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Ionic liquid-mediated microwave-assisted simultaneous extraction and distillation of gallic acid, ellagic acid and essential oil from the leaves of *Eucalyptus camaldulensis*

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ABSTRACT

The ionic liquid (IL) microwave-assisted simultaneous extraction and distillation (ILMSED) of gallic acid (GA), ellagic acid (EA) and essential oil (EO) from the powdered leaves of *Eucalyptus camaldulensis* was investigated and optimized. A wide range of imidazolium-based ILs with different cations and anions were evaluated for this process, and compared in terms of the GA, EA and EO yields. Notably, 1-butyl-3-methylimidazolium tetrafluoroborate was used as an extraction solvent in the current study. The ILMSED process for the three analytes (i.e., GA, EA and EO) was optimized by a series of single factor experiments, followed by response surface methodology analysis. The optimal conditions were determined to be a liquid-solid ratio, microwave irradiation time and microwave power of 50 mL/g, 20 min and 440 W (0.34 W/g at a $[C_4mim]BF_4$ concentration of 0.5 M), respectively. The main constituents found in the EO extracted from the leaves of *E. camaldulensis* were globulol and aromadendrene. A comparison of our ILMSED process with an existing hot water extraction and distillation process revealed that the former approach was much more efficient in terms of being time-saving and low energy. Satisfactory yields of GA (35.2 ± 1.1 mg/g), EA (7.5 ± 0.3 mg/g) and EO (5.8 ± 0.3 mg/g) were achieved.

1. Introduction

Eucalyptus camaldulensis is an important species of the Eucalyptus that belongs to the Myrtaceae family. Although *E. camaldulensis* originates from Australia, it is currently grown throughout the world, particularly in Africa, Southern Europe, West Asia, Southeast Asia and the provinces to the south of the Yangtze River in China [1]. It distributes widely in the world due to the nature of its easy adaptability and fast growth [2]. The leaves of *E. camaldulensis* are one of the main byproducts produced by the papermaking and timber manufacturing industries. Considerable research efforts have consequently been directed towards the recovery of commercially valuable compounds from the leaves of *E. camaldulensis*, including terpenes, phenolic acids and flavonoids, with a view to improve the overall utility of this plant. The main product of *E. camaldulensis* leaves is their essential oil (EO), which has been reported to exhibit insecticidal activity against a number of different insects, including mosquitoes [3], schistosomes [4], moths [5] and weevils [6]. The EO of *E. camaldulensis* leaves has been reported to show antimicrobial activity against RNA antiviruses [4], human pathogenic bacteria [4,7], human pathogenic fungi [4,8] and plant pathogenic and wood rot fungi [9], as well antioxidant and antidiabetic activities [8]. The EO of *E. camaldulensis* leaves has also been used as an aroma enhancer in food and cleaning products and in cosmetic formulations [10].

The results of several studies have shown that the functional properties of *E. camaldulensis* leaves can be attributed to the polyphenolic ingredients found in the leaves, including gallic acid (GA) [11–13] and ellagic acid (EA) [12,13], which are water-soluble phenolic acid and fat-soluble hexahydroxydiphenic acid species, respectively. Numerous studies have been conducted to develop efficient methods for the extraction of GA, EA and EO from the leaves of *E. camaldulensis*. The results of a previous study revealed that non-volatile liposoluble EA, non-volatile hydrosoluble

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GA and volatile EO could be successfully extracted using independent processes. Traditional hydrodistillation [8], steam distillation [9] and Soxhlet extraction techniques involving organic solvents have also been used to isolate these different components [14]. GA has previously been extracted using a variety of different techniques, including Soxhlet extraction [15], reflux extraction [15], microwave-assisted extraction [16], leakage extraction [15], maceration extraction [16,17], ultrasound-assisted extraction [15,16] with methanol, ethanol, acetone or diethyl ether as the extraction solvent. GA has also been extracted with supercritical carbon dioxide using methanol as a co-solvent [16]. Soxhlet extraction [18], reflux extraction [19] and ultrasound-assisted extraction [20] techniques have also been reported for the extraction of EA using a volatile organic solvent such as methanol or ethanol. However, it is noteworthy that the requirement for large volumes of toxic organic solvents has limited the application of these traditional extraction approaches, making them inefficient and environmentally unappealing. There is therefore an urgent need for the development of an efficient and environmentally friendly process for the extraction of the valuable components from the leaves of *E. camaldulensis*.

Microwave technology is becoming increasingly popular for the extraction of the EOs of different plant materials [21,22], and previous studies have demonstrated promising applicability of ionic liquid based microwave-assisted simultaneous extraction and distillation in the obtaining of EO and non-volatile lipophilic or hydrophilic components such as carnosic acid and rosmarinic acid [23], proanthocyanidins [24] and lignans [25] from rosemary leaves, cinnamomi barks and *Schisandra chinensis* fruits, respectively. In addition, some acidic ionic liquids were also used as a dual solvent-catalyst in the hydrolysis processes under microwave irradiation [26,27]. These microwave-assisted extraction (MAE) techniques currently represent promising alternatives to traditional extraction processes [28]. It is well known that the cell types of different plant tissues were quietly different, and these differences usually could lead to the different degrees of difficulty for the extraction of the same components from different plant materials [29–32], specially this phenomenon also exists in the same plant [33,34]. To our knowledge, none of these authors has studied the application of ionic liquid in the extraction of EO and non-volatile compounds from the *E. camaldulensis* leathery wide leaf matrix, which requires further understanding. Ionic liquids (ILs) typically consist of nitrogen-containing organic cations and inorganic anions and have a low melting temperature (below 100 °C). ILs have been used as solvents in a variety of different fields, including synthesis, catalysis [35] and separation sciences [36,37]. ILs have negligible vapor pressures, which means that they can be readily isolated from most reaction mixtures with very little release into the environment. ILs are alternative extraction solvents in terms of multifarious active ingredients extraction from medicinal plants, such as essential oils [38], alkaloids [39], polyphenolic compounds [23]. In light of their attractive properties, considerable research efforts have been directed towards the use of ILs as solvents in liquid extraction processes. The results of numerous microwave experiments have shown that polar solvents can absorb microwave radiation much more effectively than non-polar solvents, allowing them to warm at a much greater rate. Given that ILs are strongly polar materials they can rapidly absorb microwave radiation, allowing for a rapid increase in the temperature of their solutions, which could be used to promote the distillation of EOs and the rapid dissolution of GA and EA.

The purpose of this paper was to develop a rapid and efficient IL microwave-assisted simultaneous extraction and distillation (ILMSED) process to separate the EO, EA and GA from the leaves of *E. camaldulensis*. Nine ionic liquids based on 1-alkyl-3-methylimidazolium cations, as well as some representative of simple (Br^- and Cl^-) and complex (NO_3^-, BF_4^- and Ac^-) anions have been evaluated as extraction solvents for this process, and the main influential parameters were optimized systematically. The determination of GA and EA in the extracts together with the quantity and quality of the EO were used to evaluate the results of our newly developed ILMSED process. A conventional hot water extraction and distillation (HED) approach was also evaluated to allow for a comparison with our newly developed ILMSED approach.

2. Experiments

2.1. Materials and reagents

E. camaldulensis was collected in October 2014 from Yuanmou (Yunnan, China) and identified by Prof. Kailin Mo from the Sichuan Academy of Forestry, China. The leaves were placed in the shade to dry at room temperature. The dry leaves with moisture of 10.8% were subsequently pulverized in a blender to give a powder (40–80 mesh) prior to being used. Analytical standards of GA (⩾98% purity), EA (⩾95% purity), aromadendrene (⩾97% purity) and globulol (⩾98.5% purity) were purchased from Sigma Aldrich (St. Louis, MO, USA). Acetonitrile and formic acid were purchased as the analytical grade from Thermo Fisher Scientific (Shanghai, China). A series of 1-alkyl-3-methylimidazolium ILs with ethyl, butyl, hexyl, octyl or decyl as the alkyl group, and Cl^-, Br^-, NO_3^-, BF_4^- or Ac^- as the cation, were purchased from Chengjie (Shanghai, China). Deionized water was purified using a Milli-Q water purification system (Millipore, MA, USA).

2.2. Apparatus

The simultaneous extraction and distillation process for the isolation of GA, EA and EO was conducted using an UWave-1000 microwave extraction system (XTrust, Shanghai, China). Notably, it was possible to adjust the power (2.45 GHz of frequency and 700 W of maximum power) of this system in a dynamic manner through power feedback [40]. A Clevenger-type apparatus was connected to a 2 L round bottom flask inside the microwave oven through a hole in the side of the oven. The entire operating environment was held at atmospheric pressure. To investigate the influence of the microwave power on the outcome of the extraction process, we evaluated five different set power levels, including 700, 560, 385, 230 and 120 W.

2.3. Ionic liquid-based microwave-assisted simultaneous extraction and distillation (ILMSED) process

The ILMSED process was conducted in the microwave system described above. A sample (20 g) of the powdered *E. camaldulensis* leaves was mixed with an IL in the 2 L round bottom flask for 2 h. 2 h was a soak time which was conducive to the dissolution of the effective constituents. The resulting suspension was then irradiated with microwave energy. To identify the optimum operating conditions for this process, we evaluated several influencing factors, including the type and concentration of IL used in the process; the microwave power and time; and the liquid-solid ratio of the system. In terms of the concentration of the IL, we investigated concentrations of 0.25, 0.5, 1.0, 1.5 and 2.5 M. We also considered microwave irradiation times of 5, 10, 15, 20, 30, 40, 50 and 60 min (It was recorded when the sample was boiling). For the liquid-solid ratio, we evaluated ratios of 20, 30, 40, 50 and 60 mL/g. The extracts prepared using the different methods were rapidly cooled to room temperature before being filtered through a 0.45 μm membrane filter (Guangfu, Tianjin, China) and analyzed by HPLC.