

Physical Chemistry

Formation of Long-Chain and Macrocyclic Compounds during Catalytic Conversion of Geraniol on Micro- and Micro-Mesoporous BEA-Type Zeolite

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ABSTRACT. The present paper studies catalytic transformations of the terpene alcohols used in the perfumery industry, transformation of geraniol on micro- and micro-mesoporous BEA-type zeolites. Experiments were carried out with the use of various mass ratios of catalyst/geraniol (0.0075–0.053 g/g), in the inert atmosphere (nitrogen, argon) and at temperatures from 27 to 150°C. The analysis of the products of catalytic transformations was carried out by the gas chromatography – mass spectrometry (GC-MS) method; conversion of geraniol, yield of products and selectivity were calculated from experimental data. The reaction products contain mainly unconverted trans-Geraniol, β -Linalool, trans,trans-Farnesol and (2E,6E)-6,11-Dimethyl-2,6,10-dodecatrien-1-ol, small quantities of β -Myrcene, D-Limonene, trans- β -Ocymene, β -Ocymene, α -Terpineol, cis-Geraniol (Nerol), cis-Isogeraniol, trans,trans,trans-Geranylgeraniol, p- and m-Camphorene (Dimyrcene), and unidentified isomer of trans-geranylgeraniol are present. It is established that by one-pot method in “zeolitic reactor” it is possible not only to receive long-chain C_{14} – C_{20} molecules, but to produce macrocycles. © 2018 Bull. Georg. Natl. Acad. Sci.

Key words: geraniol, catalytic transformation, zeolite beta, micro- and micro-mesoporous materials

Catalytic transformation of terpene alcohols $C_{10}H_{18}O$ used in the perfumery industry (linalool, geraniol, nerol, etc.) includes not only isomerization, but also their dehydration, cyclization and condensation. These processes

were studied by us earlier for linalool with the use of micro- and micro-mesoporous BEA-type zeolites as catalysts [1]. Our next research [2] was devoted to consideration of catalytic transformations of geraniol on the same zeolites characterized

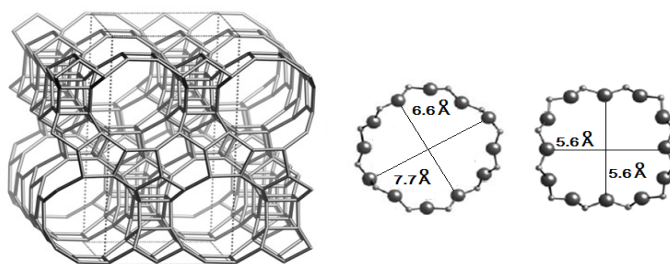


Fig. 1. The polymorph A of BEA framework viewed along [010] and cross sections of wide and tortuous channels [6].

by different chemical ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, total acidity) and structural (surface area, micro and meso pore volumes, amount of weak and strong acid centers) properties. It has been established that along with products of isomerization-cyclisation ($\text{C}_{10}\text{H}_{18}\text{O}$) and dehydration ($\text{C}_{10}\text{H}_{16}$) some substances $\text{C}_{14} - \text{C}_{20}$ with higher molecular mass are formed, and discussion of opportunities of formation of long chains and macrocycles on micro- and micro-mesoporous BEA-type zeolite was a main objective of this contribution.

Zeolite BEA (beta) based catalysts are widely used for transformation of various organic compounds [3, 4], and now various forms of this zeolite are applied [5].

According to the data of the International Zeolite Association [6], crystal chemical formula of zeolite beta is $[\text{Na}_7] [\text{Al}_7\text{Si}_{57}\text{O}_{128}] \cdot n\text{H}_2\text{O}$. *BEA, its microporous structure [7] is a hybrid of two intergrowing polymorphs termed A and B and having the three-dimensional 12-membered ring pore system with two straight channels, each with a cross section of 0.77×0.66 nm, parallel to [100] and [010], and a channel of 0.56×0.56 nm, which runs along the [001] direction. The polymorphs grow as two-dimensional sheets and the sheets randomly alternate between the two. The intergrowth of the polymorphs does not significantly affect the pores in X and Y dimensions, but in the Z direction of the faulting, the pore becomes tortuous, but not blocked. The hypothetical polymorph A is depicted

in Fig. 1, where cross sections of channels are also shown.

Compared with other zeolites, BEA has a high density of stacking defects, which arise from the successive interconnection of layers in the [001] planes, where they link either in a left- or right-handed fashion. When a tertiary building unit in a layer rotates over 90° around the [001] direction with respect to the next building unit, defects, which contain partially coordinated aluminum, are created [7, 8]. These stacking faults do not affect the micropore volume, but do influence the tortuosity of the channel along [001].

Open channels of the BEA-type zeolite have rather big diameter for diffusion of comparatively large molecules. Besides, the low content of aluminum in the crystal structure leads to the fact that the number of the compensating positively charged ions located in channels is also small, and cation don't interfere with penetration of organic molecules into channels.

Materials and Methods

Reagent and chemicals. Geraniol ($\geq 97\%$, FG, trans-3,7-Dimethyl-2,6-octadien-1-ol), nerol (97%, cis-3,7-Dimethyl-2,6-octadien-1-ol), and racemic linalool (97-98%, GC, ($\pm$)-3,7-Dimethyl-1,6-octadien-3-ol) were purchased from Sigma-Aldrich (USA). Argon and nitrogen (99.999%) were used as an inert reaction medium, methanol (for HPLC, $\geq 99.9\%$, Sigma-Aldrich) was used as a solvent.

Catalysts. Parent zeolites BEA-25 and BEA-150 (Zeolyst International) were used in NH_4^+ and

Table 1. Chemical and structural properties of catalysts

Catalyst	BEA-25	RBEA-25	BEA-150	RBEA-150
$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$	25.0	23.8	150.0	176.4
S_{BET} (cm^3/g)	558	721	539	822
V (cm^3/g)	0.486	0.625	0.588	0.792
V_{micro} (cm^3/g)	0.164	0.125	0.151	0.139
V_{meso} (cm^3/g)	0.322	0.500	0.437	0.653
$a_0(\text{NH}_3)$ ($\mu\text{mol}/\text{g}$)	1200	1179	180	233
$a_{\text{weak}}(\text{NH}_3)$ ($\mu\text{mol}/\text{g}$)	725	704	97	95
$a_{\text{strong}}(\text{NH}_3)$ ($\mu\text{mol}/\text{g}$)	475	475	83	138

H-forms, respectively. Preparation of micro-mesoporous materials (RBEA-25 and RBEA-150) and characterization of all four catalysts is given in [1,2], the main characteristics are provided in Table 1, where, $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ is molar ratio of silicon and aluminum oxides in crystal structure, S_{BET} is surface area calculated from the nitrogen adsorption-desorption isotherms on the basis of Brunauer-Emmet-Teller approach, specific total pore volume V includes volume of micropores V_{micro} and volume of mesopores V_{meso} , and acidity is calculated on the basis of temperature-programmed desorption curves of ammonia and expressed as total ammonia adsorption value $a_0(\text{NH}_3)$ consisting of adsorption of ammonia on the weak acid centers $a_{\text{weak}}(\text{NH}_3)$ and the strong acid centers $a_{\text{strong}}(\text{NH}_3)$.

Hydrothermal treatment of BEA crystals was carried out to generate a secondary system of pores allowing shorter diffusion paths for the reactants and the products within the crystal, and in both cases (BEA-25→RBEA-25, BEA-150→RBEA-150) the volume of mesopores has increased approximately by one and a half times.

Geraniol conversion. Catalytic transformation of geraniol was carried out in a liquid phase in a 50 mL three-necked round-bottomed glass flask with a reflux condenser, a thermometer and with an inlet for introducing an inert gas; experiments were conducted on a magnetic stirrer with a heater under solvent-free condition at temperatures in the range of 27-150°C and under ambient pressure; duration

of run was 1-2 h, catalyst mass – 0.01-0.07 g (mass ratio of catalyst/geraniol from 0.0075 to 0.0523), catalyst was separated by centrifugation.

Catalytic activity. The progress of the geraniol conversion reaction and analysis of the reaction products was carried out by the Gas Chromatography – Mass Spectrometry method (Agilent Technologies, 7890B/5977A, USA) in the electron ionization mode, 70 eV. Helium as a carrier gas and capillary column HP-5ms, Ultra Inert, 30 m x 0.32 mm x 0.25 μm , were used. Analyses were carried out in the following program mode: holding at 80°C for 5 min, heating to 210°C at a rate of 30°C/min, holding at 210°C for 10 min.

Quantitative estimation of reaction products. The relative content of the reaction products (C_i , %) was determined using geraniol as an internal standard, also the amount of linalool, geraniol, and nerol was determined from corresponding calibration curves. Conversion of geraniol was calculated by the formula: $C_{\text{geraniol}} = (\mathbf{m}_{\text{initial geraniol}} - \mathbf{m}_{\text{unconverted geraniol}}) \times 100 / \mathbf{m}_{\text{initial geraniol}}$; the yield (Y_i , %) and selectivity to products (S_i , %) were determined according to the formulas, respectively: $Y_i = C_i \times M_{\text{geraniol}} \times 100 / 97 \times M_i$, $S_i = 100 \times Y_i / C_{\text{geraniol}}$. Where, M_{geraniol} is molar mass of geraniol, 97% – its initial concentration, $\mathbf{m}$ is the mass of substance.

Results and Discussion

Geraniol conversion data. The detailed description of geraniol conversion is given in

work [2], the main conversion products of geraniol on microporous BEA and micro-mesoporous RBEA catalysts over 60°C are the following compounds:

Isomerization products $C_{10}H_{18}O$ (mainly the products of the double bond transfer in geraniol and, to a lesser extent, cis-trans isomerization): β -Linalool and Nerol, also a very small amount (up to 0.6%) of cis-Isogeraniol ((3Z)-3,7-Dimethyl-3,6-octadien-1-ol) and cyclic product α -Terpineol (up to 1.2%); the selectivity of isomerization products decreases with increasing geraniol conversion.

Dehydration products $C_{10}H_{16}$: terpenic hydrocarbons α -Myrcene, β -Myrcene, α -Terpinolene, D-Limonene, trans- β -Ocimene, β -Ocimene, γ -Terpinene, 1,1,2-Trimethyl-3-(2-methyl-1-propen-1-ylidene)cyclopropane, α -Terpinene, (4E,6Z)-2,6-Dimethylocta-2,4,6-triene (allo-Ocimene); the selectivity of dehydration products increases with increasing geraniol conversion.

Carbon-chain-extending products C_{14} and C_{15} (sesquiterpene alcohols), selectivity of such products has an extreme dependence on the conversion of geraniol. Over the 40°C diterpene alcohols $C_{20}H_{34}O$ are formed up to 2-3%, only on the RBEA-25 and BEA-25 catalysts at 100-150°C the formation of up to 1.0-1.5% of **monocyclic diterpene alcohols** (thunbergol) and up to 0.3-0.6% of **monocyclic terpene** (cembrene) is observed.

The first three ways of transformation of geraniol are shown in the Fig. 2 where structures of isomerization, dehydration, and cyclization products are given.

Geraniol has 4 rotatable C – C bonds and energetically the most favorable conformation is “extended” when the molecule has the maximum length and the minimum “diameter” of approx. 3.8 Å [9]. The same concerns isomers of geraniol and acyclic products, but even for compounds with six-membered cycles their effective diameter generally

is defined not by the size of a ring, but of the gem-dimethyl group, so all these products can be formed in channels of the catalyst and move freely in them. It is not so obvious to long-chain compounds and, in particular, for macrocycles, and demands special consideration.

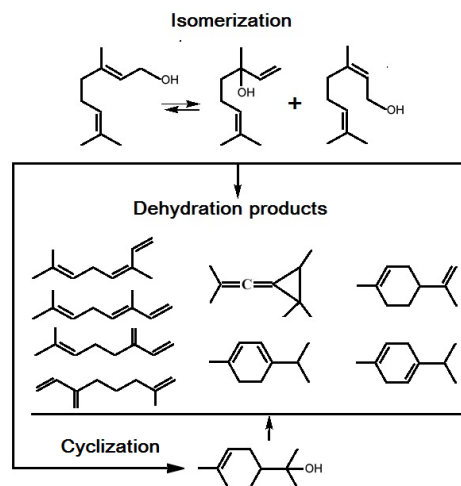


Fig. 2. Isomerization, dehydration, and cyclization of geraniol.

Long-chain compounds. According to obtained experimental data, catalytic redistribution and extension of the carbon chain results in formation of (2E,6E)-6,11-Dimethyl-2,6,10-dodecatrien-1-ol, $C_{14}H_{24}O$, and sesquiterpene alcohol (2E,6E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol, trans,trans-Farnesol, $C_{15}H_{26}O$, from monoterpene alcohol geraniol, which has a “head” at the methyl group and a “tail” at the gem-dimethyl group [10] and is freely moving in zeolite BEA channels.

Formation of sesquiterpene from monoterpene can be presented if to assume that on the used BEA-type zeolite catalysts a cracking of monoterpenes takes place with formation of the isoprene units C_5H_8 joining to other monoterpene molecules according to Ruzicka’s “isoprene rule”. It is more difficult to understand formation of $C_{14}H_{24}O$, but this compound, most likely, doesn't take part in further transformations, and from this point of view

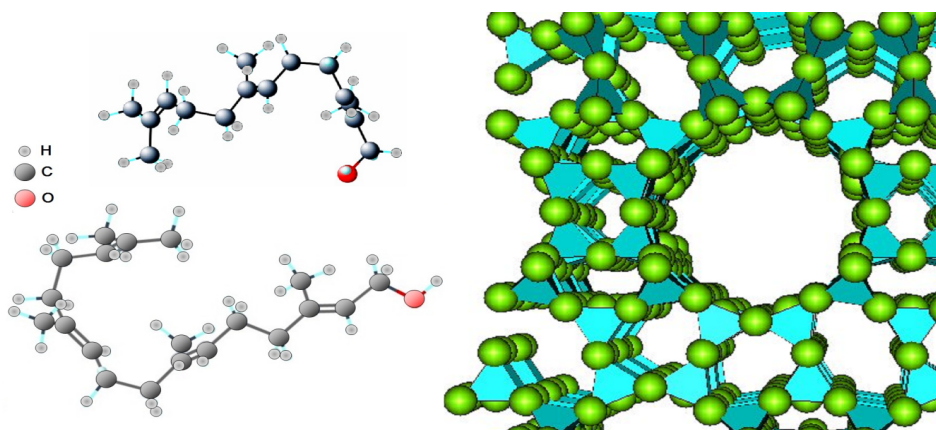


Fig. 3. Produced long-chain molecules and zeolite 12-rings.

it is a little interesting. On the contrary, the *trans,trans*-Farnesol can be involved in further transformations as it happens to this substance in the nature.

an effective “diameter” of approx. 4 Å. In this case the diterpenic alcohols formed in channels of the catalyst can freely pass through the 12-rings and diffuse not only in wide, but in narrow zeolite

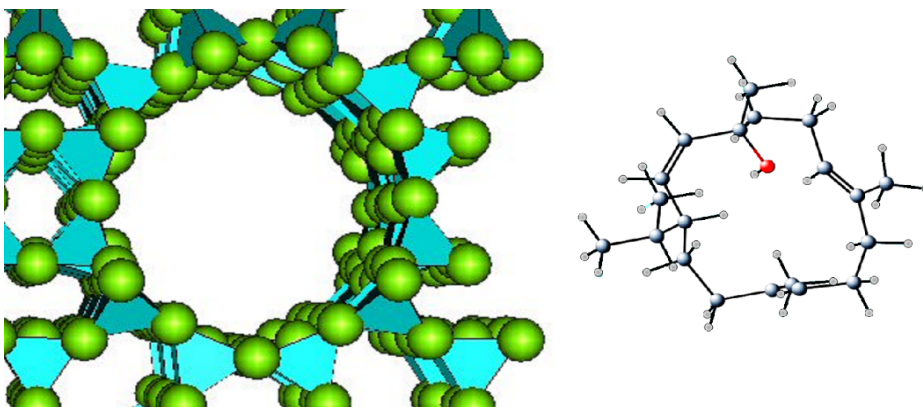


Fig. 4. Zeolite 12-ring and the thunbergol macrocycle

In biochemistry the *trans,trans*-Farnesol is considered as the biogenetic predecessor of mono-, bi-, and tricyclic sesquiterpenes, but such compounds are not found among geraniol conversion products, but diterpenic alcohols $C_{20}H_{34}O$ – *trans,trans,trans*-Geranyl-geraniol, *p*-Camphorene and unidentified isomer of *trans*-Geranylgeraniol are present in reaction mixture. The possibility of obtaining of geranylgeraniol from farnesol by allylic rearrangement under $O=W(OR)_4 \cdot \text{Ligand}$ catalysts was shown in study [11].

The molecule of *trans,trans,trans*-Geranylgeraniol has ten rotatable C – C bonds and variety of conformations including the “extended” one with

channels, like their predecessor *trans,trans*-Farnesol having seven rotatable C – C bonds. However, staying in energetically most probable conformations [12], these molecules can move only in a wide channels, as shown in Fig. 3.

Macrocyclic compounds. Among products of conversion of geraniol there are monocyclic compounds having the sizes (averaged “diameter” of the C_{14} -ring 6.8 Å) comparable to the sizes of the $(SiO)_2$ -ring of catalyst (see Fig. 4).

Formation of thunbergol and its isomer isocembrol (1*R*,2*E*,4*S*,7*E*,11*E*)-4-Isopropyl-1,7,11-trimethyl-cyclotetradeca-2,7,11-trienol, $C_{20}H_{34}O$, in zeolite channels is possible by

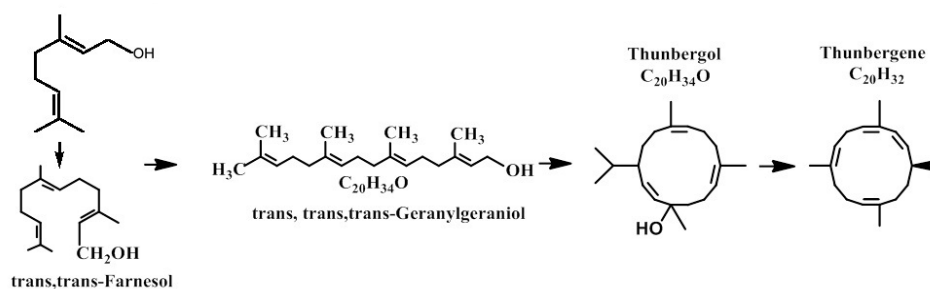


Fig. 5. Ways of geraniol transformation through farnesol into long-chain and macrocyclic molecules

transformation of *trans,trans,trans*-Geranylgeraniol arranging bond between the C1 and C14 carbon atoms, as it was shown earlier in [13]. Most likely, formation of diterpenic alcohols is followed by dehydration into cembrene (thunbergene, (1*E*,3*Z*,6*E*,10*E*)-3,7,11-trimethyl-14-(propan-2-yl) cyclotetradeca-1,3,6,10-tetraene, $C_{20}H_{32}$).

The proposed scheme of formation of long-chain and macrocyclic molecules is submitted in the Fig. 5.

Conclusion

Thus, it is established, that by one-pot method in “zeolitic reactor” it is possible to receive such long-chain molecules as *trans,trans*-Farnesol and

(2*E*,6*E*)-6,11-dimethyl-2,6,10-dodecatrien-1-ol at a relatively low temperature, and with selectivity up to 37 and 52%, respectively. Moreover, *trans,trans*-Farnesol attaches one more isoprene unit to form the long-chain molecule of *trans,trans,trans*-Geranylgeraniol which can form a macrocycle of thunbergol $C_{20}H_{34}O$, which is dehydrated into diterpene thunbergene $C_{20}H_{32}$.

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ფიზიკური ქიმია

ნახშირბადის გრძელჯაჭვიანი და მაკროციკლური ნაერთების წარმოქმნა გერანიოლის კატალიზური გარდაქმნის დროს მიკრო- და მიკრო-მეზოფოროვან ბეტა ტიპის ცეოლითებზე

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**ივანე ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო

§ ლომონოსოვის მოსკოვის სახელმწიფო უნივერსიტეტი ქიმიის ფაკულტეტი, კინეტიკის და კატალიზის ლაბორატორია, , მოსკოვი, რუსეთის ფედერაცია

#სან დიეგოს სახელმწიფო უნივერსიტეტი საქართველოში, თბილისი, საქართველო

°ივანე ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი, ზუსტ და

საბუნებისმეტყველო მეცნიერებათა ფაკულტეტი, ქიმიის დეპარტამენტი, თბილისი, საქართველო

წარმოდგენილ სტატიაში შესწავლილია სუნამოების წარმოებაში გამოყენებული ტერპენული სპირტის გერანიოლის კატალიზური გარდაქმნები მიკრო- და მიკრო-მეზოფოროვან BEA ტიპის ცეოლითებზე.

ტერპენული პირველადი სპირტის გერანიოლის კატალიზური გარდაქმნები შესწავლილია სტატიკურ სისტემაში, ინერტულ (აზოტი, არგონი) გარემოში, კატალიზატორებისა და გერანიოლის სხვადასხვა მასური თანაფარდობებისთვის (0,0075-0,053 გ/გ) და 27-150°C ტემპერატურებზე. პროდუქტების ანალიზი ტარდებოდა ქრომატომას-სპექტრომეტრული (GC-MS) მეთოდით; ექსპერიმენტული მონაცემებიდან გამოითვლებოდა გერანიოლის გარდაქმნის ხარისხი, პროდუქტების გამოსავლიანობა და პროდუქტების შერჩევითობა.

ტრანს-გერანიოლის გარდაქმნის პროდუქტებში, გარდა გარდაუქმნელი ტრანს-გერანიოლისა, იყო მისი დეჰიდრატაციის პროდუქტები – ტერპენული ნახშირწყალბადები $C_{10}H_{16}$, გერანიოლში ორმაგი ბმის გადანაცვლებისა და ცის-ტრანს-იზომერიზაციის და აგრეთვე ციკლიზაციის პროდუქტები (β-ლინალოლი, ცის-გერანიოლი, ანუ ნეროლი და α-ტერპინოლი); ნახშირბადოვანი ჯაჭვის დაგრძელების პროდუქტები – სესკვიტერპენული სპირტები $C_{15}H_{26}O$ და $C_{14}H_{24}O$ (შესაბამისად, ტრანს, ტრანს-ფარნეზოლი, ანუ (2E,6E)-3,7,11-ტრიმეთილ-2,6,10-დოდეკატრიენ-1-ოლი და (2E,6E)-6,11-დიმეთილ-2,6,10-დოდეკატრიენ-1-ოლი); მცირე რაოდენობით – ნახშირბადის გრძელჯაჭვიანი დიტერპენული სპირტის $C_{20}H_{34}O$ გეომეტრული იზომერები – ტრანს, ტრანს, ტრანს-გერანილგერანიოლი და ტრანს, ტრანს- გერანილლინალოლი; ციკლური დიტერპენის დიმირცენის ($C_{20}H_{32}$) პარა- და მეტა-იზომერები.

კატალიზატორებზე RBEA-25 და BEA-25 100-150°C ხდება აგრეთვე მონოციკლური დიტერპენული სპირტის $C_{20}H_{34}O$, თუნბერგოლის (იზო-ცემბროლის, (1R,2E,4S,7E,11E)-4-იზოპროპილ-1,7,11-ტრიმეთილ-ციკლოტეტრადეკა-2,7,11-ტრიენოლის) და მონოციკლური ტერპენის $C_{20}H_{32}$, ცემბრენის (1E,3Z,6E,10E)-3,7,11-ტრიმეთილ-14-(პროპან-2-ილ) ციკლო-ტეტრადეკა-1,3,6,10-ტეტრაენი) წარმოქმნა.

ამგვარად, ერთსაფეხურიანი გზით კატალიზატორების BEA-150 და RBEA-150 „ცეოლითურ რეაქტორში“ შედარებით დაბალ ტემპერატურაზე ტრანს-გერანიოლიდან ხდება ნახშირბადის გრძელჯაჭვიანი სესკვიტერპენული სპირტების $C_{15}H_{26}O$ (ტრანს, ტრანს-ფარნეზოლი) და $C_{14}H_{24}O$ (2E,6E)-6,11-დიმეთილ-2,6,10-დოდეკატრიენ-1-ოლი) მოლეკულების ტრანს-იზომერების დასინთეზება, შესაბამისად, შერჩევითობით 33 და 52%, როცა გერანიოლის გარდაქმნის ხარისხებია 18-34 და 42-61%. გარდა ამისა, სავარაუდოა, რომ მაღალი მჟავურობის კატალიზატორებზე BEA-25 და RBEA-25 გერანიოლიდან წარმოქმნილ ტრანს, ტრანს-ფარნეზოლთან კიდევ ერთი იზომერული ჯგუფის მიერთებით წარმოიქმნება ტრანს, ტრანს, ტრანს-გერანილგერანიოლი, რომელიც წარმოქმნის თუნბერგოლის $C_{20}H_{34}O$ მაკროციკლურ მოლეკულას, რომლის დეჰიდრატაციით მიიღება ციკლური მოლეკულა თუნბერგენი, $C_{20}H_{32}$.

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