



Short Communication

Selective aerobic hydroxylation of *p*-menthane to dihydroterpineols catalyzed by metalloporphyrins in solvent and additive free system



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ABSTRACT

Metallodeuteroporphyrins (MDPs) were employed as the catalysts for aerobic hydroxylation of *p*-menthane in absence of solvents and additives under ambient pressure. Tertiary C–H bonds were found to be more active than secondary and primary C–H bonds. Thus, dihydroterpineols (DHTs) could be conveniently obtained in high selectivity. The influences of reaction temperature and catalyst concentration on this reaction were investigated. The impact of central metal on the yield and selectivity of DHTs was discussed. It was found that ferric deuteroporphyrin dimethyl ester (FeClDPDME) and cobalt deuteroporphyrin dimethyl ester (CoDPDME) exhibited higher catalytic activity than other catalysts.

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1. Introduction

DHTs (Scheme 1, 1a–c) are commercially important materials for cosmetic, detergent, perfumery and fine chemical industries [1,2]. In addition, monoterpenols with a *p*-menthane (Scheme 2, 2) skeleton were identified as bioactive compounds and used widely as vital components in disinfectants and antiseptics [1,3]. Generally, DHTs are mainly produced chemically, starting from pinene (3) or crude turpentine oil by acid catalyzed hydration of them to terpene hydrate (4), followed by partial dehydration of 4 to terpineol (5a–e) and the catalyzed hydrogenation of 5a–e to 1a–c (Scheme 1) [4,5]. Besides high-cost issues associated with the complex synthetic procedure, a large amount of chemical waste was produced in these reaction systems and caused great environmental impacts.

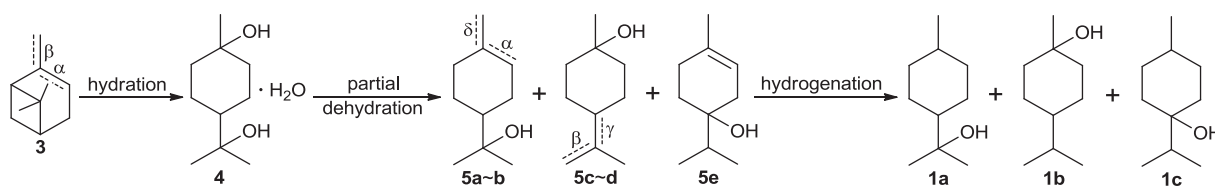
Catalyzed hydroxylation of hydrocarbons with dioxygen is an important industrial process for fine chemicals because of their commercial importance and eco-friendly characterization and provides

a potential convenient preparation approach for *p*-menthane type monoterpenols from *p*-menthane [6–8]. But it still faces very fundamental challenging problems related with the kinetically inert and low selectivity of C–H bonds [9,10]. Therefore, considerable efforts have been made to investigate efficient oxidation methods with high selectivity.

During the last decade years, numerous researches have shown that metalloporphyrins are efficient catalysts for direct oxidation of alkanes by air to alcohols and/or carbonyl compounds in absence of any solvents and additives (cocatalysts, reductants, stoichiometric oxidants or other additives) [11–14]. However, the selective hydroxylation of substrates with different kind C–H bonds in one molecule was rarely reported. Furthermore, the application of this catalysis system under ambient pressure has not been reported before.

In this paper, an efficient MDPs catalyzed aerobic hydroxylation of *p*-menthane (possessing 7 different active sites) in the absence of solvents and additives under ambient pressure was established. DHTs could be obtained in high selectivity because of the higher reactivity of tertiary C–H bonds than other C–H bonds in this hydroxylation system. The effects of various reaction parameters on the yield and selectivity of DHTs were optimized and investigated in detail.

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Scheme 1. Chemical synthesis of dihydroterpineols.

2. Experimental

2.1. Reagents and apparatus

All reagents and solvents were of analytical grade obtained commercially. Organic solvents were dried before use. Ferric deuteroporphyrin (Fig. 1, FeDP, **6**), deuteroporphyrin dimethyl ester (DPDME, **7**) and FeClDPDME (**8a**) were synthesized according to published literatures [15–17]. Other MDPs (**8b–e**) were synthesized from **7** by a standard metal insertion method [18]. The structures of them were identified by ^1H -NMR, IR, MS and UV–vis. *p*-Menthane was obtained from Zhuzhou Sonbon Forest Chemical Co. and redistilled before use.

^1H NMR spectra were obtained on a Bruker Avance III spectrometer (Bruker, German). A Thermo Nicolet IS10 IR instrument (Thermo, USA) was applied for IR spectra. ESI-MS results were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer (Finnigan, USA). UV–vis spectra were recorded on a Lambda-35 UV-spectrofluorimeter (Perkin-Elmer, USA). GC analysis was performed using a Shimadzu GC-2014AF (Shimadzu, Japan) equipped with a 0.25 mm i.d. \times 30 m quartz capillary column and a flame ionization detector. GC-MS spectra were measured using an Agilent 6890N/5973N GC-MS instrument (Agilent, USA) equipped with a 0.25 mm i.d. \times 30 m quartz capillary column.

2.2. Hydroxylation procedure

The oxidation of *p*-menthane was carried out in liquid phase in a 250 mL four-necked glass flask equipped with a heating magnetic whisk, a reflux condenser, a thermometer and a breather pipe. Air was fed to the reactor through the air bottle and the flow rate was measured by a rotameter. In a typical procedure, 100 g *p*-menthane and a certain amount of metalloporphyrin were added. When the reaction temperature reached 100–160 $^\circ\text{C}$, air was pumped into the mixture with a flow rate of 20–100 mL/min. The reaction mixture was sampled and identified by GC or GC-MS every 1 h. The selectivity (*S*) of DHTs in hydroxylation products and the relative activity (*RA*) between tertiary and secondary C–H bonds are defined as Eqs. (1) and (2):

$$S = \frac{\text{GC peak area of DHTs}}{\sum \text{GC peak area of all hydroxylation products}} \times 100\% \quad (1)$$

$$RA = \frac{\text{the yield of all tertiary C–H bonds hydroxylation products} / \text{the number of all tertiary C–H bonds}}{\text{the yield of all secondary C–H bonds hydroxylation products} / \text{the number of all secondary C–H bonds}} \quad (2)$$

p-Menthane hydroperoxides (PMHPs) were analyzed by a modified iodometric method (Appendix A.) and quantified according to Eq. (A.1) [19].

3. Results and discussion

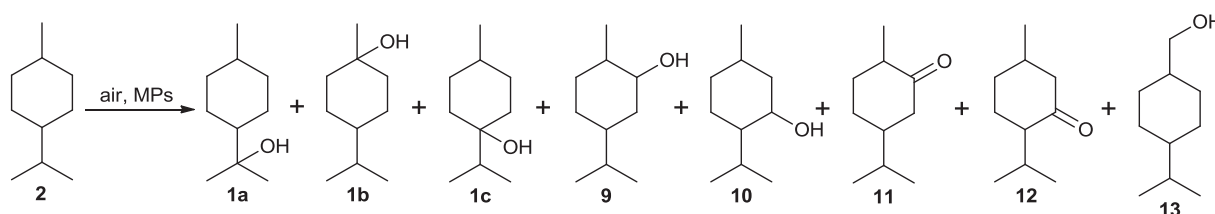
3.1. Aerobic hydroxylation of *p*-menthane under the catalysis of MPs

Scheme 2 formulated the main hydroxylation products of *p*-menthane over the catalysis of FeCl-DPDME in this system. The content of different hydroxylation products was listed in Table 1. The results indicated that the hydroxylation products of tertiary C–H bonds (**1a–1c**) were the predominant components and only trace amount of primary C–H bond hydroxylation product (**13**) was found in this protocol. The *RA* value between tertiary and secondary C–H bonds in this system is 8.80, implying that tertiary C–H bonds has much higher reactivity

than secondary and primary C–H bonds. It has been widely accepted that in MPs catalyzed hydroxylation reactions, alkyl radicals were formed after the activation of C–H bonds in alkane molecules [13,20,21]. The high selectivity of tertiary C–H bonds in this reaction might attribute to the lower activation energy of tertiary C–H bonds than others.

3.2. Optimization of reaction conditions

The critical step in metalloporphyrin catalyzed hydroxylation of alkane C–H bonds is the formation of active high-spin unsteady state metalloporphyrin intermediates, which could activate dioxygen in



Scheme 2. Aerobic hydroxylation of *p*-menthane under the catalysis of MPs.

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