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Solvent and additive-free selective aerobic allylic hydroxylation 2

- of β -pinene catalyzed by metalloporphyrins 3
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turpentine, β -pinene (1, Fig. 1) contributes to 30% in raw

turpentine materials [4]. Due to the presence of a double bond

and a strained four-membered ring, β -pinene can be transformed

readily to produce a number of useful products for pharmaceutical

pinocarveol (3) are valuable pharmaceuticals, fragrance ingre-

dients or chemical intermediates [8,9]. Generally, direct allylic

oxidation of β -pinene by stoichiometric oxidants such as peracids,

 SeO_2 or H_2O_2 is the most efficient processes for the production

 β -Pinene oxidation products such as myrtenol (2) and

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ABSTRACT

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10 1. Introduction

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of 2 and 3 [10-12]. These procedures have been now rejected because a large amount of toxic waste could be produced in these With the rapid decrease of the fossil resources, there is an everincreasing interest for the utilization of renewable biomass resources in making more valuable products [1,2]. Turpentine, obtained by collecting and isolating the oleosus exudates of living pine trees, is the most important and cheapest monoterpene resources all over the world [3]. As the major component of

systems and caused great environmental impacts. In contrast to stoichiometric oxidants, molecular oxygen is an excellent oxidant due to its inexpensive, eco-friendly and easily available characteristics [13]. However, because of the inertness of molecular oxygen and the complex molecular structure of β -pinene, selective aerobic oxidation of β -pinene by molecular oxygen is still amongst the major challenges in academic and industrial research [14]. Metalloporphyrins (MPs) are efficient selective catalysts

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Metallodeuteroporphyrins (MDPs) were employed as the catalysts for aerobic oxidation of β -pinene in

absence of solvents and additives. Allylic hydroxylation products were found to be the main products

from this protocol. The catalytic activity of MDPs with different metal nuclei and the influences of

technological conditions on this reaction were investigated. This catalytic system has bright application

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prospect since only eco-friendly and readily available dioxygen were needed.

applied widely for direct aerobic allylic oxidation of hydrocarbons [15–17]. But most are used under the assistance of solvents, reductants and cocatalysts. MPs catalyzed aerobic oxidation of hydrocarbons in absence of solvents and additives has bright industry application prospect since only eco-friendly and readily available molecular oxygen were needed. Aerobic oxidation of simple hydrocarbons catalyzed by MPs in solvent and additive free system has been studied [18,19]. However, to the best of our knowledge, selective allylic oxidation of complex alkenes in MPs catalyzed aerobic oxidation systems in absence of solvents and additives has not been reported before.

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and other industrial applications [5-7].

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Fig. 1. Structure of β -pinene and its aerobic oxidation products over the catalysis of metallodeuteroporphyrins (MDPs).

49 In this work, an efficient metallodeuteroporphyrins (MDPs) 50 catalyzed selective aerobic allylic oxidation method of β -pinene 51 (Fig. 1, containing one C=C bond and six different C-H bonds in a 52 molecule) was established. Allylic hydroxylation products could be 53 obtained with high selectivity under the catalyzing of metal-54 lodeuteroporphyrin dimethyl esters (Fig. 2, MDPDMEs, 4a-4d) in 55 absence of solvents and additives because of the high reactivity of 56 allylic C—H bonds of β -pinene in this aerobic oxidation system. 57 The effects of reaction parameters and metal nuclei of MDPDMEs 58 on this reaction were investigated. The possible reaction mecha-59 nism and the role of MDPDMEs in this procedure were initially 60 discussed.

⁶¹ **2. Results and discussion**

⁶² 2.1. Aerobic oxidation of β -pinene under the catalysis of MDPs

63 According to GC, GC-MS and chemical analysis data, the 64 oxidation products consisted of 2, 3, pinocarvone (5) and trace 65 amount of 2,10-epoxypinane (6) and hydroperoxides (HPs). HPs are 66 proved to be myrtenyl-hydroperoxide (7) and pinocarvyl-hydro-67 peroxide (8) [4]. Products 2, 3 and 5 belonged to the oxidation of 68 allylic C—H bonds. Product 6 was attributed to the epoxidation of 69 π -bond. Products **7** and **8** belonged to the hydroperoxidation of 70 allylic C—H bonds. β -Pinene could be oxidized by dioxygen in the 71 absence of any catalysts under similar parameters (Table 1). But the



Fig. 2. Formula of MDPDMEs mentioned in the text. M = FeCl (**4a**), Co (**4b**), MnCl (**4c**), Cu (**4d**).

Table 1

Comparison for aerobic hydroxylation oxidation of $\beta\mbox{-pinene}$ at different reaction temperatures.

E	Entry	Cat.	T (°C)	C (%)	Product selectivity (%)			S _{hydroxyl} (%)	TON
					2	3	5		
1	l	4a	70	5.1	30.5	20.0	11.8	50.5	4700
2	2	4a	80	16.9	59.9	25.1	6.9	85.0	15,400
3	3	4a	90	18.6	60.9	24.9	4.9	85.8	17,000
4	1	Non	90	18.5	34.6	11.3	2.6	45.9	-
5	5	4a	100	20.8	63.3	16.4	4.7	79.7	19,000
6	6	4 a	110	21.8	59.8	14.6	1.6	74.4	19,900

Reaction conditions: β -pinene 0.73 (m), FeClDPDME 8 (μ m), temperature 90 (° C), ambient pressure, oxygen flow rate 60 (mL/min), time 5 (h).

selectivity (*S*) of allylic hydroxylation products is much lower than the values under the catalysis of MDPs, indicating that MDPs acted as critical regioselective catalysts in this reaction. The accumulation of HPs was detected at the initial of this reaction. But HPs could be decomposed under the catalysis of MPs [19]. When this reaction proceeded for 5 h, the yield of HPs decreased to a stable value of about 0.5% while the conversion (*C*) value of β -pinene reached 18.6%, indicating a completely decomposition of HPs in this protocol.

2.2. Optimization of the working conditions

MPs are important biomimetic catalysts with bright industry application prospect. In order to obtain the optimal reaction conditions, FeClDPDME was selected as a model to investigate the influence of various working conditions on this reaction. Table 1 listed the C values of β -pinene and the S values of various oxidation products of this reaction at different temperatures. The results showed that the **C** values increased with reaction temperature at the temperature range from 70 °C to 110 °C. The total selectivity of allylic hydroxylation products 2 and 3 reached a maximal value of 85.8% at 90 °C. It has been reported that only high-spin unsteady state perfluorinated or poly-halogenated MPs can activate molecular oxygen under ambient pressure in this solvent and additive free system [18]. The reductive potentials of simple MPs such as metallotetraphenylporphyrines (MTPPs) and MDPs are so low that they can be easily reduced to their high-spin unsteady state by thermal decomposition reduction [18,19]. Thus, the catalytic of MDPs on aerobic oxidation of β -pinene at low reaction temperatures plays a trivial role, which leads to the decrease of **S** values of hydroxylation products 2 and 3. When the reaction temperature was higher than 100°C, the selectivity of 2 and 3 decreased dramatically due to the over-oxidation of initial oxidation products.

In our previous research, catalyst concentration was found to be a critical factor in MPs biomimetic catalyzed reactions. Fig. 3 showed the conversion of β -pinene and the selectivity of various oxidation products over the catalysis of different concentration MDPs from 1 ppm to 9 ppm. The results indicated that the



Fig. 3. Effects of catalyst concentration *C* and *S* values of this reaction. Reaction conditions: temperature 90 (°C), ambient pressure and time 5 (h).

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Fig. 4. Effects of oxygen flow rate on *C* and *S* values of this reaction. Reaction conditions: β -pinene 0.73 mol, FeClDPDME 8 μ mol, temperature 90 °C, ambient pressure and time 5 h.

conversion of β -pinene and the selectivity of allylic C–H oxidation products increased with the increasing of FeClDPDME concentration when the catalyst concentration was lower than 5 ppm. Higher concentration of FeClDPDME would lead to the formation of inactive μ -oxo metalloporphyrin dimers [20,21]. Therefore, although more catalyst was added, the efficient concentration of active catalyst reduced and caused the decrease of *C* and *S* values in this reaction.

The effect of oxygen flow rate on conversion and product selectivity were also investigated. As illustrated in Fig. 4, the conversion of β -pinene increased with the increase of the flow rate of oxygen at flow rate less than 60 mL/min. If the oxygen flow rate was higher than 80 mL/min, the selectivity of product **2** and **3** decreased evidently with the increase of oxygen flow rate. This phenomenon might be explained as follows: The dissolved oxygen in liquid phase increased with the increase of the oxygen flow rate. Thus, the production of **2** and **3** increased with the increase of oxygen would accelerate the over-oxidation of **2** and **3** to other by-products.

¹²⁸ 2.3. Effect of central metal of MDPs

129 As reported in our previous work. MPs with different central 130 metal possess different catalytic activities. Table 2 summarized the 131 data obtained from the aerobic oxidation of β -pinene under the 132 catalysis of various MDPs. The results showed that the S values of 133 allylic hydroxylation products varied dramatically with the change 134 of central metal nuclei. Under the catalysis of various correspond-135 ing metal salts, the S values were much lower, indicating this 136 variation is mainly caused by the different catalytic abilities of 137 MDPs, which follows a sequence of FeClDPDME > CoDPDME > 138 MnClDPDME > CuDPDME. It has been reported that the catalytic 139 activity of MPs can be influenced by the stability and redox 140 potential of central metal nuclei, resulting to the higher selectivity

Table 2

Comparison for aerobic oxidation of $\beta\mbox{-pinene}$ under the catalysis of different MDPs. a

Entry	Catalyst	C (%)	Product selectivity (%)			S _{hydroxyl} (%)	TON
			2	3	5		
1	4a	18.6	60.9	24.9	4.9	85.8	17,000
2	FeCl ₃ ·6H ₂ O	17.8	43.2	14.4	2.4	57.6	16,200
3	4b	17.1	54.7	21.3	2.5	76.0	15,600
4	CoCl ₂ ·6H ₂ O	18.4	42.0	14.6	1.6	56.6	16,800
5	4c	17.2	48.1	22.1	2.8	70.2	15,700
6	MnCl ₂ ·4H ₂ O	18.3	38.0	14.5	1.3	52.5	16,700
7	4d	17.5	49.1	14.9	3.5	64.0	16,000
8	CuCl ₂ ·2H ₂ O	17.5	39.8	18.1	1.4	57.9	16,000

 a Reaction conditions: β -pinene 0.73 mol, MDPs and metal salts 8(µmol, temperature 90 °C, ambient pressure, oxygen flow rate 60 mL/min, time 5 h.

for allylic hydroxylation products in our procedure [19,20]. This phenomenon might be attributed to the different redox potential of various MDPs.

2.4. Probable reaction mechanism

Aerobic oxidation of hydrocarbons in presence and in absence of catalysts has been widely investigated in previous researches. It is widely accepted that these processes are initiated by different active radical intermediates, which generated from the decomposition of HPs [4,22]. These radicals remove hydrogen atoms in substrate molecules, yielding corresponding resonance-stabilised alkyl radicals. As it is mentioned above, β -pinene could be oxidized by oxygen in or in absence of MPs. Aerobic oxidation of β -pinene in absence of catalysts has been explicitly investigated by Hermans and coworkers and found to be propagated by different peroxyl radicals [4]. These radicals abstract weakly bonded *a*-hydrogen atoms in the substrate, yielding the corresponding hydroperoxides and resonance-stabilised alkyl radicals (Scheme 1). O2 adds to these allyl radicals and generates allylic hydroperoxidation, allylic hydroxylation and epoxidation porducts via complex approaches.

161 In MPs biomimetic catalyzed system, β-pinene might be 162 oxidized in a different procedure. Under the catalyst of MPs. HPs 163 could decomposed rapidly by MPs to corresponding hydroxylation 164 products (Scheme 2a). Meanwhile, MPs transformed to high-165 valence MP radicals (e.g. ferric(IV) porphyrin radicals, $[FeP^{IV} = O^+]$, 166 Scheme 2b) [19]. These radicals are regarded as the active species 167 to initiate this reaction, which removes hydrogen atoms in alkyls 168 and yields caged pair of alkyl radicals and high-valence MPs. The 169 caged pair collapses to alcohol or over-oxidized ketone products 170 via a complex oxygen transfer process [19,23]. Perhaps, this is the 171 main reason for the high selectivity of allylic hydroxylation 172 products in this catalytic oxidation system. Aerobic oxidation of 173 β-pinene in absence of catalysts might occur as a competing 174 reaction in this system. Therefore, the increasement of the flow 175 rate increased the selectivity of HPs and other over-oxidation



Scheme 1. Aerobic oxidation of β-pinene in absence of catalysts.

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Scheme 2. Aerobic oxidation of $\beta\mbox{-pinene}$ under the catalysis of FeP.

products. MPs with different central metal nuclei possess different
activities in this biomimetic catalytic process. Higher reactive
catalysts could promote the decomposing of HPs and the
propagating of MPs catalyzed process, resulting to the different
selectivity for allylic hydroxylation products.

¹⁸¹ **3. Conclusion**

182 Aerobic oxidation of β -pinene catalyzed by MDPs in absence of 183 solvents and additives at ambient pressure was studied. The 184 optimal reaction conditions of this protocol were evaluated to be 185 90°C, 5 ppm and 60 mL/min. The catalyst active of MDPs with 186 different central metal nuclei followed a sequence FeClDPDME> 187 CoDPDME > MnClDPDME > CuDPDME. This catalytic system has 188 bright application prospect since only eco-friendly and readily 189 available dioxygen were needed.

¹⁹⁰ **4. Experimental**

191 ¹H NMR spectra were determined on a Bruker Avance III 192 500 MHz spectrometer (Bruker, German). IR spectra were charac-193 terized by a Thermo Nicolet IS10 IR instrument (Thermo, USA). ESI-194 MS/MS spectra were recorded on a Finnigan TSO Quantum Ultra 195 AM mass spectrometer (Finnigan, USA). GC detection were 196 performed through a Shimadzu GC-2014AF (Shimadzu, Japan) 197 GC instrument. GC-MS analysis was performed on an Agilent 198 6890N/5973N GC-MS instrument (Agilent, USA).

199 Hemin (purity > 98.5%) was obtained from Tianjin Institute of 200 Life Sciences Applications (China). β-pinene obtained from 201 Zhuzhou Sonbon Forest Chemical Co. was redistilled and purified 202 to over 98.5% before use. Other chemicals were of analytical grade 203 obtained commercially and used without further purification. 204 Organic solvents were dried before use. MDPDMEs and their 205 intermediates were synthesized from hemin according to the 206 literatures published in our previous work [19-25] and identified 207 by ¹H NMR, IR and ESI⁺-MS.

²⁰⁸ 4.1. Aerobic oxidation procedure

209 03 Aerobic oxidation of β-pinene was carried out in a 250 mL four-210 necked glass flask containing a reflux condenser, a thermometer 211 and a breather pipe. β -Pinene (100g, 0.73 mol) and a certain 212 amount of MDPs were added. When the flask was heated to a 213 certain temperature (60–110 °C), oxygen was fed into the mixture 214 with a flow rate of 20-100 mL/min. The reaction was sampled 215 every one-hour and analyzed by GC using *n*-nonane as an inert 216 internal standard. Hydroperoxides were determined according to 217 the method reported in our previous work [19]. Other components 218 were identified by GC-MS.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.cclet.2016.11.020.

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