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# Transformations of 6,7-Epoxy Derivatives of Citral and Citronellal in Various Acidic Media

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**Abstract**—The transformations of 6,7-epoxy derivatives of widely spread in the nature unsaturated aldehydes, citral and citronellal, in various acidic media both under conditions of homogeneous and heterogeneous catalysis were investigated. A number of previously unknown products belonging to different classes of organic compounds was obtained. Probable mechanisms of the products formation are discussed.

The extensive study of terpenes and their derivatives in the modern chemistry is due both to their polyfunctionality and therefore versatile reactivity and to application of this class compounds to many fields of human activity, for instance, to medicine and perfumery [1]. Investigations on epoxides of the terpene series that are able to transform into alcohols, aldehydes, ketones, and heterocycles is a very promising field in the terpene chemistry. Besides the introduction of an epoxy group into a molecule of a complex polyfunctional natural compound can mark the place where arises a cationic center thus providing a possibility of making assumptions on the mechanism of carbocationic reactions and of comparison with the acid-catalyzed reactions of the original olefins.

The objects of this study were citral and citronellal epoxidized at the 6,7-double bond. The transformations of the original unsaturated aldehydes in the acidic media were formerly investigated. It is known from the published data [2] that under treatment with acids citral (**I**) and citronellal (**II**) undergo cyclization to afford *p*-cymene and isopulegol respectively. Besides it was shown earlier [3] that at dissolution of isomeric aldehydes **I** in a system HSO₃F–SO₂FCl at –120°C under "long life" conditions a mixture of two carboxonium ions (A) and (B) was formed, and the dissolution of isomers **I** in a system SbF₅–HSO₃F–SO₂FCl at –95°C resulted in dications (C) and (D). The dissolution of citronellal (**II**) in the fluorosulfonic acid (HSO₃F–SO₂FCl at –120°C) furnished an allyl ion (E). The NMR spectra of the observed ions did not change from –100 to –60°C (Scheme 1).

**Scheme 1.**
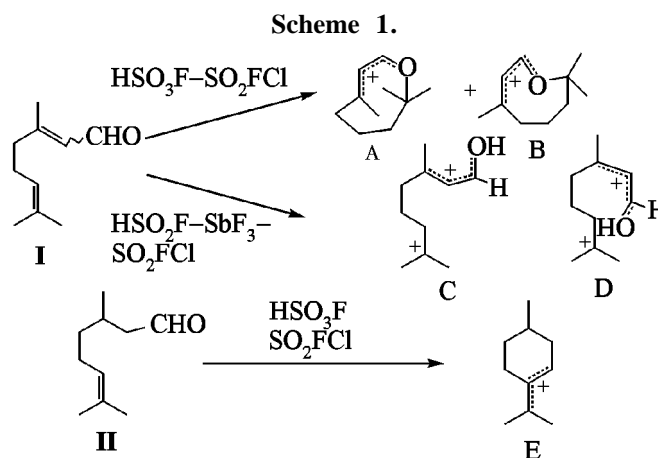


We showed before [4] that treating of citral with peracetic acid provided 6,7-derivatives of geranial (*cis*-citral) (**III**) and neral (*trans*-citral) (**IV**). Alongside these epoxides formed (*E*)- (**V**) and (*Z*)- (**VI**) 2,6-dimethyl-5,6-epoxy-1-heptenyl formates arising from epoxidation and Bayer–Williger reaction (Scheme 2).*

**Scheme 2.**
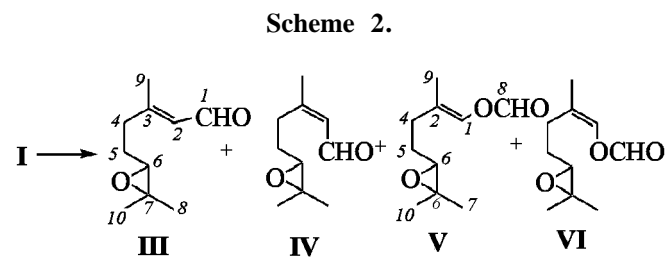


We studied reactions of epoxides **III** and **IV** in various acidic media. The equimolar mixture of isomers **III** and **IV** was dissolved in fluorosulfonic acid

**Table 1.** Ratio of reaction products **VII**–**XV** depending on reaction conditions

| Reaction conditions | VII | VIII | IX | X | XI | XII | XIII | XIV | XV | III |
|---|---|---|---|---|---|---|---|---|---|---|
| HSO₃F–SO₂FCl, –115°C | 25 | 75 | – | – | – | – | – | – | – | – |
| Dioxane–H₂O–H₂SO₄ 40:6:1, 1 min | – | – | 70 | 30 | – | – | – | – | – | – |
| Dioxane–H₂O H₂SO₄ 40:6:1, 1 h | – | – | 30 | 70 | – | – | – | – | – | – |
| CH₃COCH₃–H₂O–H₂SO₄ 40:6:1, 1 min | – | – | 43 | 36 | 7 | 14 | – | – | – | – |
| CH₃COCH₃–H₂O–H₂SO₄ 40:6:1, 1 h | – | – | 13 | 26 | 21 | 40 | – | – | – | – |
| Askanite–bentonite clay, 5 min | – | – | – | – | – | – | 45 | 5 | – | 50 |
| Zeolite β, 5 min | – | – | – | – | – | – | 30 | 20 | – | 50 |
| TiO₂/SO₄²⁻, 10 min | 18 | 30 | 7 | 17 | – | – | – | – | 30 | – |

$^{a}$ Percent according to GLC data at 1:1 ratio of the original epoxides **III** and **IV**.

at molar ratio HSO₃F to aldehyde mixture **III** + **IV** 20:1, SO₂FCl–HSO₃F at a ratio 4:1 by volume, and reaction temperature –115°C. On quenching the acid solution with a mixture methanol–ethyl ether, 5:2, a mixture was obtained of (*E*)- (**VII**) and (*Z*)- (**VIII**) 3,7-dimethyl-6-oxo-2-octenals (Scheme 3). The dissolution of epoxides **III** and **IV** in a system dioxane–water–H₂SO₄ at volume ratio 40:6:1 with subsequent neutralization of the acid by sodium carbonate resulted in formation of (2*R*,5*R*)- (**IX**) and (2*S*,5*R*)- (**X**) 5-(1-hydroxy-1-methylethyl)-2-methyltetrahydro-furan-2-acetaldehydes. The ratio of the arising products essentially depended on the reaction time and is independent of the initial reagent ratio. If the reaction is stopped in 1 min the main product is compound **IX**, and neutralization of the reaction mixture in 1 h and more affords predominantly compound **X** (Table 1). The mechanism of compounds **IX** and **X** formation we assumed is shown on Scheme 3. It is suggested that a molecule of water adds to primarily arising cations (F) and (G) with subsequent protonation of the 2,3-double bond resulting in ion (H). The latter undergoes cyclization to furnish the substituted tetra-hydrofurans **IX** and **X**. This mechanism assuming formation of the same ion (H) from two different compounds explains why the initial ratio of epoxides **III** and **IV** does not influence the reaction products ratio. With no acid compound **IX** does not isomerize, and at dissolution of the isolated substance **IX** in the system dioxane–water–H₂SO₄ compound **X** also does not form. Semiempirical calculations of the thermodynamic stability for isomers **IX** and **X** show that compound **X** is more thermodynamically stable [$\Delta H_f^0$ (**IX**) –151.10 kcal mol$^{-1}$, $\Delta H_f^0$ (**X**) –152.26 kcal mol$^{-1}$; MOPAC].

At dissolving epoxides **III** and **IV** in a system acetone–water–H₂SO₄ at molar ratio 40:6:1 alongside the isomeric substituted tetrahydrofurans **IX** and

**X** were obtained (*E*)- (**XI**) and (*Z*)- (**XII**) 3,7-dimethyl-6,7-isopropylidenedioxy-2-octenals. Cations (H) and (G) arising on the opening of the epoxy ring either react with the external nucleophile (acetone) affording ketals **XI** and **XII** or cyclize to give the tetrahydrofuran derivatives **IX** and **X**. It should be noted that the ratio of ketals **XI** and **XII** does not depend either on the reaction time or the ratio of the initial epoxides evidencing the existence of the acid-catalyzed equilibrium between (H) and (G) ions. At the same time the relative amount of compounds **IX, X** versus (**XI** + **XII**) depends on the duration of the process in the acidic medium.

We studied further the isomerization of epoxides **III** and **IV** under conditions of heterogeneous catalysis. It was demonstrated, that application of equimolar mixture of compounds **III** and **IV** dissolved in CH₂Cl₂ on zeolite β or askanite–bentonite clay for 5 min at room temperature did not cause isomerization of epoxide **III** with *trans*-located substituents at the double bond, whereas epoxide **IV** apparently due to its spatial arrangement suffered a transformation into cyclic products, 4,8,8-trimethyl-7,9-dioxabicyclo[4.2.1]non-4-ene (**XIII**) and 2,2,6-trimethyl-3,9-dioxabicyclo[4.2.1]non-4-ene (**XIV**). Depending on the type of the acid catalyst used compounds **XIII** and **XIV** were obtained in different amounts.

As seen from the mechanism we proposed in Scheme 3 for the formation of bicyclic ethers the stabilization of cationic center on ion (G) arising at the rupture of the epoxy ring occurs through its reaction with the carbonyl oxygen resulting in a cyclic ion (I). Further the OH group of ion (I) either reacts with the carbon atom $C^2$ to yield compound **XIII** or with the atom $C^4$ providing compound **XIV**. The comparison with published data shows that ion (I) is structurally similar to cyclic ions (A) and (B) arising

**Scheme 3.**
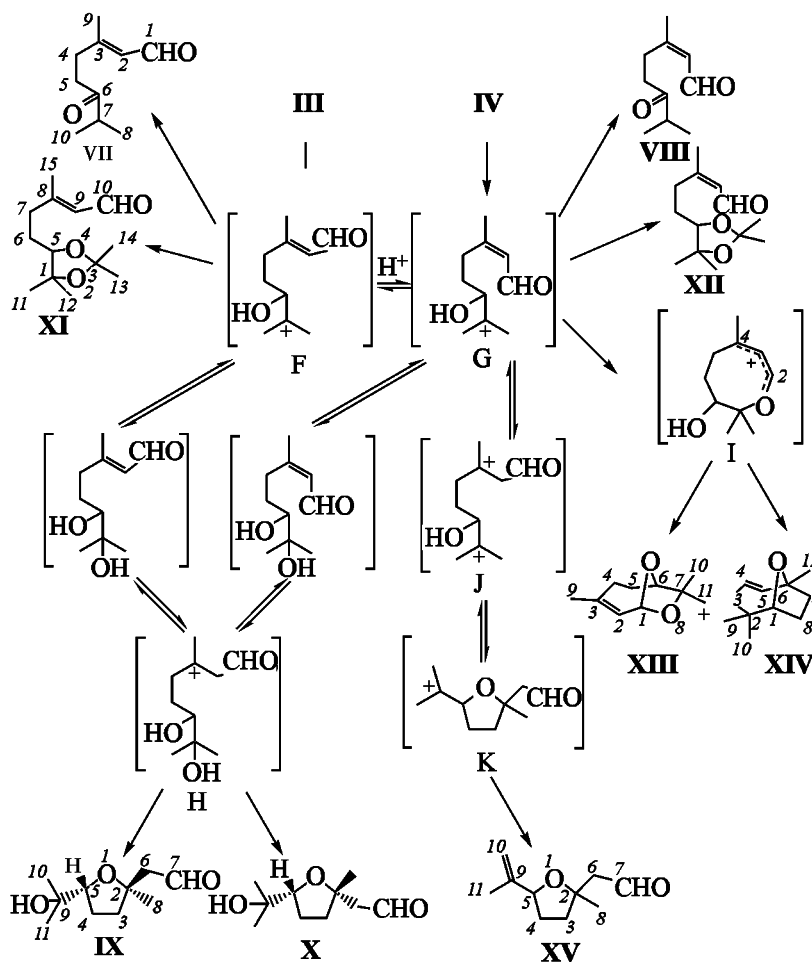


from the initial compound **I** in the system HSO$_3$F–SO$_2$FCl at –120°C [3]. The stabilization of a carbocationic center by reaction with a carbonyl oxygen yielding carboxonium ions as with compound **I** is fairly common for cyclization reactions of acyclic terpenoids containing a carbonyl group [5].

At the use of another solid catalyst, solid superacid TiO$_2$/SO$_4^{2-}$, the isomerization of epoxides **III** and **IV** gives rise to ketoaldehydes **VII** and **VIII**, tetrahydrofuran derivatives **IX** and **X**, and also to a mixture (4 : 1) of diastereomers 5-isopropenyl-2-methyltetrahydrofuran-2-acetaldehydes (**XV**). The ratio of the forming products is weakly sensitive to the type of the solid superacid used and to the duration of the reaction. Note that keeping compounds **IX** and **X** with the heterogeneous catalyst does not afford compounds **XV**. We believe that on the route to isomers **XV** arises dication (J) of structure similar to that of ions (C) and (D). This dication cyclizes to give the tetrahydrofuran skeleton. It was remarked [3] that an

important factor influencing the formation of dications or cyclic ions from aldehydes **I** was the ratio of acid to the initial compound. Yet it is known that the acidity of the solid superacid is significantly stronger than that of the clay and the zeolite we used. This fact may testify to the mechanism of compounds **XV** formation via a dication, but the possibility of the other mechanisms cannot be excluded.

We showed further that at dissolving the epoxides **V** and **VI** mixture at 2 : 1 ratio in a system HSO$_3$–SO$_2$FCl at –115°C arose a mixture of (*E*)- (**XVI**), (*Z*)- (**XVII**) 2,6-dimethyl-oxo-1-heptenyl formates, and 2,6-dimethyl-5-oxoheptanal (**XVIII**) in 2 : 1 : 4 ratio respectively (Scheme 4). The shortening of the chain by one atom as in compound **XVIII** was previously observed by Prilezhaev [6] in oxidation of the original aldehyde **I** with perbenzoic acid. The isomerization of epoxyformates **V** and **VI** on solid catalysts provided intractable mixtures of compounds.

**Schemes 4.**



$V + VI \longrightarrow$ **XVI** + **XVII** + **XVIII**
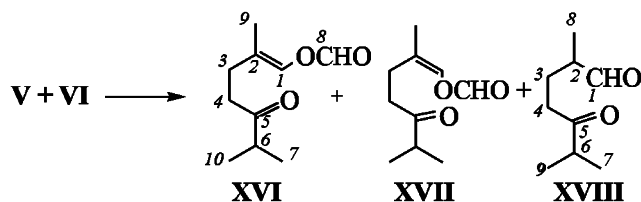
Next we studied the acid-catalyzed reactions of epoxides of citronellal (**II**), an acyclic monoterpene structurally similar to compound **I**. It was shown that at oxidation of citronellal **II** with peracids formed both 6,7-epoxy derivatives (**XIX**) as a mixture of diastereomers and the isomer of the original compound isopulegol (**XX**) (Scheme 5).
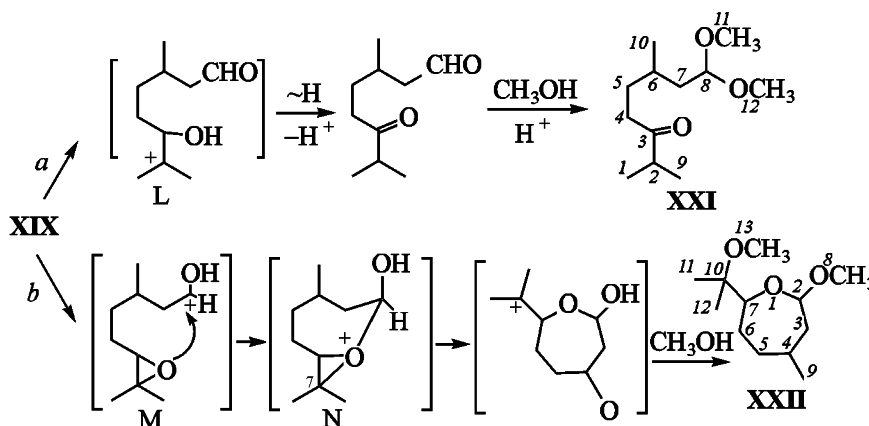
**Scheme 5.**



**II** $\xrightarrow{RCOOOH}$ **XIX** + **XX**
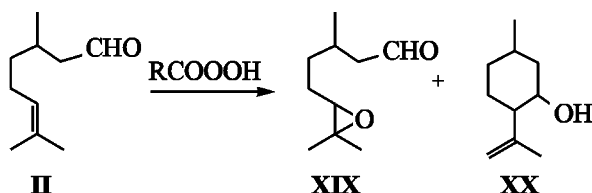
Compounds **XIX** were dissolved in fluorosulfonic acid at molar ratio $HSO_3F$ to compound **XIX** 15:1, $SO_2FCl–HSO_3F$ at a ratio 4:1 by volume, and reaction temperature –105°C. On quenching the acid solution with a mixture methanol–ethyl ether, 5:2, were obtained 2.6-dimethyl-8,8-dimethoxyoctan-3-one (**XXI**) and 4-methyl-2-methoxy-7-(1-methoxy-1-methylethyl)1-oxacycloheptane (**XXII**) (Scheme 6).

The presumable mechanism of this reaction is shown in Scheme 6. It follows from the Scheme that in a superacid epoxides **XIX** can undergo transformation

by the paths *a* and *b*. According to path *a* the epoxide ring first opens to form ion (L), and then it suffers further transformation into compound **XXI**. Along path *b* in the first stage occurs a protonation of carbonyl group giving ion (M), then the reaction of the epoxy oxygen with the cationic center gives rise to trialkyloxonium ion (N). The rupture of $C^7$–O bond in the latter furnishes a cyclic cation (O), and its quenching with a mixture methanol–ether yields compound **XXII**. The mechanism of ion (N) formation we assumed basing on the published data. Formerly a stable trialkyloxonium ion (P) was generated from α-bisabolol (**XXIII**) in a system $SO_2FCl–HSO_3F$ at –80°C [7], and trialkyloxonium ion (Q) was assumed as an intermediate in isomerization of 2,3-epoxygeraniol (**XXIV**) in the system $SO_2FCl–HSO_3F$ at –100°C [8] (Scheme 7).

Dissolving epoxides **XIX** in a system acetone–water–$H_2SO_4$ at molar ratio 40:6:1 gave rise to 3,7-dimethyl-6-oxooctanal (**XXV**) and 3,7-dimethyl-6,7-isopropylidenedioxyoctanal (**XXVI**) as a mixture of diastereomers (Scheme 8). The isomerization of epoxides **XIX** on heterogeneous acid catalysts, such as zeolite β, askanite–bentonite clay, and solid superacid $TiO_2/SO_4^2$, afforded alongside the ketoaldehyde **XXV** also 4,8,8-trimethyl-7,9-dioxabicyclo[4.2.1]-nonane (**XXVII**) as a mixture of isomers. The reaction products **XXV** and **XXVII** formed in different

**Scheme 6.**

**Scheme 7.**



**XXIII**  →  **P**

**XXIV**  →  **Q**  → →
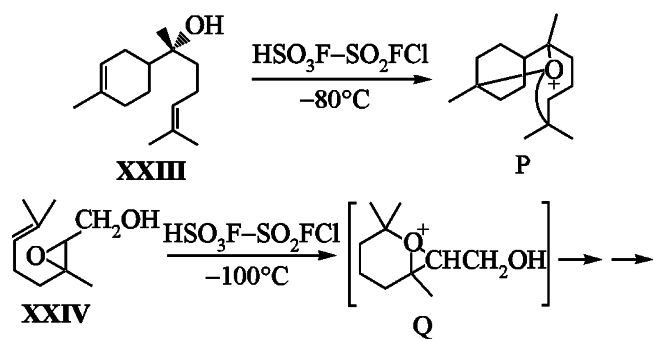
ratios depending on the type of catalyst used (Table 2). The formation of cyclic compound **XXVII** evidences that in the intermediate stage arises a cyclic ion (R) with a structure similar to that of ion (I) from epoxide **IV**.
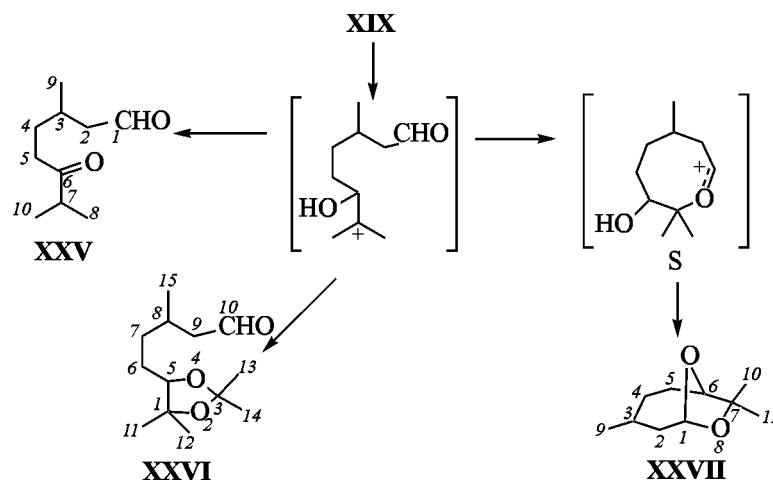
It is remarkable that bicyclic ketals obtained by us **XIII, XIV, XXVII** are structural analogs of well-known pheromones **XXVIII–XXXIV**. Intramolecular bicyclic ketals frontalin (**XXVIII**), *exo-* (**XXIX**) and

*endo-* (**XXX**) brevicomin (**XXX**), α- and β-multistearin (**XXXI**) are active components of pheromone compositions controlling the aggregation of bark beetles from the genera *Dendroctonus* and *Dryocoetes* and of bark beetles from the genus *Scolytus* [9]. Besides the three-component pheromone of male hepialid moth *Hepialus hecta* is known to contain two unsaturated compounds of the 2,9-oxabicyclo[3.2.1]-non-7-ene series, **XXXII** and **XXXIII**, and unsaturated analog of the *exo*-brevicomin **XXXIV** is a multifunctional pheromone of house mice *Mus musculus*.
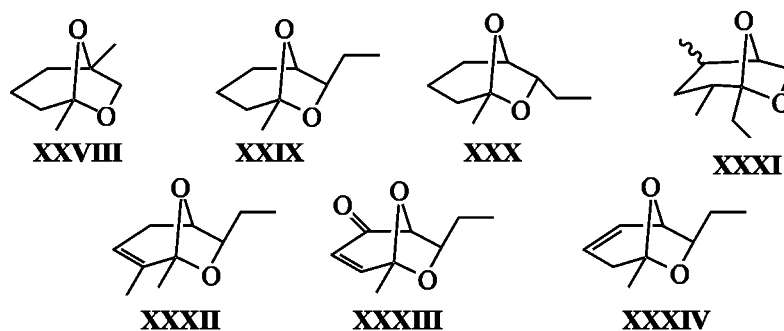
Let us discuss some details of structure determination for the compounds obtained. The ^{1}H NMR spectrum of compound **III** is identic to that published [10].

The assignment of respective *trans-* and *cis*-structures to compounds **IX** and **X** was done by analogy with the chemical shifts of carbons in the published ^{13}C NMR spectra of compounds with related *trans-* and *cis*-structures **XXXV** and **XXXVI** [11]. The alternative pyran type structures **XXXVIIa, b** were

**Scheme 8.**



**XXV**        **XIX**        **S**

**XXVI**        **XXVII**

**Scheme 9.**



**XXVIII**    **XXIX**    **XXX**    **XXXI**

**XXXII**    **XXXIII**    **XXXIV**

rejected after comparison of the NMR spectra with the corresponding spectra from the literature [12] belonging to compounds of analogous structure **XXXVIIIa, b**. The choice between the alternative structures **XXII** and **XXXIX** was done basing on the LRJMD spectrum that permitted rejection of structure **XXXIX**. Decoupling from protons of methoxy groups performed separately for signals at 3.18 and 3.26 ppm resulted in appearance in the first case only of a singlet from carbon atom at 76.61 ppm ($C^{10}$ in structure **XXI**), and in the second case was observed a doublet signal at 102.67 ppm assigned to carbon atom $C^2$. The decoupling from methoxy group signal at 3.18 ppm should have resulted for compound **XXXIX** by appearance in the LRJMD spectrum of a doublet belonging to carbon atom $C^7$ at 75.56 ppm, and that was not actually observed.



XXXV    XXXVI

XXXVIIa, b    XXXVIIIa, b

XXXIX
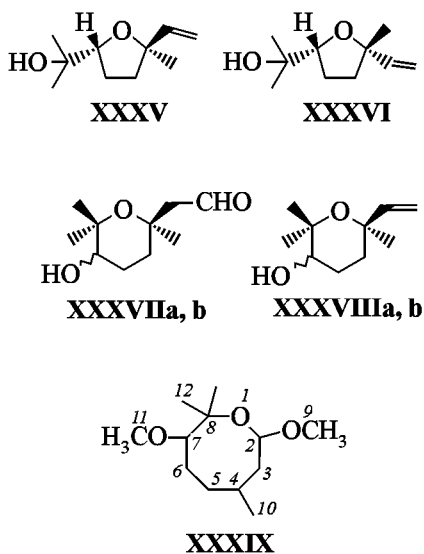
Thus in this study the acid-catalyzed reactions of 6,7-epoxides prepared from the aldehydes widely spread in the nature, citral (**I**) and citronellal (**II**), were investigated under various homogeneous and heterogeneous conditions. Owing to the polyfunctional character of terpenoid molecules they possess versatile reactivity that depends on the reaction conditions. Therewith in these strongly bonded multi-center systems relatively small structural changes result in significant variations. In keeping with the type of the acid catalyst the reaction products can belong to various classes of organic compounds; it is besides demonstrated that varying the nature of the acid catalyst and the duration of the reaction it is possible to change the ratio of the forming substances.

**Table 2.** Ratio of reaction products **XXI, XXII, XXV–XXVII** (% according to GLC ) depending on isomerization conditions of epoxyaldehyde **XIX**

| Reaction conditions | XXI | XXII | XXV | XXVI | XXVII | XIX |
|---|---|---|---|---|---|---|
| $HSO_3F$–$SO_2FCl$, –115°C | 80 | 20 | – | – | – | – |
| $CH_3COCH_3$–$H_2O$–$H_2SO_4$ 40:6:1, 10 min | – | – | 10 | 90 | – | – |
| Askanite–bentonite clay, 5 min | – | – | 40 | – | 30 | 30 |
| zeolite β, 15 min | – | – | 30 | – | 45 | 25 |
| $TiO_2/SO_4^{2-}$, 10 min | – | – | 60 | – | 40 | – |

## EXPERIMENTAL

$^1$H and $^{13}$C NMR spectra were registered on spectrometer Bruker AM-400 at 400.13 and 100.61 MHz respectively from solutions of compounds in $CDCl_3$ or in a mixture $CCl_4$–$CDCl_3$ (~1:1). The chloroform signals served as internal reference (δ 7.24, $\delta_C$ 76.90 ppm). The structures of compounds obtained were established by analysis of the coupling constants in the NMR spectra of double resonance $^1$H–$^1$H, and by analysis of $^{13}$C NMR spectra with the use of spectra with selective and off-resonance protons irradiation, two-dimensional correlation spectra $^{13}$C–$^1$H on direct constants (COSY, the applied value of $^1J_{C,H}$ 135 Hz), and unidimensional spectra $^{13}$C–$^1$H with correlation on remote constants (LRJMD, $J_{C,H}$ 10 Hz). Data on $^{13}$C NMR spectra are presented in Table 3.

The analysis of reaction products and checking of the initial compounds purity was performed by GLC on "Biokhrom-1" chromatograph equipped with several columns: (a) glass capillary column 53000 × 0.26 mm, stationary phase XE-60; (b) quartz capillary column 13000×0.22 mm, stationary phase SE-54; (c) quartz capillary column 20000×0.27 mm, stationary phase BS-30 (analogous to SE-30); flame-ionization detector, carrier gas helium. The ratios of product formed from epoxides **III, IV** under acid catalysis are given in Table 1, those arising from epoxides **XIX** in Table 2. The separation of reaction products was carried out by column chromatography on $SiO_2$ (Czech Republic, 40–100 and 100–160 μ). The ratio of crude product to the sorbent was 1:20–

1:40. The elemental composition of compounds obtained was derived from the high resolution mass spectra registered on Finnigan MAT 8200 instrument.

The solutions of ion salts were prepared in twice distilled $HSO_3F$ (bp 158–161°C). The diluent, $SO_2FCl$, was purified by passing through sulfuric acid. As nucleophile for quenching was used a mixture methanol–ethyl ether, 5:2 by volume. The procedures for preparation of salts solutions and their quenching are described in [13]. The askanite–bentonite clay used as catalyst was prepared by acid activation of clay from Askane group of deposits, State Standard OCT 113–12-86-82, and it was dried directly before experiments at 110°C for 3 h. As catalysts were also used titanium oxide sulfate $(TiO_2/SO_4^{2-})$ (calcined at 400°C for 3 h) or wide-porous zeolite β $(SiO_2/Al_2O_3$ 22.4) with pore size 0.75–0.80 nm, weight content of oxides $Na_2O$ 0.01%, $Al_2O_3$ 4.50%, $SiO_2$ 59.20%, $Fe_2O_3$ 0.08% (manufactured at TsIN Zeosit, Novosibirsk). Zeolite was calcined before use for 3 h at 500°C. The following reagents were used in the study: citral Fluka containing no less than 97% of the main product, ratio of cis to trans isomers 1:2 ($^1H$ NMR data); technical-grade citral containing 13% of dehydrolinalool, ratio of *cis* to trans isomers 1:1 ($^1H$ NMR data); citronellal Fluka with content of the main substance 85–90%.

**Reaction of citral (I) with peracetic acid.** To 2.12 g (0.014 mol) of compound **I** (with *cis*-to-trans ratio 1:2) in 3 ml of $CH_2Cl_2$ and 8 g of anhydrous $Na_2CO_3$ was added slowly at vigorous stirring 24 ml (0.021 mol) of $CH_3COOOH$ dissolved in $CH_2Cl_2$. The peracetic acid was preliminary prepared by extraction from the mixture of 200 ml $CH_3COOH$, 200 ml of 30% $H_2O_2$, and 10 ml of $H_2SO_4$, and its concentration was determined by iodometry. After the end of peracetic acid addition the reaction mixture was vigorously stirred for 50 min at 20°C. The epoxides were extracted from the reaction mixture by ethyl ether, the extract was treated with saturated solution of $Na_2CO_3$, washed with water till neutral, and dried on $Na_2SO_4$. The weight of crude product 2.08 g. In the mixture epoxides **III, IV, V**, and **VI** were present in 28, 21, 30, 21% amount respectively according to GLC. The products were separated by column chromatography on $SiO_2$ (100–160 μ), gradient elution with hexane–ethyl ether mixture, ether content from 5 to 30%. We obtained 0.75 g of compounds **III** and **IV** mixture in 2:1 ratio, and 1.28 g of compounds **V** and **VI** mixture in 2:1 ratio. Mass spectra of isomers **III** and **IV** are identic. Found $[M]^+$ 168.11495. $C_{10}H_{16}O_2$. Calculated $M$

168.11502. $^1H$ NMR spectrum of 6,7-epoxygeranial (III) (δ, ppm, $J$, Hz): 1.18 s and 1.21 s ($C^8H_3$, $C^{10}H_3$), 1.54–1.74 m ($2H^5$), 2.11 d ($C^9H_3$, $J_{9,2}$ 1.2), 2.20–2.37 m ($2H^4$), 2.63 d.d ($H^6$, $J_{6,5}$ 7, $J_{6,5'}$ 5), 5.81 d.m ($H^2$, $J_{2,1}$ 8), 9.89 d ($H^1$, $J$ 8). $^1H$ NMR spectrum of 6,7-epoxyneral (IV) (δ, ppm, $J$, Hz): 1.23 s and 1.26 s ($C^8H_3$, $C^{10}H_3$), 1.66–1.78 m ($2H^5$), 1.96 d ($C^9H_3$ $J_{9,2}$ 1.2), 2.63–2.76 m ($2H^4$, $H^6$), 5.88 br.d ($H^2$, $J_{2,1}$ 8), 9.93 d ($H^1$, $J$ 8).

Mass spectrum of compounds **V, VI** mixture (2:1): $m/z$ 156.11493 (fragment ion $[M–CO]^+$) $C_9H_{16}O_2$. Calculated. $([M–CO]^+)$ 156.11502. $^1H$ NMR spectrum of (*E*)-2,6-dimethyl-5,6-epoxy-1-heptenyl formate (V) (δ, ppm, $J$, Hz): 1.17 s and 1.21 s ($C^7H_3$, $C^{10}H_3$), 1.57 m ($2H^4$), 1.63 d ($C^9H_3$, $J_{9,1}$ 1.5), 1.98–2.15 m ($2H^3$), 2.60 t ($H^5$, $J_{5,4}$ 6), 6.93 m ($H^1$, $J_{1,3}$ 1.5, $J$ 1.5), 7.96 s ($H^8$). $^1H$ NMR spectrum of (*Z*)-2,6-dimethyl-5,6-epoxy-1-heptenyl formate (VI) (δ, ppm, $J$, Hz): 1.22 s and 1.25 s ($C^7H_3$, $C^{10}H_3$), 1.60 m ($2H^4$), 1.64 d ($C^9H_3$, $J_{9,1}$ 1.5), 2.26 br.t ($2H^3$, $J_{3,4}$ 7.5, $J_{3,1}$ 1), 2.67 t ($H^5$, $J_{5,4}$ 6), 6.94 m ($H^1$, $J$ 1.5, 1), 8.00 s ($H^8$).

**Transformation of epoxides III, IV in $HSO_3F$–$SO_2FCl$ at –115°C.** To a solution of 2.8 g (1.6 ml) of $HSO_3F$ in 6.4 ml of $SO_2FCl$ was added at –115°C a solution of 0.3 g of epoxides **III, IV** mixture (with the ratio of *E* and *Z* isomers 2:1) in 1.8 ml of $CH_2Cl_2$. The reaction mixture was vigorously stirred for 5 min at the same temperature, and then poured into a mixture of methanol with ethyl ether. Yield of the crude reaction product 0.9 g. By column chromatography on $SiO_2$ (eluent hexane) was separated 0.05 g of a mixture of compounds **VII** and **VIII** in 3:1 ratio. Found $[M]^+$ 168.11495. $C_{10}H_{16}O_2$. Calculated $M$ 168.11502. $^1H$ NMR spectra (recorded from the mixture of compounds **VII** and **VIII** in the ratio ~3:1), δ, ppm ($J$, Hz): (*E*)-3,7-dimethyl-6-oxo-2-octenal (**VII**), 1.082 d ($C^8H_3$, $C^{10}H_3$, $J$ 7), 2.17 d ($C^9H_3$, $J_{9,2}$ 1.2), 2.43 br.t ($2H^4$, $J_{4,5}$ 7.5), 2.57 septet ($H^7$, $J$ 7), 2.63 t ($2H^5$, $J$ 7.5), 5.77 d.q.t ($H^2$, $J_{2,1}$ 7.5, $J$ 1.2, $J_{2,4}$ 1.2), 9.93 d ($H^1$, $J_{2,1}$ 7.5); (*Z*)-3,7-dimethyl-6-oxo-2-octenal (**VIII**), 1.079 d ($C^8H_3$, $C^{10}H_3$, $J$ 7), 1.93 d ($C^9H_3$, $J_{9,2}$ 1.2), 2.55 septet ($H^7$, $J$ 7), 2.63 m ($2H^5$), 2.79 br.t ($2H^4$, $J_{4,5}$ 7), 2.82 br.d ($H^2$, $J_{2,1}$ 7.5), 9.91 d ($H^1$, $J$ 7.5).

**Isomerization of the epoxides III and IV mixture in a system dioxane–water–$H_2SO_4$.** To 1.5 ml of a mixture dioxane–water–$H_2SO_4$ (40:6:1 by volume)

**Table 3.** $^{13}C$ NMR spectra of compounds **III–XIX, XXI, XXII, XXV–XXVII**, $\delta_C$, ppm[a]

| Number of carbon atom | **III**[b] | **IV**[b] | **V**[b] | **VI**[b] | **VII**[c] | **VIII**[c] | **IX**[c] | **X**[c] | **XI**[c] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 190.94 d | 190.31 d | 128.96 d | 128.91 d | 190.04 d | 189.72 d | – | – | 79.91 s |
| 2 | 127.15 d | 128.55 d | 122.38 s | 122.55 s | 126.98 d | 128.64 d | 80.99 s | 81.05 s | – |
| 3 | 162.54 s | 162.73 s | 30.54 t | 26.35 t | 161.44 s | 161.22 s | 37.93 t | 38.15 t | 106.79 s |
| 4 | 37.01 t | 29.30 t | 26.77 t | 26.44 t | 33.66 t | 26.52 t | 26.03 t | 25.89 t | – |
| 5 | 26.35 t | 27.88 t | 63.35 d | 63.64 d | 37.31 t | 38.67 t | 86.09 d | 85.63 d | 82.46 d |
| 6 | 63.08 t | 63.10 t | 57.97 s | 58.15 s | 211.44 s | 211.44 s | 54.00 t | 54.09 t | 26.99 t |
| 7 | 58.29 s | 58.47 s | 18.44 q | 18.52 q | 40.89 d | 40.86 d | 200.59 d | 200.90 d | 37.78 t |
| 8 | 18.42 q | 18.55 q | 157.66 d | 157.72 d | 18.26 q | 18.19 q[e] | 27.56 q | 26.89 q | 162.08 s |
| 9 | 17.34 q | 24.77 q | 13.48 q | 17.26 q | 17.91 q | 24.79 q | 70.31 s | 70.58 s | 127.30 d |
| 10 | 24.45 q | 24.54 q | 24.49 q | 24.65 q | 18.26 q | 18.26 q[e] | 24.31 q[e] | 24.63 q[e] | 190.36 d |
| 11 | | | | | | | 27.39 q[e] | 27.48 q[e] | 22.92 q[e] |
| 12 | | | | | | | | | 25.97 q[e] |
| 13 | | | | | | | | | 26.89 q[f] |
| 14 | | | | | | | | | 28.51 q[f] |
| 15 | | | | | | | | | 17.63 q |

| Number of carbon atom | **XII**[c] | **XIII**[c] | **XIV**[c] | **XV**[c] | **XVI**[b] | **XVII**[b] | **XVIII**[b] | **XIXa**[c] | **XIXb**[c] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 79.76 s | 100.11 d | 83.02 d | – | 129.09 d | 128.91 d | 204.32 d | 200.66 s | 200.59 s |
| 2 | – | 125.95 d | 81.80 s | 81.07 s | 122.49 s | 122.49 s | 45.47 d | 50.63 t | 50.80 t |
| 3 | 106.88 s | 142.66 s | – | 37.83 t | 27.74 t | 23.75 t | 24.05 t | 27.69 d | 27.69 d |
| 4 | – | 30.34 t | 141.12 d | 31.00 t | 38.15 t | 37.66 t | 36.97 t | 33.54 t | 33.54 t |
| 5 | 81.74 d | 28.71 t | 114.13 d | 82.45 d | 213.33 s | 213.61 s | 213.67 s | 26.23 t | 26.23 t |
| 6 | 27.84 t | 80.67 d | 80.67 s | 54.25 t | 40.81 d | 40.69 d | 40.76 d | 63.53 d | 63.55 d |
| 7 | 29.76 t | 80.35 s | 41.04 t | 200.36 d | 18.06 q | 18.08 q | 18.06 q | 57.60 s | 57.50 s |
| 8 | 161.73 s | – | 25.08 t | 27.81 q | 157.81 d | 157.74 d | 13.34 q | 18.66 q | 18.62 q |
| 9 | 129.18 d | 26.10 q | 25.65 q[e] | 145.12 s | 13.77 q | 17.32 q | 18.06 q | 19.87 q | 19.74 q |
| 10 | 190.36 d | 27.96 q[e] | 23.42 q[e] | 110.53 t | 18.06 q | 18.08 q | | 24.74 q | 24.74 q |
| 11 | 22.97 q[e] | 21.10 q[e] | 26.23 q | 18.07 q | | | | | |
| 12 | 25.89 q[e] | | | | | | | | |
| 13 | 26.76 q[f] | | | | | | | | |
| 14 | 28.51 q[f] | | | | | | | | |
| 15 | 24.68 q | | | | | | | | |

| Number of carbon atom | **XXI**[c] | **XXII**[c] | **XXV**[b] | **XXVIa, b**[c] | **XXVIIb**[b] | **XXVIIb**[b] |
|---|---|---|---|---|---|---|
| 1 | 18.20 q[e] | – | 200.63 s | 79.86 s | 102.32 d | 104.03 d |
| 2 | 40.69 d | 102.67 d | 50.90 t | – | 43.27 t | 43.13 t |
| 3 | 214.37 s | 38.15 t | 27.62 d | 106.44 s | 30.49 d | 28.57 d |
| 4 | 37.66 t | 28.97 d | 30.47 t | – | 32.16 t | 31.92 t |
| 5 | 30.64 t | 42.87 t | 37.57 t | 83.26 d, 83.42 d | 30.81 t | 26.52 t |
| 6 | 28.67 d | 29.22 t | 212.59 s | 26.87 t | 81.70 d | 80.21 d |
| 7 | 39.20 t | 75.56 d | 40.76 d | 34.23 t, 34.31 t | 79.72 s | 81.32 s |
| 8 | 102.86 d | 55.80 q | 18.34 q[e] | 28.11 d, 28.19 d | – | – |
| 9 | 18.17 q[e] | 24.31 q | 19.86 q | 50.89 t, 50.91 t | 23.34 q | 22.88 q |
| 10 | 19.56 q | 76.61 s | 18.32 q[e] | 200.63 d, 200.67 d | 26.29 q[e] | 27.52 q[e] |
| 11 | 52.52 q[f] | 22.54 q[e] | | 22.92 q[e] | 20.98 q[e] | 22.19 q[e] |
| 12 | 52.22 q[f] | 20.77 q[e] | | 26.14 q[e] | | |
| 13 | | 49.11 q | | 26.93 q[f] | | |
| 14 | | | | 28.63 q[f] | | |
| 15 | | | | 19.99 q | | |

[a] The chemical shift values with the same superscripts (e, f) probably would be interchanged within the same column.
[b] In $CDCl_3$. [c] In $CCl_4+CDCl_3$ (1:1).

was added 0.1 g of epoxides **III** and **IV** mixture (1:1). In 1 min the reaction mixture was washed with a saturated $Na_2CO_3$ solution, the reaction products were extracted into ethyl ether. The crude product weighted 0.07 g, the ratio of compound **IX** to **X** 2.3:1 (GLC) was not influenced by the ratio of the original epoxides **III** and **IV**. Found $[M]^+$ 186.11495. $C_{10}H_{16}O_2$. Calculated $M$ 186.11502. The products were subjected to column chromatography on $SiO_2$, gradient elution with hexane–ethyl ether mixture, ether content from 0.5 to 25%. We obtained 0.021 g of compounds **IX** and **X** mixture in 3:1 ratio. At keeping 0.15 g of the epoxides mixture in 2.3 ml of the system dioxane–water–$H_2SO_4$ for 1 h 0.12 g of crude product was isolated with compound **IX** to **X** ratio 1:2.3. By chromatography on $SiO_2$, gradient elution with hexane–ethyl ether mixture, ether content from 0.5 to 25%, 0.04 g of compounds **IX** and **X** mixture, 1:3, was isolated.

The NMR spectra were registered from mixtures with one or another isomer prevailing. $^1$H NMR spectrum of (2*R*,5*S*)-5-(1-hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-acetaldehyde (**IX**) (δ, ppm, *J*, Hz): 1.05 s, 1.14 s ($C^{10}H_3$, $C^{11}H_3$), 1.27 s ($C^8H_3$), 1.70–1.95 m ($2H^3$, $2H^4$), 2.00 br.s (OH), 2.49 d.d ($H^6$, $J_{6,6'}$ 15, $J_{6,7}$ 3) and 2.54 d.d ($H^{6'}$, $J$ 15, $J_{6',7}$ 3) *AB* system, 3.72 m ($H^5$), 9.72 t ($H^7$, $J$ 3). $^1$H NMR spectrum of (2*S*,5*R*)-5-(1-hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-acetaldehyde (**X**) (δ, ppm, *J*, Hz): 1.02 s, 1.14 s ($C^{10}H_3$, $C^{11}H_3$), 1.31 s ($C^8H_3$), 1.70–2.00 m ($2H^3$, $2H^4$), 2.22 br.s (OH), 2.53 d ($2H^6$, $J_{6,7}$ 3), 3.73 m ($H^5$), 9.76 t ($H^7$, $J$ 3).

**Reaction of epoxides III and IV mixture with a system acetone–water–$H_2SO_4$.** To 1.88 ml of the mixture acetone–water–$H_2SO_4$ (40:6:1 by volume) was added 0.4 g of epoxides **III, IV** mixture (1:1). In 1 h the reaction mixture was washed with a saturated solution of $Na_2CO_3$, the reaction products were extracted into ethyl ether. The weight of crude product was 0.22 g. The content of the main reaction products (by GLC data) as a function of the reaction duration is indicated in Table 1. The products were subjected to column chromatography on $SiO_2$, gradient elution with hexane–ethyl ether mixture, ether content from 0 to 90%. We isolated 0.066 g of compounds **IX** and **X** mixture in 1:2 ratio (GLC), and 0.042 g of compounds **XI** and **XII** mixture in 1.4:1 ratio (NMR), compounds were unstable and tarring occurred at room temperature. Compounds **XI** and **XII** mixture. Found: $[M]^+$ 226.11509. $C_{13}H_{22}O_3$. Calculated $M$ 226.11512. $^1$H NMR spectrum of (*E*)-3,7-dimethyl-6,7-isopropylidenedioxy-2-octenal

(**XI**) (δ, ppm, *J*, Hz): 1.05 s, 1.20 s ($C^{11}H_3$, $C^{12}H_3$), 1.26 s, 1.35 s ($C^{13}H_3$, $C^{14}H_3$), 1.50 d.d.d.d ($H^6$, $J_{6,6'}$ 13.5, $J_{6,7}$ 10.5, $J_{6,7}$ 6, $J_{6,5}$ 3), 1.65 d.d.d.d ($H^{6'}$, $J$ 13.5, $J_{6',5}$ 10, $J_{6',7}$ 10, $J_{6',7'}$ 5), 2.16 d ($C^{15}H_3$, $J_{15,9}$ 1.5), 2.23 d.d.d.d ($H^7$, $J_{7,7'}$ 15, $J$ 10, 6, $J_{7,9}$ 1), 2.44 d.d.d.d ($H^{7'}$, $J$ 15, 10.5, 5, $J_{7',9}$ 1), 3.58 d.d ($H^5$, $J$ 10, 3), 5.85 d.m ($H^9$, $J_{9,10}$ 8), 9.95 d ($H^{10}$, $J$ 8). $^1$H NMR spectrum of (*Z*)-3,7-dimethyl-6,7-isopropylidenedioxy-2-octenal (**XII**2) (δ, ppm, *J*, Hz): 1.04 s, 1.18 s ($C^{11}H_3$, $C^{12}H_3$), 1.23 s, 1.35 s ($C^{13}H_3$, $C^{14}H_3$), 1.51 m ($H^6$), 1.68 m ($H^{6'}$), 1.96 d ($C^{15}H_3$, $J_{15,9}$ 1.5), 2.58 d.d.d.d ($H^7$, $J_{7,7'}$ 13, $J_{7,6'}$ 8, $J_{7,6}$ 5, $J_{7,9}$ 0.5), 2.83 d.d.d ($H^{7'}$, $J$ 13, $J_{7',6}$ 8, $J_{7,6'}$ 8), 3.57 d.d ($H^5$, $J_{5,6'}$ 10.5, $J_{5,6}$ 3), 5.86 d.m ($H^9$, $J_{9,10}$ 8), 9.92 d ($H^{10}$, $J$ 8).

**Isomerization of the epoxides III and IV mixture on zeolite.** To 0.40 g of calcined zeolite in 6 ml of dried $CH_2Cl_2$ was added at stirring 0.25 g of epoxides **III** amd **IV** mixture (1:1) in 1 ml of $CH_1Cl_2$. After 5 min of stirring the catalyst was filtered off and washed with ethyl ether. The solvent was removed from the combined organic solution to afford 0.22 g of crude product. The products were subjected to column chromatography on $SiO_2$, gradient elution with pentane–ethyl ether mixture, ether content from 0 to 30%. We isolated 0.036 g of compound **XIII**, 0.018 g of compound **XIV**, and 0.10 g of unreacted epoxide **III**.

**4,8,8-Trimethyl-7,9-dioxabicyclo[4.2.1]non-4-ene (XIII).** $^1$H NMR spectrum (δ, ppm, *J*, Hz): 1.22 s, 1.32 s ($C^{10}H_3$, $C^{11}H_3$), 1.71 d ($C^9H_3$, $J_{9,2}$ 1.5), 1.81 m ($H^5$), 1.88 m ($H^{5'}$), 2. 18 d.d.d.d ($H^4$, $J_{4,4'}$ 16, $J_{4,5}$ 7.5, $J_{4,5'}$ 4.5, $J_{4,2}$ 1) and 2.34 d.d.d.d.q ($H^{4'}$, $J$ 16, $J_{4',5'}$ 9.0, $J_{4',5}$ 4.5, $J_{4',2}$ 1.5, $J_{4',9}$ 1) *AB* system, 3.91 d.d ($H^6$, $J_{6,5'}$ 6, $J_{6,5}$ 4), 5.38 d ($H^1$, $J_{1,2}$ 4), 5.48 m ($H^2$, $J_{2,1}$ 4, $J_{2,9}$ 1.5, $J_{2,4'}$ 1.5, $J_{2,4}$ 1). Found $[M]^+$ 168.11470. $C_{10}H_{16}O_2$. Calculated $M$ 168.11502. **2,2,6-Trimethyl-3,9-dioxabicyclo[4.2.1]-non-4-ene (XIV).** $^1$H NMR spectrum (δ, ppm, *J*, Hz): 1.15 s, 1.30 s ($C^9H_3$, $C^{10}H_3$), 1.37 s ($C^{11}H_3$), 1.60 m and 1.89 m ($2H^7$), 1.92–2.08 m ($2H^8$), 3.97 d.d ($H^1$, $J_{1,8k}$ 8.5, $J_{1,8h}$ 4), 4.55 d ($H^5$, $J_{5,4}$ 8), 5.76 d ($H^4$, $J$ 8). Found $[M]^+$ 168.11461. $C_{10}H_{16}O_2$. Calculated $M$ 168.11502.

**Isomerization of the epoxides III and IV mixture on clay.** To 0.50 g of clay in 8 ml of dried $CH_2Cl_2$ was added at stirring 0.30 g of epoxides **III** and **IV** mixture (1:1) in 2 ml of $CH_1Cl_2$. After 5 min of stirring the catalyst was filtered off and washed

with ethyl ether. The solvent was removed from the combined organic solution to afford 0.26 g of crude product. The products were subjected to column chromatography on $SiO_2$, gradient elution with pentane–ethyl ether mixture, ether content from 0 to 30%. We isolated 0.043 g of compound **XIII**, 0.010 g of compound **XIV**, and 0.09 g of unreacted epoxide **III**.

**Isomerization of the epoxides III and IV mixture on solid superacid $TiO_2/SO_4^{2-}$.** To 0.40 g of sulfated titanium oxide in 10 ml of dried $CH_2Cl_2$ was added at stirring 0.40 g of epoxides **III** amd **IV** mixture (1:1) in 5 ml of $CH_2Cl_2$. After 10 min of stirring the catalyst was filtered off and washed with ethyl ether. The content of the main products (by GLC data) is indicated in Table 1. On removing the solvent we obtained 0.36 g of crude product. The products were subjected to column chromatography on $SiO_2$, gradient elution with hexane–ethyl ether mixture, ether content from 0 to 50%. From the reaction mixture were separated the following substances: 0.11 g of compounds **VII** and **VIII** mixture, 0.09 g of compounds **IX** and **X** mixture, and 0.03 g of compound **XV** as an isomer mixture in 4:1 ratio.

**5-Isopropenyl-2-methyltetrahydrofuran-2-acetaldehyde (XV).** ^{1}H NMR spectrum of the prevailing isomer ($\delta$, ppm, $J$, Hz): 1.31 s ($C^8H_3$), 1.68 br.s ($C^{11}H_3$), 1.70–1.92 m ($2H^3$, $H^4$), 2.03 m ($H^{4'}$), 2.51 d.d ($H^6$, $J_{6,6'}$ 15, $J_{6,7}$ 3) and 2.55 d.d ($H^{6'}$, $J$ 15, $J_{6',7}$ 3) $AB$ system, 4.31 br.d.d ($H^5$, $J_{5,4'}$ 8, $J_{5,4}$ 6.5), 4.73 m ($H^{10}$, $J_{10,10'}$ 2, $J_{10,11}$ 1.5, $J_{10,5}$ 1), 4.94 m ($H^{10'}$, $J$ 2, $J_{10',5}$ 1, $J_{10',11}$ 1), 9.76 t ($H^7$, $J$ 3). Found $[M]^+$ 168.11461. $C_{10}H_{16}O_2$. Calculated $M$ 168.11502.

**Transformation of epoxides V, VI in $HSO_3F$–$SO_2FCl$ at –115°C.** To a solution of 3.48 g (2 ml) of $HSO_3F$ in 8 ml of $SO_2FCl$ was added at –115°C a solution of 0.42 g of epoxides **V, VI** mixture (with the ratio of *E40 and Z* isomers 2:1) in 2 ml of $CH_2Cl_2$. The reaction mixture was vigorously stirred for 5 min at the same temperature, and then poured into 35 ml of a mixture of methanol with ethyl ether. Yield of the crude reaction product 0.26 g. GLC analysis showed that the mixture consisted of compounds **XVIII**. **XVI**, and **XVII** at a ratio ~4:2:1. By column chromatography on $SiO_2$ (gradient elution with a mixture pentane–ethyl ether, the latter from 0 to 30%) we isolated 0.1 g of compound **XVIII** and 0.09 g of compounds **XVI** and **XVII** mixture in 1.3:1 ratio.

**The mixture of (E)- (XVI) and (Z)- (XVII) 2,6-dimethyl-5-oxo-1-heptenyl formates.** ^{1}H NMR spectra were recorded for the mixture of compounds **XVI** and **XVII**. ^{1}H NMR spectrum of compound **XVI** ($\delta$, ppm, $J$, Hz): 1.063 d ($C^7H_3$, $C^{10}H_3$, $J$ 7), 1.67 d ($C^9H_3$, $J_{9,1}$ 1.5), 2.23 t.d ($2H^3$, $J_{3,4}$ 8, $J_{3,1}$ 1.2), 2.54 t ($2H^4$, $J$ 8), 2.57 septet ($H^6$, $J$ 7), 6.95 m ($H^1$, $J$ 1.5, 1.2), 8.01 s ($H^8$). ^{1}H NMR spectrum of compound **XVII** ($\delta$, ppm, $J$, Hz): 1.064 d ($C^7H_3$, $C^{10}H_3$, $J$ 7), 1.62 d ($C^9H_3$, $J_{9,1}$ 1.5), 2.36 br.t ($2H^3$, $J_{3,4}$ 8), 2.52 t ($2H^4$, $J$ 8), 2.58 septet ($H^6$, $J$ 7), 6.91 m ($H^1$), 8.00 s ($H^8$). Found $[M$-CO$]^+$ 156.11493. $C_9H_{16}O_2$. Calculated $[M$-CO$]$ 156.11502.

**2,6-Dimethyl-5-oxoheptanal (XVIII).** ^{1}H NMR spectrum ($\delta$, ppm, $J$, Hz): 1.04 d ($C^7H_3$, $C^9H_3$, $J$ 7), 1.07 d ($C^8H_3$, $J_{8,2}$ 7), 1.63 d.t.d ($H^3$, $J_{3,3'}$ 14, $J_{3,4}$ 7, $J_{3,2}$ 6), 1.90 d.t.d ($H^{3'}$, $J$ 14, $J_{3',4}$ 7, $J_{3',2}$ 7), 2.32 d.q.d.d ($H^2$, $J$ 7, 7, 6, $J_{2,1}$ 2), 2.46 m ($2H^4$), 2.54 septet ($H^6$, $J$ 7), 9.56 d ($H^1$, $J$ 2). Found $[M]^+$ 156.11493. $C_9H_{16}O_2$. Calculated $M$ 156.11502.

**Reaction of citronellal (II) with peracetic acid.** A mixture of 2.50 g of compound **II**, 33 ml (0.028 mol) of $CH_3COOOH$ solution in $CH_2Cl_2$, and 6 g of anhydrous $Na_2CO_3$ was vigorously stirred for 1 h. The peracetic acid was preliminary prepared by extraction from the mixture of 200 ml $CH_3COOH$, 200 ml of 30% $H_2O_2$, and 10 ml of $H_2SO_4$, and its concentration was determined by iodometry. In 1 h the reaction mixture was treated with saturated solution of $Na_2CO_3$, washed with water till neutral, and dried on $Na_2SO_4$. The isolated product of 1.38 g contained compounds **II, XX**, and **XIX** in 1:1:6 ratio. By column chromatography on $SiO_2$ (gradient elution with a mixture hexane–ethyl ether, the latter from 0 to 30%) was isolated 0.13 g of unreacted aldehyde **II**. 0.22 g of alcohol **XX**, and 0.75 g of epoxides **XIX** as a mixture of diastereomers **XIXa, XIXb** in a ratio ~2:1.

**3,7-Dimethyl-6,7-epoxyoctanal (XIX).** ^{1}H NMR spectrum of prevailing isomer A ($\delta$, ppm, $J$, Hz): 0.91 d ($C^9H_3$, $J_{9,3}$ 6.5), 1.16 s, 1.20 s ($C^8H_3$, $C^{10}H_3$), 1.31–1.50 m ($2H^4$, $2H^5$), 2.03 m ($H^3$), 2.16 d.d.d ($H^2$, $J_{2,2'}$ 16.5, $J_{2,3}$ 8, $J_{2,1}$ 2.5), 2.33 d.d.d ($H^{2'}$, $J$ 16.5, $J_{2',3}$ 6, $J_{2',1}$ 2), 2.53 t ($H^6$, $J_{6,5}$ 6), 9.65 d.d ($H^1$, $J$ 2.5, 2). NMR spectrum ^{1}H of minor isomer B ($\delta$, ppm, $J$, Hz): 0.90 d ($C^9H_3$, $J_{9,3}$ 6.5), 1.15 s, 1.20 s ($C^8H_3$, $C^{10}H_3$), 1.31–1.50 m ($2H^4$, $2H^5$), 2.03 m ($H^3$), 2.17 d.d.d ($H^2$, $J_{2,2'}$ 16.5, $J_{2,3}$ 8, $J_{2,1}$ 2.5), 2.31 d.d.d ($H^{2'}$, $J$ 16.5, $J_{2',3}$ 6, $J_{2',1}$ 2), 2.53 t ($H^6$, $J_{6,5}$ 6), 9.65 d.d ($H^1$, $J$ 2.5, 2). Found $[M]^+$ 170.11509. $C_{10}H_{18}O_2$. Calculated $M$ 170.11512.

**Transformation of epoxides XIX in HSO$_3$F–SO$_2$FCl.** To a solution of 2.61 g (1.5 ml) of HSO$_3$F in 7 ml of SO$_2$FCl was added at –105°C a solution of 0.30 g of isomer mixture of epoxides **XIX** in 2 ml of dried CH$_2$Cl$_2$. The reaction mixture was vigorously stirred for 5 min at the same temperature, and then poured into 30 ml of a mixture of methanol with ethyl ether (5:2 by volume). The reaction products were extracted into ethyl ether, the solution was dried with MgSO$_4$. We isolated 0.25 g of mixture of compounds **XXI** and **XXII**. By column chromatography on SiO$_2$ with gradient elution with hexane containing from 0 to 5% of ethyl ether was isolated 0.06 g of compound **XXI** and 0.01 g of compound **XXII**.

**2,6-Dimethyl-8,8-dimethoxyoctan-3-one (XXI).** $^1$H NMR spectrum ($\delta$, ppm, $J$, Hz): 0.87 d (C$^{10}$H$_3$, $J_{10,6}$ 6.5), 1.04 d (C$^1$H$_3$, C$^9$H$_3$, $J$ 7), 1.33 d.d.d (H$^7$, $J_{7,7'}$ 13, $J_{7,6}$ 7, $J_{7,6'}$ 5), 1.35 m (H$^5$), 1.50 m (H$^6$), 1.52–1.62 m (H$^{5'}$, H$^{7'}$), 2.40 m (2H$^4$), 2.55 septet (H$^2$, $J$ 7), 3.25 s and 3.26 s (2 OCH$_3$), 4.39 d.d (H$^8$, $J_{8,7'}$ 7, $J$ 5). Found [$M$–OCH$_3$]$^+$ 185.11509. C$_{11}$H$_{21}$O$_2$. Calculated [$M$–OCH$_3$] 185.11512.

**4-Methyl-2-methoxy-7-(1-methoxy-1-methylethyl)-1-oxacycloheptane (XXII).** $^1$H NMR spectrum ($\delta$, ppm, $J$, Hz): 0.91 d (C$^9$H$_3$, $J_{9,4}$ 6.5), 1.08 m (H$^3$), 1.10 s and 1.16 s (C$^{11}$H$_3$, C$^{12}$H$_3$), 1.36 m and 1.82 m (2 H$^6$) 1.54 m and 1.78 m (2H$^5$), 1.62 m (H$^4$), 1.76 br.d.d (H$^{3'}$, $J_{3',3}$ 13.5, $J_{3',2}$ 5), 3.18 s (OC$^{13}$H$_3$), 3.36 s (OC$^8$H$_3$), 3.63 br.d (H$^7$, $J_{7,6}$ 10), 4.61 d.d (H$^2$, $J_{2,3}$ 9, $J$ 5). Found [$M$–OCH$_3$]$^+$ 185.11509. C$_{11}$H$_{21}$O$_2$. Calculated [$M$–OCH$_3$] 185.11512.

**Transformations of epoxides XIX in a system acetone–water–H$_2$SO$_4$.** To 0.94 ml of the mixture acetone–water–H$_2$SO$_4$ (40:6:1 by volume) was added 0.29 g of epoxides **XIX**. After 10 min the reaction mixture was treated with saturated Na$_2$CO$_3$ solution, the reaction products were extracted into ethyl ether, and the extract was dried with MgSO$_4$. On removing ether we obtained 0.126 g of substance. By column chromatography on SiO$_2$ with gradient elution with hexane containing from 0 to 10% of ethyl ether was isolated 0.026 g of compound **XXV** and 0.06 g of compound **XXVI** as a mixture of diastereomers in 1:1 ratio.

**3,7-Dimethyl-6-oxooctanal (XXV).** $^1$H NMR spectrum ($\delta$, ppm, $J$, Hz): 0.93 d (C$^9$H$_3$, $J_{9,3}$ 6.5), 1.05 d (C$^8$H$_3$, C$^{10}$H$_3$, $J$ 7), 1.44 d.t.d (H$^4$, $J_{4,4'}$ 14, $J_{4,5}$ 7.5, $J_{4,3}$ 6.5), 1.57 d.t.d (H$^{4'}$, $J$ 14, $J_{4',5}$ 7, $J_{4',3}$ 6), 2.00 m (H$^3$), 2.21 d.d.d (H$^2$, $J_{2,2'}$ 16.5, $J_{2,3}$ 7.5, $J_{2,1}$

2.5) and 2.35 d.d.d (H$^{2'}$, $J$ 16.5, $J_{2',3}$ 6, $J_{2',1}$ 2) $AB$ system, 2.40 m (2H$^5$), 2.53 septet (H$^7$, $J$ 7), 9.69 d.d (H$^1$, $J$ 2.5, 2). Found [$M$]$^+$ 170.11509. C$_{10}$H$_{18}$O$_2$. Calculated $M$ 170.11512.

**3,7-Dimethyl-6,7-isopropylidenedioxyoctanal (XXVI).** The NMR spectra of compound **XXVI** are presented without assignment to one or another isomer for we failed to isolate them as individual compounds or at least with the prevalence of one isomer ($\delta$, ppm, $J$, Hz): 0.94 d, 0.95 d (2C$^{15}$H$_3$, $J$ 6.5), 1.01 s (6H) and 1.16 s (6H, 2C$^{11}$H$_3$ and 2C$^{12}$H$_3$), 1.23 s (6H) and 1.31 s (6H, 2C$^{13}$H$_3$ and 2C$^{14}$H$_3$), 2.05 m (2H$^8$), 2.19 d.d.d ($J$ 16, 8, 2) and 2.20 d.d.d (2H$^9$, $J_{9,9'}$ 16, $J_{9,8}$ 8, $J_{9,10}$ 2), 2.36 d.d.d ($J$ 16, 5.5, 2) and 2.38 d.d.d (2H$^{9'}$, $J$ 16, $J_{9',8}$ 5.5, $J_{9',10}$ 2), 3.52 d.d ($J$ 9, 3.5) and 3.53 d.d (2H$^5$, $J_{5,6}$ 9, $J_{5,6'}$ 3.5), 9.69 d.d (2H$^{10}$, $J$ 2, 2). Found: [$M$]$^+$ 216.11512. C$_{13}$H$_{24}$O$_3$. Calculated: $M$ 216.11525.

**Isomerization of epoxides XIX on zeolite-β.** To 0.60 g of calcined zeolite in 8 ml of dry CH$_2$Cl$_2$ was added 0.40 g of epoxides **XIX** in 2 ml of CH$_2$Cl$_2$. After 10 mi of stirring the mixture was filtered, the catalyst was washed with ethyl ether. On removing the solvents we obtained 0.31 g of products. By column chromatography on SiO$_2$ with gradient elution with hexane containing from 0 to 30% of ethyl ether was isolated 0.043 g of compound **XXVII** as a mixture of diastereomers in 2:1 ratio, 0.05 g of compound **XXV**, and 0.09 g of initial epoxides **XIX**.

**4,8,8-Trimethyl-7,9-dioxabicyclo[4.2.1]nonane (XXVII).** $^1$H NMR spectrum of prevailing isomer ($\delta$, ppm, $J$, Hz): 0.89 d (C$^9$H$_3$, $J_{9,3}$ 7), 1.21 s and 1.30 s (C$^{10}$H$_3$, C$^{11}$H$_3$), 1.29 m (H$^2$), 1.39 m (H$^4$), 1.63–1.79 m (H$^{4'}$, 2H$^5$), 1.91 m (H$^3$), 1.97 m (H$^{2'}$, $J_{2',2}$ 13.5, $J_{2',3}$ 6, $J_{2',1}$ 4.5, $J_{2',4}$ 1.5), 3.92 br.d (H$^6$, $J_{6,5}$ 4), 5.42 d (H$^1$, $J$ 4.5). $^1$H NMR spectrum of minor isomer ($\delta$, ppm, $J$, Hz): 0.93 d (C$^9$H$_3$, $J_{9,3}$ 7), 1.25 s and 1.30 s (C$^{10}$H$_3$, C$^{11}$H$_3$), 1.47 m (2H$^4$), 3.94 d.d (H$^6$, $J_{6,5}$ 8, $J_{6,5'}$ 2), 5.47 t (H$^1$, $J_{1,2}$ 2); the signals of the other protons coincide with those of the main isomer. Found $M$ 170.11468. C$_{10}$H$_{16}$O$_2$. Calculated $M$ 170.11504.

### ACKNOWLEDGMENT

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