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## ARTICLE

# Fe(III)-catalyzed $\alpha$ -terpinyl derivatives synthesis from $\beta$ -pinene via reactions with hydrogen peroxide in alcoholic solutions

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In this work, an novel and environmentally benign Fe(III)-catalyzed terpinyl derivatives synthesis using hydrogen peroxide in alcohol solutions (i.e methyl, ethyl, propyl, isopropyl and butyl alcohols) was investigate. Brønsted-acid catalysts were avoid and  $\beta$ -pinene was the starting reactant. High conversions (*ca.* 90 %) and combined selectivities for the  $\alpha$ -terpineol and terpinyl alkyl ethers (*ca.* 70-73 %) were obtained, when Fe(NO<sub>3</sub>)<sub>3</sub> was the catalyst. The role of each component catalyst system was studied, with special focus on the solvent. The use of biodegradable and renewable origin solvent (ethyl alcohol), added to an inexpensive and little toxic catalyst and a green oxidant are main positive features of this process.

## Introduction

Monoterpenes are abundant raw material present in all the plants, and the valorization them in the presence of active and cheap catalysts, is potentially a cost-effective and environmentally friendly process, that can supply of feedstock the fine chemical industries such as flavors, drugs, pesticide and pharmaceutical industries [1-3]. In addition, some oxygenated derivatives of monoterpenes have agreeable organoleptic properties;  $\alpha$ -terpinyl methyl or propyl ethers have smells of fresh grass,  $\alpha$ -terpinyl ethyl ether has citrus fragrance whilst  $\alpha$ -terpinyl butyl ether has woody aroma [4]. On the other hand,  $\alpha$ -terpineol is a compound highly attractive for pharmacological applications or as food and fragrances ingredient, and its synthesis has been extensively studied either in homogeneous as well as in heterogeneous catalytic processes [5-8].

In this sense,  $\alpha$ -pinene and limonene are always the starting materials used in the synthesis of terpinyl derivatives [9,10]. In those reactions, the most part of heterogeneous catalysts are acid solid catalysts such as zeolites, sulfated carbon activate and heteropolyacids [9-12]. Similar to the  $\alpha$ -pinene,  $\beta$ -pinene is as well as also an important constituent of turpentine oil, which is industrially obtained by the distillation of pine tree resins or as a by-product of the Kraft cellulose pulping processes [13].  $\beta$ -pinene is raw material for industrial processes that produce a number of important chemicals, and have been selected as model molecule in several works [14-16].

In addition to the alkoxylation or hydroxylation processes, monoterpenes oxidation is also a reaction used to add value to this feedstock [16,17]. Besides oxygen, hydrogen peroxide is an environmentally benign oxidant giving virtually no waste, produce water as the only by-product, differently of others corrosive and

hardly handling organic peroxides [18,19]. Moreover, hydrogen peroxide is a powerful liquid oxidant and an inexpensive chemical commodity [20]. Thus, because of the highest percentage of available oxygen, besides the non-flammability and compatibility with a large scope of catalysts, hydrogen peroxide is employed at industrial scale [21,22].

Transition metal catalysis has been of utmost importance to convert renewable and cheap feedstock into more valuable products. In general, homogenous catalysts are more active and selective than heterogeneous ones, although serious drawbacks are still found when attempting to recovery and reuse these catalysts [23]. Noble metals are broadly used as homogeneous catalysts in organic synthesis and industrial processes. Nevertheless, to develop alternative process based on cheap metal catalysts is always a goal to be pursue. On this regard, iron salts are inexpensive, environmentally friendly and commercially available, often offering relevant advantages in terms of sustainable chemistry, being hence attractive catalysts to be employed in organic synthesis [24,25].

Considering all these aspects, in this work we wish describe the synthesis of  $\alpha$ -terpinyl derivatives trough of Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed reactions of  $\beta$ -pinene with H<sub>2</sub>O<sub>2</sub> in alcoholic solutions. A special emphasis was dedicate to the reactions in ethyl alcohol, who is a renewable, cheap, greener and less toxic solvent. Additionally, reactions were also carried out in others alcohols (i.e. methyl, propyl, isopropyl and butyl alcohols), which resulted in the selective formation of  $\alpha$ -terpineol and  $\alpha$ -terpinyl alkyl ethers. The effects of the main parameters of reaction (i.e. reactants concentration, catalyst nature, temperature) and mainly the solvent role were evaluated. A brief discussion on iron-catalyzed isomerization and rearrangement of carbon skeletal undergo by  $\beta$ -pinene was performed. Remarkably, after a short time reaction (*ca.* 120 min), the Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed

reactions of  $\beta$ -pinene with  $\text{H}_2\text{O}_2$  achieved high conversions (*ca.* 80 to 97 %), and combined selectivity (i.e. 60 to 70 %) for two valuable products:  $\alpha$ -terpineol and  $\alpha$ -terpinyl alkyl ethers.

## Experimental Procedures

### Materials and physical methods

All the chemicals and solvents were used as received.  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  (98.5 % w/w);  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$  (97 % w/w);  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (97 % w/w) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (99 % w/w) were acquired from Sigma-Aldrich.  $\beta$ -pinene (99 %) and the alkyl alcohols (i.e. methyl, ethyl, propyl, isopropyl and butyl alcohols, 99.5 to 99.8 % w/w) were also purchased of Sigma-Aldrich. The active oxygen content of the hydrogen peroxide (aqueous solutions, 34 % w/w, Vetec) was quantified by titration with  $\text{KMnO}_4$  solution (*ca.*  $0.10 \text{ mol}\cdot\text{L}^{-1}$ ) before the use.

### Catalytic runs

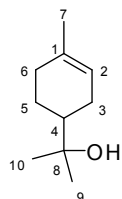
Catalytic runs were carried out under air in a glass reactor (50 mL) fitted with reflux condenser and sampling septum, under heating and magnetic stirrer. Typically, iron catalyst adequate and  $\beta$ -pinene were dissolved in alcohol (*ca.* 25 mL), and the reactor temperature was adjusted to 333 K. Then, the reaction was started by adding of  $\text{H}_2\text{O}_2$  solution (*ca.* 34 % w/w).

The progress of the reaction was followed taking aliquots at regular time intervals and analyzing them by chromatography gas, in a Shimadzu 2010 plus gas chromatograph instrument fitted with a FID detector and a CP-WAX capillary chromatographic column ( $25 \text{ m} \times 0.32 \text{ mm} \times 0.30 \mu\text{m}$ ). Toluene was internal standard. The conversions were calculate comparing the corresponding GC peak areas to ones the calibrating curve built with substrate and main pure products.

### Products chromatographic separation and characterization

The main products of reaction were identified by GC/MS analyses (Shimadzu MS-QP 2010 ultra, mass spectrometer, electronic impact mode at 70 eV, coupled to a Shimadzu 2010 plus, GC) and by comparison with the authentic samples. The major products were isolated by column chromatography (silica, 60G) and then characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Varian 300 spectrometer), and IR spectroscopy analyses (Varian FTIR 660). The NMR spectra were obtained in  $\text{CDCl}_3$  solutions, using the Varian 300 spectrometer at 300.13 and 75.47 MHz, respectively. Chemical shifts were expressed in  $\delta$  (ppm) relative to tetramethylsilane, used as an internal reference.

### Spectroscopy data of major products



1a

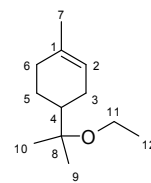
**Figure 1.** Structure and carbons numeration of  $\alpha$ -terpineol (**1a**) (4-methylcyclohex-3-enyl)propan-2-ol)

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.15 (s, 3H, H-9 or H-10), 1.17 (s, 3H, H-9 or H-10), 1.20-1.28 (m, 1H, H-5), 1.42-1.54 (m, 1H, H-4), 1.55 (s, 1H, OH), 1.64 (s, 3H, H-7), 1.70-2.10 (m, 5H, H-3/ H-5/ H-6), 5.36 (br s, 1H, H-2)

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  23.3 (C7); 23.9 (C5); 26.2 (C10), 26.8 (C3), 27.4 (C9), 31.0 (C6); 44.9 (C4); 72.7 (C8); 120.5 (C2); 133.9 (C1).

*MS* ( $m/z$ /int.rel.): 154/0.08 ( $\text{M}^+$ ); 136/54; 121/46; 107/6; 93/37; 81/21; 67/19; 59/100; 55/18; 43/52; 41/27; 39/17; 31/10.

*FT-IR* (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3381, 2965, 2923, 2833, 1631, 1438, 1376, 1157.



1b

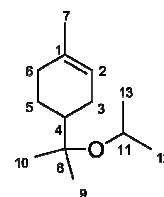
**Figure 2.** Structure and carbons numeration of 4-(2-ethoxypropan-2-yl)-1-methylcyclohex-1-ene (**1b**)

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.09 (s, 3H, H-9 or H-10), 1.11 (s, 3H, H-9 or H-10), 1.14(t, 3H,  $J = 7.0 \text{ Hz}$ , H-12), 1.18-1.32 (m, 1H, H-4), 1.64 (s, 3H, H-7), 1.65-1.99 (m, 6H, H-3/ H-5/ H-6), 3.37 (quart., 2H,  $J = 14.0$ ,  $J = 7.0 \text{ Hz}$ , H-11), 5.38 (br s, 1H, H-2).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.2 (C12); 22.7 (C7); 23.0 (C10); 23.4 (C9); 24.0 (C5); 26.9 (C3); 31.1 (C6); 41.6 (C4); 55.8 (C11); 76.4 (C8); 120.9 (C2); 133.9 (C1).

*MS* ( $m/z$ /int.rel.): 180/0 ( $\text{M}^+$ ); 167/2; 136/58; 121/35; 107/4; 93/22; 87/70; 79/8; 67/11; 59/100; 53/11; 43/34; 41/31; 39/12; 31/11.

*FT-IR* (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2972, 2926, 2892, 2874, 1631, 1455, 1378, 1159, 1071.



1c

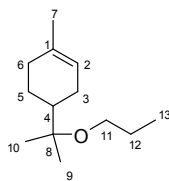
**Figure 3.** Structure and carbons numeration of 4-(2-isopropoxypropan-2-yl)-1-methylcyclohex-1-ene (**1c**)

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.09 (s, 3H, H-13 or H-12); 1.10 (s, 3H, H-9 or H-10); 1.10 (s, 3H, H-9 or H-10); 1.12 (s, 3H, H-12 or H-13); 1.20-1.25 (m, 1-H, H-5); 1.53-1.59 (m, 1H, H-4); 1.65 (s, 3H, H-7); 1.72-1.97 (m, 5H, H-3/ H-5/ H-6); 3.76-3.88 (m, 1H, H-11); 5.40 (br s, 1H, H-2).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 22.8 (C10); 23.4 (C7); 23.7 (C9); 24.0 (C5); 25.0 (C13); 25.2 (C12); 27.2 (C3); 31.1 (C6), 43.0 (C4); 62.7 (C11); 77.1 (C8); 120.9 (C2); 134.1 (C1).

MS ( $m/z$ /int.rel.): 196/0 ( $\text{M}^+$ ); 181/1; 136/20; 121/19; 101/32; 93/17; 81/10; 67/6; 59/100; 43/16; 41/11.

FT-IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2985, 2928, 1548, 1450, 1351, 1119, 1004.



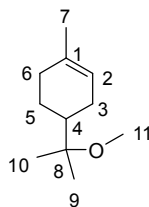
**Figure 4.** Structure and carbons numeration of 4-(2-propoxypropan-2-yl)-1-methylcyclohex-1-ene (**1d**)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.90 (t, 3H,  $J = 7.4$  Hz, H-13); 1.11 (s, 3H, H-9 or H-10); 1.14 (s, 3H, H-9 or H-10); 1.22-1.30 (m, 1H, H-5); 1.46-1.58 (m, 2H, H-12); 1.66 (s, 3H, H-7); 1.71-2.00 (m, 6H, H-3/ H-4/ H-5/ H-6); 3.26 (t, 2H,  $J = 6.7$  Hz, H-11); 5.41 (br s, 1H, H-2).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 10.8 (C13); 22.6 (C10); 22.9 (C9); 23.4 (C7); 23.8 (C12); 24.0 (C5); 26.8 (C3); 31.1 (C6), 41.9 (C4); 62.3 (C11); 76.2 (C8); 121.0 (C2); 134.0 (C1).

MS ( $m/z$ /int.rel.): 196/0 ( $\text{M}^+$ ); 181/1; 136/26; 121/20; 101/46; 93/18; 81/9; 67/6; 59/100; 43/19; 41/13.

FT-IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2961, 2918, 2870 ( $\nu_{\text{s}}$  e  $\nu_{\text{as}}$  - $\text{CH}_2$  e - $\text{CH}_3$ ); 1664 ( $\nu$  C=C); 1458, 1367 ( $\delta$ - $\text{CH}_2$  e - $\text{CH}_3$ ); 1078 ( $\nu_{\text{as}}$  C-O); 1003 ( $\nu_{\text{s}}$  C-O).



**Figure 5.** Structure and carbons numeration of 4-(2-methoxypropan-2-yl)-1-methylcyclohex-1-ene (**1e**)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.39 (s, 1H, H-2); 3.17 (s, 2H, H-11); 2.05-1.65 (m, 6H, H-3/ H-4/ H-6); 1.64 (s, 3H, H-11); 1.35-1.10 (m, 1H, H-5); 1.09 (s, 6H, H-9/ H-10).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 134.0 (C1); 120.8 (C2); 76.6 (C8); 48.7 (C11); 41.5 (C4); 31.1 (C6); 26.8 (C3); 23.9 (C5); 23.4 (C7); 22.3 (C9 ou C10); 21.8 (C10 ou C9).

FT-IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2967; 2926; 2828; 1438; 1378; 1362; 1074.

MS ( $m/z$ /int.rel.): 153/2; 136/34; 121/23; 93/29; 73/100; 59/12; 55/13; 43/31; 41/28.

The NMR  $^1\text{H}$ ,  $^{13}\text{C}$  of spectra (i.e. HSQC, COSY, And DEPT 135) are provided as supplementary material.

## Results and Discussion

### General aspects

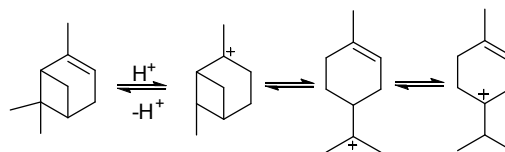
Nowadays, to develop the concepts of atom economy and green chemistry has resulted in catalytic processes where all the components have a minimum environmental impact. In this sense, a system to oxidize monoterpenes using  $\text{Fe(III)}/\text{H}_2\text{O}_2$  in methyl alcohol solution was recently described by us [26]. Nevertheless, we realize that products obtained in that system were alkoxylation and hydroxylation products.

Herein, the  $\text{Fe(NO}_3)_3/\text{H}_2\text{O}_2$  system was useful to synthesize alcoxide derivatives of  $\beta$ -pinene, a renewable raw material of great interest on behalf of several chemical industries. Our focus was to study the reactions in ethyl alcohol, an inexpensive and green solvent. Additionally, we also investigate reactions with other alcohols.

A more deep assessment revealed that  $\text{Fe(III)}$  cations successfully promoted the  $\beta$ -pinene isomerization under non-corrosive and Brønsted acid-free conditions. The  $\text{Fe(NO}_3)_3/\text{H}_2\text{O}_2/\text{C}_2\text{H}_5\text{OH}$  system employs  $\text{Fe(III)}$  salts catalysts, an inexpensive, easy to handle and affordable reactant of low toxicity. The alkoxylation reactions were effective mainly when carried out in  $\text{C}_2\text{H}_5\text{OH}$ , who is a renewable origin solvent. Moreover, hydrogen peroxide, a friendly environmentally and highly efficient-atom oxidant has a highlighted role in the reactions studied.

### Assessment the role of system components in the $\text{Fe(NO}_3)_3$ -catalyzed $\beta$ -pinene reaction with hydrogen peroxide in $\text{C}_2\text{H}_5\text{OH}$

In general, the majority of reactions that synthesizes  $\alpha$ -terpineol starting from  $\alpha$ -pinene works with water as nucleophilic reactant and Brønsted acids as catalysts [10-12]. Under acidic conditions,  $\alpha$ -pinene undergo carbon skeletal rearrangement generating a tertiary carbocation (Figure 6). Nucleophiles as water or alcohol presents in the reaction medium may then attack this intermediate in further steps, resulting in  $\alpha$ -terpineol or alkyl ethers as main products.



**Figure 6.** Brønsted acid-catalyzed skeletal rearrangement of  $\alpha$ -pinene (adapted) [27]

Herein, the  $\text{Fe(III)}$  cations were used by us as Lewis acid catalyst, whereas  $\beta$ -pinene was substrate instead of  $\alpha$ -pinene. In addition, as an aqueous solution of hydrogen peroxide (34 % w/w) was used, two nucleophiles (i.e.  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{O}$ ) may contribute for the  $\alpha$ -terpineol formation. On the other hand, as the iron nitrate is also an oxidant might himself oxidize the olefin. All these key-aspects were addressed in Table 1 carrying reactions under different experimental conditions.

We find out that in absence of  $\text{Fe(NO}_3)_3$  catalyst, no conversion of  $\beta$ -pinene was detected, regardless reaction time (Runs 1 and 4, Table 1) or presence of  $\text{H}_2\text{O}_2$  (Run 2, Table 1). Conversely, despite low conversion achieved (ca. 21 %) in ethyl alcohol solutions, the

Fe(NO<sub>3</sub>)<sub>3</sub> converted β-pinene to α-terpinyl ethyl ether (**1b**) with high selectivity (ca. 86%) in absence of water or peroxide (Run 3, Table 1). Remarkably, the combination Fe(NO<sub>3</sub>)<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> converted the β-pinene to two main products with good selectivities (ca. 32 and 44 %, α-terpineol (**1a**) and α-terpinyl ethyl ether (**1b**), respectively), achieving high conversion (ca. 84 %, Run 6, Table 1). It means that the presence of H<sub>2</sub>O<sub>2</sub> in the Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed reactions is more favorable to form α-terpineol than presence of alone “alone” H<sub>2</sub>O; α-terpineol selectivity increased considerably (ca. 8 to 32 %), when we replaced water by hydrogen peroxide. Moreover, in water presence it was require a larger reaction time than in presence of peroxide (ca. 24 against 8 hours, Runs 5 and 6, Table 1).

**Table 1.** Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reaction with hydrogen peroxide in C<sub>2</sub>H<sub>5</sub>OH

Run	Fe(NO <sub>3</sub> ) <sub>3</sub> (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	Convers. <sup>d</sup> (%)	Selectivity <sup>d</sup> (%)			
				1a	1b	Iso.	ni
1 <sup>b</sup>	-	-	0	-	-	-	-
2	-	30.0	0	-	-	-	-
3	0.04	-	21	-	86	10	4
4 <sup>c</sup>	-	-	0	-	-	-	-
5 <sup>c</sup>	0.21	-	92	8	36	33	23
6	0.21	20.0	84	32	44	17	7

<sup>a</sup>Reaction conditions: β-pinene (5 mmol), ethyl alcohol solution (15 mL), 333 K, 8 hours reaction.

<sup>b</sup>Run carried out during a 24 hours.

<sup>c</sup>Test catalytic carried out during a 24 hours in presence of water (ca. 20.0 mmol)

<sup>d</sup>Conversion determined by CG; α-terpineol (**1a**), α-terpinyl ethyl ether (**1b**); terpinene isomers (equimolar amounts of α- and γ-terpinene); ni (complex mixture of minority products).

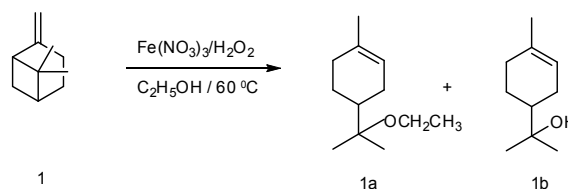
The mechanism of Fe(III)-catalyzed isomerization of β-pinene remains unclear. Although H<sup>+</sup> cations could be generated herein from reaction H<sub>2</sub>O<sub>2</sub> with Fe(III) species, via Haber-Weiss mechanism, it is important to note that even in absence of peroxide the α-terpinyl ethyl ether (**1b**) was selectively obtained, probably via reaction between tertiary carbocation (Figure 6) and ethyl alcohol [28]. Indeed, high selectivity for formation of α-terpinyl tertiary carbocation derivatives (i.e., **1a** and **1b** products) may be attributed to stabilization of this intermediate by the polar solvent (i.e. ethyl alcohol) (Figure 7). Nevertheless, the mechanism for formation of this carbocation in the presence only of Fe(NO<sub>3</sub>)<sub>3</sub> and alcohol is being investigated and remains not totally understood.

There are some recent works that described the activity of iron catalysts under heterogeneous conditions (i.e. iron-modified mesoporous silicates; Fe-MCM), in reactions acid-catalyzed such as α-pinene oxide isomerization [29,30]. Gusevskaya et al showed that acidity properties of MCM samples were significantly increased by the introduction of iron cations, which were nominated by them as catalytically active species (i.e. Fe<sup>+2</sup>-MCM or Fe<sup>+3</sup>-MCM) in the acid-catalyzed transformations undergone by substrate (i.e. isomerization, skeletal rearrangement, opening ring) [30]. Actually, they verified that the unmodified MCM-41 samples have no

sufficient acidity to promote any transformation of moiety α-pinene oxide.

### Effect of catalyst concentration on the Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reaction with hydrogen peroxide in C<sub>2</sub>H<sub>5</sub>OH

To evaluate the efficiency of Fe(NO<sub>3</sub>)<sub>3</sub> catalyst in the reactions in C<sub>2</sub>H<sub>5</sub>OH, were accomplished reactions within broad range of concentration (i.e., 0.010 to 0.612 mmol). The data of conversion, TON and selectivity are shown in Table 2.



**Figure 7.** Main products obtained in the Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reaction with H<sub>2</sub>O<sub>2</sub> in C<sub>2</sub>H<sub>5</sub>OH

Any significance changes on reaction selectivity was triggered by variation of catalyst concentration. The formation of these products occurred always in virtually equimolar amounts (i.e. **1a** and **1b**), with combined selectivity ranging of ca. 68 to 73 %.

**Table 2.** Effect of catalyst concentration on Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reaction with H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CH<sub>2</sub>OH<sup>a</sup>

Run	Fe(NO <sub>3</sub> ) <sub>3</sub> (mmol)	TON	Convers. <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)			
				Isomers	1a	1b	Ni
1	0.612	8	97	17	34	34	15
2	0.412	11	94	16	36	35	13
3	0.212	21	90	15	38	35	12
4	0.112	38	84	16	37	34	13
5	0.070	56	79	18	35	35	12
6	0.040	80	64	17	33	37	13
7	0.030	95	57	18	33	37	12
8	0.020	143	57	17	32	38	13
9	0.010	255	51	18	38	32	12
10 <sup>d</sup>	0.010	475	95	14	39	34	13

<sup>a</sup>Reaction conditions: β-pinene (5 mmol), H<sub>2</sub>O<sub>2</sub> (30.0 mmol), ethyl alcohol solution (15 mL), 333 K, 8 hours reaction.

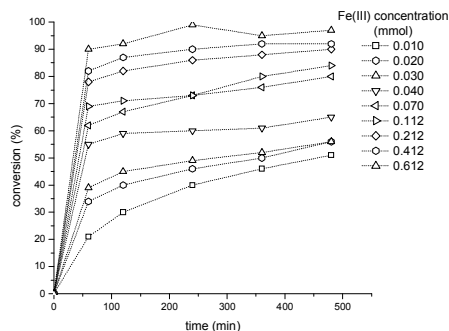
<sup>b</sup>Determined via GC analyses

<sup>c</sup>Determined via GC-MS analyses; α-terpineol (**1a**), α-terpinyl ethyl ether (**1b**); terpinene isomers (ca. equimolar amounts of α- and γ-terpinene); ni (complex mixture of minority products).

<sup>d</sup>24 hours reaction.

Table 2 shows that the reaction conversions decreases when Fe(NO<sub>3</sub>)<sub>3</sub> load is reduced, demonstrating that reaction equilibrium was not reached after a 8 hours reaction. In addition, regardless catalyst concentration, any significance changes on selectivity occurred after this reaction time. Conversely, high TON values were achieved, in the reactions with low catalyst concentration, mainly if compared to TON obtained in Brønsted

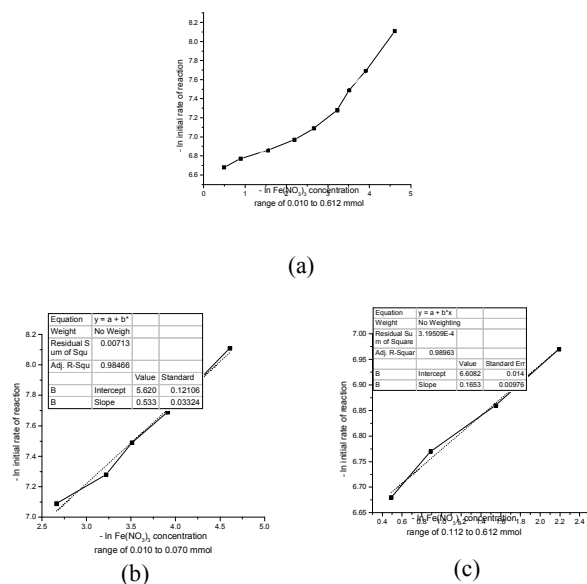
acid-catalyzed reactions [31]. When we carried out reactions with lowest catalyst concentration throughout 24 hours (run 10, Table 2), we observed that high conversion was reached (*ca.* 97 %). It is suggestive that catalyst remained active even after long reaction time.



**Figure 8.** Kinetic curves of  $\text{Fe}(\text{NO}_3)_3$ -catalyzed  $\beta$ -pinene reaction with  $\text{H}_2\text{O}_2$  in  $\text{C}_2\text{H}_5\text{OH}$  using different catalyst load<sup>a</sup>.

<sup>a</sup>Reaction conditions:  $\beta$ -pinene (5 mmol),  $\text{H}_2\text{O}_2$  (30.0 mmol), ethyl alcohol solution (15 mL), 333 K, 8 hours reaction.

To assess the catalyst activity we taking in account the reaction initial rates achieved after 30 minutes using different catalyst concentrations. These data were obtained from the slopes of the conversion vs time data collected at the reaction beginning (*ca.* 30 min). From these curves shown in the Figure 8, we built a linear plot of  $\ln$  (reaction initial rate) calculated in terms of mmol  $\beta$ -pinene consumed/ 3600 seconds *versus*  $\ln$  ( $\text{Fe}(\text{NO}_3)_3$  concentration), expressed in mmol, as showed in the Figure 9.



**Figure 9.** Order of reaction in respect to catalyst concentration: (a) 0.010 to 0.612 mmol; (b) 0.010 to 0.070 mmol; (c) 0.112 to 0.612 mmol.

In principle, the slope of the curve  $\ln$  (conversion) *versus*  $\ln$  ( $\text{Fe}(\text{NO}_3)_3$  concentration) give order in relation to catalyst concentration. The data shown in Figure 9 (a) suggest that the effect of catalyst concentration on reaction conversion varied from non-linear way within concentration range of 0.010 to 0.612 mmol. An attempt to linearize result in low linear coefficient ( $R^2 = 0.90$ ), which was omitted by simplification (Figure 9 (a)).

However, a careful analysis reveals that a split in two concentration ranges seems be more adequate, as shown in the Figures 9 b and 9 c. The slope of the curve  $\ln$  (reaction initial rate) *versus*  $\ln$  ( $\text{Fe}(\text{NO}_3)_3$  concentration) was approximately 0.53 ( $R^2 = 0.985$ ), when a low concentration of  $\text{Fe}(\text{NO}_3)_3$  was employed (*ca.* 0.010 to 0.070 mmol). Conversely, using a catalyst load higher than 0.070 (0.112 to 0.612 mmol), a dependence equal to 0.19 ( $R^2 = 0.990$ ) in relation to  $\text{Fe}(\text{NO}_3)_3$  concentration can be considered (Figure 9 c). The high linearity coefficient indicate that this was an acceptable approach.

Several aspects may be behind of this different behavior. Probably, peroxide concentration variation or of the pH values are key aspects that may affect these reactions. Volumetric titration measurements were carried out with  $\text{KMnO}_4$  and shows that after the first 30 minutes of reaction, almost all hydrogen peroxide was consumed. It was possible that peroxide intermediates could have formed in the reaction. Shullpin et al proposed a test to verify the presence of hydroperoxides intermediates that are not detectable by GC analysis, via adding phosphine [35]. In according with these authors, the phosphine react with hydroperoxides resulting in the alcohol formation and consequently increase the GC peak corresponding. Thus, we added phosphine to the aliquots of reaction and verifying if GC peak of  $\alpha$ -terpineol has undergone or not some changes. We found that no alkylperoxide intermediate was formed.

Although during the reaction beginning, the pH values measured keeps almost constant (*ca.* 1.35 to 1.44 after 30 reaction minutes), this initial value depends on  $\text{Fe}(\text{NO}_3)_3$  initial amount. We supposed that both  $\text{Fe}(\text{III})$  and ( $\text{H}^+$ ) ions may act catalyzing this reaction. Thus, low  $\text{Fe}(\text{III})$  concentrations result on high dependence in relation to  $\text{Fe}(\text{NO}_3)_3$  catalyst concentration because there is low  $\text{H}^+$  concentration. Conversely, when high amount of iron catalyst is present, a great amount of  $\text{H}^+$  ions is produced. Therefore, a low dependence in relation to iron catalyst concentration was observed.

In spite of different reaction initial rates achieved, analyzing kinetic curves shown in Fig. 8 we can note that in general, the catalytic runs that attained high reaction initial rates were the same that reached the high conversion after 8 hours reaction.

The isomerization of monoterpenes has been described in presence of Lewis or Brønsted acid catalysts [32,33]. In this work,  $\text{H}^+$  cations were not added at the beginning of the reaction, because only  $\text{Fe}(\text{III})$  cations were used as catalyst. Nevertheless, it is well known that  $\text{Fe}(\text{III})$  cations can react with peroxides to give  $\text{Fe}(\text{II})$  and  $\text{H}^+$  cations and OOH radical [34]. Consequently, herein either Lewis or Brønsted catalysts may have promoted the  $\beta$ -pinene isomerization.

The kinetic curves show that initial rates of reaction were notably affected by the decreasing on catalyst concentration (Figure 8). However, ranging the catalyst load between 21.2 to 0.112 mmol (*i.e.*, 12.0 to 4.0 mol %), high conversions between 91 and 97 % were achieved. Even though decreasing on the catalyst concentration has resulted in a lower conversion, the TON's obtained were higher than those achieved in the Brønsted acid-catalyzed  $\alpha$ -pinene alkoxylation/ hydroxylation reactions [9-11].

### $\text{Fe}(\text{NO}_3)_3$ -catalyzed $\beta$ -pinene reactions with hydrogen peroxide in $\text{C}_2\text{H}_5\text{OH}$ : Effect of hydrogen peroxide concentration

The effect of H<sub>2</sub>O<sub>2</sub> concentration on the conversion and selectivity of β-pinene reactions was investigated in the range of 30.0 to 5.0 mmol, and main results are summarized in Table 3.

**Table 3.** Effect of H<sub>2</sub>O<sub>2</sub> concentration in Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reactions in C<sub>2</sub>H<sub>5</sub>OH<sup>a</sup>

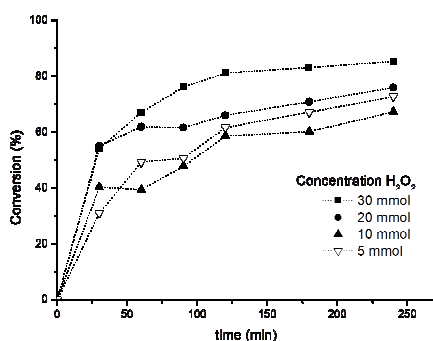
Run	H <sub>2</sub> O <sub>2</sub> (mmol)	Conversion <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)			
			Isomers	1a	1b	ni
1	30.0	85	17	26	28	29
2	20.0	76	18	28	37	17
3	10.0	67	24	17	40	19
4	5.0	73	30	9	41	20

<sup>a</sup>Reaction conditions: β-pinene (5.0 mmol), Fe(NO<sub>3</sub>)<sub>3</sub> (0.21 mmol), ethyl alcohol solution (15 mL), 333 K, 4 hours reaction.

<sup>b</sup>Determined via GC analyses

<sup>c</sup>Determined via GC-MS analyses; α-terpineol (**1a**), α-terpinyl ethyl ether (**1b**); terpinene isomers (*ca.* equimolar amounts of α- and γ-terpinene); ni (complex mixture of minority products).

We would expect that an increase of the amount of H<sub>2</sub>O<sub>2</sub> aqueous solution may favor the formation of water addition products (*i.e.* α-terpineol), because we would also be increasing the water content in the reaction medium. Indeed, the selectivity for α-terpineol drops from *ca.* 9 to 26 % when H<sub>2</sub>O<sub>2</sub> load increases from 5 to 30 mmol. Moreover, competitive reactions such as isomerization seem to have been favored; it was observed that a higher selectivity for isomers was achieved when the amount of aqueous hydrogen peroxide was lowered from 30.0 to 5.0 mmol.



**Figure 10.** Effect of H<sub>2</sub>O<sub>2</sub> amount on the Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reaction with H<sub>2</sub>O<sub>2</sub> in C<sub>2</sub>H<sub>5</sub>OH solution<sup>a</sup>

<sup>a</sup>Reaction conditions: β-pinene (5.0 mmol); Fe(NO<sub>3</sub>)<sub>3</sub> (0.212 mmol); ethyl alcohol (15 mL); 333 K; 4 hour reaction.

In addition to changing the conversion and reaction selectivity, an increase in H<sub>2</sub>O<sub>2</sub> concentration also resulted in an improved initial rate of reaction, as shown in Figure 10. Nevertheless, carrying out the reaction with H<sub>2</sub>O<sub>2</sub> concentration equal to 20.0 mmol during longer times than 4 hours (*i.e.* 8 hours, Table 2), it was

possible to note that the reaction selectivity for goal products (*i.e.* **1a** and **1b** products) was enhanced (*i.e.* 65 to 73 % of combined selectivity).

In general, we can note that different from Fig. 8 where after the initial period of the reaction the conversion remains almost constant, in Fig. 10 we observe a slight increase in conversion throughout the reaction when a lower concentration than 30.0 mmol of H<sub>2</sub>O<sub>2</sub> was employed. It can be attributed to the conversion rate of alkyl intermediate to products which is lower when a low peroxide concentration is used.

#### Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reaction with H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>OH: Effect of temperature

The decreasing of temperature affected notably the final conversion of reactions; whilst 85 % were achieved heating the reaction to 333 K, only a poor conversion of 37 % was reached at room temperature (Table 4). Likewise, the products selectivity was also drastically changed; at room temperature the selectivity for α-terpinyl ethyl ether (**1b**) was the lowest (Run 1, *ca.* 7 %). It is relevant to note that Fe(NO<sub>3</sub>)<sub>3</sub> solubility at room temperature in ethyl alcohol was only partial, a fact that certainly compromised catalyst activity.

**Table 4.** Effect of temperature on the conversion and selectivity of Fe(NO<sub>3</sub>)<sub>3</sub>-catalyzed β-pinene reaction with hydrogen peroxide in ethyl alcohol<sup>a</sup>

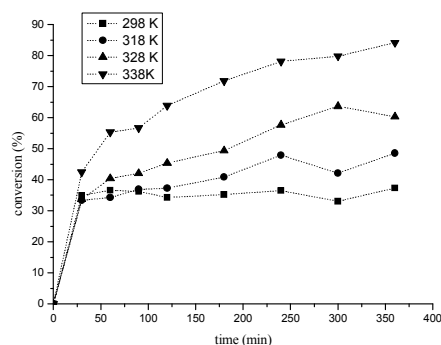
Run	Temperature (K)	Conversion <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)			
			isomers	1a	1b	ni
1	298	37	21	33	7	31
2	313	49	25	34	24	17
3	323	61	25	35	26	15
4	333	85	23	36	27	14

<sup>a</sup>Reaction conditions: β-pinene (5.0 mmol); Fe(NO<sub>3</sub>)<sub>3</sub> (0.212 mmol); H<sub>2</sub>O<sub>2</sub> (20.0 mmol); ethyl alcohol (15 mL); 8 hours reaction.

<sup>b</sup>Determined via GC analyses

<sup>c</sup>Determined via GC-MS analyses; α-terpineol (**1a**), α-terpinyl ethyl ether (**1b**); terpinene isomers (*ca.* equimolar amounts of α- and γ-terpinene); ni (complex mixture of minority products).

The kinetic curves obtained at different temperatures show that the initial rates of reaction were relatively close within the initial 45 minutes of reaction. Afterward, the run performed at the highest temperature was visibly more favored (Figure 11).



**Figure 11.** Effect of temperature on  $\text{Fe}(\text{NO}_3)_3$ -catalyzed  $\beta$ -pinene reaction with  $\text{H}_2\text{O}_2$  in ethyl alcohol<sup>a</sup>

<sup>a</sup>Reaction conditions:  $\beta$ -pinene (5.0 mmol),  $\text{Fe}(\text{NO}_3)_3$  (0.212 mmol), ethyl alcohol (15.0 mL), 6 h reaction.

### Effect of iron catalyst nature on the reaction of $\beta$ -pinene with $\text{H}_2\text{O}_2$ in $\text{C}_2\text{H}_5\text{OH}$

The Table 5 display results obtained using different iron salts as catalysts. The solubility of the catalysts affected drastically their efficiency and consequently compromised the conversions of the  $\beta$ -pinene throughout reactions.

**Table 5.** Effects of iron catalyst nature in the  $\beta$ -pinene reaction with  $\text{H}_2\text{O}_2$  in ethyl alcohol<sup>a</sup>

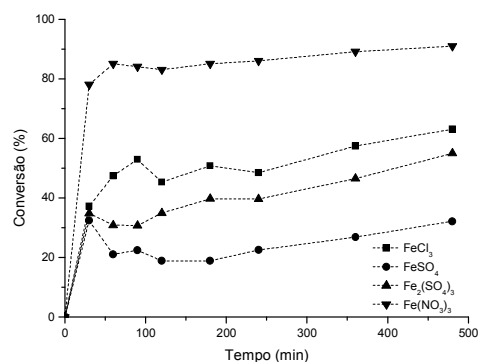
Run	Catalyst	Conversion <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)			
			1a	1b	isomers	Ni
1	$\text{Fe}(\text{NO}_3)_3$	91	34	34	17	15
2	$\text{FeCl}_3$	63	16	22	11	51
3	$\text{Fe}_2(\text{SO}_4)_3$	55	20	27	16	37
4	$\text{FeSO}_4$	32	13	17	12	58

<sup>a</sup>Reaction conditions:  $\beta$ -pinene (5.0 mmol); catalyst (0.612 mmol);  $\text{H}_2\text{O}_2$  (20.0 mmol); ethyl alcohol (15 mL); 60 °C; 8 h.

<sup>b</sup>Determined via GC analyses

<sup>c</sup>Determined via GC-MS analyses;  $\alpha$ -terpineol (**1a**),  $\alpha$ -terpinyl ethyl ether (**1b**); terpinene isomers (*ca.* equimolar amounts of  $\alpha$ - and  $\gamma$ -terpinene); ni (complex mixture of minority products).

The lowest conversion was achieved in presence of  $\text{Fe}_2(\text{SO}_4)_3$  catalyst, which was virtually insoluble in the reaction medium (Run 3, Table 5). Similarly, the  $\text{FeSO}_4$  was not completely soluble, and lowest conversion was reached (Run 4, Table 5). The highest iron content per mol of iron (III) sulfate justifies the higher activity than ones of iron (II) sulfate. This different solubility hamper a straight comparison between the activity of these catalysts or a possible discussion about the effect of iron oxidation state on the reactions. Conversely, both catalysts  $\text{FeCl}_3$  and  $\text{Fe}(\text{NO}_3)_3$  were totally soluble. However, even being used at the same concentration, the  $\text{Fe}(\text{NO}_3)_3$  catalyst was much more efficient than  $\text{FeCl}_3$  (Fig. 12).



**Figure 12.** Kinetic curves of the  $\beta$ -pinene reactions with  $\text{H}_2\text{O}_2$  in ethyl alcohol varying iron catalyst<sup>a</sup>.

<sup>a</sup>Reaction conditions:  $\beta$ -pinene (5.0 mmol); catalyst (0.612 mmol);  $\text{H}_2\text{O}_2$  (20.0 mmol); ethyl alcohol (15 mL); 333 K; 8 h.

Although the motive for this high activity remains blurred, we suppose that the nitrate anions may have acted becoming more electrophilic the Fe(III) cations, favoring the cleavage of 4 members-ring of  $\beta$ -pinene, which should be a step-key in formation **1a** or **1b**.

### Effect of alcohol nature on the $\text{Fe}(\text{NO}_3)_3$ -catalyzed $\beta$ -pinene reaction with $\text{H}_2\text{O}_2$

The impact of alcohol chain on conversion and selectivity of reactions was assessed (Table 6). As the catalyst was insoluble, the reaction do not proceed in butyl alcohol.

**Table 6.** Effects of alcohol nature in the  $\text{Fe}(\text{NO}_3)_3$ -catalyzed  $\beta$ -pinene reaction with  $\text{H}_2\text{O}_2$ <sup>a</sup>

Run	alcohol	Conver. <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)			
			Isom.	1a	Alkyl terpinyl ether	ni
1	Methyl	97	17	18	50	15
2	Ethyl	84	23	36	27	14
3	Propyl	88	17	33	34	16
4	isopropyl	75	26	15	36	23
5	butyl	<5	-	-	-	100

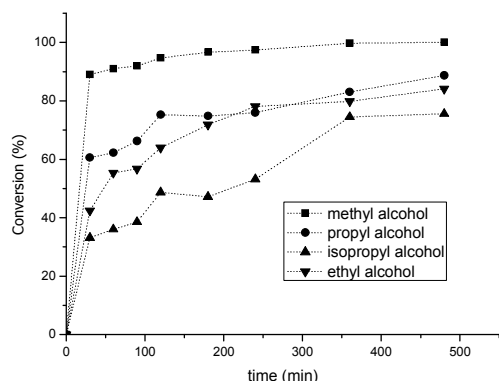
<sup>a</sup>Reaction conditions:  $\beta$ -pinene (5.0 mmol); catalyst (0.212 mmol);  $\text{H}_2\text{O}_2$  (20.0 mmol); alcoholic solution (15 mL); 333 K; 8 h.

The results obtained in the reaction with methyl alcohol are in agreement with those published by us [26]. Nevertheless, although not novel, they are included herein for comparison. The methyl alcohol quickly react to give respective alkyl ether with highest selectivity and an almost complete conversion (Run 1, Table 6).

Ethyl and propyl alcohols reacted with similar rates providing the respective alkyl ethers with selectivity very close (Figure 13). However, unlike in the case of isopropyl alcohol the steric hindrance on carbon tertiary bonded to the hydroxyl group



hampered the formation of  $\alpha$ -terpinyl isopropyl ether (Run 4, Table 6).



**Figure 13.** Kinetic curves of the  $\beta$ -pinene reactions with  $\text{H}_2\text{O}_2$  in alcoholic solutions<sup>a</sup>.

<sup>a</sup>Reaction conditions:  $\beta$ -pinene (5.0 mmol); catalyst (0.212 mmol);  $\text{H}_2\text{O}_2$  (20.0 mmol); ethyl alcohol (15 mL); 333 K; 8 h.

In general, we can conclude that the system  $\text{Fe}(\text{NO}_3)_3/\text{H}_2\text{O}_2$  is efficient to convert alcohol of short carbon chain and carbon less sterically hindered to their terpinyl derivatives (i.e. alcoxydes or alcohol products).

## Conclusion

A novel process to convert  $\beta$ -pinene to terpinyl derivatives using non-corrosive Brønsted acid-free conditions was developed. In presence of catalytic amounts of  $\text{Fe}(\text{NO}_3)_3$  dissolved in alcoholic solutions containing hydrogen peroxide, the  $\beta$ -pinene was converted to  $\alpha$ -terpineol and  $\alpha$ -terpinyl alkyl ethers with high conversions (ca. 90 %) and combined selectivity ranging of 60 to 80 % for two main products (i.e.  $\alpha$ -terpinyl alkyl ethers and  $\alpha$ -terpineol). The high TON achieved reveals that this homogeneous catalyst is notably more effective than other catalysts described in literature. Among iron salts investigate,  $\text{Fe}(\text{NO}_3)_3$  was the most active catalyst. The use of biorenewable solvent (ethyl alcohol), an environmentally benign oxidant (i.e.  $\text{H}_2\text{O}_2$ ), and an inexpensive catalyst are positive features of this process.

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## Notes and references

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