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Green and solvent-free simultaneous ultrasonic-microwave assisted extraction of essential oil from white and black peppers

Ying Wang, Rong Li, Zi-Tao Jiang*, Jin Tan, Shu-Hua Tang, Ting-Ting Li, Lu-Lu Liang, Hai-Jun He, Yu-Miao Liu, Jiu-Tian Li, Xing-Cheng Zhang

Tianjin Key Laboratory of Food Biotechnology, College of Biotechnology and Food Science, Tianjin University of Commerce, Tianjin 300134, People's Republic of China

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A B S T R A C T

Essential oils were extracted from white and black peppers (*Piper nigrum* L.) by green and solvent-free ultrasonic-microwave assisted extraction (UMAE), microwave assisted extraction (MAE) and ultrasonic assisted extraction (UAE), and the efficiency and free radical scavenging activities of the essential oils by different extraction methods were compared in order to illuminate their advantages and disadvantages. The oil yield and superoxide radical scavenging activity of white pepper by UMAE were both significantly higher than those oil extracted by MAE and UAE, implying that UMAE was far more efficient extracting method than MAE and UAE. The same trends were also found for black pepper. Meanwhile, the bioactive compounds of the essential oils from white and black peppers were also characterized and compared by GC coupled with mass spectrometry (GC–MS) and electronic nose based on fast gas chromatography (GC). The essential oil from black pepper contained more monoterpenes than the oil from white pepper, while white pepper oil showed higher content of sesquiterpenes than black pepper. For the different extraction methods, generally, UMAE could obtain more monoterpenes and sesquiterpenes than MAE and UAE. UMAE should be an emerging effective green extraction technique for essential oil from *P. nigrum* because of the maximum extraction yields, shortest extraction time and solvent-free. The electronic nose has been proven as a useful tool for quick analysis and discrimination of the essential oils by different extraction methods.

1. Introduction

Peppers (*Piper nigrum* L.) are one of the most abundant herbal spices in Hainan and Guangdong Province, China, which are very common and important spices, preservatives and insecticides in China and throughout the world. From economical point of view, the cheapest and the most abundant plants or/and plant waste are usually chosen as the extraction raw materials will favor the price of product (Şahin, 2015). White and black peppers (*Piper nigrum* L.) are different in their harvest time and in their modes of processing (Freire et al., 2000; Jagella and Grosch, 1999; Omafuvbe and Kolawole, 2004; Prabhu et al., 2015). White pepper is produced from ripe fruit by removal of the pulp, while the black pepper is processed by drying unripe fruit until a wrinkled skin formed, i.e., black pepper is with the pulp (Agbor et al., 2006). The flavor of black pepper is stronger than that of the white one (Jagella and Grosh, 1999). They are not only used as spices and preservatives, but also as insecticides and as well as applied in herbal medicine with antibacterial, antifungal and antiprotozoan properties and in cosmetic industry (Agbor et al., 2006; Ahmad et al., 2012; Gasparetto et al., 2017; Sauter et al., 2012).

Moreover, bioactive substances, such as piperine, flavonoids, polyphenols and amides, especially essential oils, are plentiful in white and black peppers (Jin et al., 2013; Jirovetz et al., 2002; Rathod and Rathod, 2014). Agbor et al. (2006) found that the hydrolyzed and nonhydrolyzed extracts of black pepper contained significantly more polyphenols compared with those of white pepper. The essential oils of *P. nigrum* have been analyzed by some researchers, they identified α-pinene, β-pinene, linalool, phellandrene, limonene, myrcene, caryophyllene and α-copaene etc. as the more potent odorants of pepper essential oil (Jagella and Grosch, 1999; Orav et al., 2004; Wang et al., 2009). However, the composition of essential oil could vary with the development phase of the plant (Martinelli et al., 2017; Sangwan et al., 2001), and there was seldom study special focusing on the different compositions of essential oil in white and black peppers. Only Orav

* Corresponding author.
E-mail addresses: yingwang@tjcu.edu.cn (Y. Wang), lirong@tjcu.edu.cn (R. Li), ztjiang@tjcu.edu.cn (Z.-T. Jiang), tanjin@tjcu.edu.cn (J. Tan), shtang103@tjcu.edu.cn (S.-H. Tang), LEE5886@163.com (T.-T. Li), dachengzizyyx@163.com (L.-L. Liang), 1720625096@qq.com (H.-J. He), 774611035@qq.com (Y.-M. Liu), 2507774323@qq.com (J.-T. Li), 1553320813@qq.com (X.-C. Zhang).

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et al. (2004) reported that the composition of the essential oil from white and black peppers extracted by using a simultaneous distillation and extraction micromethod for oil isolation. Essential oils are reviewed to have antioxidant, antifungal, antiviral, antibacterial or insecticidal components (Bakkali et al., 2008). For examples, Souto et al. (2012) reported the insecticidal activity of the essential oil of *P. aduncum*, *P. marginatum*, *P. divaricatum* and *P. callosum* against the fire ant *Solenopsis saevissima* and identified various compounds by GC–MS. Kapoor et al. (2009) demonstrated antioxidant and scavenging activity of *P. nigrum* essential oil, and thus makes it important in applications in cosmetic chemistry. Pepper oil also could inhibit fungal growth and toxin production by 50% at the 100-ppm level, and both black and white pepper could be considered as poor substrates for fungal growth (Madhyastha and Bhat, 1984). It is also evident that white pepper could inhibit fungal growth better than black pepper. Thus, it is very important to develop extraction method with high efficiency for the essential oil of white and black peppers.

Many techniques including traditional methods such as steam distillation, hydrodistillation and solvent extraction, and as well as emerging innovative and promising methods such as supercritical fluid extraction, microwave assisted extraction (MAE) and ultrasonic assisted extraction (UAE) are applied to the extraction of essential oils (Martinelli et al., 2017). The composition and quantity of the essential oil might vary with different extraction methods (Bakkali et al., 2008; Wang et al., 2009). Among those extraction methods, hydrodistillation is the main method for obtaining essential oils, but traditional method requires long processing time with low efficiency and low extraction yield (Bakkali et al., 2008). In recent years, microwave assisted extraction (MAE) of bioactive phytochemicals has arisen researchers' tremendous interest (Mandal et al., 2007; Thomas et al., 2015). Microwaves are non-ionizing electromagnetic waves with frequency 300 MHz–300 GHz. Polar molecules such as H_2O inside plant cell are heated instantly by microwave, in which process evaporation generate tremendous pressure in plant cell walls. This pressure pushes and stretches the cell wall and finally destroys it, which facilitates the leaching out of phytochemicals from the broken cells, and thus improving the extraction yield (Mandal et al., 2007). On the other hand, ultrasonic assisted extraction (UAE) was also applied for the isolation of bioactive phytoconstituents (Şahin and Şamlı, 2013; Tiwari, 2015), which uses high frequency (20–50 kHz) sound waves to create minipores in the plant cell wall and causes high strength mechanical and thermal effects, leading to the release of phytoconstituents from plant materials (Thomas et al., 2015; Tiwari, 2015). By now we know that MAE and UAE could accelerate the extracting process and improve bioactive phytochemicals extraction (Bonrath, 2004; Chemat et al., 2017b; Hoang et al., 2007; Proestos and Komaitis, 2008; Rodrigues et al., 2008; Stanisavljević et al., 2007), e.g., MAE heat the extracts rapidly and accelerate the extraction process for adsorption and desorption of the targeted compounds from matrix (Zhang and Liu, 2008). Although the above two extraction techniques have their own advantages, MAE has the problem of inhomogeneous heating, while the thermal effect of UAE is relatively weak. All these shortcomings restrict the further application and promotion of these two methods. Consequently, combining MAE with UAE to ultrasonic-microwave assisted extraction (UMAE) is a complementary extraction technique with both advantages of MAE and UAE, i.e., the effects of the mechanical oscillation and stirring action of ultrasonic wave could effectively make up for the defect of uneven heating by microwave, vice versa, excellent thermal effect by microwave could effectively compensate for the problem of shortage of insufficient heat production by ultrasound (Zhang and Liu, 2008). Last but not least, with the development of “Green Chemistry” concept these years, “green and environmental friendly” techniques in extraction are more and more attractive, which typically characterized by faster extraction rate, less time consuming, less solvent and energy use, easier mass and heat transfer and ensuring a safe and purified product (Boukroufa et al., 2015; Chemat et al., 2017a; Jacotet-Navarro et al., 2016; Şahin, 2015). Among all above green points, Industrials sometimes are looking for green processes extract bioactive compounds from plants without organic solvent. Therefore, in the present study, an alternative solvent-free extraction process with both ultrasonic wave and microwave by using only water has been investigated. The efficiency of the essential oils of white pepper extracted by MAE, UAE and UMAE were compared in order to illuminate the advantages and disadvantages of the extraction techniques. The present study also aimed to compare the essential oils of white and black peppers extracted by UMAE. The electronic nose (E-nose) is a nowadays emerging technology for different fields. For example, E-nose has been applied to discrimination of different wines from different origins (Cozzolino et al., 2005; Santos et al., 2005), the identification of different types of teas (Yu and Wang, 2007) and classification of cheese (Cevoli et al., 2011) and propolis (Cheng et al., 2013). However, there were few attempts to identify volatile components of essential oil by E-nose (Gorji-Chakespari et al., 2017; Ravi et al., 2013). Furthermore, to our best knowledge, no studies have been reported about the application of E-nose to the discrimination of different essential oils extracted by different methods. Therefore, the other aim of this study was to characterize the bioactive compounds of the essential oil by different extraction methods of white and black peppers by chromatography (GC) coupled with mass spectrometry (GC–MS) and electronic nose based on fast GC.

2. Materials and methods

2.1. Plant materials

The fresh and healthy fruits of white and black peppers (*P. nigrum*) were collected from Hainan province, China. The fruits were ground by a laboratory grinder (IKA A10 laboratory grinder, Germany) to 40 mesh, and the ground powders were stored in a desiccator in dark at room temperature before use.

2.2. Chemicals

The *n*-alkane mixtures of C_6-C_{16} (Alpha MOS, Toulouse, France) and C_8-C_{40} (AccuStandard Inc., CT, USA) were utilized for electronic nose and GC–MS analysis, respectively. Other chemicals used were of analytical reagent grade. Distilled water was used throughout.

2.3. Methods

2.3.1. Separation of white and black pepper essential oils by UMAE method

UMAE processes were carried out with ultrasonic and microwave extracting apparatus (CW-2000, Shanghai Xintuo Microwave Instrument Co. Ltd., China). The schematic diagram of UMAE apparatus is shown (Fig. 1). The microwave energy input by the generator was at a maximum delivered power of 800 W, while the ultrasonic wave energy input by an ultrasonic transducer was with a fixed power of 50 W/40 KHz. They were used simultaneously to extract essential oil from peppers: 10 g of plant sample was transferred into the flask, and then 100 mL distilled water was added, i.e., the ratio of plant material to water was 1:10 (g/mL). The flask was then transferred into the chamber of the apparatus and connected it with water-oil separator and condenser. Other conditions were set as follows: Extraction temperature was 100 °C; microwave and ultrasonic powers were 500 W and 50 W (fixed by the apparatus), respectively; and extraction time was 7 min. These extraction conditions were derived from our previous experiment base on statistical experiments such as single factor experiments and response surface analysis (Wang et al., 2017). With the functions of microwave and ultrasonic wave together, the essential oil was volatilized with the evaporation of water. After cooling down by the condenser, essential oil and distilled water were gathered into the water-oil separator (as shown in Fig. 1). Due to the relatively lower density than