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Dedicated to Full Member of the Russian Academy of Sciences N.S. Zefirov on His 70th Anniversary

Transformations of Isocaryophyllene Diepoxide under Conditions of Homogeneous and Heterogeneous Acid Catalysis

O. V. Salomatina[1], O. I. Yarovaya[2], D. V. Korchagina[2], Yu. V. Gatilov[2], M. P. Polovinka[2], and V. A. Barkhash[2]

[1] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*
e-mail: ana@nioch.nsc.ru

[2] *Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia*

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Abstract—Transformations of isocaryophyllene diepoxide (an isomer of widely spread natural sesquiterpene) were studied in various acidic media under conditions of homogeneous and heterogeneous catalysis. A number of previously unknown compounds were thus obtained. The experimental data were compared with the results of molecular-mechanics and quantum-chemical simulation of the most probable transformation paths.

We previously studied acid-catalyzed transformations of diepoxy derivatives of caryophyllene (which is one of the most widely spread natural sesquiterpenes) over solid catalysts and under homogeneous conditions [1]. With a view to elucidate how the substrate structure affects the results of transformations, in the present work we examined transformations of isomeric isocaryophyllene diepoxide under conditions of homogeneous and heterogeneous catalysis. Isocaryophyllene (**I**) is the *cis* isomer of caryophyllene with respect to the 4(5)-double bond; like caryophyllene, compound **I** readily undergoes cyclization in the presence of acids; however, the composition of the cyclization products is different due to the lack of strain at the endocyclic 4(5)-double bond [2, 3].

Treatment of diene **I** with a peroxy acid gives rise to epimeric epoxy derivatives as a result of oxidation of the 4(5)-double bond, 4β,5β- (**II**) and 4α,5α-epoxyisocariophyllenes. Compound **II** was isolated from the reaction mixture by recrystallization from hexane; its oxidation with monoperoxyphthalic acid afforded diepoxy derivative **III** (Scheme 1) [2]. It should be noted that epoxidation of caryophyllene 4β,5α-epoxide gave two epimeric diepoxy derivatives. The reaction of **II** with peroxy acid was stereoselective.

The most stable conformations of diepoxide **III** are almost equally strained αα and βα forms. The low barrier to interconversion between the conformers (as in the case of initial diene **I**) [4] rules out conformationally controlled reaction. The stable conformers were revealed using Dreiding models and molecular dynamics calculations. The heats of formation of possible conformers were estimated in terms of the PM3 semiempirical method, and the most stable conformers (within 5 kcal/mol) were calculated by the DFT method (B3LYP/6□31G*). Scheme 1 shows the best (within 2 kcal/mol) conformers according to the DFT calculations.

The synthesis of diepoxy derivative **III** and its transformations in nucleophilic media were described in [5]. It was shown that the 4,5-epoxy group is stable in alkaline medium; therefore, the corresponding 8,13-diol is formed, and the latter undergoes intramolecular cyclization to give tricyclic product (Scheme 1). Acid-catalyzed transformations of diepoxide **III** were not studied previously.

Isomerization of compound **III** over solid catalysts (such as β-zeolite or askanite–bentonite clay) leads to formation of dialdehyde **IV** and tricyclic hydroxy aldehyde **Va**; in addition, compounds **VI** and **VII** at a ratio of 1:0.4 (according to the ^{1}H NMR data) were isolated from the reaction mixture. Compound **IV** and tricyclic hydroxy aldehyde **Vb** (which is stereoisomeric to **Va**) were obtained previously as a result of acid-catalyzed

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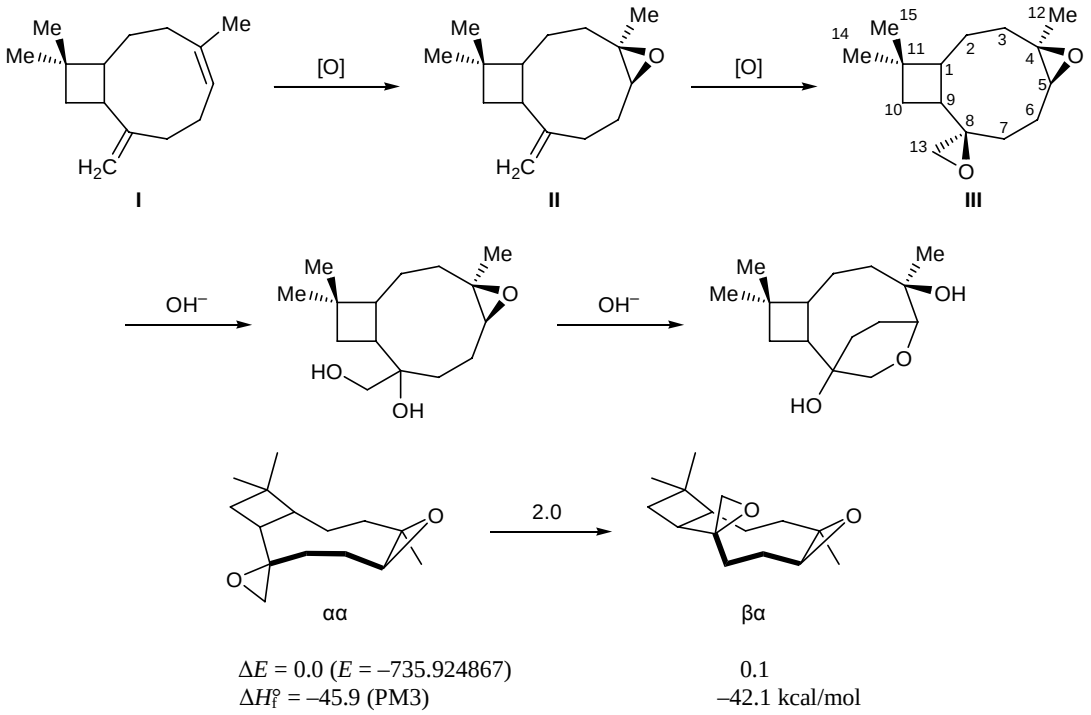
Scheme 1.



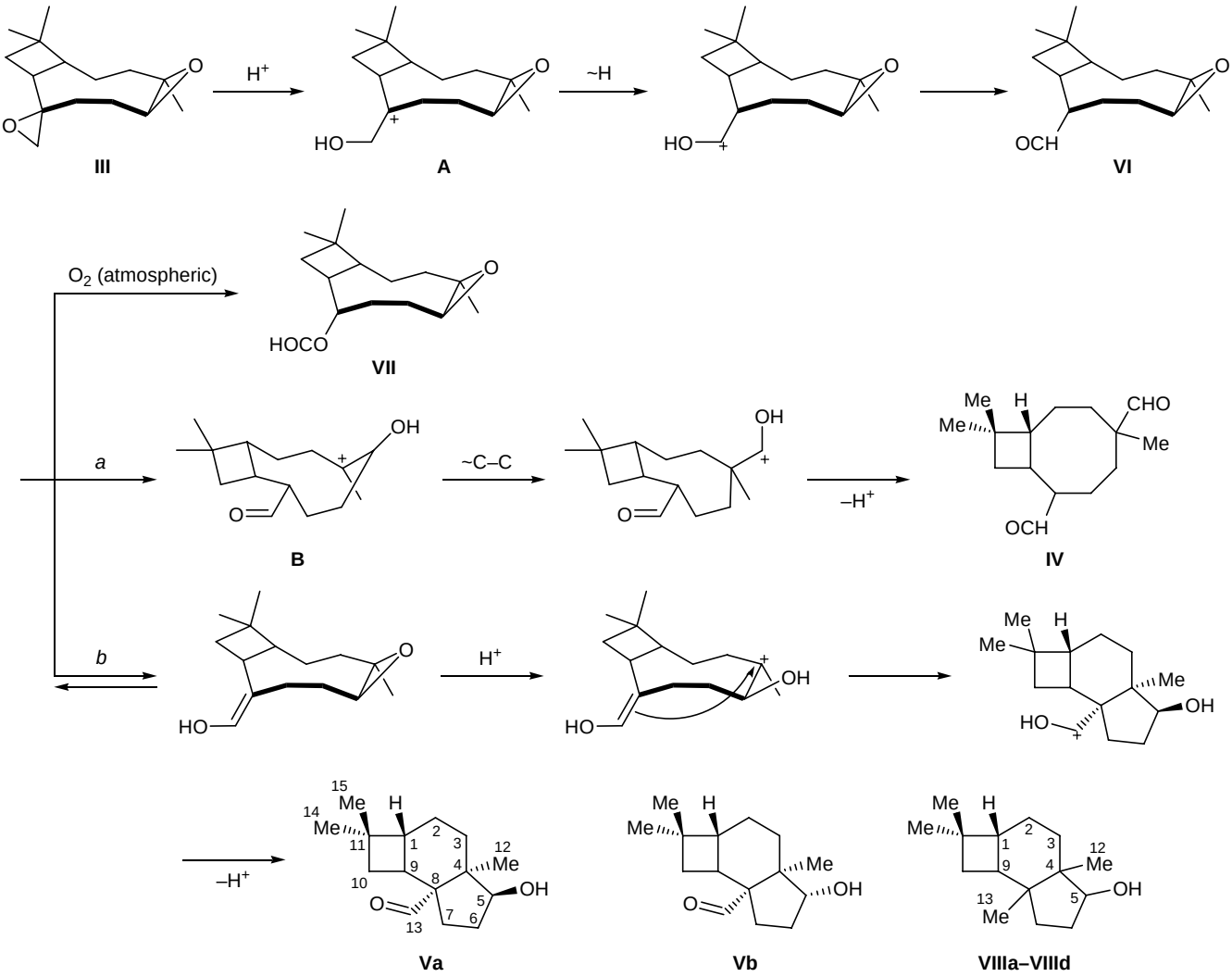
ΔE = 0.0 (E = –735.924867) 0.1
ΔH_f° = –45.9 (PM3) –42.1 kcal/mol

transformations of caryophyllene diepoxides [1]. Scheme 2 illustrates a probable mechanism of transformations of compound **III** in acid medium. In the first stage, protonation of 8,13-epoxy ring gives cation **A** which undergoes rearrangement to epoxy aldehyde **VI**. Further transformations of compound **VI** follow two pathways, *a* and *b*, which lead to dialdehyde **IV** and hydroxy aldehyde **Va**, respectively. Pathway *a* includes protonation of the 4,5-epoxy ring with formation of ion **B**, and the subsequent C–C bond migration is accompanied by contraction of the 9-membered ring to produce compound **IV** (via elimination of proton). Along pathway *b*, enolization of the aldehyde group, followed by opening of the oxirane ring and cyclization, gives rise to tricyclic skeleton of **V**. The proposed reaction scheme which begins with opening of the 8,13-epoxy ring is supported by the facts that compound **VI** in the presence of β-zeolite is converted into **IV** and **Va** and that epoxy acid **VII** is formed from aldehyde **VI** via oxidation with atmospheric oxygen.

Next we examined transformations of diepoxy derivative **III** in homogeneous acid media. Dissolution of compound **III** in the system acetone–water–sulfuric acid led to formation of tricyclic ether **IX** as a result of intramolecular heterocyclization. The transformation of isocaryophyllene diepoxide (**III**) in formic acid or in the system formic acid–dioxane afforded a mixture of compounds **IX** and **X** at a ratio of 1:1. Scheme 3 shows a probable mechanism of acid-catalyzed transformations of diepoxy derivative **III** under homogeneous conditions. According to the results of quantum-chemical and molecular-mechanics calculations, the reactivity of the 8,13-epoxy ring is higher; therefore, it is cleaved in the first stage. Further addition of water molecule from the α-side is more favorable, and the product is epoxy diol with a heat of formation of –130.9 kcal/mol. Opening of the 4,5-epoxy ring and the subsequent transannular cyclization can occur through both secondary and tertiary carbocation to give more stable oxonium ion, ΔH_f° = 13.8 kcal/mol. Carbocation with ΔH_f° = 2.3 kcal/mol is not formed, presumably for kinetic reasons.

Thus we have shown that isomerization of isocaryophyllene diepoxide over solid catalysts either yields bicyclic dialdehyde **IV** via contraction of the 9-membered ring to 8-membered (compound **IV** is also formed by isomerization of caryophyllene diepoxides) or involves rearrangement to hydroxy aldehyde **Va** having a tricyclic skeleton. The isolation of epoxy aldehyde **VI** from the reaction mixture supports our assumptions concerning possible transformation pathways of diepoxy derivative **III** over acid β-zeolite. Acid-catalyzed isomerization of compound **III** under homogeneous conditions leads to formation of intramolecular heterocyclization products **IX** and **X**.

Scheme 2.



VIII, α-$C^{12}H_3$, β-OH, α-$C^{13}H_3$ (**a**); α-$C^{12}H_3$, α-OH, α-$C^{13}H_3$ (**b**); β-$C^{12}H_3$, α-OH, β-$C^{13}H_3$ (**c**); β-$C^{12}H_3$, β-OH, β-$C^{13}H_3$ (**d**).

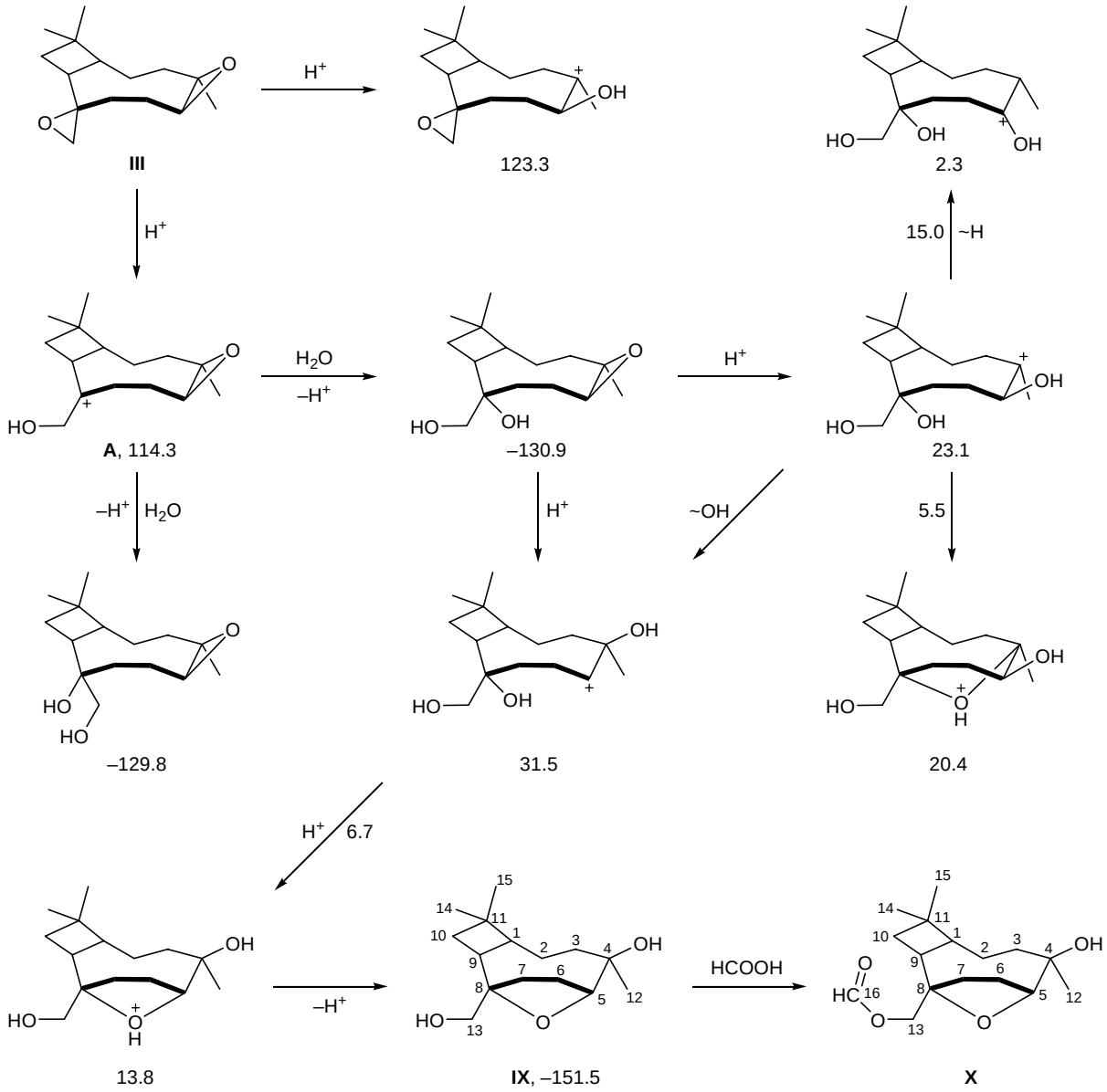
The structure of the newly synthesized compounds was established on the basis of their ^1H and ^{13}C NMR spectra. Comparison of the NMR spectra of compound **Va** with the corresponding data for isomer **Vb** and four isomeric alcohols **VIIIa**–**VIIId** [6] allowed us to assign α-orientation of the substituents on C^4 and C^8 and β-orientation of the substituent on C^5.

The presence of a hydroxy group on C^4 and of 5,8-epoxy bridge in molecule **IX** is confirmed by the ^{13}C NMR spectrum of a solution of **IX** in a CCl_4–$CDCl_3$ mixture containing D_2O. Isotope effect due to replacement of the OH group by OD induces upfield shift of the singlet at δ_C 75.39 ppm ($\Delta\delta_C$ = 0.12 ppm) belonging to C^4 and of the triplet at δ_C 65.90 ppm ($\Delta\delta_C$ = 0.12 ppm) belonging to C^{13}. Otherwise, when the hydroxy group is attached to C^5 and the oxygen bridge links C^4 and C^8, the doublet at δ_C 86.64 ppm should be displaced upfield in the ^{13}C NMR spectrum recorded in the presence of D_2O. α-Orientation of the methyl group on C^4 and of the 5,8-oxygen bridge may be assumed on the basis of the configuration of the 4,5-epoxy group in the initial diepoxide, which is also confirmed by the calculations. Identical stereochemical structures of compounds **IX** and **X** follow from similarity in their ^1H and ^{13}C NMR spectra.

EXPERIMENTAL

The initial compounds and reaction products were analyzed by GLC on a Biokhrom-1 chromatograph equipped with a flame-ionization detector using SE-54 (13 000 × 0.22 mm) and VS-30 (an analog of SE-30;

Scheme 3.



20000×0.27 mm) quartz capillary columns; carrier gas helium. The product mixtures were separated by column chromatography on silica gel (100–160 μm; Czechia). The specific optical rotations were measured on a Polamat A polarimeter. The elemental compositions were determined from the high-resolution mass spectra which were recorded on a Finnigan MAT-8200 instrument.

The reactions were carried out over wide-pore β-zeolite (SiO_2/Al_2O_3 22.4; pore size 0.75–0.80 nm; oxide concentrations: Na_2O 0.01, Al_2O_3 4.50, SiO_2 59.20, Fe_2O_3 0.08 wt %; manufactured by *Tseosit*, Novosibirsk); the catalyst was calcined for 3 h at 500°C before use.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400.13 MHz for ^1H and 100.61 MHz for ^{13}C) from solutions in CCl_4–$CDCl_3$ (1:1); the chemical shifts were measured relative to the chloroform signals (δ 7.24, δ_C 76.90 ppm). The structure of the products was determined by analysis of the ^1H NMR spectra (including ^1H–^1H double resonance technique), ^{13}C NMR spectra with selective and off-resonance decoupling from protons, two-dimensional ^{13}C–^1H correlation spectra (COSY, direct coupling constants $^1J_{CH}$ = 135 Hz), and unidimensional ^{13}C–^1H correlation spectra (LRJMD, long-range coupling constants J_{CH} = 10 Hz). The atom numbering used below corresponds to those given in Schemes 1–3.

The barriers to conformational transitions were calculated by the PM3 method; the heats of formation of carbocations and the barriers to rearrangements were calculated by the AM1 method. The B3LYP/6-31G* calculations were performed using GAMESS program [7] at the Information Technologies Department, Novosibirsk State University.

Caryophyllene isolated from clove oil was used, $[\alpha]_{580}^{20} = -13.8°$ (c = 4.3, $CHCl_3$).

Isomerization of caryophyllene into isocaryophyllene [8]**.** A mixture of 20 g of caryophyllene and 0.2 g of finely powdered selenium was heated for 5 h at 180–190°C under argon. The crude product, 19 g, was subjected to column chromatography on silica gel using hexane as eluent to isolate 16 g (80%) of isocaryophyllene (**I**), $[\alpha]_{580}^{20} = -15.0°$ (c = 5.4, $CHCl_3$).

Isocaryophyllene diepoxide (III) was synthesized according to the procedure described in [2]. Treatment of 6.70 g (0.032 mol) of isocaryophyllene (**I**) with a solution of monoperoxyphthalic acid (0.0385 mol) in diethyl ether (c = 0.0007 M), followed by recrystallization from hexane, gave 2.50 g (35%) of 4β,5β-monoepoxide **II**. Epoxidation of the latter afforded 2.57 g (95.5%) of compound **III**, $[\alpha]_{580}^{20} = -21.1°$ (c = 1.9, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.88 s ($C^{14}H_3$), 0.91 s ($C^{15}H_3$), 1.26 s ($C^{12}H_3$), 1.78 m (1β-H), 1.28–1.38 m (3-H, 2-H), 1.42–1.62 m (7-H, 2'-H, 6-H), 1.88–2.03 m (7'-H, 3'-H, 9-H, 6'-H), 1.32 d.d (10-H, $J_{10,10'}$ = 10, $J_{10,9}$ = 10), 1.48 d.d (10'-H, J = 10, $J_{10',9}$ = 8), 2.41 d (13-H, $J_{13,13'}$ = 5), 2.54 d.d (13'-H, J = 5, 1), 2.63 d.d.d (5-H, $J_{5,6}$ = 11, $J_{5,6'}$ = 2.5, $J_{5,3'}$ = 1). ^{13}C NMR spectrum, δ_C, ppm: 48.10 d (C^1), 25.73 t (C^2), 33.45 t (C^3), 60.89 s (C^4), 64.10 d (C^5), 23.55 t (C^6), 30.94 t (C^7), 58.33 s (C^8), 40.78 d (C^9), 34.71 t (C^{10}), 33.82 s (C^{11}), 22.30 q (C^{12}), 55.58 t (C^{13}), 22.41 q (C^{14}), 29.58 q (C^{15}). Found: m/z 236.11748 $[M]^+$. $C_{15}H_{24}O_2$. Calculated: M 236.11762.

Isomerization of isocaryophyllene diepoxide (III) over β-zeolite. A solution of 0.40 g of compound **III** in 10 ml of methylene chloride was added to 0.70 g of freshly calcined β-zeolite. The mixture was stirred for 50 min and filtered. According to the GLC data, the mixture contained compounds **IV**, **Va**, and **VI** at a ratio of 3:2:1. The product mixture, 0.39 g, was subjected to column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0 to 80% of the latter) to isolate 0.07 g (18%) of compound **IV**, 0.12 g (31%) of **Va**, and 0.04 g of mixture **VI/VII** (1:0.4). The spectral parameters of compound **IV** were reported in [1].

(2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-5-Hydroxy-2,2,4a-trimethyldecahydrocyclobuta[*e*]indene-7a-carbaldehyde (Va). $[\alpha]_{580}^{20} = -10.0°$ (c = 2.1, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.05 s ($C^{15}H_3$), 1.10 s ($C^{12}H_3$), 1.14 s ($C^{14}H_3$), 1.21 d.d (10-H, $J_{10,9}$ = 11, $J_{10,10'}$ = 10), 1.28–1.50 m (4H, 2-H, 3-H), 1.52 m (1-H), 1.54 d.d (10'-H, J = 10, $J_{10',9}$ = 7), 1.66 m (6-H), 1.72–1.87 m (7-H), 2.13 m (6'-H, $J_{6',6}$ = 13, $J_{6',5}$ = 8), 2.30 d.d.d (9-H, $J_{9,1}$ = 12, $J_{9,10}$ = 11, $J_{9,10'}$ = 7), 3.73 d.d (5-H, $J_{5,6}$ = 9, $J_{5,6'}$ = 8), 9.51 s (13-H). ^{13}C NMR spectrum, δ_C, ppm: 46.71 d (C^1), 23.00 t (C^2), 30.93 t (C^3), 48.53 s (C^4), 80.39 d (C^5), 29.90 t (C^6), 19.41 t (C^7), 60.04 s (C^8), 35.49 d (C^9), 37.55 t (C^{10}), 39.63 s (C^{11}), 19.70 q (C^{12}), 205.87 d (C^{13}), 20.83 q (C^{14}), 30.37 q (C^{15}). Found: m/z 236.11748 $[M]^+$. $C_{15}H_{24}O_2$. Calculated: M 236.11762.

We failed to distinguish signals from some protons for each compound in the ^{1}H NMR spectrum of mixture **VI/VII** due to their superposition.

{(1*R*,4*R*,6*S*,9*S*,10*R*)-4,12,12-Trimethyl-5-oxatricyclo[8.2.0.0^{4,6}]dodec-9-yl}acetaldehyde (VI). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.94 s ($C^{15}H_3$), 0.97 s ($C^{14}H_3$), 1.29 s ($C^{12}H_3$), 1.22–1.35 m (2-H, 3-H), 1.34 d.d (10-H, $J_{10,10'}$ = 10, $J_{10,9}$ = 10), 1.55 d.d (10'-H, J = 10, $J_{10',9}$ = 8), 2.48 m (9-H), 2.58 d.d.d (8-H, $J_{8,9}$ = 11, $J_{8,7}$ = 6, $J_{8,7'}$ = 3), 2.63 d.d (5-H, $J_{5,6}$ = 12, $J_{5,6'}$ = 3), 9.54 s (13-H), 1.48–2.15 m (other protons). ^{13}C NMR spectrum, δ_C, ppm: 49.67 d (C^1), 25.97 t (C^2), 34.53 t (C^3), 61.17 s (C^4), 63.79 d (C^5), 23.53 t (C^6), 18.81 t (C^7), 49.25 d (C^8), 37.44 d (C^9), 34.91 t (C^{10}), 36.13 s (C^{11}), 22.09 q (C^{12}), 202.30 d (C^{13}), 21.01 q (C^{14}), 29.80 q (C^{15}).

{(1*R*,4*R*,6*S*,9*S*,10*R*)-4,12,12-Trimethyl-5-oxatricyclo[8.2.0.0^{4,6}]dodec-9-yl}acetic acid (VII). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.92 s ($C^{15}H_3$), 0.93 s ($C^{14}H_3$), 1.31 s ($C^{12}H_3$), 2.42 m (9-H), 2.67 d.d (5-H, $J_{5,6}$ = 12, $J_{5,6'}$ = 3), 3.73 d.d.d (8-H, $J_{8,9}$ = 11, $J_{8,7}$ = 6, $J_{8,7'}$ = 4), 1.22–2.08 m (other protons). ^{13}C NMR spectrum, δ_C, ppm: 48.75 d (C^1), 25.90 t (C^2), 34.60 t (C^3), 61.26 s (C^4), 63.67 d (C^5), 23.64 t (C^6), 20.88 t (C^7), 41.64 d (C^8), 39.27 d (C^9), 34.87 t (C^{10}), 36.13 s (C^{11}), 22.09 q (C^{12}), 179.55 s (C^{13}), 20.98 q (C^{14}), 29.80 q (C^{15}).

Transformations of isocaryophyllene diepoxide (III) under homogeneous conditions. *a. In the system acetone–water–sulfuric acid.* Compound **III**, 0.20 g, was dissolved in 3 ml of a mixture of acetone, water, and sulfuric acid at a ratio of 50:6:1 (by volume). After 2 h, the mixture was treated with a saturated aqueous solution of Na_2CO_3 and extracted with diethyl

ether (3×30 ml), and the extract was dried over $MgSO_4$. According to the GLC data, the extract contained compound **IX**. The solvent was distilled off, and the residue, 0.16 g, was subjected to column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0 to 100% of the latter) to isolate 0.08 g (37%) of compound **IX**.

(1*S*,2*S*,5*R*,8*R*,9*S*)-1-Hydroxymethyl-4,4,8-trimethyl-12-oxatricyclo[7.2.1.0^{2,5}]dodecan-8-ol (IX). $[\alpha]_{580}^{20}$ = –10.0° (*c* = 1.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.95 s ($C^{14}H_3$), 0.96 s ($C^{15}H_3$), 1.27 s ($C^{12}H_3$), 1.42 br.d.d (1β-H, $J_{1,2}$ = 10, $J_{1,9}$ = 10), 1.14–1.25 m and 1.47–1.56 m (1H each, 2-H), 1.56–1.70 m (2H, 3-H), 3.95 t (5-H, $J_{5,6}$ = 7.5), 2.08–2.16 m (2H, 6-H), 1.82–1.93 m (2H, 7-H), 1.92 d.d.d (9α-H, $J_{9,1}$ = 10, $J_{9,10}$ = 10, $J_{9,10'}$ = 8), 1.07 d.d (10-H, $J_{10,10'}$ = 10, $J_{10,9}$ = 10), 1.46 d.d (10'-H, *J* = 10, 8), 2.27 br.s (2H, OH), 3.18 d and 3.33 d (1H each, 13-H, *AB* system, *J* = 11.5). ^{13}C NMR spectrum, δ_C, ppm: 47.83 d (C^1), 25.78 t (C^2), 39.14 t (C^3), 75.39 s (C^4), 86.64 d (C^5), 26.44 t (C^6), 26.01 t (C^7), 87.62 s (C^8), 44.78 d (C^9), 35.51 t (C^{10}), 35.58 s (C^{11}), 27.38 q (C^{12}), 65.90 t (C^{13}), 20.92 q (C^{14}), 29.87 q (C^{15}). Found, *m*/*z*: $[M]^+$ 254.13174. $C_{15}H_{26}O_3$. Calculated: *M* 254.13067.

b. In the system HCOOH–dioxane. Compound **III**, 0.50 g, was dissolved in a mixture of 0.5 ml of formic acid and 0.5 ml of dioxane. After 30 min, the mixture was treated with a saturated aqueous solution of Na_2CO_3 and extracted with diethyl ether (3×30 ml). The extract was dried over $MgSO_4$. According to the GLC data, it contained compounds **IX** and **X** at a ratio of 1:1. The solvent was distilled off from the extract, and the residue, 0.40 g, was subjected to column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0 to 100% of the latter) to isolate 0.05 g (9%) of compound **IX** and 0.03 g (6%) of **X**.

(1*S*,2*S*,5*R*,8*R*,9*S*)-8-Hydroxy-4,4,8-trimethyl-12-oxatricyclo[7.2.1.0^{2,5}]dodec-1-ylmethyl formate (X). $[\alpha]_{580}^{20}$ = –5.2° (*c* = 1.9, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.96 s ($C^{14}H_3$), 0.97 s ($C^{15}H_3$), 1.30 s ($C^{12}H_3$), 1.42 br.d.d (1β-H, $J_{1,2}$ = 10, $J_{1,9}$ = 10), 1.17–1.27 m and 1.49–1.54 m (2H, 2-H), 1.54–1.71 m (2H, 3-H), 3.99 t (5-H, $J_{5,6}$ = 7.5), 2.08–2.20 m (2H, 6-H), 1.76 d.d.d (7-H, $J_{7,7'}$ = 12, $J_{7,6}$ = 12, $J_{7,6'}$ = 10), 1.96–2.03 m (7'-H), 2.04 d.d.d (9α-H, $J_{9,1}$ = 10, $J_{9,10}$ = 10, $J_{9,10'}$ = 8), 1.12 d.d (10-H, $J_{10,10'}$ = 10, $J_{10,9}$ = 10), 1.47 d.d (10'-H, *J* = 10, 8), 3.89 d.d (13-H, $J_{13,13'}$ = 12, $J_{13,16}$ = 1), 3.99 d.d (13'-H, *J* = 12, $J_{13',16}$ = 1), 8.06 t (16-H, $J_{16,13}$ = 1). ^{13}C NMR spectrum, δ_C, ppm: 47.81 d (C^1), 25.64 t (C^2), 39.07 t (C^3), 75.30 s (C^4), 85.63 d (C^5), 26.03 t (C^6), 27.33 t (C^7), 85.08 s (C^8), 44.63 d (C^9), 35.78 t (C^{10}), 35.36 s (C^{11}), 27.33 q (C^{12}), 67.26 t (C^{13}), 20.82 q (C^{14}), 29.76 q (C^{15}), 160.79 d (C^{16}). Found, *m*/*z*: $[M - CHO]^+$ 237.16868. $C_{15}H_{25}O_3$. Calculated: $[M - CHO]^+$ 237.16979.

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