FULL PAPER

The Convenient Way for Obtaining Geranial by Acid-Catalyzed Kinetic Resolution of Citral

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A new simple method has been developed for isolation of geranial from citral, which is a mixture of two isomeric aldehydes, geranial and neral. The storage of citral in the presence of *K10* montmorillonite clay has been demonstrated to result in an almost complete conversion of neral to dimeric and oligomeric products, with most geranial remaining unconverted. This enables isolation of geranial with the yield of up to 94%, based on the amount of geranial originally present in citral.

Keywords: Citral, Geranial, Neral, Montmorillonite *K10* clay, Kinetic resolution.

Introduction

Citral (3,7-dimethylocta-2,6-dienal) is an acyclic α,β-unsaturated monoterpenoid aldehyde, which is a mixture of (*E*)- (geranial (**1**)) and (*Z*)- (neral (**2**)) isomers (*Fig.*) in approximately equal proportions. Citral is the main component of many essential oils, *e.g.*, the content of citral in lemongrass oil is 70 – 80%. Synthetic citral is industrially produced from isobutene and HCHO [1]. Citral and its derivatives are used in perfumery as flavors and perfumes; they are valuable raw materials for synthesis of L-menthol (BASF process [2]), β-ionone, and vitamin A [1], and also possess diverse biological activity [3]. Citral isomers are often used as model compounds for studies of a wide range of reactions due to the presence of several unsaturated groups. Citral is usually used as a mixture of geranial (**1**) and neral (**2**), without separation of the isomers. However, it is often necessary to use the citral isomers as individual compounds, which is particularly important for synthesis of biologically active compounds [4] and L-menthol [2].

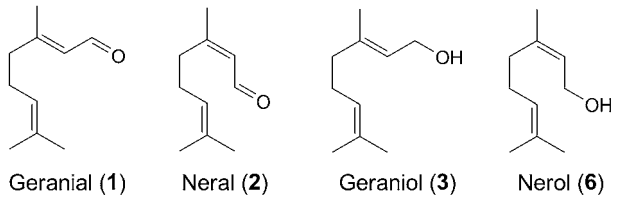

Figure. Structures of geranial (**1**), neral (**2**), geraniol (**3**), and nerol (**6**).

Various approaches have been used to solve the problem of producing the individual citral isomers. The industrial synthesis of menthol (BASF process) is based on separation of geranial (**1**) and neral (**2**) by dynamic distillation of citral [2b]. Thus obtained individual citral isomers, preferably neral (**2**), are used for synthesis L-menthol which comprises the following steps *i*) asymmetric catalytic hydrogenation of neral (**2**) and/or geranial (**1**) to form citronellal [2c – e]; *ii*) acid-catalyzed cyclization of citronellal to isopulegol; and *iii*) catalytic hydrogenation of isopulegol to form menthol [2]. But in laboratory scale distillative separation is a challenging task due to the close boiling points of the isomers (90 °C/5 Torr or 100 °C/6 Torr for geranial (**1**), and 88 °C/5 Torr or 96 °C/6 Torr for neral (**2**)) [5] as well as the ability of these aldehydes to undergo partial mutual isomerization when heated. Geranial (**1**) was isolated from citral by high-performance liquid chromatography [6]. The most common laboratory method for production of geranial (**1**) is the selective oxidation of geraniol (**3**) using different systems, such as MnO_2 [7], the *Dess–Martin* reagent [8], [bis(acetoxy)iodo]-benzene [9], oxygen in the presence of catalysts containing noble metals (Pd, Pt, Au, Ru, and Rh) [10], or the *Swern*, *Corey–Kim* [11], and *Oppenauer* oxidation reactions [12]. The disadvantages of the existing methods of obtaining individual citral isomers by oxidation of the appropriate alcohols include high cost reagents, stringent requirements for the reaction conditions, difficulties in handling of reaction mixtures and catalysts regeneration, and the need of special equipment.

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Transformations of citral in the presence of homogeneous acid catalysts have been studied quite well. For example, treatment of citral with dilute aqueous acids is known to lead to the formation of cyclization products, with the conversion degree of starting citral and the number and ratio of products being dependent on the medium pH. The main conversion products were hydrocarbons, alcohols, and diols with the *p*-menthane framework. For example, acid treatment of citral at pH 1.8 under nitrogen for 22 h gave rise to *p*-cymene (**4**) and *p,α*-dimethylstyrene (**5**) (*Scheme 1*) [13]. Remarkably, under certain conditions, the conversion of one of the citral isomers is higher than that of the other. For example, treatment of citral with *ca.* 1.5:1 isomers ratio at pH 3.3 under nitrogen for 6 h gave rise to a reaction mixture containing *ca.* 70% of the original aldehyde with the approximately 4.5:1 ratio of the (*E*)- and (*Z*)-isomers [13].

The aim of this study was to search for acid catalysts, the use of which would lead to the preferential conversion of only one from the citral geometric isomers, thus providing the opportunity to isolate the remaining isomer as an individual compound by kinetic resolution.

Results and Discussion

We used both *Lewis* ($BF_3 \cdot Et_2O$) and *Brønsted* (AcOH, CF_3COOH, and TsOH) acids as well as solid catalysts (montmorillonite *K10*, bentonite-SF, laponite, and zeolite beta). The reaction was carried out by storing a solution of citral in CH_2Cl_2 in the presence of acid catalyst at room temperature, until almost complete utilization of neral (**2**) was reached (0.5 – 2 h). Once the reaction mixture was processed, the composition and ratio of the reaction products were analyzed by gas chromatography/mass spectrometry (*Table 1*). The yield of the reaction mixture was determined as the ratio of the weight of all reaction products to the weight of initial citral.

The experiments have demonstrated that citral is not affected by exposure to acetic acid, bentonite-SF, and laponite. The citral conversion in the presence of TsOH results in the formation of *p*-cymene (**4**) and *p,α*-dimethylstyrene (**5**), with initial aldehydes being completely converted. However, the use of $BF_3 \cdot Et_2O$, CF_3COOH, *K10*, or zeolite beta as catalysts leads to the formation of reaction mixtures primarily consisting of geranial **1**, products of citral cyclization ($m/z \leq 152$) and oligomerization ($m/z \geq 268$), and also a small amount of neral **2**. Based on the data, we have concluded that the most promising conversion catalyst is the montmorillonite *K10*, the use of which results in a high yield of the reaction mixture and a preferential conversion of neral (**2**) to dimers (that can be easily separated from the intact geranial (**1**)), but not to the cyclization products (*Table 1*). It should be noted that montmorillonite clays are widely used nowadays as catalysts for monoterpenoid transformations [14].

We have then examined the influence of time and amount of the used *K10* on the reaction course (*Table 2*). We have found that an almost complete conversion of neral (**2**) is achieved within 2 – 4 h for the 1:1 citral/*K10* ratio. Changing the citral/*K10* ratio from 1:1 to 2:1 leads, on the one hand, to a higher content of geranial (**1**) in the reaction mixture, but on the other hand, to a higher content of neral (**2**) and cyclization products as well as a lower content of polymerization products that may complicate isolation of aldehyde **1**. Conversions of neral (**2**) proceed very slowly for the 10:1 citral/*K10* ratio. Therefore, the best conditions have been found to be stirring a solution of citral in CH_2Cl_2 in the presence of *K10*

Scheme 1. Products of citral transformations in acid medium [13].

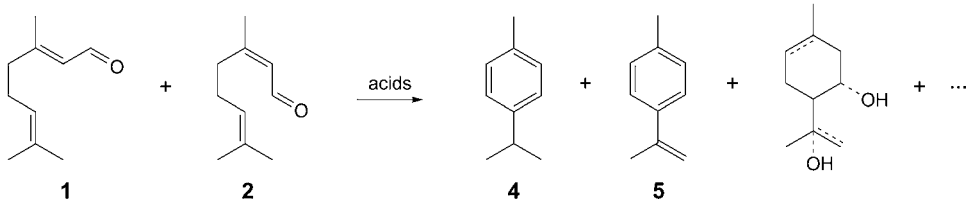


Table 1. Transformations of citral in the presence of acid catalysts

Catalysts	Reaction time [h]	Yield of the reaction mixture [%]	Composition of the reaction mixture [%][a])			
			1	**2**	Cyclization products, $m/z \leq 152$	Oligomers, $m/z \geq 268$
$BF_3 \cdot Et_2O$	0.5	67	15.0	0.4	4.7 (4 compounds)	80.0 (*ca.* 30 compounds)
CF_3COOH	2.0	81	33.3	1.7	15.4 (6 compounds)	42.5 (*ca.* 10 compounds)
Montm.*K10*	2.0	98	34.5	2.0	4.0 (2 compounds)	58.6 (15 compounds)
Zeolite beta	0.5	54	61.1	1.6	37.4 (2 compounds)	–

[a]) The percentage of the mixtures was calculated by peak areas without correction coefficients.

Table 2. Transformations of citral on *K10* clay

Citral/*K10* [by weight]	Reaction time [h]	Composition of the reaction mixture [%][a])			
		1	**2**	Cyclization products, $m/z \leq 152$	Oligomers, $m/z \geq 268$
1:1	0.5	32.9	7.0	7.3	50.1
	1	33.2	5.3	7.0	52.9
	2	33.1	3.9	6.7	54.4
	4	31.6	2.2	4.7	59.6
2:1	2	56.0	12.6	18.2	13.2
	4	45.5	7.3	12.7	34.6
10:1	2	48.2	41.2	6.8	3.9
	4	40.3	32.3	11.4	1.4

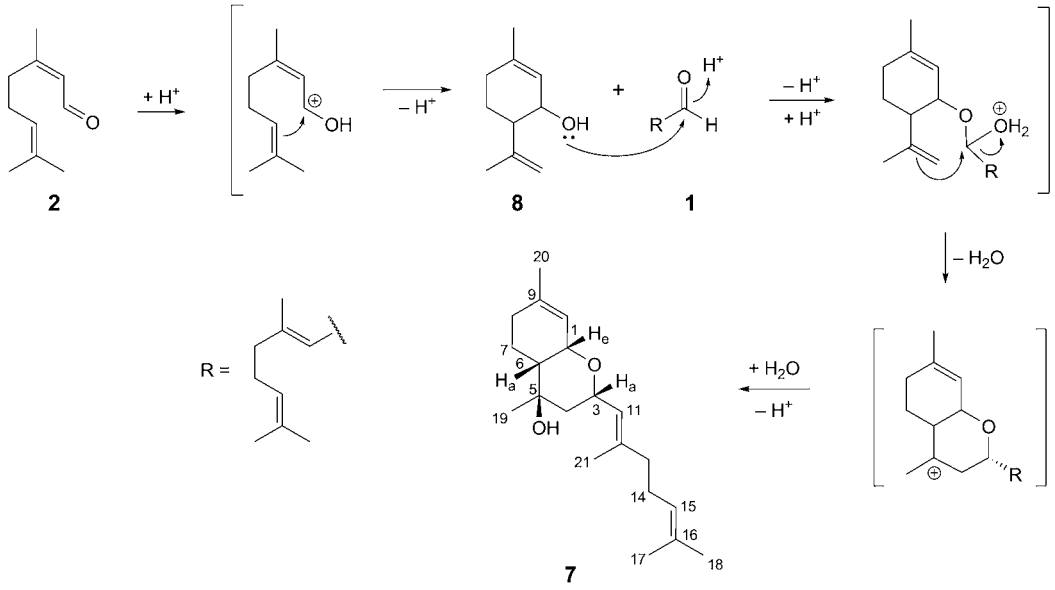
[a]) The percentage of the mixtures was calculated by peak areas without correction coefficients.

montmorillonite clay (1:1 citral/*K10* by weight) at room temperature for 2 – 4 h.

Isolation of geranial (**1**) from a reaction mixture can be performed by column chromatography or distillation under reduced pressure. Separation using SiO_2 column chromatography enables isolating geranial (**1**) with the yield of 94% (based on the content of geranial (**1**) in the initial mixture) and the purity of 98%, with neral (**2**) being the only impurity. In addition, we have been able to isolate major component from large amount of the oligomerization products – racemic compound **7** with a hexahydro-2*H*-chromene framework. Ring fusion and the relative arrangement of the substituents for one of the enantiomers of **7** are presented in *Scheme 2*. Previously, we observed the formation of compounds with a similar type of a framework in reactions of *p*-menthane diol with aldehydes on *K10* clay [15]. Evidently, the reaction starts with an intramolecular cyclization of neral (**2**) into alcohol **8** formation of which from citral is well-known [16]. Alcohol **8** may further react with an aldehyde molecule giving rise to compound **7** *(Scheme 2)*. Apparently, it is the ability of *K10* clay to catalyze both the conversion of neral (**2**) to an alcohol with the *p*-menthane framework and further intermolecular conversions of the alcohol that explains the unique efficiency of this catalyst in the kinetic isomer resolution leading to the production of geranial (**1**).

Isolation of geranial (**1**) from the reaction mixture by distillation *in vacuo* is somewhat less effective (the yield of geranial (**1**) is 55% and the purity is 96%), presumably, due to secondary reactions occurring during the distillation. The distillation residue consists mainly of dimerization products (more than 20 compounds with $m/z \geq 268$), with compound **7** being the main component (33% according to GC/MS). It should be noted that, in contrast to the data of paper [17], we have not observed the

Scheme 2. Possible mechanism of formation of compound **7**.



formation of isocitrals during distillation neither in the distillate nor in the distillation residue.

To explore the possibility of converting neral (**2**) to geranial (**1**) under the reaction conditions, we have incubated aldehyde **2**, produced by nerol (**6**) oxidation by MnO_2 [7], in the presence of *K10*. We have found that neral (**2**) completely converts to cyclization and oligomerization products as early as after 15 min, with no geranial (**1**) being present in the reaction mixture. Therefore, neral (**2**) is not converted to geranial (**1**) on *K10* clay under these conditions, *i.e.*, geranial (**1**) is the product of kinetic resolution of citral.

Conclusions

Therefore, we have developed a new simple method for isolation of geranial from citral. The storage of citral in the presence of *K10* clay, $BF_3 \cdot Et_2O$, CF_3COOH, or zeolite beta results in the preferential conversion of neral (**2**), with geranial (**1**) remaining intact, thereby leading to kinetic resolution of the isomers. The use of *K10* clay as a conversion catalyst enables isolation of up to 94% of geranial (**1**) initially present in citral.

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Experimental Part

General

Reagents and solvents were purchased from commercial suppliers and used as received. Citral (*ABCR*, Karlsruhe, Germany) ((*E*/*Z*) = 1:1, ^{1}H-NMR); purity 96%. Neral (**2**) was synthesized from nerol (**6**) (*Acros*, Geel, Belgium) according to previously described methods [7]. Montmorillonite *K10* (*Aldrich*, St. Louis, Missouri, USA) was calcined at 105 °C for 3 h before the reaction. Zeolite beta (*Zeosit*, Novosibirsk, Russia) was calcined at 500 °C for 2 h before the reaction. CH_2Cl_2 was passed through calcined Al_2O_3. Column chromatography (CC): silica gel (SiO_2; 60 – 200μm; *Macherey-Nagel*, Duren, Germany); hexane/AcOEt 100:0 → 0:100. GC/MS (purity control and product analysis): *Agilent* (Santa Clara, CA, USA) *7890A* gas chromatograph with a quadrupole mass spectrometer (*Agilent 5975C*) as a detector, *HP-5MS* (*Agilent* (Santa Clara, CA, USA)) quartz column, 30 × 9 0.25 mm, He as carrier gas. ^{1}H- and ^{13}C-NMR spectra: *Bruker* (Rheinstetten, Germany) *DRX-500* apparatus at 500.13 MHz (^{1}H) and 125.76 MHz (^{13}C), $CDCl_3$; δ in ppm rel. to residual $CHCl_3$ (δ(H) 7.24, δ(C) 76.90), *J* in Hz. The structure of the products was determined by analyzing the ^{1}H- and ^{13}C-NMR spectra, ^{1}H,^{1}H double-resonance spectra and ^{13}C,^{1}H-type 2D-COSY (^1J(C,H) = 160 Hz and COLOC ($^{2,3}J$(C,H) = 10 Hz). HR-MS: *DFS Thermo Scientific* (Waltham, MA, USA) spectrometer in a full scan mode (15 – 500 *m*/*z*, 70 eV electron impact ionization, direct sample administration). Spectral and analytical investigations were carried out at Collective Chemical Service Center of Siberian Branch of Russian Academy of Sciences.

Acid-Catalyzed Transformations of Citral

Homogeneous Catalysts. To a solution of catalyst (0.7 mmol in 3 ml of CH_2Cl_2), a solution of citral (0.7 mmol in 2 ml of CH_2Cl_2) was added. The mixture was then stirred for 0.5 – 2 h at room temperature. The mixture was washed with a sat. soln. of $NaHCO_3$, then with H_2O, and Na_2SO_4 was used for drying. The solvent was distilled off and the obtained reaction mixture was analyzed by GC/MS.

Heterogeneous Catalysts. To a suspension of the catalysts (0.10 g in 3 ml of CH_2Cl_2), a solution of citral (0.10 g in 2 ml of CH_2Cl_2) was added. The mixture was stirred for 0.5 – 4 h at room temperature. The catalyst was filtered off and the solvent was distilled off. The obtained reaction mixture was analyzed by GC/MS.

Isolation of Geranial **1** from Citral

To a suspension of *K10* clay (0.50 g) in 10 ml of CH_2Cl_2, a solution of citral (0.50 g in 5 ml of CH_2Cl_2) was added. The mixture was stirred for 2 h at room temperature and then AcOEt (7 ml) was added. *K10* clay was filtered off, the solvent was distilled off and the residue was separated by SiO_2 CC to isolate geranial (**1**) (0.235 g, 94% based on the content of isomer **1** in initial mixture) containing 2% neral (**2**) as impurity (^{1}H-NMR data), and (2*S*,4*R*,4a*R*,8a*S*)-2-[(1*E*)-2,6-dimethylhepta-1,5-dien-1-yl]-3,4,4a,5,6,8a-hexahydro-4,7-dimethyl-2*H*-1-benzopyran-4-ol (**7**) (0.035 g, 4%).

(2*S*,4*R*,4a*R*,8a*S*)-2-[(1*E*)-2,6-Dimethylhepta-1,5-dien-1-yl]-3,4,4a,5,6,8a-hexahydro-4,7-dimethyl-2*H*-1-benzopyran-4-ol (**7**). $[\alpha]_{580}^{20}$ = 0 (*c* = 3, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 1.22 (*s*, Me(19)); 1.28 (br. *dd*, *J*(6a,7a) = 13.2, *J*(6a,7e) = 3.2, H_a–C(6)); 1.34 (*ddd*, ^2J = 14.0, *J*(4e,3a) = 2.5, *J*(4e,6a) = 1.6, H_e–C(4)); 1.46 – 1.53 (*m*, H_e–C(7)); 1.48 (*dd*, ^2J = 14.0, *J*(4a,3a) = 11.4, H_a–C(4)); 1.55 (br. *s*, Me(18)); 1.59 – 1.64 (*m*, H_a–C(7)); 1.64 (*m*, all $J \leq 2.0$, Me(17)); 1.65 (*d*, *J*(21,11) = 1.4, Me(21)); 1.66 (br. *s*, Me(20)); 1.91 – 2.01 (*m*, CH_2(8), CH_2(13)); 2.02 – 2.08 (*m*, CH_2(14)); 4.23 (br. *d*, *J*(1e,10) = 5.5, H_e–C(1)); 4.48 (*ddd*, *J*(3a,4a) = 11.4, *J*(3a,11) = 8.1, *J*(3a,4e) = 2.5, H_a–C(3)); 5.05 (*tqq*, *J*(15,14) = 7.0, *J*(15,17) = *J*(15,18) = 1.5, H–C(15)); 5.16 (*dq*, *J*(11,3a) = 8.1, *J*(11,21) = 1.4, H–C(11)); 5.58 (*dq*, *J*(10,1) = 5.5, *J*(10,20) = 1.4, H–C(10)). ^{13}C-NMR ($CDCl_3$): 68.2 (*d*, C(1)); 69.9 (*d*,C(3)); 40.9 (*t*, C(4)); 71.1 (*s*, C(5)); 45.0 (*d*, C(6)); 19.7 (*t*, C(7)); 31.2 (*t*, C(8)); 138.3 (*s*, C(9)); 121.2 (*d*, C(10)); 125.4 (*d*, C(11)); 140.1 (*s*, C(12)); 39.3 (*t*, C(13)); 26.2 (*t*, C(14)); 124.0 (*d*, C(15)); 131.3 (*s*, C(16)); 25.5 (*q*, C(17)); 17.5 (*q*, C(18)); 29.0 (*q*, C(19)); 23.3 (*q*, C(20)); 16.7 (*q*, C(21)). HR-MS:

304.2392 (M^+, $C_{20}H_{32}O_2^+$; calc. 304.2397). *cis*-Fusion of rings of **7** was established similar to our previous work [15a]. The coupling constants $^3J(6,7)$ = 13.2 and 3.2 suggest that the H–C(6) is axial in the cyclohexene ring, hence the H–C(1) has an equatorial conformation ($^3J(1,10)$ = 5.5). The coupling constants $^3J(3,4)$ = 11.4 and 2.5 suggest that the H–C(3) is axial in the pyran ring. Based on these data and taking into account the rings fusion, one can assume only *cis*-arrangement of H–C(6) and H–C(3).

To a suspension of *K10* clay (10.0 g) in 100 ml of CH_2Cl_2 at 10 °C, a solution of citral (12.0 g in 200 ml of CH_2Cl_2) was added. The mixture was stirred for 3 h at room temperature and then AcOEt (50 ml) was added. *K10* clay was filtered off and the solvent was distilled off. The residue was distilled at 69 – 72 °C (2 Torr) to isolate geranial (**1**) (3.28 g, 55% based on the content of isomer **1** in initial mixture) containing 4% neral (**2**) as impurity (^{1}H-NMR data). The distillation residue consisted of *ca*. 20 compounds ($m/z \geq 268$, GC/MS).

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