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# Acid-Catalyzed Reactions of Epoxides Derived from Citronellene

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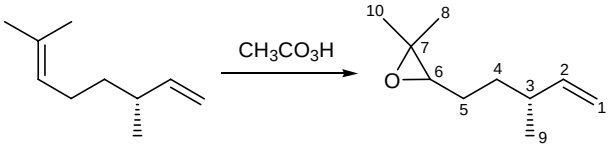
**Abstract**—Transformations of epoxy derivatives of citronellene in the presence of acid catalysts ($ZrO_2/SO_4^{2-}$, $SnCl_4$, $H_2SO_4$) in methylene chloride, acetone, and acetonitrile give rise to various oxygen- and nitrogen-containing compounds.

Acid-catalyzed reactions of epoxy terpenoids attract attention from the synthetic viewpoint. Variation of the reaction conditions makes it possible to obtain a number of oxygen-containing compounds belonging to different classes from a single accessible precursor. We previously studied rearrangements of epoxides derived from linalool over solid acid catalysts and synthesized various oxygen-containing compounds. It was shown that the key stage in these transformations is heterocyclization involving oxygen atom of the hydroxy group [1]. In the present work we examined acid-catalyzed reactions of epoxides derived from citronellene (**Ia**, **Ib**), which are structurally related to 6,7-epoxy derivatives of linalool but contain only a double bond in addition to the epoxy ring. Initial epoxy derivatives **Ia** and **Ib** were synthesized by oxidation of (–)-β-citronellene (**II**) with peroxyacetic acid in methylene chloride (Scheme 1); according to the $^1$H NMR data, the ratio of diastereoisomers **Ia** and **Ib** was ~1:1.

Unlike epoxides derived from linalool, compounds **Ia** and **Ib** in the presence of $ZrO_2/SO_4^{2-}$ at room temperature were converted into (6*R*)-2,6-dimethyloct-7-en-3-one (**III**) and (5*R*)-2,2,5-trimethyl-6-heptenal (**IV**) at a ratio of ~3:1 (GLC). The formation of the 5*S* isomer of **IV** as by-product (which was identified by the IR spectrum of the reaction mixture) in the reaction of epoxy derivatives of (+)-β-citronellene with $LiClO_4$ was noted in [2]. We isolated compound **IV** as individual substance.

**Scheme 1.**




**II** **Ia**, **Ib**

It is known that epoxy derivatives of geraniolene and geranyl acetate undergo various cyclizations by the action of Lewis acids, e.g., $SnCl_4$ [3, 4]. Citronellene epoxides **Ia** and **Ib** turned out to behave differently. Isomerization of epoxy derivatives **Ia** and **Ib** in the presence of $SnCl_4$ at 0°C afforded a mixture of acyclic compounds **III** and **IV** at a ratio of ~1:2 (GLC–MS). The following scheme of formation of compounds **III** and **IV** can be proposed (Scheme 2). Opening of the oxirane ring in **Ia** or **Ib** gives tertiary carbocation **A**; the subsequent hydride shift or C–C shift to the positively charged center $C^7$, followed by deprotonation, yields ketone **III** or aldehyde **IV**, respectively.

Compounds **Ia** and **Ib** are readily involved in intermolecular transformations catalyzed by sulfuric acid. In the system acetone–water–sulfuric acid (40:6:1, by volume), (5*R*,*S*)-2,2,4,4-tetramethyl-5-[(3*R*)-methyl-4-pentenyl]-1,3-dioxolanes **Va** and **Vb** were obtained. The (3*S*)-isomers of compounds **Va** and **Vb** were previously synthesized from (+)-β-citronellene epoxides in two steps [5].

The use of the Ritter reaction for the synthesis of substituted dihydrooxazoles from 6,7-epoxy derivatives of citral is quite promising [6]. Under analogous conditions ($CH_3CN$, $H_2SO_4$), compounds **Ia** and **Ib** were converted into mixtures of (5*R*,*S*)-2,4,4-tri-

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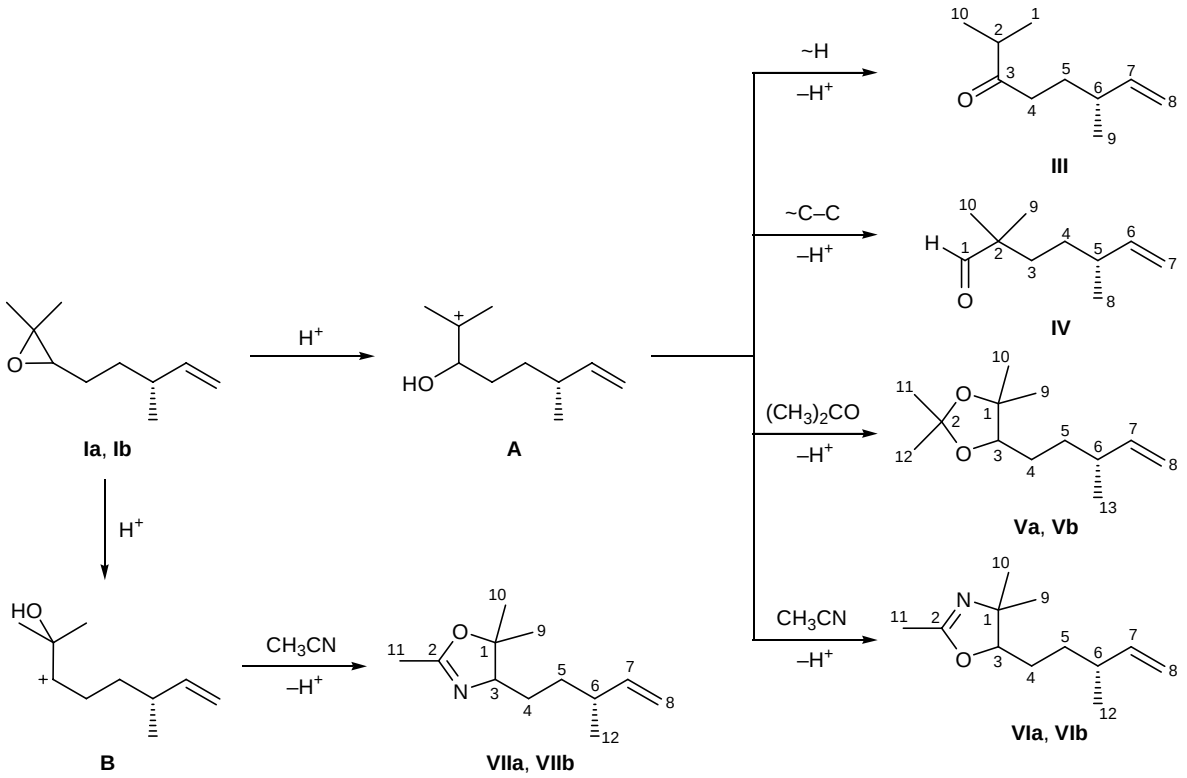
**Scheme 2.**




methyl-5-[(3*R*)-methyl-4-pentenyl)-4,5-dihydrooxazoles **VIa** and **VIb**, (4*R*,*S*)-2,5,5-trimethyl-4-[(3*R*)-methyl-4-pentenyl)-4,5-dihydrooxazoles **VIIa** and **VIIb**, and ketone **III** at a ratio of ~3.5:1 (**VI**+**VIIb**:**III**; GLC). Compounds **VIa**, **VIb**, **VIIa**, and **VIIb** were not reported previously. Thus the transformation of epoxides **Ia** and **Ib** via reaction of intermediate cations **A** and **B** with acetonitrile, which leads to structures **VIa**, **VIb**, **VIIa**, and **VIIb**, is accompanied by intramolecular rearrangement of cation **A**, resulting in formation of ketone **III**. Analogous opening of the oxirane ring at the $C^6$–O and $C^7$–O bonds was observed in the isomerization of linalool 6,7-epoxides over $ZrO_2/SO_4^{2-}$ [1].

According to the $^1H$ and $^{13}C$ NMR spectra of compounds **VIa**, **VIb**, **VIIa**, and **VIIb**, the strongest changes in the chemical shifts are observed for the 3-H proton and $C^1$ and $C^3$ atoms; these variations are consistent with those expected for formation of oxazole ring via cleavage of either $C^6$–O or $C^7$–O bond in the initial epoxides. In going from compounds **VI** to **VII**, the 3-H signal in the $^1H$ NMR spectra shifts upfield ($\Delta\delta$ ~0.65 ppm), the $C^1$ signal in the $^{13}C$ NMR spectrum shifts downfield ($\Delta\delta$ ~4.7 ppm), and the $C^3$ signal shifts upfield ($\Delta\delta$ ~10 ppm) due to different effects of the oxygen and nitrogen atoms.

## EXPERIMENTAL

The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.13 and 100.61 MHz, respectively, from solutions in $CDCl_3$–$CCl_4$ (~1:1) using the solvent signals ($CHCl_3$, $\delta$ 7.24, $\delta_C$ 76.90 ppm) as internal reference. The structure of the products was determined by analysis of spin–spin coupling constants in the $^1H$–$^1H$ double resonance spectra, as well as of the $^{13}C$ NMR spectra recorded with selective decoupling from protons, off-resonance spectra, differential spectra modulated by long-range $^{13}C$–$^1H$ coupling (LRJMD, $^nJ_{CH}$ = 10 Hz, $n$ = 2, 3), and two-dimensional $^{13}C$–$^1H$ heteronuclear correlation spectra (COSY, $^1J_{CH}$ = 135 Hz).

The purity of the initial compounds and products was checked by GLC on a Biokhrom-1 chromatograph equipped with a flame ionization detector and an SE-54 quartz capillary column (13000×0.22 mm); carrier gas helium, oven temperature 70–180°C. The elemental compositions were determined from the high-resolution mass spectra which were recorded on a Finnigan MAT-8200 spectrometer. Gas chromatographic–mass spectrometric analysis was performed on a Hewlett–Packard 618100A instrument. The optical rotations were measured on a Polamat A spectro-

polarimeter from solutions in $CHCl_3$. The procedure for the preparation of $ZrO_2/SO_4^{2-}$ was described in [7]; the solvent was passed through a column charged with calcined aluminum oxide. (–)-β-Citronellene (**II**) from Fluka, $[\alpha]_D^{20} = -9.0 \pm 1°$, containing no less than 90% of the main substance was used.

**Epoxy derivatives Ia and Ib.** A solution of 1.82 g (0.024 mol) of peroxyacetic acid in 25 ml of methylene chloride (prepared by extraction from a mixture of 200 ml of acetic acid, 200 ml of 30% hydrogen peroxide, and 10 ml of concentrated sulfuric acid and titrated with sodium thiosulfate) was added over a period of 20 min under vigorous stirring to a mixture of 2.76 g (0.020 mol) of (–)-β-citronellene (**II**) and 5.4 g of $Na_2CO_3$. The mixture was stirred for 1 h at room temperature and extracted with diethyl ether, the extract was washed with a 17% aqueous solution of $Na_2CO_3$ and water, and dried over $Na_2SO_4$, and the residue (2.67 g) was subjected to chromatography on silica gel (100–160 μm) using a solution of diethyl ether in hexane (0 to 5%) as eluent. We isolated 1.56 g (51%) of compounds **Ia** and **Ib** (a mixture of diastereoisomers at a ratio of ~1:1) $[\alpha]_{580}^{25} = -14.0°$ ($c$ = 3.64, $CHCl_3$). $^1$H NMR spectrum of **Ia**, δ, ppm: 0.90 d ($C^9H_3$, $J_{9,3}$ = 7 Hz), 1.118 s and 1.163 s ($C^8H_3$, $C^{10}H_3$), 1.34–1.45 m (4H, 4-H, 5-H), 2.06 m (3-H), 2.51 m (6-H), 4.80 d.d.d (1-H$_{cis}$, $J_{1\text{-}cis,2\text{-}cis}$ = 10, $^2J$ = 2, $J_{1\text{-}cis,3}$ = 1 Hz), 4.84 d.d.d (1-H$_{trans}$, $J_{1\text{-}trans,2\text{-}cis}$ = 17, $J$ = 2, $J_{1\text{-}trans,3}$ = 1 Hz), 5.52 d.d.d (2-H, $J$ = 17, 10, $J_{2,3}$ = 7.5 Hz) (cf. [2]. $^{13}$C NMR spectrum of **Ia**, $\delta_C$, ppm: 113.01 t ($C^1$), 143.75 d ($C^2$), 37.57 d ($C^3$), 33.22 t ($C^4$), 26.52 t ($C^5$), 63.79 d ($C^6$), 57.44 s ($C^7$), 24.65 q and 18.55 q ($C^8$, $C^{10}$), 19.95 q ($C^9$). $^1$H NMR spectrum of **Ib**, δ, ppm: 0.90 d ($C^9H_3$, $J_{9,3}$ = 7 Hz), 1.116 s and 1.160 s ($C^8H_3$, $C^{10}H_3$), 1.34–1.45 m (4H, 4-H, 5-H), 2.04 m (3-H), 2.51 m (6-H), 4.80 d.d.d (1-H$_{cis}$, $J_{1\text{-}cis,2\text{-}cis}$ = 10, $J_{1\text{-}cis,1\text{-}trans}$ = 2, $J_{1\text{-}cis,3}$ = 1 Hz), 4.85 d.d.d (1-H$_{trans}$, $J_{1\text{-}trans,2\text{-}cis}$ = 17, $J$ = 2, $J_{1\text{-}trans,3}$ = 1 Hz), 5.54 d.d.d (2-H, $J$ = 17, 10, $J_{2,3}$ = 7.5 Hz). $^{13}$C NMR spectrum of **Ib**, δ, ppm: 112.85 t ($C^1$), 143.63 d ($C^2$), 37.34 d ($C^3$), 33.01 t ($C^4$), 26.32 t ($C^5$), 63.61 d ($C^6$), 57.35 s ($C^7$), 24.67 q and 18.52 q ($C^8$, $C^{10}$), 20.15 q ($C^9$).

**Isomerization of compounds Ia and Ib in the presence of $ZrO_2/SO_4^{2-}$.** A solution of 0.275 g of stereoisomer mixture **Ia**/**Ib** in 2 ml of $CH_2Cl_2$ was added to a suspension of 0.550 g of $ZrO_2/SO_4^{2-}$ (preliminarily calcined for 2 h at 500°C) in 23 ml of methylene chloride, and the mixture was stirred for 0.5 h at 20°C. After appropriate treatment, the crude product was subjected to column chromatography on aluminum oxide (activity grade IV) to isolate 0.255 g of a mixture of compounds **III** and **IV** at a ratio of ~3:1 (GLC). This mixture was separated by double column chromatography on silica gel (40–100 μm, Czechia) using 0 to 35% of diethyl ether in hexane as eluent. We isolated 0.097 g (35%) of ketone **III** and 0.019 g (7%) of aldehyde **IV**.

Compound **III**, $[\alpha]_{580}^{25} = -9.0°$ ($c$ = 1.11, $CHCl_3$). $^1$H NMR spectrum, δ, ppm: 0.93 d ($C^9H_3$, $J_{9,6}$ = 6.5 Hz), 1.00 d ($C^1H_3$, $C^{10}H_3$, $J$ = 7 Hz), 1.42 d.d.t. (5-H, $J_{5,5'}$ = 14, $J_{5,6}$ = 8, $J_{5,4}$ = 7 Hz), 1.54 d.t.d (5'-H, $J$ = 14, $J_{5',4}$ = 8, $J_{5',6}$ = 5), 2.02 m (6-H), 2.34 d.d (2H, 4-H, $J$ = 8, 7 Hz), 2.49 sept (2-H, $J$ = 7 Hz), 4.85 d.d.d (8-H$_{cis}$, $J_{8\text{-}cis,7\text{-}cis}$ = 10, $J_{8\text{-}cis,8\text{-}trans}$ = 2, $J_{8\text{-}cis,6}$ = 1 Hz), 4.87 d.d.d (8-H$_{trans}$, $J_{8\text{-}trans,7\text{-}cis}$ = 17, $J$ = 2, $J_{8\text{-}trans,6}$ = 1 Hz), 5.53 d.d.d (7-H, $J$ = 17, 10, $J_{7,6}$ = 7.5 Hz) (cf. [2]). $^{13}$C NMR spectrum, $\delta_C$, ppm: 18.20 q and 18.15 q ($C^1$, $C^{10}$), 40.68 d ($C^2$), 213.72 s ($C^3$), 37.85 t ($C^4$), 29.96 t ($C^5$), 37.50 d ($C^6$), 143.67 d ($C^7$), 113.29 t ($C^8$), 20.30 q ($C^9$). Found: $M^+$ 154.13594. $C_{10}H_{18}O$. Calculated: $M$ 154.13576.

**Isomerization of compounds Ia and Ib in the presence of $SnCl_4$.** A mixture of 0.1 ml of $SnCl_4$ and 1 ml of dry methylene chloride was added under stirring and cooling (0°C) to a solution of 0.410 g of stereoisomer mixture **Ia**/**Ib** in 25 ml of dry methylene chloride, and the mixture was stirred for 2 h at 0°C. The mixture was diluted with chloroform, washed in succession with a 17% aqueous solution of sodium carbonate, 10% hydrochloric acid, a saturated solution of sodium chloride, and water, and dried over sodium sulfate. The solvent was distilled off, and the residue (0.329 g) was passed through a column charged with aluminum oxide (activity grade IV). The column was eluted with diethyl ether to obtain 0.222 g of a mixture containing 22% of compound **III** and 48% of **IV** (GC–MS data). The mixture was subjected to column chromatography on silica gel (40–100 μm, Czechia) using 0 to 5% of diethyl ether in hexane as eluent to isolate 0.020 g (5%) of ketone **III** and 0.025 g (6%) of aldehyde **IV**.

Compound **IV**. $[\alpha]_{580}^{25} = -9.9°$ ($c$ = 0.81, $CHCl_3$). $^1$H NMR spectrum, δ, ppm: 0.96 d ($C^8H_3$, $J_{8,5}$ = 7 Hz), 1.00 s ($C^{10}H_3$, $C^9H_3$), 1.11–1.24 m (2H, 4-H), 1.32–1.48 m (2H, 3-H), 2.02 d.q.t (5-H, $J_{5,6}$ = 8, $J_{5,8}$ = 7, $J_{5,4}$ = 7 Hz), 4.89 d.d.d (7-H$_{cis}$, $J_{7\text{-}cis,6\text{-}cis}$ = 10, $J_{7\text{-}cis,7\text{-}trans}$ = 2, $J_{7\text{-}cis,5}$ = 1 Hz), 4.91 d.d.d (7-H$_{trans}$, $J_{7\text{-}trans,6\text{-}cis}$ = 17, $J$ = 2, $J_{7\text{-}trans,5}$ = 1 Hz), 5.58 d.d.d (6-H, $J$ = 17, 10, 8 Hz), 9.37 s (1-H). $^{13}$C NMR spectrum, $\delta_C$, ppm: 205.12 d ($C^1$), 45.53 s ($C^2$), 34.89 t ($C^3$), 30.97 t

($C^4$), 38.34 d ($C^5$), 143.86 d ($C^6$), 113.30 t ($C^7$), 20.33 q ($C^8$), 21.42 q and 21.35 q ($C^9$, $C^{10}$). Found: $M^+$ 154.13594. $C_{10}H_{18}O$. Calculated: *M* 154.13576.

**Reaction of compounds Ia and Ib with acetone in the presence of sulfuric acid.** Stereoisomer mixture **Ia**/**Ib**, 0.200 g, was added to 15 ml of an acetone–water–sulfuric acid mixture (40:6:1, by volume), and the mixture was stirred for 15 min at 20°C. After appropriate treatment, we isolated 0.162 g of a crude product containing ~80% of compounds **Va** and **Vb** (GLC). It was subjected to column chromatography on silica gel (40–100 μm, Czechia) using 0 to 5% of diethyl ether in hexane as eluent to isolate 0.138 g (50%) of diastereoisomer mixture **Va**/**Vb** with one isomer slightly prevailing ($^1$H NMR), $[\alpha]_{580}^{25}$ = –2.70° (*c* 3.33, $CHCl_3$).

Isomer **Va**. $^1$H NMR spectrum, δ, ppm: 0.91 d ($C^{13}H_3$, $J_{13,6}$ = 7 Hz), 0.95 s and 1.11 s ($C^9H_3$, $C^{10}H_3$), 1.194 s and 1.277 s ($C^{11}H_3$, $C^{12}H_3$), 1.12–1.51 m (4H, 4-H, 5-H), 2.05 m (6-H), 3.50 d.d (3-H, $J_{3,4}$ = 9, $J_{3,4'}$ = 4 Hz), 4.81 d.d.d (8-$H_{cis}$, $J_{8\text{-}cis,7\text{-}cis}$ = 10, $J_{8\text{-}cis,8\text{-}trans}$ = 2, $J_{8\text{-}cis,6}$ = 1 Hz), 4.85 d.d.d (8-$H_{trans}$, $J_{8\text{-}trans,7\text{-}cis}$ = 17, $J$ = 2, $J_{8\text{-}trans,6}$ = 1.2 Hz), 5.55 d.d.d (7-H, $J$ = 17, 10, $J_{7,6}$ = 7.5 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 79.77 s ($C^1$), 106.11 s ($C^2$), 83.43 d ($C^3$), 27.04 t ($C^4$), 33.73 t ($C^5$), 37.63 d ($C^6$), 143.87 d ($C^7$), 112.90 t ($C^8$), 25.92 q and 22.68 q ($C^9$, $C^{10}$), 28.39 q and 26.68 q ($C^{11}$, $C^{12}$), 20.05 q ($C^{13}$).

Isomer **Vb**. $^1$H NMR spectrum, δ, ppm: 0.91 d ($C^{13}H_3$, $J_{13,6}$ = 7 Hz), 0.95 s and 1.11 s ($C^9H_3$, $C^{10}H_3$), 1.192 s and 1.279 s ($C^{11}H_3$, $C^{12}H_3$), 1.12–1.51 m (4H, 4-H, 5-H), 2.03 m (6-H), 3.52 d.d (3-H, $J_{3,4}$ = 9, $J_{3,4'}$ = 3.5 Hz), 4.81 d.d.d (8-$H_{cis}$, $J_{8\text{-}cis,7\text{-}cis}$ = 10, $J_{8\text{-}cis,8\text{-}trans}$ = 2, $J_{8\text{-}cis,6}$ = 1 Hz), 4.86 d.d.d (8-$H_{trans}$, $J_{8\text{-}trans,7\text{-}cis}$ = 17, $J$ = 2, $J_{8\text{-}trans,6}$ = 1.2 Hz), 5.56 d.d.d (7-H, $J$ = 17, 10, $J_{7,6}$ = 7.5 Hz) (cf. [5]). $^{13}$C NMR spectrum, $\delta_C$, ppm: 79.77 s ($C^1$), 106.11 s ($C^2$), 83.04 d ($C^3$), 26.75 t ($C^4$), 33.41 t ($C^5$), 37.97 d ($C^6$), 143.87 d ($C^7$), 112.82 t ($C^8$), 25.92 q and 22.65 q ($C^9$, $C^{10}$), 28.39 q and 26.68 q ($C^{11}$, $C^{12}$), 20.17 q ($C^{13}$). Found: $[M - CH_3]^+$ 197.15409. $C_{12}H_{21}O_2$ (fragment ion $[M - CH_3]^+$). Calculated: *M* 197.15414.

**Reaction of compounds Ia and Ib with acetonitrile in the presence of sulfuric acid.** Concentrated sulfuric acid, 0.1 ml, was added to a solution of 0.150 g of stereoisomer mixture **Ia**/**Ib** in 5 ml of acetonitrile, and the mixture was stirred for 1 h at 25°C, neutralized with a 17% aqueous solution of sodium carbonate, and extracted with diethyl ether. The extract was washed with a 17% aqueous solution of sodium carbonate and water and dried over sodium sulfate. The solvent was distilled off, and the residue, 0.146 g, contained compounds **VIa**/**VIb**+**VIIa**/**VIIb** and **III** at a ratio of ~3.5:1 (GLC). The crude product was twice distilled under reduced pressure (6 mm), a fraction boiling in the range from 80 to 110°C being collected. We thus isolated 0.064 g (33%) of a mixture of compounds **VIa**, **VIb**, **VIIa**, and **VIIb** at a ratio of ~5:5:2:2 ($^1$H NMR). Chromatographic separation of a 0.145-g portion of the same crude product on silica gel gave 0.027 g (18%) of ketone **III**; compounds **VIa**, **VIb**, **VIIa**, and **VIIb** decomposed during chromatographic separation.

Compounds **VIa**/**VIb**. $^1$H NMR spectrum, δ, ppm: 0.846 d (6H, $C^{12}H_3$, $J_{12,6}$ = 6.5 Hz); 0.845 s, 0.848 s, 1.028 s, and 1.031 s (3H each, $C^9H_3$, $C^{10}H_3$); 1.70 s (6H, $C^{11}H_3$); 1.05–1.48 m (8H, 4-H, 5-H); 1.97–2.04 m (2H, 6-H); 3.68 m (2H, 3-H); 4.74 d.m (2H, 8-$H_{cis}$, $J_{8\text{-}cis,7\text{-}cis}$ = 10 Hz); 4.77 d.m (2H, 8-$H_{trans}$, $J_{8\text{-}trans,7\text{-}cis}$ = 17 Hz); 5.45 d.d.d (2H, 7-H, $J$ = 17, 10, $J_{7,6}$ = 7.5 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: isomer **VIa**: 67.63 s ($C^1$), 161.73 s ($C^2$), 88.60 d ($C^3$), 27.40 t ($C^4$), 33.41 t ($C^5$), 37.76 d ($C^6$), 143.50 d ($C^7$), 113.09 t ($C^8$), 28.99 q and 22.60 q ($C^9$, $C^{10}$), 13.82 q ($C^{11}$), 20.14 q ($C^{12}$); isomer **VIb**: 67.63 s ($C^1$), 161.73 s ($C^2$), 88.15 d ($C^3$), 27.67 t ($C^4$), 33.41 t ($C^5$), 37.43 d ($C^6$), 143.54 d ($C^7$), 113.09 t ($C^8$), 29.03 q and 22.58 q ($C^9$, $C^{10}$), 13.82 q ($C^{11}$), 20.19 q ($C^{12}$).

Compound **VIIa**/**VIIb**. $^1$H NMR spectrum, δ, ppm: 0.824 d and 0.826 d (3H each, $C^{12}H_3$, $J_{12,6}$ = 6.5 Hz); 0.887 s, 0.894 s, 0.939 s, and 0.943 s (3H each, $C^9H_3$, $C^{10}H_3$); 1.70 s (6H, $C^{11}H_3$); 1.05–1.48 m (8H, 4-H, 5-H); 1.87–2.02 m (2H, 6-H); 3.015 d.d and 3.020 d.d (1H each, 3-H, $J_{3,4}$ = 10.5, $J_{3,4'}$ = 8Hz); 4.66–4.78 m (4H, 8-$H_{cis}$, 8-$H_{trans}$); 5.47 d.d.d and 5.45 d.d.d (2H, 7-$H_{cis}$, $J_{7\text{-}cis,8\text{-}trans}$ = 17, $J_{7\text{-}cis,8\text{-}cis}$ = 10, $J_{7,6}$ = 7.5 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: isomer **VIIa**: 72.29 s ($C^1$), 161.73 s ($C^2$), 77.51 d ($C^3$), 28.92 t ($C^4$), 33.41 t ($C^5$), 37.76 d ($C^6$), 144.11 d ($C^7$), 112.39 t ($C^8$), 26.36 q and 23.07 q ($C^9$, $C^{10}$), 13.82 q ($C^{11}$), 19.99 q ($C^{12}$); isomer **VIIb**: $\delta_C$, ppm: 72.29 s ($C^1$), 161.73 s ($C^2$), 77.98 d ($C^3$), 29.19 t ($C^4$), 33.73 t ($C^5$), 37.50 d ($C^6$), 144.32 d ($C^7$), 112.60 t ($C^8$), 26.36 q and 23.09 q ($C^9$, $C^{10}$), 13.82 q ($C^{11}$), 20.41 q ($C^{12}$). Found for mixture **VIa**/**VIb**+**VIIa**/**VIIb**: $M^+$ 195.16283. $C_{12}H_{21}NO$. Calculated: *M* 195.16230.

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