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Acid-Catalyzed Reactions of 2,3-Epoxy Derivatives of Citral with Alcohols

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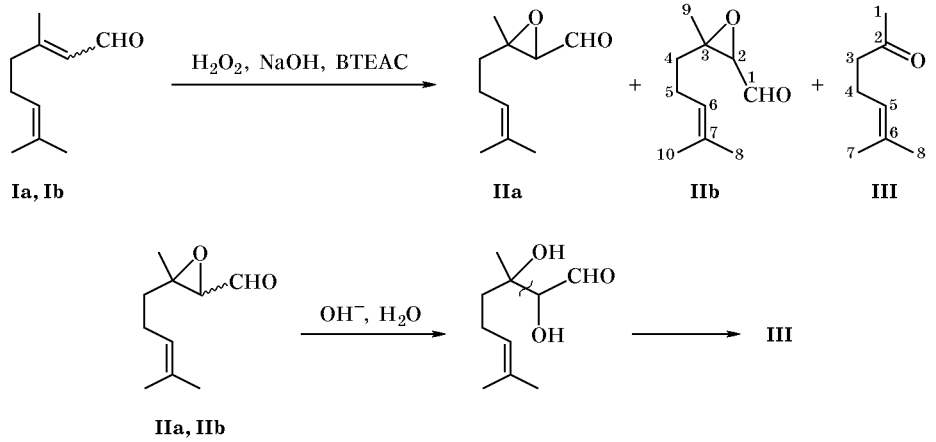
Abstract—Acid-catalyzed reactions of 2,3-epoxy derivatives of citral (which is a widely spread naturally occurring unsaturated aldehyde) with alcohols were studied under conditions of heterogeneous catalysis and in fluorosulfonic acid. A number of new products were obtained, and possible mechanisms of their formation were proposed.

Interest in chemical transformations of terpene compounds arises from their accessibility and reactivity which make it possible to obtain products having various structures [1]. Of particular interest are acid-catalyzed transformations of terpenes and their oxygen-containing analogs, for these processes are accompanied by skeletal rearrangements which open the way to selective preparation of valuable but difficultly accessible compounds or new compounds with an unusual carbon backbone. Epoxy derivatives of naturally occurring compounds could give rise to cyclic and acyclic oxygen-containing products, and studies of their transformations provide information on the reaction mechanisms and relative reactivity of such compounds.

We were the first to examine acid-catalyzed reactions of 2,3-epoxy derivatives of citral. The latter is widely spread in the nature as a mixture of *E* and *Z* isomers, geranial (**Ia**) and neral (**Ib**), and wide synthetic potential of its labile polyfunctional molecule makes the use of citral and its derivatives in the synthesis of various substances very promising.

2,3-Epoxy derivatives **II** were obtained as a mixture of diastereoisomers **IIa** and **IIb** by the known method, treatment of citral **I** with hydrogen peroxide in alkaline medium in the presence of phase-transfer

Scheme 1.



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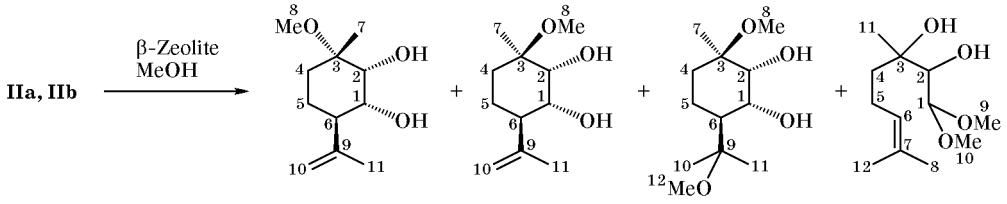
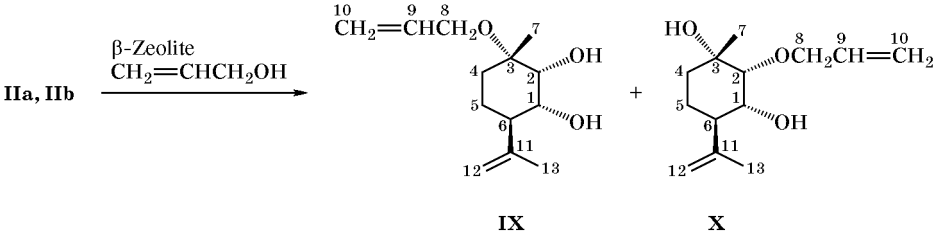
Scheme 2.



Scheme 3.



catalyst [2]. Also, 6-methyl-5-hepten-2-one (**III**) was formed as a result of decomposition of epoxy derivatives **II** (Scheme 1). Optically active 2,3-epoxides derived from geranial and neral have already been reported: They were synthesized by asymmetric epoxidation of geraniol and nerol, followed by oxidation of the alcohol moiety to aldehyde [3, 4].

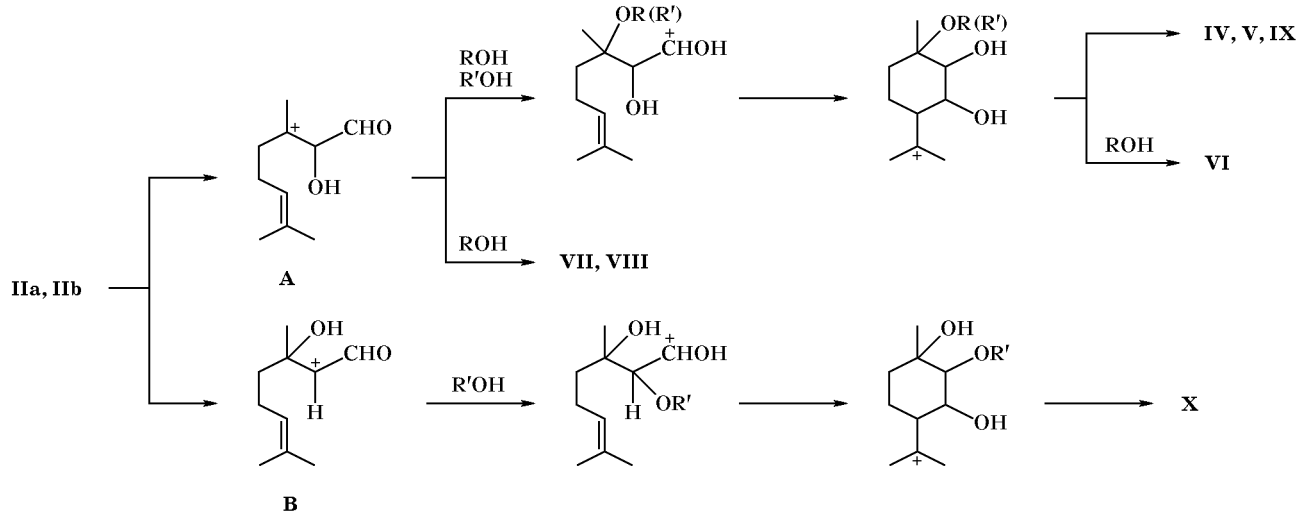
In the present work we used a racemic mixture of compounds **IIa** and **IIb** at a ratio of 1:1 and studied their reactions with methyl and allyl alcohols over acidic β-zeolite. The reaction of **IIa**/**IIb** with methyl alcohol gave a mixture of compounds **IV**–**VIII** at a ratio of 3.8:2.7:1:2.4 (hereinafter, according to the GLC data; Scheme 2). The structure of (1*R*,2*R*,3*S*,6*R*)-6-isopropenyl-3-methoxy-3-methylcyclohexane-1,2-diol (**IV**), (1*R*,2*R*,3*R*,6*R*)-6-isopropenyl-3-methoxy-3-methylcyclohexane-1,2-diole (**V**), (1*R*,2*R*,3*R*,6*S*)-3-methoxy-6-(1-methoxy-1-methylethyl)-3-methylcyclohexane-1,2-diol (**VI**), and 1,1-dimethoxy-3,7-dimethyl-6-octene-2,3-diols (**VII** and **VIII**, a mixture of isomers) was determined by NMR spectroscopy. The products were separated by column chromatography on silica gel impregnated with 20% of $AgNO_3$.

The reaction of **IIa**/**IIb** with allyl alcohol over β-zeolite resulted in formation of (1*R*,2*S*,3*S*,6*R*)-3-allyloxy-6-isopropenyl-3-methylcyclohexane-1,2-diol (**IX**) and (1*R*,2*R*,3*S*,4*R*)-2-allyloxy-4-isopropenyl-1-methylcyclohexane-1,3-diol (**X**) at a ratio of 1:2 (Scheme 3).

A probable mechanism of formation of diols **IV**–**X** is shown in Scheme 4. In the reaction with methyl alcohol, protonation of epoxy aldehydes **IIa**/**IIb** leads to opening of the oxirane ring with formation of tertiary carbenium ion **A** which immediately reacts with methanol molecule. The subsequent rearrangements either involve ring closure to give cyclic diols **IV**–**VI** or afford acyclic compounds **VII** and **VIII**. In the reaction with allyl alcohol, opening of the oxirane ring in **IIa**/**IIb** gives rise to either tertiary cation **A** or secondary cation **B**. These cations take up allyl alcohol, yielding compounds **IX** and **X**, respectively. The different pathways in the reactions of **IIa**/**IIb** with methyl and allyl alcohols may be understood in terms of different nucleophilicities of these alcohols. It should be noted that application of epoxy derivatives **IIa** and **IIb** to solid catalysts, such as β-zeolite used in our study or other acid catalysts (e.g., clays or solid superacids) in the absence of a nucleophile leads to polymerization of the substrate.

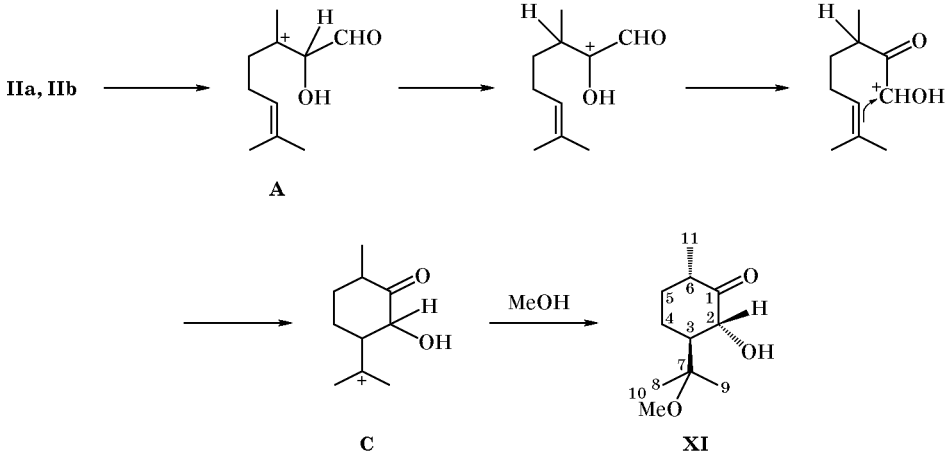
In the presence of liquid superacids, the reaction of epoxy derivatives **IIa** and **IIb** with methanol took a radically different pathway. A mixture of compounds **IIa** and **IIb** was dissolved in fluorosulfonic acid (molar ratio HSO_3F:**IIa**/**IIb** = 20:1; volume ratio SO_2FCl:HSO_3F = 4:1; –115°C), and the resulting acid solution was quenched with a mixture of methanol with diethyl ether at a ratio of 5:2. We thus obtained (2*R*,3*S*,6*S*)-2-hydroxy-6-methyl-3-(1-methoxy-1-methylethyl)cyclohexanone (**XI**). A possible mechanism of formation of compound **XI** is shown in Scheme 5. It includes opening of the oxirane ring to give tertiary cation **A** which then undergoes rearrangements leading to cation **C**. The latter takes up methanol molecule to afford product **XI**.

Scheme 4.



R = CH_3, R′ = $CH_2CH{=}CH_2$.

Scheme 5.



Thus, in fluorosulfonic acid, initial opening of the oxirane ring is followed by isomerization, cyclization, and addition of methanol molecule to cation **C**, whereas the process over acid zeolite involves reaction with alcohol immediately after opening of the oxirane ring; the main pathway in the reaction with methanol leads to formation of 1,2-dihydroxycyclohexanes, and in the reaction with allyl alcohol, to 1,3-dihydroxycyclohexanes. Compounds **IV**–**XI** have not been reported previously.

Let us consider some aspects of structure determination of the compounds prepared. By analysis of vicinal and long-range coupling constants for protons on C^1–C^6 (see Experimental) we succeeded in establishing the conformations of compounds **IV** and **V** and substituent configuration therein. In the ^{1}H NMR spectrum of **IV**, the coupling constants between 1-H and 2-H ($^3J_{1,2}$ = 3 Hz), 1-H and 6-H ($^3J_{1,6}$ = 10 Hz), and 6-H and two 5-H protons ($^3J_{6,5\text{-}ax}$ = 12, $^3J_{6,5\text{-}eq}$ = 4 Hz) indicate that the 1-H and 6-H protons occupy axial positions and that 2-H is equatorial. The presence of a long-range coupling constant between 4-H_{ax} and protons of the methyl group on C^3 suggests axial orientation of the latter. The vicinal coupling constants in the ^{1}H NMR spectrum of **V** are similar to those observed for compound **IV**; however, no long-range coupling between 4-H_{ax} and 3-CH_3 was detected even on forced narrowing of spectral lines. This means that the C^7CH_3 group occupies equatorial position. It follows from the above stated that the hydroxy groups on C^1 and C^2, methoxy group on C^3, and 6-H_{ax} are arranged *cis* with respect to each other

in molecule **IV** and that the methoxy group on C^3 in molecule **V** is axial and is arranged *trans* with respect to the above listed groups. The location of methoxy group in diols **IV** and **V** on C^3 rather than on C^1 or C^2 was proved by the LRJMD technique. Irradiation at a frequency corresponding to resonance of the OCH_3 protons (δ 3.21 and 3.13 ppm, respectively) gave rise to singlets at δ_C 76.74 (compound **IV**) and 76.93 ppm (**V**), which belong to C^3.

The positions of hydroxy groups in **VI** (at C^1 and C^2) were determined on the basis of the ^{13}C NMR data. After addition of D_2O (H–D exchange in the hydroxy groups), we observed upfield shift of two doublets at δ_C 70.72 ($\Delta\delta_C$ = 0.10) and 73.68 ppm (Δ = 0.15 ppm), which belong, respectively, to C^1 and C^2. The configuration of substituents in **VI** is the same as in **V**.

The fact that both methoxy groups in diols **VII** and **VIII** are attached to the same carbon atom follows from the LRJMD spectrum. Suppression of signals from all methoxy group protons (δ 3.41 ppm) in the LRJMD spectrum of a mixture of **VII** with **VIII** at a ratio of ~1:2 gave a response only at the C^1 signal at δ_C 104.46 and 104.27 ppm, respectively. If one or both methoxy groups were attached to C^2 and/or C^3, additional carbon signals would appear in the LRJMD spectrum at δ_C 73.92, 74.29 and/or 73.03 ppm (or only the latter).

In the ^1H NMR spectrum of **X**, the vicinal coupling constant between the 3-H and 4-H protons ($^3J_{3,4}$ = 10.5 Hz) indicates their axial orientation, and a small value of $^3J_{2,3}$ (3 Hz) suggests equatorial orientation of 2-H. Protons of the methyl group on C^1 are characterized by a coupling constant $^4J_{7,6\text{-}ax}$ of 0.6 Hz, which is typical of axial orientation of C^7H_3. Therefore, the methyl group on C^1 and isopropenyl group on C^4 are arranged *cis* with respect to each other and *trans* with respect to 2-OR and 3-OH.

On the basis of the vicinal coupling constants for 1-H–2-H and 1-H–6-H (J = 9 Hz) and the appearance of ^4J = 0.7 Hz between the C^7H_3 protons and 4-H_{ax} we concluded that the 1-H, 2-H, and 6-H protons and the 3-CH_3 group in molecule **IX** are axial. This means that the 3-CH_3 group is located *cis* with respect to 1-H and *trans* with respect to 2-H and 6-H.

The position of the allyloxy group at the C^2 atom in molecule **X** and at C^3 in **IX** follows from the LRJMD spectra. Suppression of the 8-H resonance (δ 3.94 and 3.91 ppm, respectively) gives rise in the first case to a doublet signal at δ_C 74.33 ppm (C^2) in addition to those belonging to C^9 and C^{10}, and in the second, to a singlet at δ_C 77.77 ppm (C^3).

Like other compounds, the configuration of **XI** was determined from vicinal coupling constants for the corresponding protons. 2,3-Epoxy neral derivative **IIb** was previously characterized by the ^1H and ^{13}C NMR spectra [4, 5], but no complete signal assignment was given. The chemical shifts measured in the present work are in agreement with those reported in [4, 5].

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. A mixture of CCl_4 with $CDCl_3$ (~1:1, by volume) was used as solvent, and chloroform signals were taken as reference (δ 7.24 ppm, δ_C 76.90 ppm). The structure of the products was determined by analysis of coupling constants in the ^1H–^1H double resonance spectra and by analysis of the ^{13}C NMR spectra recorded with selective decoupling from protons, off-resonance spectra, two-dimensional ^{13}C–^1H correlation spectra (COSY, direct couplings, $^1J_{C,H}$ = 135 Hz), and one-dimensional ^{13}C–^1H correlation spectra (LRJMD, long-range couplings, $J_{C,H}$ = 10 Hz). For some compounds, direct coupling constants $^1J_{C,H}$ are given, which were obtained from the monoresonance spectra; their values do not contradict the assigned structures.

The purity of the initial compounds was checked, and the product mixtures were analyzed, by GLC on a Biokhrom-1 chromatograph using the following columns: (a) XE-60 glass capillary column, 53 m × 0.26 mm, and (b) BS-30 (an analog of SE-30) quartz capillary column, 20 m × 0.27 mm; flame ionization detector; carrier gas helium. The product mixtures were separated by column chromatography on silica gel (Czechia, 40–100 and 100–160 μm), $SiO_2/AgNO_3$, and Al_2O_3. The ratio crude product–sorbent was 1:20 to 1:40. The elemental compositions were determined from the high-resolution mass spectra which were recorded on a Finnigan MAT 8200 instrument.

Doubly distilled fluorosulfonic acid (bp 158–161°C) was used for preparation of acid solutions. Fluorosulfonyl chloride (diluent) was purified by passing through sulfuric acid. The acid mixtures were quenched with a mixture of methanol with diethyl ether (5:2, by volume). The procedures for preparation and qienching of acid solutions were described in [6]. Wide-pore β-zeolite (SiO_2/Al_2O_3 22.4; pore diameter 0.75–0.80 nm; oxide concentration, %: Na_2O 0.01, Al_2O_3 4.50, SiO_2 59.20, Fe_2O_3 0.08%) was manufactured by *Tseosit* (Novosibirsk, Russia); it was calcined for 3 h at 500°C prior to use. The following reagents were used: citral (from Fluka) with

a purity of no less than 97%, *cis*/*trans* isomer ratio 1:2 (according to the ^{1}H NMR data), and technical-grade citral containing 13% of dehydrolinalool, *cis*/*trans* isomer ratio 1:1 (^{1}H NMR).

The reaction of citral with hydrogen peroxide under conditions of phase-transfer catalysis was carried out following the procedure described in [2]. From 3 g of citral we obtained 2.35 g of a crude product containing compounds **IIa**, **IIb**, and **III** at a ratio of 3.8:3.3:1. The products were separated by column chromatography on silica gel using hexane as eluent: 0.10 g of **III** and 1.95 g of a **IIa**/**IIb** mixture were isolated. Isomer mixture **IIa**/**IIb** was then separated on basic Al_2O_3 using hexane as eluent; as a result, 0.25 g of pure 2,3-epoxy derivative **IIb** was isolated. The ^{1}H and ^{13}C NMR spectra of geranial epoxide **IIa** were reported in [3].

Compound **IIb**. Found $[M]^+$: 168.11495. $C_{10}H_{16}O_2$. Calculated *M*: 168.11502. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.38 s (C^9H_3), 1.55 br.s ($C^{10}H_3$), 1.63 m (C^8H_3), 1.63 m (4-H), 1.81 d.d.d (4′-H, $J_{4',4}$ = 14, $J_{4',5}$ = 8.5, $J_{4',5'}$ = 5.5), 1.96–2.26 m (2H, 5-H), 3.11 d (2-H, $J_{2,1}$ = 5), 5.00 t.q.q (6-H, $J_{6,5}$ = 7, $J_{6,8}$ = 1.5, $J_{6,10}$ = 1.5), 9.38 d (1-H, *J* = 5). ^{13}C NMR spectrum, δ_C, ppm: 198.74 d (C^1), 64.47 d (C^2), 64.42 s (C^3), 33.27 t (C^4), 24.04 t (C^5), 122.27 d (C^6), 133.15 s (C^7), 25.44 q (C^8), 21.97 q (C^9), 17.45 q (C^{10}).

Compound **III**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.57 br.s (C^8H_3), 1.63 br.s (C^7H_3), 2.08 s (C^1H_3), 2.19 br.t.d (2H, 4-H, $J_{4,3}$ = 7, $J_{4,5}$ = 7), 2.39 t (2H, 3-H, $J_{3,4}$ = 7), 5.00 t.q.q (5-H, *J* = 7, $J_{5,7}$ = 1.5, $J_{5,8}$ = 1.5). ^{13}C NMR spectrum, δ_C, ppm: 29.70 q (C^1), 207.62 s (C^2), 43.58 t (C^3), 22.43 t (C^4), 122.76 d (C^5), 132.41 s (C^6), 25.63 q (C^7), 17.58 q (C^8).

Reaction of epoxy derivatives IIa/IIb with methanol over β-zeolite. Methanol (preliminarily dried by passing through calcined aluminum oxide), 0.5 ml, and a solution of 0.27 g of a mixture of compounds **IIa** and **IIb** (at a ratio of 1:1) in 1 ml of methylene chloride were added in succession to a mixture of 0.4 g of β-zeolite in 3 ml of methylene chloride. After 30 min, the mixture was filtered, the catalyst was washed with diethyl ether, and the filtrate was combined with the washings and evaporated to obtain 0.25 g of a crude product. The product was subjected to column chromatography, first on SiO_2 and then on $SiO_2/AgNO_3$, using hexane–diethyl ether mixtures as eluent (0.5 to 10% of diethyl ether, gradient elution) to isolate 0.044 g of compound **IV**, 0.022 g of **V**, 0.008 g of **VI**, 0.011 g of **VII**/**VIII** (isomer mixture, 4:1), 0.015 g of **VII**/**VIII** (1:2), and 0.015 g of **VII**/**VIII** (1:1).

Compound **IV**. Found $[M]^+$: 200.14099. $C_{11}H_{20}O_3$. Calculated *M*: 200.14123. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 d (C^7H_3, $J_{7,4\text{-}ax}$ = 0.7), 1.22 d.d.d.d (5-H_{ax}, $J_{5\text{-}ax,5\text{-}eq}$ = 14, $J_{5\text{-}ax,4\text{-}ax}$ = 12.5, $J_{5\text{-}ax,6\text{-}ax}$ = 12, $J_{5\text{-}ax,4\text{-}eq}$ = 3.5), 1.47 d.d.d.d (4-H_{eq}, $J_{4\text{-}eq,4\text{-}ax}$ = 12.5, *J* = 3.5, $J_{4\text{-}eq,5\text{-}eq}$ = 3.5, $J_{4\text{-}eq,2\text{-}eq}$ = 1.2), 1.55 d.d.d.d (5-H_{eq}, *J* = 14, $J_{5\text{-}eq,4\text{-}ax}$ = 4, $J_{5\text{-}eq,6\text{-}ax}$ = 4, *J* = 3.5), 1.67 d.d.d (4-H_{ax}, *J* = 12.5, 12.5, 4), 1.69 d.d ($C^{11}H_3$, $J_{11,10'}$ = 1.5, $J_{11,10}$ = 1), 2.24 br.d (1-OH, *J* = 6), 2.37 d.d.d (6-H_{ax}, *J* = 12, $J_{6\text{-}ax,1\text{-}ax}$ = 10, *J* = 4), 2.72 br.s (2-OH), 3.21 s (OCH_3), 3.45 br.m (1-H_{ax}, *J* = 10, 6, $J_{1\text{-}ax,2\text{-}eq}$ = 3), 3.70 m (2-H_{eq}, *J* = 3, 1.2), 4.77 d.d.q (10-H, $J_{10,10'}$ = 2, $J_{10,6\text{-}ax}$ = 1, $J_{10,11}$ = 1), 4.80 d.q (10′-H, *J* = 2, 1.5). ^{13}C NMR spectrum, δ_C, ppm ($^1J_{C,H}$, Hz): 70.95 d (142) (C^1), 74.13 d (146) (C^2), 76.74 s (C^3), 29.86 t (128) (C^4), 25.58 t (128) (C^5), 46.44 d (129) (C^6), 18.87 q (126) (C^7), 48.41 q (141) (C^8), 145.85 s (C^9), 112.55 t (155) (C^{10}), 19.73 q (126) (C^{11}).

Compound **V**. Mass spectrum: Found $[M-H_2O]^+$ (fragment ion): *m*/*z* 182.13049. $C_{11}H_{18}O_2$. Calculated: 182.13067. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.18 s (C^7H_3), 1.33 m (5-H_{eq}), 1.43 d.d.d.d (5-H_{ax}, $J_{5\text{-}ax,5\text{-}eq}$ = 12.5, $J_{5\text{-}ax,4\text{-}ax}$ = 12.5, $J_{5\text{-}ax,6\text{-}ax}$ = 12.5, $J_{5\text{-}ax,4\text{-}eq}$ = 4), 1.51 d.d.d (4-H_{ax}, $J_{4\text{-}ax,4\text{-}eq}$ = 12.5, *J* = 12.5, $J_{4\text{-}ax,5\text{-}eq}$ = 4), 1.58 m (4-H_{eq}), 1.69 d.d ($C^{11}H_3$, $J_{11,10'}$ = 1.5, $J_{11,10}$ = 1), 2.08 br.s and 2.66 br.s (2H, OH), 2.24 d.d.d (6-H_{eq}, $J_{6\text{-}ax,5\text{-}ax}$ = 12.5, $J_{6\text{-}ax,1\text{-}ax}$ = 11, $J_{6\text{-}ax,5\text{-}eq}$ = 4), 3.13 s (OCH_3), 3.62 d.d (2-H_{eq}, $J_{2\text{-}eq,1\text{-}ax}$ = 3, $J_{2\text{-}eq,4\text{-}eq}$ = 1), 3.75 d.d (1-H_{ax}, *J* = 11, 3), 4.81 br.s (10-H), 4.83 d.q (10′-H, $J_{10',10}$ = 2, *J* = 1.5). ^{13}C NMR spectrum, δ_C, ppm ($^1J_{C,H}$, Hz): 69.17 d (146) (C^1), 73.48 d (146) (C^2), 76.93 s (C^3), 28.17 t (128) (C^4), 24.20 t (130) (C^5), 45.87 d (127) (C^6), 20.96 q (126) (C^7), 48.12 q (141) (C^8), 146.30 s (C^9), 113.05 t (155) (C^{10}), 19.02 q (126) (C^{11}).

Compound **VI**. Mass spectrum: Found $[M-H_2O-CH_3]^+$ (fragment ion): *m*/*z* 183.13054. $C_{11}H_{19}O_2$. Calculated: 183.13067. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.10 m (5-H_{ax}), 1.15 s and 1.19 s ($C^{10}H_3$, $C^{11}H_3$), 1.18 s (C^7H_3), 1.29 d.d.t (5-H_{eq}, $J_{5\text{-}eq,5\text{-}ax}$ = 13, $J_{5\text{-}eq,6\text{-}ax}$ = 4, $J_{5\text{-}eq,4}$ = 4), 1.54 m (2H, 4-H), 1.80 d.d.d (6-H_{ax}, $J_{6\text{-}ax,5\text{-}ax}$ = 13, $J_{6\text{-}ax,1\text{-}ax}$ = 10.5, *J* = 4), 2.59 br.s and 5.10 br.s (2H, OH), 3.13 s (OC^8H_3), 3.23 s ($OC^{12}H_3$), 3.52 d (2-H_{eq}, $J_{2\text{-}eq,1\text{-}ax}$ = 3), 3.88 d.d (1-H_{ax}, *J* = 10.5, 3). ^{13}C NMR spectrum, δ_C, ppm ($^1J_{C,H}$, Hz): 70.72 d (144) (C^1), 73.68 d (145) (C^2), 76.11 s (C^3), 29.11 t (128) (C^4), 21.25 t (128)

(C^5), 43.29 d (127) (C^6), 20.89 q (126) (C^7), 48.20 q (140) (C^8), 80.44 s (C^9), 19.53 q (126) (C^{10} or C^{11}), 23.62 q (125) (C^{11} or C^{10}), 48.43 q (141) (C^{12}).

We failed to isolate pure diols **VII** and **VIII**, and the NMR spectra were recorded for their mixtures containing mainly one or another isomer (see above).

Isomer **VII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 s ($C^{11}H_3$), 1.40 d.d.d (4-H, $J_{4,4'}$ = 13.5, $J_{4,5}$ = 10, $J_{4,5'}$ = 6.5), 1.54 d.d.d (4′-H, *J* = 13.5, $J_{4',5'}$ = 10, $J_{4',5}$ = 6.5), 1.59 br.s ($C^{12}H_3$), 1.65 br.s (C^8H_3), 2.05 m (2H, 5-H), 2.41 br.s (2-OH), 2.71 br.s (3-OH), 3.41 br.d (2-H, $J_{2,1}$ = 6), 3.41 s and 3.43 s (3H each, OCH_3), 4.38 d (1-H, *J* = 6), 5.08 t.q.q (6-H, $J_{6,5}$ = 7, $J_{6,8}$ = 1.5, $J_{6,12}$ = 1.5). ^{13}C NMR spectrum, δ_C, ppm: 104.46 d (C^1), 73.92 d (C^2), 73.03 s (C^3), 38.47 t (C^4), 21.85 t (C^5), 124.90 d (C^6), 131.07 s (C^7), 25.76 q (C^8), 54.53 q (C^9 or C^{10}), 54.05 q (C^{10} or C^9), 23.18 q (C^{11}), 17.67 q (C^{12}).

Isomer **VIII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 s ($C^{11}H_3$), 1.43 m and 1.55 m (2H, 4-H), 1.59 br.s ($C^{12}H_3$), 1.65 br.s (C^8H_3), 2.00 m (2H, 5-H), 2.50 br.s (2H, OH), 3.36 br.d (2-H, $J_{2,1}$ = 6), 3.40 s and 3.42 s (3H each, OCH_3), 4.36 d (1-H, *J* = 6), 5.06 m (6-H). ^{13}C NMR spectrum, δ_C, ppm: 104.27 d (C^1), 74.29 d (C^2), 73.03 s (C^3), 38.88 t (C^4), 22.25 t (C^5), 124.85 d (C^6), 131.11 s (C^7), 25.75 q (C^8), 54.61 q (C^9 or C^{10}), 54.18 q (C^{10} or C^9), 22.44 q (C^{11}), 17.66 q (C^{12}).

Reaction of compounds IIa and IIb with allyl alcohol over β-zeolite. Allyl alcohol (preliminarily dried by boiling over K_2CO_3 and purified by fractional distillation; bp 96°C), 0.6 ml, and a solution of 0.3 g of a 1:1 mixture of compounds **IIa** and **IIb** in 1 ml of methylene chloride were added in succession under stirring to a mixture of 0.4 g of β-zeolite and 3 ml of methylene chloride. After 1 h, the mixture was filtered, the catalyst was washed with diethyl ether, and the filtrate was combined with the washings and evaporated to obtain 0.27 g of a crude product. The product was purified from tars by passing through a column charged with Al_2O_3. We thus isolated 0.156 g of a mixture containing compounds **IX** and **X** at a ratio of 1:2 and ~10% of unidentified products. This mixture was subjected twice to chromatographic separation on silica gel (gradient elution with hexane–diethyl ether, 0.5 to 50% of the latter) to isolate 0.035 g of compound **IX** and 0.042 g of **X**.

Compound **IX**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.16 s (C^7H_3), 1.31 d.d.d.d (5-H_{ax}, $J_{5\text{-}ax,5\text{-}eq}$ = $J_{5\text{-}ax,4\text{-}ax}$ = $J_{5\text{-}ax,6\text{-}ax}$ = 13, $J_{5\text{-}ax,4\text{-}eq}$ = 4), 1.49 d.d.d (4-H_{ax}, $J_{4\text{-}ax,4\text{-}eq}$ = 13, *J* = 13, $J_{4\text{-}ax,5\text{-}eq}$ = 4), 1.56 d.d.d.d (5-H_{eq}, *J* = 13, 4, $J_{5\text{-}eq,6\text{-}ax}$ = 4, $J_{5\text{-}eq,4\text{-}eq}$ = 3), 1.70 br.s ($C^{13}H_3$), 1.80 d.d.d (4-H_{eq}, *J* = 13, 4, 3), 2.04 d.d.d (6-H_{ax}, *J* = 13, $J_{6\text{-}ax,1\text{-}ax}$ = 9, *J* = 4), 2.51 br.s and 2.81 br.s (1H each, OH), 3.38 d.d (1-H_{ax}, *J* = 9, $J_{1\text{-}ax,2\text{-}ax}$ = 9) and 3.42 d (2-H_{ax}, *J* = 9) (*AB* system), 3.91 d.d.t (8-H, $J_{8,8'}$ = 12, $J_{8,9}$ = 5, $J_{8,10}$ = 1.5) and 3.96 d.d.t (8′-H, *J* = 12, $J_{8',9}$ = 5, $J_{8',10}$ = 1.5) (*AB* system), 4.79 br.s (12-H), 4.81 d.q (12′-H, $J_{12',12}$ = 2, $J_{12',13}$ = 1.5), 5.06 d.d.t (10-H_{cis}, $J_{10\text{-}cis,9}$ = 10, $J_{10\text{-}cis,10\text{-}trans}$ = 1.5, *J* = 1.5), 5.20 d.d.t (10-H_{trans}, $J_{10\text{-}trans,9}$ = 17, *J* = 1.5, 1.5), 5.84 d.d.t (9-H, *J* = 17, 10, 5). ^{13}C NMR spectrum, δ_C, ppm: 72.05 d (C^1), 79.94 d (C^2), 77.77 s (C^3), 33.95 t (C^4), 26.28 t (C^5), 50.76 d (C^6), 16.47 q (C^7), 62.42 t (C^8), 135.94 d (C^9), 115.67 t (C^{10}), 145.31 s (C^{11}), 112.67 t (C^{12}), 19.47 q (C^{13}).

Compound **X**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.20 d (C^7H_3, $J_{7,6\text{-}ax}$ = 0.6), 1.26 m (5-H_{ax}), 1.51 d.d.d.d (6-H_{eq}, $J_{6\text{-}eq,6\text{-}ax}$ = 13, $J_{6\text{-}eq,5\text{-}ax}$ = 4, $J_{6\text{-}eq,5\text{-}eq}$ = 4, $J_{6\text{-}eq,2\text{-}eq}$ = 1), 1.57 d.d.d.d (5-H_{eq}, $J_{5\text{-}eq,5\text{-}ax}$ = 13.5, $J_{5\text{-}eq,4\text{-}ax}$ = 4, $J_{5\text{-}eq,6\text{-}ax}$ = 4, *J* = 4), 1.70 br.s ($C^{13}H_3$), 1.74 d.d.d (6-H_{ax}, *J* = 13, $J_{6\text{-}ax,5\text{-}ax}$ = 13, *J* = 4), 2.32 br.s (3-OH), 2.40 d.d.d (4-H_{ax}, $J_{4\text{-}ax,5\text{-}ax}$ = 12, $J_{4\text{-}ax,3\text{-}ax}$ = 10.5, *J* = 4), 2.77 br.s (1-OH), 3.49 br.d (3-H_{ax}, *J* = 10.5), 3.74 d.d (2-H_{eq}, $J_{2\text{-}eq,3\text{-}ax}$ = 3, $J_{2\text{-}eq,6\text{-}eq}$ = 1), 3.90 d.d.t (8-H, $J_{8,8'}$ = 13, $J_{8,9}$ = 5, $J_{8,10}$ = 1.5) and 3.94 d.d.t (8′-H, *J* = 13, $J_{8',9}$ = 5, $J_{8',10}$ = 1.5) (*AB* system), 4.79 br.s (12-H), 4.82 d.q (12′-H, $J_{12',12}$ = 2, $J_{12',13}$ = 1.5), 5.10 d.d.t (10-H_{cis}, $J_{10\text{-}cis,9}$ = 10, $J_{10\text{-}cis,10\text{-}trans}$ = 1.5, *J* = 1.5), 5.22 d.d.t (10-H_{trans}, $J_{10\text{-}trans,9}$ = 17, *J* = 1.5, $J_{10\text{-}trans,8}$ = 1.5), 5.86 d.d.t (9-H, *J* = 17, 10, 5). ^{13}C NMR spectrum, δ_C, ppm: 77.23 s (C^1), 74.33 d (C^2), 70.92 d (C^3), 46.40 d (C^4), 25.45 t (C^5), 30.33 t (C^6), 19.60 q (C^7), 62.04 t (C^8), 135.24 d (C^9), 116.18 t (C^{10}), 145.78 s (C^{11}), 112.60 t (C^{12}), 19.63 q (C^{13}).

Transformation of epoxy derivatives IIa and IIb in HSO_3F–SO_2FCl at –115°C. A solution of 0.3 g of a ~1.5:1 mixture of compounds **IIa** and **IIb** in 1.8 ml of methylene chloride was added at –115°C to a solution of 2.8 g (1.6 ml) of HSO_3F in 6.4 ml of SO_2FCl. The mixture was vigorously stirred for 5 min at that temperature and was poured into 25 ml of CH_3OH–Et_2O. Yield of the crude product 0.24 g. By column chromatography on silica gel using hexane–diethyl ether as eluent (gradient elution, 0 to 20% of diethyl ether) we isolated 0.04 g of compound **XI**. IR spectrum (CCl_4), ν, cm^{-1}: 3464 (O–H),

1711 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 d ($C^{11}H_3$, $J_{11,6}$ = 6.5), 1.21 s and 1.28 s (3H each, C^8H_3 and C^9H_3), 1.25 m (5-H_{ax}), 1.52 d.d.d.d (4-H_{ax}, $J_{4\text{-}ax,4\text{-}eq}$ = 13, $J_{4\text{-}ax,5\text{-}ax}$ = 13, $J_{4\text{-}ax,3\text{-}ax}$ = 12, $J_{4\text{-}ax,5\text{-}eq}$ = 3.5), 1.72 m (3-H_{ax}, *J* = 12, $J_{3\text{-}ax,2\text{-}ax}$ = 11, $J_{3\text{-}ax,4\text{-}eq}$ = 3.5), 1.93 d.d.d.d (4-H_{eq}, *J* = 13, 3.5, $J_{4\text{-}eq,5\text{-}ax}$ = 3.5, $J_{4\text{-}eq,5\text{-}eq}$ = 3.5), 2.07 d.d.d.d (5-H_{eq}, $J_{5\text{-}eq,5\text{-}ax}$ = 13, $J_{5\text{-}eq,6\text{-}ax}$ = 6.5, *J* = 3.5, 3.5), 2.38 d.q.d.d (6-H_{ax}, $J_{6\text{-}ax,5\text{-}ax}$ = 13, *J* = 6.5, 6.5, $J_{6\text{-}ax,2\text{-}ax}$ = 1.5), 3.16 s (OCH_3), 4.02 br.m (2-H_{ax}, *J* = 11, $J_{2\text{-}ax,OH}$ = 2, *J* = 1.5). ^{13}C NMR spectrum, δ_C, ppm: 211.79 s (C^1), 76.72 d (C^2), 54.52 d (C^3), 24.10 t (C^4), 34.37 t (C^5), 43.09 d (C^6), 76.72 s (C^7), 24.34 q (C^8 or C^9), 22.54 q (C^9 or C^8), 48.65 q (C^{10}), 14.19 q (C^{11}).

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