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Efficient dehydration of 6-gingerol to 6-shogaol catalyzed by an acidic ionic liquid under ultrasound irradiation

Xingran Kou [a,c], Xingze Li [c], Md Ramim Tanver Rahman [a,c], Minming Yan [c], Huanhuan Huang [c], Hongxin Wang [a,b,c,*], Yihai Su [d]

[a] State Key Laboratory of Food Science & Technology, Wuxi 214122, People's Republic of China
[b] National Engineering Research Center for Functional Food, Wuxi 214122, People's Republic of China
[c] School of Food Science and Technology, Jiangnan University, Wuxi 214122, People's Republic of China
[d] Tongling White Ginger Development Limited Co., Tongling 244000, People's Republic of China

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ABSTRACT

6-Gingerol and 6-shogaol are the main bioactive compounds in ginger. Although 6-shogaol has more and better bioactivities than its precursor 6-gingerol, the low content of 6-shogaol in ginger restricts its bioactive effects in functional foods. The traditional preparation methods of 6-shogaol are defective because of the environmental hazards and low efficiency of the processes. In this study, an efficient, easy and eco-friendly dehydration conversion of 6-gingerol to 6-shogaol is presented using an acidic ionic liquid 1-butyl-3-methylimidazolium hydrosulfate ([Bmim]HSO_4) under ultrasound irradiation. The key parameters, including reaction temperature, reaction time, mass ratio of catalyst to substrate and ultrasonic power in each reaction process, were investigated. The yield of 6-shogaol reached as high as 97.16% under optimized condition. The catalyst could be separated from the reaction mixture and reused five times with only a slight loss of activity.

1. Introduction

Ginger, the rhizome of *Zingiber officinale* Roscoe (Zingiberaceae), is widely used as spice and food-flavouring agent in various foods and beverages across the world. As a common medicinal herb in the traditional medicines of many countries and areas, ginger has long been used to treat headaches, nausea, colds, arthritis, rheumatism, muscular discomfort and inflammation (Semwal, Semwal, Combrinck, & Viljoen, 2015). The major pungent and bioactive principles in ginger are considered to be 6-gingerol, 8-gingerol, 10-gingerol and 6-shogaol (Dugasani et al., 2010). 6-Gingeol ((5S) -5-hydroxy-1-(4-hydroxy-3-methoxyphenyl) decan-3-one), the predominant constituent of gingerols, is present in either fresh or dried ginger. However, 6-shogaol ((E)-1-(4-hydroxy-3-methoxy phenyl)dec-4-en-3-one) is hardly detected in fresh ginger and is usually transformed by the dehydration of 6-gingerol during processing or storage. This is due to the fact that 6-gingerol possesses a labile β-hydroxyl ketone functional group in its side chain. This structural feature makes 6-gingerol susceptible to conversion to 6-shogaol via a dehydration reaction (Bhattarai, Tran, & Duke, 2007).

Although 6-gingerol and 6-shogaol have similar chemical structures, and both are known to have beneficial bioactive properties, 6-shogaol is more potent. Numerous studies have shown that 6-shogaol displays greater effectiveness than 6-gingerol in many cases, such as in antioxidant activity (Bhattarai et al., 2007; Cheng, Liu, Peng, Qi, & Li, 2011; Dugasani et al., 2010; Pawar, Pai, Nimbalkar, & Dixit, 2011), anti-inflammatory activity (Dugasani et al., 2010; Pan et al., 2008a; Sang et al., 2009) anti-platelet aggregation effects (Shih et al., 2014), inhibiting muscle contraction (Kimura, Pancho, Koizumi, & Kimura, 1989; Pancho, Kimura, Unno, Kurono, & Kimura, 1989), inhibiting colorectal cancer (Pan et al., 2008b), ovarian cancer (Kim et al., 2008; Rhode et al., 2007), breast cancer (Wu, Hong, Ho, & Yen, 2015) and lung cancer (Hsu et al., 2015; Warin, Chen, Soroka, Zhu, & Sang, 2014). Furthermore, because of the presence of α,β-unsaturated ketone functional group, 6-shogaol can interact with SH groups of cysteine residues in tubulin, leading to microtubule damage, while 6-gingerol is inert (Ishiguro, Ando, Watanabe, & Goto, 2008).

Hence, more and more 6-shogaol and 6-shogoal-rich ginger products are desired for research and application in functional foods. Normally, 6-shogaol is prepared through the acid- or

* Corresponding author at: School of Food Science and Technology, Jiangnan University, Wuxi 214122, People's Republic of China.
E-mail address: wanghongxin2009@hotmail.com (H. Wang).

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heat-catalyzed dehydration of 6-gingerol, because the β-hydroxyl ketone functional group is thermally liable to form α,β-unsaturated ketone. The catalyst used in the acidic catalytic dehydration method is usually HCl or *p*-toluenesulfonic, that has the potential to lead to environmental pollution (Banno & Mukaiyama, 1976; Morera et al., 2012; Shih et al., 2014). Cheng et al. (2011) reported a steaming processing method, in which no catalyst was used. However, in this method, only around 40% of 6-gingerol transformed to 6-shogaol after steam processing for 4 h at 120 °C. Therefore, these traditional preparation methods for 6-shogaol are environmentally hazardous or poorly efficient. Recently, Guo, Zhang, Wu, and Du (2015) provided a microwave-assisted dehydration coupled with an acidic food condiment to convert gingerols to shogaols. However, the conversion rate of 6-gingerol to 6-shogaol is low (58.6%) in this method, and rigorous conditions (reaction temperature 140 °C, microwave power 1000 W) are needed.

Ionic liquids (ILs) have gained attention in many fields owing to their excellent physical and chemical properties, such as negligible vapour pressure, high thermal stability, non-flammability, nontoxicity recyclability (Welton, 1999). Due to these unique properties, ILs represent a new paradigm in green chemistry (Bao, Qiao, Tomida, & Yokoyama, 2008). ILs based on the imidazolium cation have been used as catalysts in the dehydration of carbohydrates to prepare various useful chemicals, including 5-hydroxymethylfurfural (Li et al., 2013; Ryu, Choi, Suh, Ahn, & Suh, 2012; Wei, Liu, Thushara, & Ren, 2012). Recently, Brønsted acidic ionic liquids have been successfully applied as catalysts to replace traditional acids, such as sulfuric, hydrochloric and *p*-toluenesulphonic acid, which have problems of toxicity and corrosion, and are difficult to separate or to reuse (Wang, Shao, Cheng, Yang, & He, 2008). In spite of the fact that it holds great potential to catalyze various organic reactions, [Bmim]HSO_4, which possesses both imidazolium cations and Bronsted acidic anions, has not been broadly applied (Fraga-Dubreuil, Bourahla, Rahmouni, Bazureau, & Hamelin, 2002; Whitehead, Lawrance, & McCluskey, 2004). Only a few examples of [Bmim]HSO_4 as catalyst have been reported (Gupta, Sonu, Kad, & Singh, 2007; Kumar, Dixit, & Awasthi, 2014; Singh, Gupta, Kad, & Kaur, 2006; Singh, Kaur, Sapehiyia, Singh, & Kad, 2005; Ullah, Bustam, & Man, 2015).

To the best of our knowledge, no reports have been found on an efficient, easy and eco-friendly preparation of 6-shogaol under mild conditions. In the present paper, [Bmim]HSO_4 was employed as a catalyst for the dehydration conversion of 6-gingerol to 6-shogaol in a solvent free system under ultrasound irradiation. Key parameters, including reaction temperature, reaction time, mass ratio of catalyst to substrate and ultrasonic power in the reaction process, were investigated.

2. Materials and methods

2.1. Chemicals and apparatus

Ethyl acetate, sodium bisulphate, dichloromethane, ethanol, 4 Å molecular sieves were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and redistilled water was used for all experiments. All of the solvents prepared for high-performance liquid chromatography (HPLC) were filtered through a 0.22 μm microporous membrane. [Bmim]Br ionic liquid was purchased from the Lanzhou Institute of Chemical Physics (Gansu, China). 6-Gingerol and 6-shogaol standards were purchased from Chroma-Biotechnology Co., Ltd (Sichuan, China), and the purity was >98%. The ginger samples were obtained from Tongling White Ginger Development Limited Co. (Anhui, China). A YQ-920D ultrasonic bath, purchased from Yijing Ultrasound Instruments Co. Ltd. (Shanghai), was used in the ultrasonic-assisted extraction process. The Agilent 1100 series HPLC system was from Agilent (California, USA), and a Grace Smart RP C18 column (5 μm, 4.6 × 250 mm. W. R. Grace & Co.-Conn, Columbia, Maryland, USA) was used.

2.2. Preparation of [Bmim]HSO_4

The [Bmim]HSO_4 ionic liquid was synthesized using sodium bisulphate in place of concentrated sulphuric acid by microwave irradiation (Singh et al., 2005). Briefly, equivalent moles of [Bmim]Br and $NaHSO_4{\cdot}H_2O$ were mixed in a conical flask and exposed to microwave irradiation at 70 W power for 20 s. The flask of mixture was then cooled and extracted with dichloromethane. The organic phase was dried over sodium sulphate, and evaporated, on a rotary evaporator to remove the solvent. After that the resulting viscous liquid was dried under vacuum for 3 h at 70 °C to eliminate water, a 91% yield of [Bmim]HSO_4 was obtained.

2.3. Preparation of ginger oleoresin

The oleoresin extraction method was modified from Liu, Tang, and Le (2008). Fresh ginger was washed by water, chipped and ground to a pulp with particles of around 0.3 mm. 95% ethanol was used to extract the ginger pulp, twice. Each time, the solid/liquid ratio was 1:3 and the extraction temperature and time was 50 °C and 1.5 h, respectively. After extraction, the resulting solution was filtered and then distilled under decompression to obtain a concentrated solution. Subsequently, ginger residue activated at 50 °C was added to the concentrated solution in the appropriate solid/liquid ratio and left standing for 1.5 h at room temperature. The solid phase was treated using the extraction procedure above and the re-extracted solution was concentrated to remove the solvent. A yield of approximately 3.5% of ginger oleoresin was obtained in the above procedure.

2.4. General procedure for the conversion of 6-gingerol to 6-shogaol

In the dehydration reaction, 2 g of ginger oleoresin, a certain amount of catalyst and 0.1 g of 4 Å molecular sieves were mixed in a closed 15 ml flask and heated to the desired reaction temperature under ultrasound irradiation. After dehydration, the flask was placed on ice to cease the reaction. Then the resulting mixture was extracted, five times, with 10 ml portions of ethyl acetate. The ethyl acetate extracts were combined and the solvent evaporated, by rotary evaporator at 40 °C. The dried reaction product, as well as the initial ginger oleoresin before reaction, were suspended in 100% ethanol and kept at 4 °C until analysis.

2.5. Analytical methods

All solutions were filtered through a 0.22 μm microporous membrane before direct injection into the HPLC system. The HPLC quantitative analysis for 6-gingerol and 6-shogaol was performed on the Agilent 1100 series. The sample (5 μl) was injected onto a C18 column at 25 °C, and the flow rate was kept at 1.0 ml/min. A linear gradient elution was carried out from 20% to 90% acetonitrile in water, followed by 90–100% acetonitrile over 5 min, and then isocratic 100% acetonitrile for 10 min. The column was re-equilibrated at the initial mobile phase composition for 10 min. The detection wavelength was set at 280 nm. This method was adapted from Cheng et al. (2011).

6-Shogaol yield (Y) is defined as follows:

$$Y = \frac{Moles\ of\ 6-shogaol\ formed}{Initial\ moles\ of\ 6-gingerol} \times 100\%$$