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Sequential extraction and separation using ionic liquids for stilbene glycoside and anthraquinones in *Polygonum multiflorum*

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ABSTRACT

In recent years, ionic liquids (ILs) have received more attentions in green extraction and separation process as a kind of novel environment-friendly solvent, and their application in the field of natural products needs to be extended. In this paper, a new method of the sequential extraction for stilbene glycoside and anthraquinones from *Polygonum multiflorum* was developed for the first time and different ionic liquids was used and compared. It was found two benzothiazolium ILs including [BBth][Br] and [HBth][*p*-TSA] had good selectivity and high efficiency. In addition, the important extraction conditions were also investigated and optimized. Compared with the traditional acid/alcohol-water extraction process, the extraction assisted by ionic liquid not only can obtain higher yield in shorter time, but also can realize the selective extraction for two different kinds of constituents with less consumption. Furthermore, the recovery of target compounds and recycling of ionic liquid were also studied and it was found that solvent extraction combined with cation-exchange resin had the ideal recovery performance.

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1. Introduction

Stilbene glycoside ($C_{20}H_{22}O_9$, abbreviated as SG) is a kind of polyhydroxy phenolic compound, which is one of particular constituents of *Polygonum multiflorum* in Polygonaceae family. It has been found with various bioactivities of eliminating free radicals, preventing cancer, lowering cholesterol, inhibiting atherosclerosis, protecting liver, vasodilating blood vessels and so on [1–4]. Because it is not stable, SG is easy to decompose in its aqueous solution under high temperature, and it is also unstable in acidic solution [5,6]. Anthraquinones is another kind of main components as natural medicine in *Polygonum multiflorum* besides SG, which is mainly composed of emodin, physcion, chrysophanol and rhein, etc. Especially, the content of emodin and physcion can reach 2.51% (dry weight) in total extract of *Polygonum multiflorum* [7]. They have antibacterial, anti-inflammatory, choleretic, diuretic, and immune regulation and cardiovascular protection functions [8–11]. Current methods of extracting anthraquinones mainly include water extraction, organic solvent extraction, acid extraction, and enzyme extraction. Generally, concentrated sulfuric acid or the mixture of concentrated sulfuric acid and chloroform is most popularly used [12], and both of the two solvents should be replaced in modern cleaner production for their well-known disadvantages. Moreover, their extraction efficiency is low and duration is long. Furthermore, the polarity and stability of SG and anthraquinones are very different; the subsequent separation of them will be unavoidable if the nonselective system is employed (just like alcohol-water) after one-step extraction. In a word, the new and cleaner method for the extraction of the two different natural products is urgently needed at present.

In recent years, ionic liquids (ILs) have received more attentions in green technology and process as a kind of novel solvent, and there have been enough successful examples. On the basis of their unique advantages of ideal thermal stability, selective extraction ability, comprehensive dissolving capacity, negligible vapor pressure, excellent structural designability and so on, ILs have been successfully applied in academia and industry fields. Especially in the extraction of bioactive natural products, ILs are being regarded as an attractive and effective replacement or alternative of conventional volatile organic solvents. Traditional alcohol-water system will extract most of constituents in herbs without any selectivity, and the great amount of coexisting impurities can result in the difficulty of obtaining target compounds. Moreover, if they belong to different structural types and need further separation, conventional extraction techniques cannot meet this requirement. Currently, the application of ILs in the field of natural bioactive products is attracting more and more attention for their extraction, separation together with hydrolysis [13,14]. For instance, 2.065 mol/L [BMim][HSO_4] or 2.565 mol/L acidified [BMim]Br solution was selected for the extraction of myricetin and quercetin from *Myrica rubra* leaves

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[15]; the extraction performance of three kinds of 1-alkyl-3-methylimidazolium ILs was investigated and compared for isoflavones from *Iris tectorum* Maxim [16]; Wang and his coworkers used 2.0 mol/L [BMim]Br (1-butyl-3-methylimidazolium bromide) solution to extract anthraquinones in Rhubarb for their UPLC analysis [17]. More recently, imidazolium ILs were found to have good performance in the extraction for three antioxidant acids (gallic acid, vanillic acid and syringic acid) from their aqueous solution [18] and [BMim][BF_4]-based homogenate system was applied to extract orientin and vitexin from *Trollius chinensis* flowers [19]. Through the comprehensive searching in ISI Web of Science©2016 THOMSON REUTERS, [BMim][Br] and [BMim][BF_4] are found as two most-frequently used ILs in the reported applications of extraction, and number of the literatures of flavonoids > phenols/acids > alkaloids > other types of natural products. However, most of these studies only focused on imidazolium-type ILs and their extraction ability for one kind of compounds with similar structures; and the separation of related products and the recovery of ILs were not be investigated and explored simultaneously. A comprehensive comparison is still necessary to search for the valuable relationships and regularity closely related with extraction. High selectivity, efficiency, recyclability and designability of ILs have not been exhibited fully in published research, so more and more new methods and findings about the structure-activity relationship of ILs are expected in their further applications for natural constituents.

Based on the above background, different ionic liquids would be investigated and compared for the extraction of stilbene glycoside and anthraquinones from *Polygonum multiflorum* in this paper. The selectivity and recyclability of ILs would be fully utilized in order to develop the sequential extraction method. Then related effects of ILs structure and the other important extraction conditions would be explored on the extraction efficiency for target compounds. Moreover, the extraction process would be optimized by response surface method and compared with traditional ways. Finally, the recovery of target products and recycling of ionic liquid would be also studied. The following study is expected to provide new meaningful reference for the extraction of similar compounds.

2. Experimental

2.1. Materials

All chemicals involved in this study were at least of analytical reagent grade. Methanol used for HPLC was of chromatographlic grade and purchased from Chemical reagents factory, Chengdu, China. Experimental water was redistilled and deionized. D001 resin was obtained from Bohong Technology Co, Ltd. (Tianjin, China), D113 and 732 resins were supplied by Guangfu chemical institute (Tianjin, China) and Kelong Chemical reagents factory, respectively. All of these cation-exchange resins were pretreated before use, and their Na-form (carrying Na^+ cation) could be converted to H-form (carrying H^+ cation) through treatment with 5% HCl aqueous solution. All of standard compounds used for HPLC were purchased from RuiQi Biological Technology Company (Shanghai, China). Rhizome of *Polygonum multiflorum* originated from Danba county in Tibetan Autonomous Prefecture of Garzê in Sichuan province and was purchased from local drug market, and then the herbal raw materials were milled and dried. The sample powders passed through a stainless steel sieve and the particle size was controlled in 60 mesh. All samples were stored in closed desiccators until use.

2.2. Apparatus

Morphology of herbal powders was observed with JSM-7001F scanning electron microscopy (JEOL Co., Ltd., Tokyo, Japan). SHA-CT thermostatic oscillator (Jinli instrumental Co., Ltd., Tianjin, China) and KQ-2200DA ultrasonic extractor (Kunshanshumei Co., Ltd., Jiangsu, China) were used in the extraction step. HPLC analysis was performed with an LC-20AT pump, a SPD-M20A PDA detector (Shimadzu, Kyoto, Japan), a Symmetry C18 column (Waters, Massachusetts, USA), and an HCT-360 LC columncooler/heater (HengaoTech & Dev, Tianjin, China). A Class-VP workstation (Shimadzu, Kyoto, Japan) was used for data acquisition. The pH meter was provided by ShiNuo physical optical instrument Co., Ltd. (Shanghai, China).

2.3. Synthesis of various ionic liquids

Three great series of imidazolium, benzothiazolium and tropinium ILs (as shown in Table 1) were synthesized according to the reported procedures [20–22] except for [BnMim][Cl]. It was synthesized according to the following procedure: under the protection of highly pure N_2, 4.15 g 1-methyl imidazole (0.05 mol) was mixed with 20 mL redistilled toluene, and 12.6 g benzyl chloride (0.l mol) was added dropwisely during the reaction at 40 °C. After refluxing for 12 h, the organic layer was washed with absolute ether repeatedly, and then the solvent was removed by evaporation. Finally, the pale yellow viscous liquid was obtained as the product of [BnMim][Cl]. All the ILs were dried for 4 h under vacuum at 90 °C and stored in closed desiccators before use. The purity of ILs was firstly checked by proton nuclear magnetic resonance, and then the HPLC analysis for various ILs was was carried out on Waters C18 chromatographic column (3.9 × 150 mm, 5 μm i.d.) at column temperature of 25 °C; the mobile phase was composed of methanol-water (23:77, *V*/V) for benzothiazolium ILs, or acetonitrile-water (20:80, *V*/V) for imidazolium ILs, or acetonitrile-water (12:88, *V*/V) for tropine-based ILs; the flow rate was 1.0 mL/min and injection volume was 10 μL. A 2000ES evaporative light scattering detector (Alltech, San Diego, USA) was used to analyze these ILs. As the result, the purities of all the investigated ILs were in the range of 96.5–99.2%.

2.4. Extraction procedure

0.50 g powders (60 mesh) of *Polygonum multiflorum* were weighed accurately and placed in 50 mL Erlenmeyer flask; the selected ionic liquid was dissolved in a certain amount of deionized water and then the concentration of 0.1–1.2 mol/L of its solution was obtained. Then:

(1) Under the certain ratio of solid to liquid (g/mL, 1:5, 1:10, 1:20, 1:30, 1:40), the herbal powders was mixed with the IL solution and extracted for various duration (1, 3, 5, 10, 30, 60, 120 min) in the thermostatic oscillator under room temperature. After extraction, the solution was filtered and the filtrate was diluted with chromatographic methanol to 50 mL, and then the sample solution was filtered with a microporous membrane of 0.45 μm before HPLC analysis.
(2) Under the certain ratio of solid to liquid (g/mL, 1:5, 1:10, 1:20, 1:30, 1:40), the herbal powders was mixed with the IL solution and extracted for various duration (5, 10, 20, 30, 60, 90, 120 min) in the ultrasonic extractor with the power of 40, 60, 80, 100 and 120 W. After extraction, the solution was filtered and the filtrate was diluted with methanol of chromatographic grade to 50 mL, and then the sample solution was filtered with a microporous membrane of 0.45 μm before HPLC analysis.

2.5. Quantitative analysis of stilbene glycoside and anthraquinones

(1) The HPLC analysis for stilbene glycoside was developed according to Chinese Pharmacopoeia (2015 edition), which was carried out on C18 chromatographic column (3.9 × 150 mm, 5 μm i.d.) at column temperature of 25 °C; the mobile phase was composed of acetonitrile and water (25:75, *V*/V) and the flow rate was 1.0 mL/min. Detection wavelength was set at 320 nm and injection volume was 10 μL. Retention time of standard compound of stilbene glycoside was nearly 6 min.

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