2$], 0.93 (s, 3 H, C_8—CH_3); 1.68 (s, 3 H, C_{13}—CH_3); 1.95 (s, 3 H, OAc); 3.05-3.75 (s, 3 H, —$CHOCH_2CH_3$); 4.48 (br.s, 2 H, CH_2OAc).

B. A solution of 65 mg of the alcohol (XI) [3] in 5 ml of dry pyridine was treated with 0.15 ml of acetic anhydride and the mixture was left at room temperature for 4.5 h and was then worked up as described above. This gave 70.4 mg of the ethoxy acetate (VII), identical according to TLC, IR, and PMR with the product described in paragraph A.

15-Acetoxyisoagath-13-en-12-one (VIII) and (14R)-Acetoxyisoagath-12-en-15-al (I). Chromatographic fraction 4 (Table 1) was rechromatographed on a column containing 6 g of silica gel. Petroleum ether—ethyl acetate (19:1) eluted 80.3 mg of 15-acetoxyisoagath-13-en-12-one (VIII) in the form of a viscous liquid, $C_{22}H_{34}O_3$, $[\alpha]_D^{19}$ −65.8° (c 4.6). IR spectrum (cm^{-1}); 1613, 1670 (conjugated keto group), 1224, 1740 (OAc). PMR spectrum (δ, ppm): 0.83 (s, 3H), 0.87 (s, 3 H) [C_4—$(CH_3)_2$]; 0.93 (s, 3 H, C_{10}—CH_3); 1.10 (s, 3 H, C_8—CH_3); 1.71 (s, 3 H, C_{13}—CH_3); 2.02 (s, 3 H, OAc); 2.23 (d, 1 H, J = 3 Hz); 2.38 (s, 1 H, C_{11}—CH_2); 4.63 (s, 2 H, C_{15}—CH_2). Then the same solvent eluted from the column 52.5 mg of a mixture of compounds (VIII) and (I), followed by 234.8 mg of (14R)-15-acetoxyisoagath-12-en-16-al (I) in the form of a colorless viscous liquid with $[\alpha]_D^{23}+6.3^\circ$ (*c* 2.1).

IR spectrum (cm^{-1}): 1633, 1680, 2700 (conjugated CHO group); 1223, 1725 (OAc). PMR spectrum (δ, ppm): 0.82 (s, 3 H, C_{10}—CH_3); 0.83 (s, 3 H), 0.86 (s, 3 H) [C_4—$(CH_3)_2$]; 0.96 (s, 3 H, C_8—CH_3); 1.88 (s, 3 H, OAc); 4.27 (d, 2 H, J = 18 Hz, C_{15}—CH_2); 4.43 (m, 1 H, C_{14}—H); 6.71 (br.s, 1 H, C_{12}—H); 9.33 (s, 1 H, CHO).

According to the literature [1] $[\alpha]_D+4.2^\circ$ ($CHCl_3$).

(12S)-15-Acetoxy-12-hydroxyisoagath-13-ene (IX) and (14R)-15- Axetoxy-16-hydroxyisoagath-12-ene (X). Fraction 5 (Table 1) was rechromatographed on a column containing 15 g of silica gel. Petroleum ether—ethyl acetate (93:7) eluted 383.7 mg of (12S)-15-acetoxy-12-

*PMR spectra marked with an asterisk were taken on a Bruker WP-200SY instrument (200 MHz).

TABLE 1. Chromatographic Separation of the Products of the Oxidation of Compound (VI) with Selenium Dioxide

Solvent on the column	Weight of the fraction mg	Composition of the fraction according to TLC and GLC
1. Petroleum ether	50,2	Mixture of hydrocarbons Not investigated
2. Petroleum ether–ethyl acetate (97:3)	126,4	The initial acetate (VI)
3. Petroleum ether–ethyl acetate *	1056	15-Acetoxy-12-ethoxyisogath-13-ene (VII)
4. Petroleum ether–ethyl acetate (93:7)	373,5	Mixture of compounds (VIII) and (I)
5. Petroleum ether–ethyl acetate (17:3)	807,5	Mixture of hydroxy acetates(IX) and (X)
6. Diethyl ether	97,3	Mixture of polar substances Not investigated

*No ratio given in Russian original – Publisher.

hydroxyisoagath-13-ene, $C_{22}H_{36}O_3$ (IX); mp 133-134°C (from petroleum ether), IR spectrum (CCl_4, cm^{-1}): 1233, 1735 (OAc); 1010, 3452 and 3600 (OH). PMR spectrum (δ, ppm): 0.78 (s, 3 H, C_{10}–CH_3); 0.83 [s, 6 H, C_4–$(CH_3)_2$]; 0.91 (s, 3 H, C_8–CH_3); 1.71 (s, 3 H, C_{13}–CH_3); 1.97 (s, 3 H, OAc); 3.68 (br.s, 1 H, $W_1/_2$ = 5 Hz, C_{12}–pseudoeq. H); 4.51 (s, 2 H, C_{15}–CH_2). Mass spectrum (m/z, intensity, %): 348 (M^+, 0.5), 304 (M–CH_3CHO, 5), 288 (M–AcOH, 100), 272(17), 257(9), 255(8), 245(7), 231(9), 219(9), 192(19), 191(48), 177(24), 159(13), 149(24), 137(42), 135(42), 119(47).

Then the solvent eluted from the column 308.4 mg of a mixture of the hydroxy acetates (IX) and (X), and petroleum ether–ethyl acetate (9:1) eluted 198.9 mg of a yellowish viscous liquid – (14R)-15-acetoxy-16-hydroxyisoagath-12-ene, $[\alpha]_D^{20}$ –16.2° (*c* 2.5). IR spectrum (cm^{-1}): 1232, 1735 (OAc); 1020, 3460 (OH band); 1667 $\left(>C=C<_H\right)$. PMR spectrum (δ, ppm): 0.81 (s, 3 H, C_{10}–CH_3); 0.84 (s, 3 H), 0.86 (s, 3 H) [C_4–$(CH_3)_2$]; 0.87 :s, 3 H, C_8–CH_3); 1.99 (s, 3 H, OAc); 3.3-4.7 (m, 5 H, C_{14}–H, C_{15}–CH_2 and C_{16}–CH_2); 5.81 (br.s, 1 H, C_{12}–H).

Oxidation of (12S)-15-Acetoxyisoagath-13-en-12-ol (IX). A solution 54 mg of the alcohol (IX) in 2 ml of dry CH_2Cl_2 was treated with 50 mg of the complex $CrO_3 \cdot 2C_5H_5N$ [5]. The mixture was stirred at room temperature for 5 h, and then the solid matter was filtered off and washed with ether and the solvent was distilled off from the filtrate. The residue (43.6 mg) was chromatographed on a column containing 1 g of SiO_2. Petroleum ether–ethyl acetate (97:3) eluted 38.6 mg (yield 71.9%) of the keto acetate (VIII) identical with the product described above.

Oxidation of (14R)-15-Axetoxy-16-hydroxyisoagath-12-ene (X). A solution of 68.4 mg of the hydroxy acetate (X) in 3 ml of dry CH_2Cl_2 was treated with 70 mg of the complex $CrO_3 \cdot 2C_5H_5N$, and the mixture was stirred at room temperature for 6.5 h and was then worked up as described above. The reaction product (65.2 mg) was chromatographed on a column containing 1 g of SiO_2. Petroleum ether–ethyl acetate (24:1) eluted 57.2 mg (yield 84.1%) of a compound identical with the acetoxy aldehyde (I) described above.

(14S)-15-Acetoxyisoagath-12-ene (XII). A solution of 1.00 g of (14S)-isoagath-12-en-15-ol (V) [2] in 5 ml of dry pyridine and 0.45 ml of acetic anhydride was left at room temperature for 14 h and was then worked up as described above. This gave 1.1 g (96.1%) of the acetate of (14S)-isoagath-12-en-15-ol, $C_{22}H_{36}O_2$ (XII): mp 49-50°C (from CH_3CN), $[\alpha]_D^{19}$ +68.6° (*c* 2.4). IR spectrum (cm^{-1}): 1223, 1735 (OAc). PMR spectrum* ($CDCl_3$, δ, ppm): 0.83 (s, 3 H, C_{10}–CH_3); 0.89 [s, 9 H, C_4–$(CH_3)_2$ and C_8–CH_3]; 1.72 (d, J = 1.4 Hz, 3 H, C_{13}–CH_3); 2.01 (s, 3 H, OAc); 4.12 (d, J = 2 Hz, 2 H, C_{15}–CH_2); 5.36 (s, 1 H, C_{12}–H).

Oxidation of the Acetate of (14S)-Isoagath-12-en-15-ol (XII) with Selenium Dioxide. A solution of 300 mg of the acetate (XII) in 2.7 ml of ethanol was treated with 42 mg of SeO_2, and the mixture was boiled under reflux for 68 h. The mixture was worked up as described above and the product (288 mg) was chromatographed on a column containing 8.5 g of silica gel. Petroleum ether–ethyl acetate (19:1) eluted 246.6 mg of the initial acetate (XII). A 17:3 mixture of the same solvents eluted 30.8 mg of a colorless viscous liquid which was (14S)-15-acetoxyisoagath-12-en-16-ol $[\alpha]_D^{20}$ + 22.2° (*c* 2.1). IR spectrum, (cm^{-1}): 1020, 3485 (band), 3600 (OH); 1227, 1730 (OAc); 1670 $\left(>C=C<_H\right)$. PMR spectrum (δ, ppm): 0.85 (s, 3 H, C_{10}–CH_3); 0.88 (s, 3 H, C_4–CH_3); 0.93 (s, 6 H, C_4– and C_8–CH_3); 1.98 (s, 3 H, OAc); 2.30 (br.s,

*See footnote on p. 44 – Publisher.

1 H, —OH); 3.80-4.22 (m, 4 H, C_{15}—CH_2 and C_{16}—CH_2); 5.65 (br.s, 1 H, C_{12}—H).

(14S)-15-Acetoxyisoagath-12-en-16-al (XIV). A. (14S)-15-Hydroxyisoagath-12-en-16-al (XV) [3] (150 mg) was acetylated with a mixture of 1 ml of acetic anhydride and 5 ml of dry pyridine at room temperature for 21 h. The reaction product (168.3 mg) was chromatographed on a column containing 6.3 g of silica gel. Petroleum ether—ethyl acetate (97:3) eluted 153.4 mg (89.9%) of (14S)-15-acetoxyisoagath-12-en-16-al, $C_{22}H_{34}O_3$ (XIV); mp 59.5-61°C (from CH_3CN); $[\alpha]_D^{24}$ +47.5° (*c* 6.5) . IR spectrum (cm^{-1}): 1644, 1685 (conjugated CHO group); 2700 (CHO); 1735 (OAc). PMR spectrum (δ, ppm); 0.79 (s, 3 H, C_{10}—CH_3), 0.82 (s, 3 H), 0.86 (s, 3 H), [C_4—$(CH_3)_2$]; 0.92 (s, 3 H, C_8—CH_3); 1.90 (s, 3 H, OAc); 3.12-4.48 (m, 3 H, C_{14}—H and C_{15}—CH_2); 6.76 (t, 1 H, J = 3.5 Hz, C_{12}—H); 9.37 (s, 1 H, CHO). Mass spectrum (m/z, intensity, %): 346 (M^+, 25), 304(100), 286(46), 271(37), 243(7), 192(30), 177(36).

B. A solution of 20 mg of (14S)-15-acetoxyisoagath-12-en-16-ol (XIII) in 1.5 ml of dry CH_2Cl_2 was treated with 25 mg of the complex $CrO_3 \cdot 2C_5H_5N$, and the reaction mixture was left at room temperature for 3 h and was then worked up as described above. The reaction product (18.4 mg) was chromatographed on a column containing 0.4 g of silica gel. Petroleum ether—ethyl acetate (19:1) eluted 16.1 mg (80.9%) of the acetoxy aldehyde (XIV), identical with that obtained above.

(14R)-Isoagath-12-ene-15,16-dial (II). With stirring at —(60-62)°C a solution of 86 mg of DMSO in 0.25 ml of CH_2Cl_2 was added to a solution of 76.8 mg of oxalyl chloride in 1.2 ml of dry CH_2Cl_2. The solution was stirred at the same temperature for 5 min and then a solution of 35 mg of (14R)-isoagath-12-ene-15,16-diol (XVI) [7] in 0.25 ml of CH_2Cl_2 was added to it at the same temperature. The reaction mixture was stirred at the same temperature for 45 min, and then 228 mg of triethylamine was added to it, with continuous stirring; it was then kept at —60°C for 10 min, after which the temperature was gradually allowed to rise to that of the room. The mixture was diluted with 20 ml of water, washed with water to neutrality, and dried, and the solvent was distilled off. The residue (33.4 mg) was chromatographed on a column containing 0.9 g of silica gel. Petroleum ether—ethyl acetate (9:1) eluted 5.4 mg of a mixture of weakly polar substances which was not investigated, and a 17:3 mixture of the same solvents eluted 27.5 mg (79.1%) of (14R)-isoagath-12-en-15,16-dial (II): mp 143-145°C (from hexane), $[\alpha]_D^{21}$ +517° (*c* 2.1) . IR spectrum (cm^{-1}): 1644, 1680 (conjugated CHO); 1722, 2713 (CHO). PMR spectrum (δ, ppm): 0.83 (s, 3 H, C_{10}—CH_3); 0.90 [s, 6 H, C_4—$(CH_3)_2$]; 0.95 (s, 3 H, C_8—CH_3); 7.02 (br.s 1 H, C_{12}—H); 9.40 (s, 1 H, C_{13}—CHO); 9.41 (d, 1 H, J = 10 Hz, C_{15}—CHO). According to the literature [1]: mp 139-142°C, $[\alpha]_D$ +48° ($CHCl_3$).

(14S)-Isoagath-12-ene-15,16-dial (III). A. A solution of 170 mg of (14S)-isoagath-12-ene-15,16-diol (XVII) [3] in 8 ml of CH_2Cl_2 was treated with 300 mg of the complex $CrO_3 \cdot 2C_5H_5N$, and the mixture was stirred at room temperature for 6.5 h and was worked up as described above. The product (166.3 mg) was chromatographed on a column containing 6 g of silica gel. Petroleum ether—ethyl acetate (97:3) eluted 154 mg (91.6%) of (14S)-isoagath-12-ene-15,16-dial (III); mp 118-119.5°C (from petroleum ether), $[\alpha]_D^{23}$ +203.6° (*c* 3.2) . IR spectrum (cm^{-1}): 1655, 1685 (conjugated CHO); 1725 and 2705 (CHO). PMR spectrum (δ, ppm): 0.81 (s, 3 H, C_{10}—CH_3); 0.85 (s, 3 H, C_4—CH_3); 0.90 (s, 6 H, C_4—CH_3 and C_8—CH_3); 3.15 (br.s, 1 H, C_{14}—H); 6.96 (t, 1 H, J = 4 Hz, C_{12}—H); 9.36 (s, 1 H, C_{16}—CNO): 9.80 (d, J = 3 Hz, C_{14}—CHO). Mass spectrum (m/z, intensity, %): 302 (M^+, 7), 287 (5), 274 (100), 259 (45), 191 (18), 177 (25). According to the literature [1]: mp 115-118°C; $[\alpha]_D$ +190° ($CHCl_3$).

B. A solution of 53 mg of (14S)-15-hydroxyisoagath-12-ene-16-al (XV) [3] was treated with 85 mg of the $CrO_3 \cdot 2C_5H_5N$, and the mixture was stirred at room temperature for 5 h. It was worked up as described above. The product (50.5 mg) was chromatographed on a column containing 1.2 g of silica gel. Petroleum ether—ethyl acetate (97:3) eluted 44.7 mg (84.9%) of the dialdehyde (III), identical with the product obtained in paragraph A.

SUMMARY

The synthesis of (14R)-15-acetoxyisogath-12-3n-16-al and of (14R)- and (14S)-isoagath-12-ene-15,16-dials, metabolites of the marine sponge *Spongia officinalis*, and of substances related to them has been effected.

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ISOMERIZATION EQUILIBRIUM OF THE p-MENTHADIENES IN THE VAPOR PHASE

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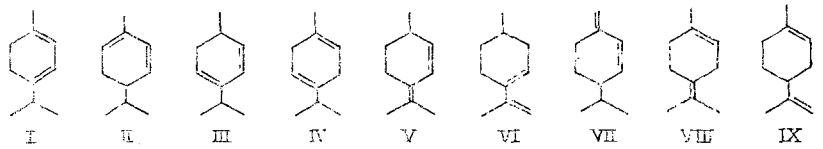
UDC 547.596.7+541.62

The isomerization equilibrium between nine p-menthadienes has been studied in the vapor phase at 250°C and their equilibrium ratios have been determined. A method for the quantitative GLC analysis of mixtures of isomeric p-menthadienes has been developed.

The contact of α-pinene with catalysis of the acidic type leads to the formation of, with other products, dipentene and p-menthadienes isomeric with it [1]. The mutual transformations of the p-menthadienes have been studied repeatedly [2, 3], but the equilibrium concentrations for the liquid phase are given in only two publications [4, 5]. In [4], the ratio of three isomers on potassium isobutanolate in dimethyl sulfoxide (50°C) is evaluated. Bates et al. [5] achieved equilibria of six p-menthadienes at 200°C on potassium tert-butanolate in tert-butanol and of four compounds at 67°C in the presence of dilute sulfuric acid. Equilibrium isomerization in the vapor phase on acidic catalysts has not been performed because of the considerable development of aromatization and polymerization processes.

We have studied the equilibrium of the isomerization of α-terpinene (I), α-phellandrene (II), mentha-2,4-diene (III), γ-terpinene (IV), isoterpinolene (V), mentha-3,8-diene (VI), β-phellandrene (VII), terpinolene (VIII), and dipentene (IX) in the vapor phase at 250°C on alumina.



I II III IV V VI VII VIII IX

The experiments were performed by the pulse method in a microreactor included in the gas line of a chromatograph. This permitted the reaction to be performed in an inert oxygen-free medium with strong dilution of the sample with carrier gas (argon) and thus enabled the polymerization of the products to be avoided to a considerable degree. The time of contact of the substances with the catalyst was regulated by the length of the catalyst bed in a tubular reactor with a constant space velocity of the carrier gas. The conditions of the experiment excluded the establishment of a chromatographic regime of the working of the microreactor [6].

The equilibrium ratios were reached from the direction of different p-menthadienes and from α- and β-pinenes (XI and XII) (Table 1), regardless of the amount of p-cymene in the

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Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 51-54, January-February, 1985. Original article submitted April 16, 1984.

0009-3130/85/2101-0047$09.50