Professor Claudio Júnior

IFMG, Campus São João Evangelista, MG

	1 M	2 M	Intervalo Manhã	3 M	4 M	5 M	6 M	Almoço	1 T	2 T	Intervalo Tarde	3 T	4 T	5 T	6 T	Intervalo Vespertino	1N	2N	Intervalo Noite	3N	4N	5N
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Certificamos que **CLÁUDIO JÚNIOR ANDRADE RIBEIRO** orientou o trabalho intitulado **"IMPLANTAÇÃO DE FOSSAS SÉPTICAS BIODIGESTORAS PARA REDUÇÃO DA DESIGUALDADE SOCIAL"** apresentado na VIII Feira de Ciências realizada no prédio de aulas Oswaldo Pimenta durante a VIII Semana Nacional de Ciência e Tecnologia do Instituto Federal de Minas Gerais-*Campus* São João Evangelista.

São João Evangelista, 01 de Novembro de 2018.

Márcia Ferreira da Silva
Coordenadora Geral do Ensino Médio e Técnico
IFMG – *Campus* São João Evangelista

Tiago de Oliveira Dias
Diretor de Desenvolvimento Educacional
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Registrado sob nº 388 do livro de registro de certificados da CGEMT-02, página 125.

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VIII FEIRA DE CIÊNCIAS DO IFMG-SJE

DECLARAÇÃO

Declaro que **CLÁUDIO JÚNIOR ANDRADE RIBEIRO** é docente do Instituto Federal de Minas Gerais – *Campus* São João Evangelista e ministrou a disciplina Química II em regime de Progressão Parcial no segundo semestre do ano letivo de 2018.

São João Evangelista, 07 de fevereiro de 2019.

_____
Márcia Ferreira da Silva
Coordenadora Geral de Ensino Médio e Técnico
IFMG – *Campus* São João Evangelista

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PORTARIA Nº 190 DE 11 DE SETEMBRO DE 2018

> **Dispõe sobre a alteração na Portaria nº 44 de 12 de março de 2018, através da inclusão de membros no Colegiado da Área de Ciências da Natureza do IFMG – *Campus* São João Evangelista.**

O DIRETOR GERAL SUBSTITUTO DO INSTITUTO FEDERAL DE EDUCAÇÃO, CIÊNCIA E TECNOLOGIA DE MINAS GERAIS – CAMPUS SÃO JOÃO EVANGELISTA, no uso das atribuições que lhe são conferidas pela Portaria IFMG-SJE nº 102, de 28 de julho de 2016, publicada no Diário Oficial da União de 02 de agosto de 2016, Seção 2, página 19; e considerando a Portaria IFMG nº 475, de 06 de abril de 2016, publicada no DOU de 15 de abril de 2016, Seção 2, pág.17, retificada pela Portaria IFMG nº 805, de 04 de julho de 2016, publicada no DOU de 06 de julho de 2016, Seção 2, pág. 22, e pela Portaria IFMG nº 1078, de 27 de setembro de 2016, publicada no DOU de 04 de outubro de 2016, Seção 3, pág. 20,

Considerando o Memorando nº 14/2018/SJR-DDE/SJR-DG/SJR/IFMG,

RESOLVE:

Art. 1º INCLUIR os servidores **MICHELLE PIRES TANNURE**, Professor de Ensino Básico, Técnico e Tecnológico, Matrícula SIAPE nº 1122752, e **CLÁUDIO JÚNIOR ANDRADE RIBEIRO**, Professor de Ensino Básico, Técnico e Tecnológico, Matrícula SIAPE nº 189900, no Colegiado da Área de Ciências da Natureza do IFMG – *Campus* São João Evangelista, constituído pela Portaria nº 44 de 12 de março de 2018.

Art. 2º. Determinar que a presente Portaria seja devidamente publicada no Boletim de Serviços do IFMG - *Campus* São João Evangelista.

Art. 3º. Esta Portaria entra em vigor na data de sua publicação.

acao=documento_conferir&id_orgao_acesso_externo=0 informando o código verificador **0143167** e o código CRC **616C5D3B**.

23214.000410/2018-48

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PORTARIA Nº 1223 DE 14 DE NOVEMBRO DE 2018

> Dispõe sobre Constituição de Comissão Eleitoral para conduzir o processo de escolha do membros da CPPD.

O REITOR DO INSTITUTO FEDERAL DE EDUCAÇÃO, CIÊNCIA E TECNOLOGIA DE MINAS GERAIS, no uso das atribuições que lhe são conferidas pelo **Estatuto da Instituição, republicado com alterações no Diário Oficial da União do dia 08/05/2018, Seção 1, Páginas 09 e 10,** e pelo Decreto de 16 de setembro de 2015, publicado no DOU de 17 de setembro de 2015, Seção 2, página 01.

RESOLVE:

Art. 1º CONSTITUIR a Comissão Eleitoral para conduzir o processo de escolha dos membros titulares e suplentes dos grupos de trabalho permanente locais para composição da Comissão Permanente de Pessoal Docente - CPPD.

Art. 2º Nomear os servidores abaixo para, sob a Presidência do primeiro, para compor a referida comissão que disciplinará e coordenará o processo de escolha, por seus pares, dos docentes que farão parte da Comissão Permanente de Pessoal Docente (CPPD) do IFMG.

Servidor	Matrícula Siape	Campus
Reginato Fernandes dos Santos	1692108	Ouro Preto
Cláudio Júnior Andrade Ribeiro	1899007	São João Evangelista

Lucélia Aparecida Radin	1520884	Santa Luzia
Mônica Lana da Paz	2145473	Reitoria
Vinícius Barbosa de Paiva	2228571	Piumhi

Art. 3º Determinar que os trabalhos desta Comissão Eleitoral sejam finalizados conforme cronograma do edital.

Art. 4º Determinar que a Pró-Reitoria de Gestão de Pessoas adote as providências cabíveis à aplicação desta Portaria.

Art. 5º Determinar que esta Portaria seja publicada no Boletim de Serviços do IFMG.

Art. 6º Esta Portaria entra em vigor na data de sua publicação.

Documento assinado eletronicamente por **Kleber Gonçalves Glória**, **Reitor**, em 14/11/2018, às 17:03, conforme art. 1º, III, "b", da Lei 11.419/2006.

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Catalysis Today

Heteropoly acid catalysts in upgrading of biorenewables: Synthesis of *para*-menthenic fragrance compounds from α-pinene oxide

Cláudio J.A. Ribeiro [a], Matheus M. Pereira [a], Elena F. Kozhevnikova [b], Ivan V. Kozhevnikov [b], Elena V. Gusevskaya [c] 👤 ✉, Kelly A. da Silva Rocha [a] 👤 ✉

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Highlights

- Cs PW is a versatile heterogeneous catalyst for the isomerization of α-pinene oxide.

- Reaction selectivity is determined by the solvent nature and reaction conditions.

- In acetone, the reactions give either *trans*-sobrerol or pinol in 60–80% yield each.

- In 1,4-dioxane, the main product is *trans*-carveol obtained in up to 60% yield.

- CsPW can be recovered and reused without loss of its activity and selectivity.

Abstract

The isomerization of α-pinene oxide in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) heteropolysalt as solid acid catalyst is reported. The reactions were performed in various solvents, which allowed to obtain *trans*-carveol, *trans*-sobrerol and pinol in 60–80% yield each, which exceed the yields reported so far. The CsPW catalyst could be recovered and reused without loss of its activity and selectivity.

Graphical abstract

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Keywords

Biomass-based feedstock; Isomerization; Heterogeneous catalysis; Heteropoly compounds; α-pinene oxide

1. Introduction

Terpenic compounds are natural products available from essential oils of various plants and flowers at a relatively low cost [1,2]. α-Pinene, for example, is a major constituent of the turpentine oil obtained from coniferous trees and also available as a by-product of the paper industry. The epoxidation of α-pinene provides α-pinene oxide, which can be transformed in acidic media into a wide variety of valuable products with many industrial applications [3,4]. The isomerization of α-pinene oxide is one of the most important reactions in the fragrance industry; however, the development of processes which are selective to specific products is always a challenge because α-pinene oxide is highly reactive in the presence of acids.

Most of the studies on the catalytic isomerization of α-pinene oxide have been directed towards the synthesis of campholenic aldehyde [[5], [6], [7], [8], [9], [10]], which is used in the manufacture of sandalwood fragrances such as Sandalore® and Javanol® (Givaudan), Bacdanol® (IFF), Brahmanol® (Dragoso) and Polysantol® (Firmenich) [3]. Other products, such as *trans*-carveol, *trans*-sobrerol, isopinocamphone and pinol, are usually obtained from α-pinene oxide in low selectivities along with campholenic aldehyde. In spite of the commercial importance, only a few reports have been focused on the selective synthesis of these compounds from α-pinene oxide [4,[11], [12], [13], [14], [15], [16]]. For example, *trans*-carveol, found in the Valencia orange essential oil, is an expensive ingredient of perfume and food flavor compositions. The highest reported yield of *trans*-carveol in the isomerization of α-pinene oxide over solid acid catalysts is 45% [4,11,13]. *trans*-Sobrerol, found in the turpentine oil, is a well-known mucolytic drug, which also attracts an increasing attention for its other important biological activities [17]. In our previous work [15], *trans*-sobrerol was obtained in 70% yield in the isomerization of α-pinene oxide over heterogeneous cerium and tin catalysts, the best result so far to our knowledge. Pinol, is a natural monoterpenic ether found in small concentrations in essential oils of various plants (e.g. *Citrus aurantifolia*, *Labdanu*) [18,19]. Bicyclic ethers with oxabicyclo[3.2.1]octene units usually show interesting fragrance properties [20,21] and biological and herbicidal activities [22,23]. Pinol has a great application potential in various segments of the chemical industry, which is, however, limited by the lack of sustainable synthetic methods for its production. In previous works on the isomerization of α-pinene oxide (except for our report [14]), pinol has been detected only as a minor product in less than 10% selectivity.

Heteropoly acids of the Keggin series (HPAs) are well known as promising catalysts for the clean synthesis of fine and specialty chemicals in homogeneous and heterogeneous systems. [[24], [25], [26]]. HPA catalysts were applied in various reactions of terpenic compounds [24], including the isomerization of α-pinene oxide [7,14,27]. We have found a remarkable effect of the solvent polarity and basicity on the isomerization of α-pinene oxide in the presence of heteropoly acid $H_3PW_{12}O_{40}$ (PW), which allowed to control the reaction selectivity for specific products [7,14]. In non-polar cyclohexane, campholenic aldehyde was obtained in 70% selectivity over heterogeneous PW/SiO$_2$ catalyst. In polar solvents (dimethylacetamide and acetone), the reaction was switched to the products with a *para*-menthenic skeleton. In polar basic solvents (dimethylacetamide) *trans*-carveol was the major product, whereas in polar weakly basic solvents (e.g. acetone), the

favored route was the formation of *trans*-sobrerol and pinol. Although we previously reported that the PW catalyst allowed to obtain *trans*-carveol, *trans*-sobrerol and pinol in ca. 70% yield each using an appropriate solvent [14], the reactions were performed under homogeneous conditions due to the high solubility of PW in polar solvents. These results encouraged us to work further on the isomerization of α-pinene oxide in order to develop heterogeneous catalytic processes for the synthesis of products other than campholenic aldehyde with a sufficient selectivity for practical use.

To design heterogeneous catalytic processes in polar solvents, excellent alternatives for HPAs could be their acidic salts which are insoluble in such media [[28], [29], [30]]. In particular, successful use of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), a compound which combines strong Brønsted acidity and a large surface area, as a heterogeneous acid catalyst has been reported by our group [[31], [32], [33], [34]].

In this work, we report the isomerization of α-pinene oxide in the presence of CsPW as a heterogeneous catalyst. The reactions were performed in various solvents, which allowed to obtain *trans*-carveol, *trans*-sobrerol or pinol, each in 60–80% yield. These compounds are valuable ingredients for the fragrance and pharmaceutical industries. To our knowledge, no attempt to use CsPW as the catalyst for this reaction has been made before; moreover, such high yields of *trans*-carveol and pinol have not been achieved with heterogeneous catalysts. The selectivity obtained for *trans*-sobrerol in the present work is comparable with the best results reported previously in both homogeneous and heterogeneous systems [14,15].

2. Experimental

2.1. Chemicals

All chemicals were purchased from commercial sources and used as received, unless specially indicated. α-Pinene oxide, dimethylcarbonate and $H_3PW_{12}O_{40}$ (PW) hydrate were from Aldrich, Aerosil 300 silica from Degussa and solvents from VETEC or Synth. In some experiments (indicated in Tables), commercial acetone (0.5 wt% of water) was dried for 24 h over molecular sieve (4 Å) activated for 3 h at 100 °C.

2.2. Catalyst preparation and characterization

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) was synthesized by the dropwise addition of aqueous solution of cesium carbonate (0.47 M) to aqueous solution of PW (0.75 M) at room temperature with stirring, as described previously [35]. The precipitated CsPW was aged in the aqueous mixture for 48 h at room temperature and dried in a rotary evaporator at 45 °C/3 kPa then in an oven at 150 °C/0.1 kPa for 1.5 h. The BET surface area of the prepared catalyst was 111 $m^2\,g^{-1}$, the pore volume 0.07 $cm^3\,g^{-1}$ and the average pore diameter 24 Å. The acid properties of CsPW have been characterized calorimetrically by ammonia and pyridine adsorption and discussed previously [35,36]. The

catalyst was also characterized by ^{31}P MAS NMR (Bruker Avance DSX 400 NMR, room temperature, spinning rate of 4 kHz, 85% H_3PO_4 as the reference), X-ray diffraction (XRD, Rigaku Geigerflex-3034 diffractometer with CuK_α radiation) and nitrogen physisorption (Micromeritics ASAP 2010 instrument). The content of tungsten and phosphorus in the catalyst was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP) on a Spectro Ciros CCD instrument.

2.3. Catalytic tests

The catalytic tests were run under air in a 10 mL glass reactor equipped with a reflux condenser to avoid solvent evaporation. In a typical run, a mixture of the substrate (0.45–1 mmol), dodecane (GC internal standard, 0.30 mmol) and the catalyst CsPW (2.5–25 mg, 0.75–7.50 μmol), in a specified solvent (5.0 mL) was magnetically stirred at 15–40 °C for a specified time. The reaction mixture was periodically analyzed by gas chromatography (GC, Shimadzu QP-2014 instrument, Rtx-Wax capillary column, flame ionization detector). Due to the small volume of the samples taken for the GC analysis (5 μL) the changes in catalyst bulk density were insignificant. Conversions and selectivities were calculated from GC analysis using dodecane as the internal standard. The difference in mass balance (if any) was attributed to high-boiling products (probably oligomers which could not be detected by GC). The reaction rate was not dependent on the intensity of stirring within the range used, suggesting the absence of mass transfer limitations. In order to control any contribution of homogeneous reactions and catalyst leaching, the catalyst was separated from the reaction mixture by centrifugation (25 °C, 18,000 rpm) and the reaction was allowed to proceed with another portion of α-pinene oxide. The lack of substrate conversion indicated the absence of any significant catalyst leaching. In our previous works, the stability of CsPW in polar solvents was confirmed by various techniques [33,34].

The products were identified by the comparison with authentic samples (co-injection tests) and/or GC–MS (Shimadzu, GCMS-QP2010-PLUS instrument operating at 70 eV). Major reaction products were isolated by a column chromatography (silica gel 60) using mixtures of hexane and ethyl acetate as eluents and identified by GC–MS (Shimadzu QP2010-PLUS spectrometer, 70 eV), ^{1}H, and ^{13}C-NMR (Bruker 400 MHz spectrometer, CDCl$_3$, TMS). Spectroscopic data for campholenic aldehyde (**2**), *trans*-carveol (**3**), *trans*-sobrerol (**4**) and pinol (**5**) have been reported previously [7,14].

3. Results and discussion

Acid-catalyzed transformations of α-pinene oxide (**1**) can yield several products, such as campholenic aldehyde (**2**), *trans*-carveol (**3**), *trans*-carveol (**4**) and pinol (**5**) (Scheme 1), as well as *p*-cymene, isopinocamphenol, and isopinocamphone. Most of the reported work aimed to obtain campholenic aldehyde, whereas other products have been usually detected in low yields. In contrast, this work was focused on the development of heterogeneous catalytic protocols for the synthesis of *para*-menthenic compounds **3**, **4** and **5** from α-

pinene oxide. Our previous studies [[14], [15], [16]] suggested that the chemoselectivity of the α-pinene oxide rearrangements in acidic solutions could be controlled by solvent and that the formation of *para*-menthenic products would be favored in polar solvents such as acetone. In modern solvent selection guides, acetone is ranked as an environmentally friendly solvent [37], as it is biodegradable and, although is currently made from fossil sources, can be produced from biomass. In addition, low boiling point of acetone allows an easy solvent recovery during the isolation of reaction products.

1
α–pinene
oxide

2
campholenic
aldehyde

3
trans-carveol

4
trans-sobrerol

5
pinol
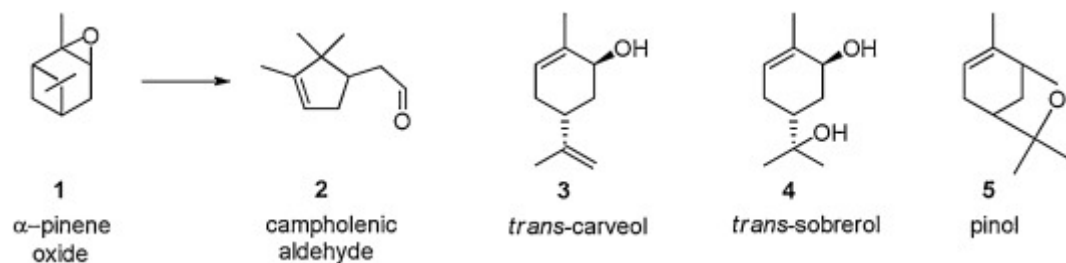
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Scheme 1. Products of the acid-catalyzed transformations of α-pinene oxide.

Representative data on the isomerization of α-pinene oxide in acetone solutions are shown in Table 1. In the absence of catalyst, no significant substrate conversion was observed in 6 h at 25 and 40 °C (less than 3%, not shown in Table 1). In the presence of CsPW, α-pinene oxide reacted very rapidly. At 25 °C, only 0.06 wt% of CsPW (based on the whole reaction mixture) effected complete conversion of α-pinene oxide in 5 min (Table 1, run 1). This corresponds to a turnover number (TON) of 2000. The TON values were calculated in moles of the substrate converted per mole of protons in CsPW. The 5-min reaction gave *trans*-sobrerol **4** as a major product (44%) along with campholenic aldehyde **2** and *trans*-carveol **3** (ca. 20% each) and small amounts of pinol **5**. However, the product selectivity gradually changed with the reaction time. After 3 h, pinol **5** became the main reaction product (43% selectivity) at the expense of *trans*-carveol and *trans*-sobrerol (Table 1).

Table 1. Isomerisation of α-pinene oxide (**1**) in acetone solutions.[a]

Run	CsPW	Substrate	Added water	T	Time	Product selectivity (%)	TON[b]

Run	HPW (μmol)	Substrate (mmol)	Added water (mmol)	(°C)	Time (min)	Product selectivity (%)				TON[b]
						2	3	4	5	
1	0.75	0.75	none	25	5	19	21	44	7	2000
					180	19	9	5	43	
2	3.00	0.75	none	25	5	17	22	48	12	500
					180	14	7	3	47	
3[c]	7.50	0.75	none	25	5	17	22	9	45	200
					180	19	5	–	70	
3a[c]	7.50	0.75	none	25	5	15	24	7	44	200
					180	21	5	–	68	
3b[c]	7.50	0.75	none	25	5	18	21	9	46	200
					180	18	5	–	71	
3c[c]	7.50	0.75	none	25	5	17	22	8	42	200
					180	20	5	–	68	
4	7.50	1.50	none	25	5	20	22	8	31	400
					180	18	6	–	49	
5[d]	7.50	3.75	none	25	5	20	22	9	45	1000
					180	22	5	–	68	
6	7.50	0.75	none	40	5	20	18	11	31	200
					180	18	–	–	61	
7	3.00	0.75	none	40	5	17	16	10	55	500
					180	15	–	–	80	

Run	CsPW	Substrate	Added water	T	Time	Product selectivity (%)				TON[b]
	(μmol)	(mmol)	(mmol)	(°C)	(min)	2	3	4	5	
8[e]	7.50	0.75	none	40	5	17	–	11	62	200
					120	17	–	–	75	
9	7.50	0.75	0.11	40	5	16	16	53	15	200
					180	18	6	7	58	
10	7.50	0.75	0.55	40	5	10	12	70	5	200
					180	13	–	8	77	
11	7.50	0.75	5.50	25	5	16	23	52	5	200
					180	15	21	60	–	

a

α-Pinene oxide conversion was 100% in 5 min in all runs presented in Table 1. Total volume of the reaction mixture: 5 mL.

b

TON (turnover number) in moles of α-pinene oxide converted per mole of protons in CsPW.

c

After the run, the catalyst was centrifuged (25 min, 18,000 rpm), washed with chloroform, dried at 60 °C in air and reused 3 times under the same conditions without significant loss in activity and selectivity (runs 3a, 3b and 3c). The filtrate was charged with a new portion of the substrate and allowed to react further. No conversion was observed for 180 min.

d

The substrate was added in five portions of 0.75 mmol and each reaction was run for 180 min. The conversions and product selectivity were almost the same in all five reactions; the average values are presented.

e

Acetone was dried before the reaction.

At higher catalyst loadings, the conversion of initially formed *trans*-carveol and *trans*-sobrerol into pinol was faster and almost complete in 3 h (Table 1, runs 2 and 3). As a result, a 70% yield of pinol was achieved, which is probably the best result reported for this reaction with heterogeneous catalysts. It is important that the combined selectivity for campholenic aldehyde and pinol was as high as 90%. The concentration of campholenic aldehyde among the products remained unchanged after complete substrate conversion, whereas *trans*-carveol and *trans*-sobrerol appeared to be intermediate products in this reaction (Fig. 1). In a special experiment performed using *trans*-carveol as the substrate instead of α-pinene oxide under the conditions of run 3 in Table 1, a slow conversion of *trans*-carveol to a mixture of *trans*-sobrerol and pinol was observed.
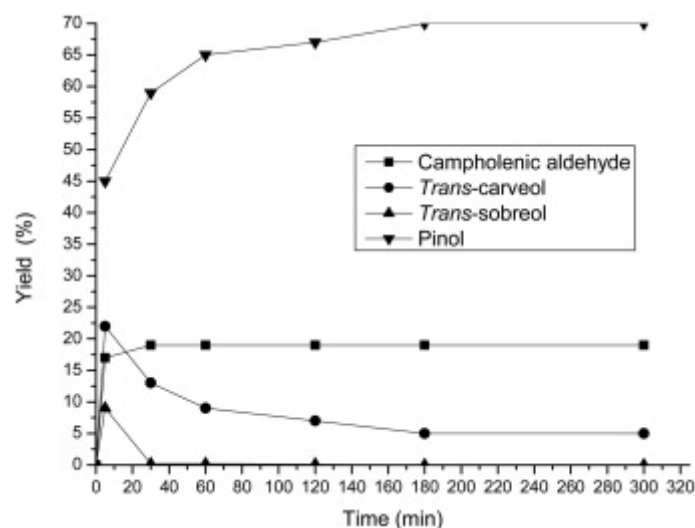
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Fig. 1. Time course for α-pinene oxide isomerization in acetone solutions: 25 °C, α-pinene oxide (0.15 M, 0.75 mmol), CsPW (25 mg, 7.50 μmol), total volume of reaction solution: 5 mL. The substrate conversion was 100% in 5 min.

Although CsPW is insoluble in acetone, the possibility of catalyst leaching under the reaction conditions was verified. After run 3 (Table 1), the reaction mixture was centrifuged for 20 min (25 °C, 18 000 rpm) in order to separate the catalyst, the supernatant was charged with a

new portion of the substrate and allowed to react further. No conversion of α-pinene oxide was observed for 3 h, which indicates the lack of catalyst leaching in this system. The spent catalyst after reaction was washed with chloroform, dried at 60 °C in air and reused three times under the same conditions without significant loss in its activity and selectivity (Table 1, runs 3a, 3b and 3c).

To improve the catalyst efficiency in terms of TON, the amount of the substrate was doubled (Table 1, run 4). However, at the higher substrate concentration, the selectivity to pinol and the combined selectivity to products **2**, **3**, **4** and **5** were poorer probably due to formation of high-boiling products (oligomers), which were not detectable by GC. The higher contribution of the oligomers at higher substrate concentrations can be explained by the suggestion that the rate of the oligomerization reaction depends more strongly on the substrate concentration (probably, second order) than the isomerization reaction (probably, first order). For this reason, in the next run, the substrate was added to the reaction solution in five portions (0.75 mmol each) and each reaction was run for 3 h. The conversion and product selectivity were almost the same in all five reactions, resulting in the total TON of 1000 (Table 1, run 5). The TON values were calculated considering the total amounts of protons in the CsPW catalyst, whereas the real efficiency of the surface proton sites available for the reaction was probably higher. Further optimization of reaction temperature and catalyst loading allowed us to obtain pinol in 80% yield, with the combined yield for both campholenic aldehyde and pinol being as high as 95% (Table 1, run 7).

A proposed mechanism for the acid-catalyzed transformations of **1** into **2**–**5** is given in Scheme 2. Protonation of α-pinene oxide results in epoxy ring cleavage to give carbenium ion **A**, which can rearrange into carbenium ions **B** and **C** through electron pair transfer from the same carbon-carbon σ-bond to either C-6 or C-1. The C-2–C-3 bond cleavage in **B** followed by proton loss results in campholenic aldehyde **2**. Carbocation **C** can undergo several competing reactions. Deprotonation of C results in *trans*-carveol **3** (route (a)). In addition, **C** can undergo an external nucleophilic attack by water to give *trans*-sobrerol **4** (route (c)) or an internal nucleophilic attack by the hydroxyl group to give pinol **5** (route (c)). Both alcohols, *trans*-carveol **3** and *trans*-sobrerol **4,** are intermediate reaction products, i.e., both can transform to pinol at a longer reaction time. Thus, we assume that *trans*-sobrerol can undergo an acid-catalyzed dehydration under the reaction conditions and *trans*-carveol an intramolecular cyclization via the nucleophilic attack of the hydroxyl group on the (protonated) olefinic moiety. Both transformations give pinol **5**, as shown in Scheme 2.
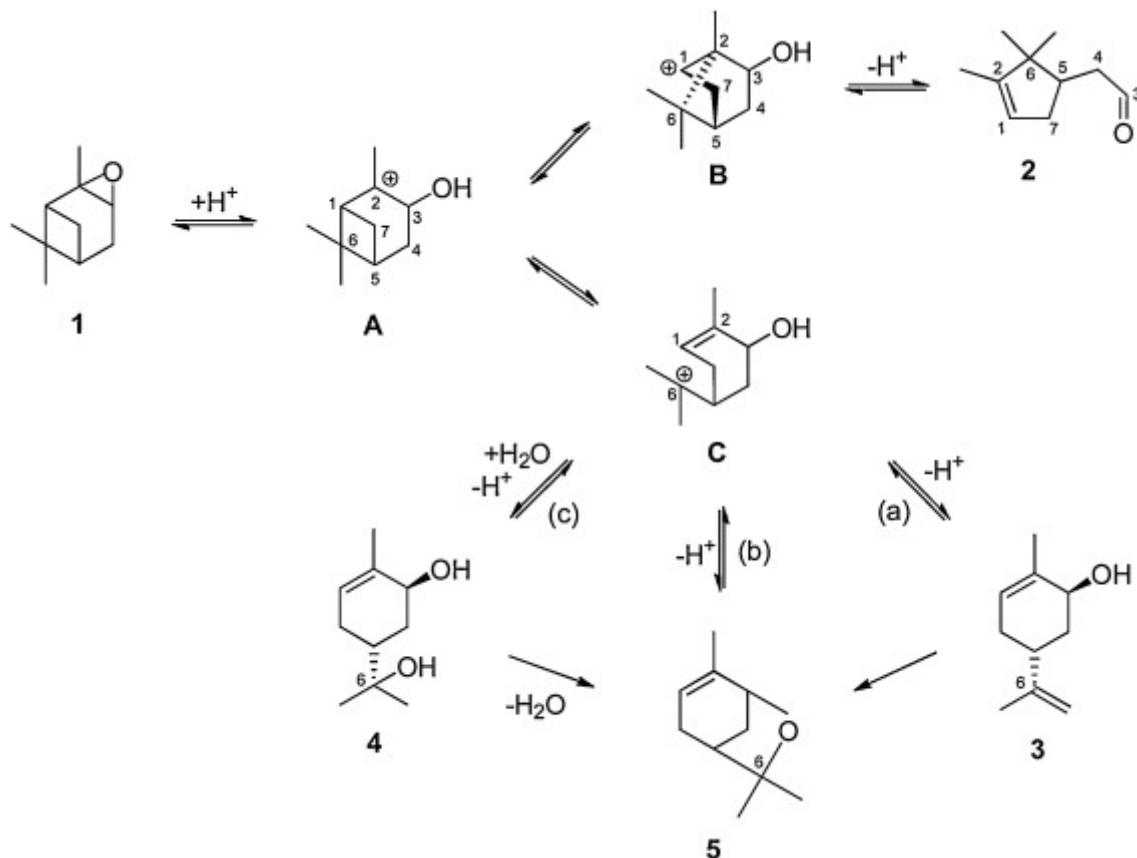
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Scheme 2. Proposed mechanism of the acid-catalyzed transformations of α-pinene oxide.

The ratio between aldehyde **2** and *para*-menthenic products **3**, **4** and **5** is determined by the relative contribution of transformations of carbeniun ion **A** into cyclopentanic cation **B** and *para*-menthenic cation **C**. The tertiary carbeniun ion **C** should be more stable thermodynamically than the secondary ion **B**; thus, the formation of aldehyde **2** should be kinetically controlled. The preferential formation of *para*-menthenic products in polar solvents, such as acetone, can be facilitated by stabilization of cation **A** by a polar solvent to favor the rearrangement of **A** into more stable cation **C**. The distribution between *para*-menthenic products **3**, **4** and **5**, on the other hand, should depend on the solvent basicity affecting the deprotonation of **C** and also on the concentration of water in the reaction mixture. It should be

mentioned that, generally, water was not added to the reaction system. The amount of residual water present in the commercial α-pinene oxide and solvent (ca. 1.5 mmol in 5 mL) was sufficient for the formation of *trans*-sobrerol.

In attempts to direct the reaction to one particular *para*-menthenic product, we changed the concentration of water in the reaction system. When the zeolite-dried acetone was used as the solvent, the formation of pinol occurred much faster than in the untreated commercial acetone (Table 1, run 8 vs. run 6). The yield of pinol reached 62% within only 5 min and then gradually increased to 75%, at the expense of *trans*-sobrerol and *trans*-carveol. Thus, decreasing the residual water concentration in acetone solutions favors the intramolecular cyclization of **C** before the proton loss allowing for the fast selective synthesis of pinol from α-pinene oxide over the CsPW catalyst.

In contrast, addition of extra water to the reaction solution favored the formation of *trans*-sobrerol at the expense of pinol allowing for 60–70 % yield of *trans*-sobrerol (Table 1, runs 9, 10 and 11). With nearly stoichiometric amounts of added water (with respect to the substrate), *trans*-sobrerol formed initially slowly converted into pinol resulting in its 80% yield (Table 1, run 10). On the other hand, at higher water concentration (1 M) in the reaction mixture, no formation of pinol was observed in 3 h reaction time (Table 1, run 11). It is interesting that neither cyclization nor hydration of *trans*-carveol was observed in aqueous acetone solutions, with *trans*-carveol concentration remaining unchanged after complete substrate conversion regardless of the reaction time (Table 1, run 11). Therefore, in acetone solutions, *trans*-sobrerol and pinol can be obtained from α-pinene oxide in a 70–80% yield varying the concentration of water and reaction time.

The reaction was also performed in other solvents in attempts to obtain other products and demonstrate a versatility of the CsPW catalyst (Table 2). In the absence of catalyst, no significant substrate conversion was observed in 6 h at 40 °C in all the solvents tested. In the expectation to obtain high selectivity to campholenic aldehyde, the reaction was run in nonpolar solvents such as cyclohexane, dimethylcarbonate and 1,4-dioxane. To our surprise, the major product in these reactions at 15 °C was *trans*-carveol (36–60% yield) (Table 2, runs 1–4). Thus, low temperatures are favorable for the preferential transformation of carbocation **A** into thermodynamically more stable tertiary carbocation **C** rather than secondary cyclopentanic cation **B**, which would enhance the formation of *trans*-carveol (Scheme 2). At 15 °C, even in a weakly polar dichloroethane solvent, campholenic aldehyde and *trans*-carveol were formed in comparable amounts with excellent combined selectivity of 87% (Table 2, run 5). As no water is required for the formation of these products, we suppose that addition of water would not influence the reaction. The yields obtained for *trans*-carveol in these runs (up to 60%) represent the best results reported for this product in the isomerization of α-pinene oxide over heterogeneous catalysts. As stated above, in acetone solutions under appropriate conditions, *trans*-sobrerol and pinol can be obtained from α-pinene oxide in 70 and 80% yield, respectively (runs 6 and 7, Table 2).

Table 2. Effect of solvent on isomerisation of α-pinene oxide.[a]

Run	Solvent	CsPW	T	Time	Product selectivity (%)				TON[b]
		(μmol)	(°C)	(min)	2	3	4	5	
1	cyclohexane	3.00	15	30	30	50	–	–	500
2	dimethylcarbonate	3.00	15	10	23	36	18	–	500
3	1,4-dioxane	3.00	15	10	18	54	1	–	500
4	1,4-dioxane	1.50	15	10	22	60	7	–	1000
5	dichloroethane	3.00	15	10	40	47	–	–	500
6	acetone	3.00	40	180	15	–	–	80	500
7[c]	acetone	7.50	40	5	10	16	70	5	200

a

Reaction conditions: 0.15 M (0.75 mmol) of α-pinene oxide, 5 mL total volume of the reaction mixture. Conversion was 100% in all runs in Table 2.

b

TON (turnover number) in moles of α-pinene oxide converted per mole of protons in CsPW.

c

Water (0.55 mmol) was added.

4. Conclusions

The results obtained in the present work showed that the nature of solvent can profoundly affect the reaction pathways and product composition in the isomerization of α-pinene oxide. The acidic heteropolysalt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was found to be a versatile heterogeneous catalyst for this reaction allowing to obtain *trans*-carveol, *trans*-sobrerol or pinol, each in 60–80% yield, under appropriate conditions. These products are highly valuable fragrance and/or pharmaceutical ingredients. To our knowledge, none of the previous studies have

achieved such high selectivities for *trans*-carveol and pinol with heterogeneous catalysts. The selectivity obtained for *trans*-sobrerol in the present work was comparable with the best results reported previously in both homogeneous and heterogeneous systems [14,15].

Acknowledgments

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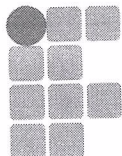
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Declaro que **CLÁUDIO JÚNIOR ANDRADE RIBEIRO** participou da comissão organizadora da VIII Semana de Ciência e Tecnologia do IFMG-*Campus* São João Evangelista no período de julho a novembro de 2018.

São João Evangelista, 11 de Fevereiro de 2019.

_____

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