



Highly selective menthol synthesis by one-pot transformation of citronellal using Ru/H-BEA catalysts



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ABSTRACT

The one-pot transformation of citronellal to menthol requires a combined cyclization–hydrogenation step for which Ru/H-BEA catalysts were identified as highly active and selective catalysts. After identifying zeolite H-BEA as the most promising heterogeneous catalyst for the cyclization of citronellal to the intermediate isopulegol, bifunctional metal/H-BEA catalysts were investigated in the one-pot transformation of citronellal to menthols. Using Pd undesired defunctionalization prevailed, while using Pt and Ru, the formation of menthols predominated. Finally, for Ru/H-BEA catalysts, the effect of catalyst composition (Si:Al ratio, Ru content) and reaction conditions (temperature, hydrogen pressure, and solvent) was investigated to diminish citronellal hydrogenation, dimerization, and defunctionalization. Accordingly, with a 1%Ru/H-BEA-25 catalyst (Ru particle size = 1 nm) in dioxane at 15 bar hydrogen pressure and 373 K, a very high selectivity to menthols of 93% at nearly full conversion was obtained. The catalyst is also highly diastereoselective producing 79% of the desired (±)-menthol.

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1. Introduction

With an annual production of about 20,000 tons (2007), menthol is one of the world's most common aroma compounds [1]. It is used in pharmaceuticals, toothpastes, and tobacco, with secondary applications in chewing gum, cosmetics, and confectionery [1,2]. Natural menthol, which accounts for more than half of the whole menthol production, is extracted from *Mentha arvensis* or *Mentha piperita* in India, China, Japan, Brazil, and Taiwan [2]. Because of its three chiral centers in the cyclohexane ring, menthol has four stereoisomeric pairs (Fig. 1). But only (–)-menthol has the typical strong odor and the characteristic cooling effect [1]. Consequently, the other stereoisomers (±)-neo-menthol, (±)-iso-menthol and (±)-neiso-menthol as well as (+)-menthol are less valuable and undesired. While natural menthol exists as the pure (–)-menthol [1], for synthetic menthol, it is either necessary to treat the racemic menthol in a separation crystallization process (Haarmann–Reimer process) or to use a chiral homogeneous catalyst (Takasago and BASF process) [2,3].

Due to the disadvantages of homogenous catalysts such as separation and the high prices for the homogenous metal complexes, the use of heterogeneous catalysts can be a more attractive alternative. A promising route to produce menthol with heterogeneous

catalysts is the one-pot transformation of citronellal to menthol (Fig. 1). This reaction involves two crucial steps: the cyclization of citronellal to isopulegols (ISPs; route 1) and the hydrogenation of the obtained isopulegols to menthols (MTs; route 2). Note that using racemic citronellal as reactant, only racemic menthols (and isopulegols) can be obtained.

Due to the existence of the four enantiomeric pairs of isopulegol and menthol, it is necessary to avoid the formation of the non-valuable isomers. Furthermore, the following reactions should be avoided: hydrogenation of citronellal (route 3), dimerization of citronellal via aldol condensation (Fig. 1, route 4b), dimerization of isopulegol to di-isopulegol ethers (route 4c), and the defunctionalization of isopulegols to p-menthadienes, p-menthenes, and p-menthanes (route 4a).

For the cyclization of citronellal, several Lewis and Brønsted acids were investigated in prior studies, for example supported or non-supported Lewis acids such as ZnBr₂, ZnCl₂, FeSO₄ [4–6], supported or non-supported heteropoly acids [7,8] sulfated or phosphated zirconia [9,10], ZrO₂ dispersed in SiO₂ – montmorillonite [11] and zeolites [9,12–15]. Very high isopulegol yields were achieved with most catalysts, but the distribution of the four isopulegol diastereomers differed strongly. In all cases, the desired stereoisomer (±)-isopulegol was obtained as the predominant isomer. But using solid acids such as zeolites, fractions of (±)-isopulegol of about 70–75% [9,13,14] were obtained, which represents the thermodynamic equilibrium [13]. Higher (±)-isopulegol

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fractions of >90% were obtained with Lewis acids such as ZnBr_2 [2,6], Sn-BEA [15], or Zr-BEA [14].

For the one-pot transformation of citronellal to menthols, several bifunctional metal/solid acid catalysts and silica-supported bifunctional systems have been investigated.

For example, using Ru/ $\text{ZnBr}_2/\text{SiO}_2$ [16], Pt/Ga/MCM-4 [17], or Pd/ $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ [18], menthol yields of around 90% were obtained, and with a physical mixture of $\text{ZnBr}_2/\text{Al}_2\text{O}_3$ and Ni/ Al_2O_3 , a yield of 75% was reached [19]. Furthermore, bifunctional metal organic frameworks (MOFs; Pd@MIL-101) converted citronellal with a yield of 86% [20].

The highest menthol selectivities of around 93% were obtained with metal/zeolite catalysts, for example, Ni/Zr-BEA [21], Pt/H-BEA [22], and Ir/H-BEA [23,24].

Using the metals Pt and Ir, conditions such as loading of the active metal, temperature, pressure, and solvent had an enormous

effect on the obtained product distribution. While in both cases, the influence of loading, temperature, and pressure shows the same dependencies (a low hydrogen pressure, a low loading, and a temperature of 353–373 K lead to high menthol selectivities), the solvent shows different dependencies. While using Ir/H-BEA nonpolar solvents as cyclohexane improves the selectivity to menthols [24], using Pt/H-BEA polar aprotic solvents as dioxane leads to high menthol selectivities [22].

The present work systematically investigates the first step of menthol synthesis, i.e. the cyclization of citronellal, where H-BEA was identified as useful catalyst, and then the one-pot transformation of citronellal to menthols on bifunctional metal (Pd, Pt, and Ru)/H-BEA catalysts. Characterization was carried out by means of CO chemisorption and temperature-programmed desorption of ammonia (NH_3 -TPD). Using Ru/H-BEA, whose ability for the title reaction is unknown so far, the influence of the Si:Al ratio as well

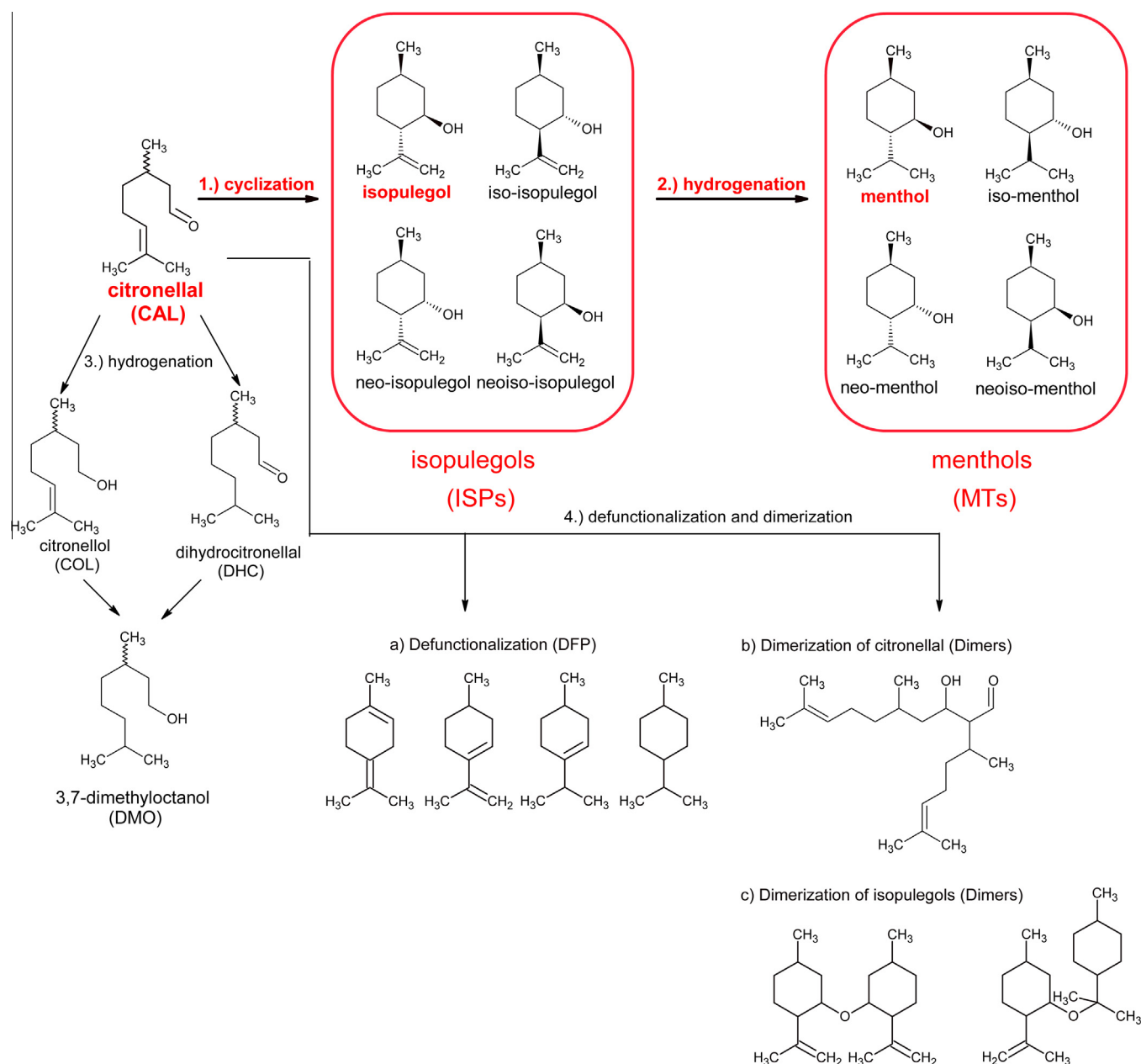


Fig. 1. Reaction network of the transformation of citronellal to menthol. Note that the name *menthols* involves the group of the menthol stereoisomers, whereas *menthol* is used for enantiomeric menthol pair. Only one enantiomer is shown in each case.

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