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A green ionic liquid-based vortex-forced MSPD method for the simultaneous determination of 5-HMF and iridoid glycosides from *Fructus Corni* by ultra-high performance liquid chromatography

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ABSTRACT

A simple and green ionic liquid-based vortex-forced matrix solid phase dispersion (IL-VFMSPD) method was presented to simultaneously extract 5-hydroxymethyl furfurol (5-HMF) and iridoid glycosides in *Fructus Corni* by ultra-high performance liquid chromatography. Ionic liquid was used as a green elution reagent in vortex-forced MSPD process. A few parameters such as the type of ionic liquid, the type of sorbent, ratio of sample to sorbent, the concentration and volume of ionic liquid, grinding time and vortex time, were investigated in detail and an orthogonal design experiment was introduced to confirm the best conditions in this procedure. With the final optimized method, the recoveries of the target compounds in *Fructus Corni* were in the range of 95.2–103% (RSD $<$ 5.0%) and the method displayed a good linearity within the range of 0.8–200 μg mL^{-1} for morroniside, sweroside, loganin, cornuside and 1.2–300 μg mL^{-1} for 5-HMF. The limits of detection ranged from 0.02 to 0.08 μg mL^{-1} for all compounds. The results showed that the newly established method was efficiently applied to extract and determine iridoid glycosides and 5-HMF for quality control of *Fructus Corni*.

1. Introduction

Fructus Corni, dry ripe sarcocarp of *Cornus officinalis Sieb. et Zucc* (*Cornaceae*), is one of famous health food. *Fructus Corni* is used not only as prevailing health food to tonify liver and kidney (National Pharmacopoeia Committee, 2015), but also as traditional Chinese medicine to treat illness of dementia and some other age-related diseases in China (Han, Yang, Shi, & Tian, 2014; Jiang, Li, Jiang, Gu, & Wang, 2013; Zhang, Qiao, & Guo, 2012). It plays a crucial pharmacological role in a few herbal prescriptions as a simon-pure traditional Chinese medicine. Iridoid glycosides are a group of bioactive ingredients such as morroniside, sweroside, loganin and cornuside in *Fructus Corni*. It was reported that the iridoid glycosides have a series of pharmacological activities covering glycemic lowering, antiarrhythmia, memory improving, immune regulation, and neuroprotection (Cao et al., 2011; Yamabe, Noh, Park, et al., 2010; Yao, Zhang, Wang, & Li, 2009). 5-hydroxymethylfurfural (5-HMF) is one of neoformed contaminants which are formed during heating processes and exhibit possible harmful effects to humans (Capuano & Fogliano, 2011). 5-HMF also has antioxidative activity, the improvement of hemorheology and the restraining of red blood cell sickling (Lin et al., 2008; Okpala, 2006; Villela, Cabrales, Tsai, & Intaglietta, 2009; Li, Li, Qian, Kim, & Kim, 2009). Therefore, extraction and quantitative determination of 5-HMF and iridoid glycosides (Fig. 1) are especially beneficial for physiological and pharmacological investigations.

There are a series of methods for the extraction of 5-HMF and iridoid glycosides from *Fructus Corni* up to now, such as ultrasonic extraction (Cai, Cao, & Cai, 2013; Jiang et al., 2016; Li & Liu, 2010), solid phase extraction (SPE) (Cao et al., 2012), microwave-based extraction (He, Liu, Mou, Zhan, & Zhang, 2011) etc. However, these methods normally require much organic reagent, abundant sample, excessive time and extra practices. They may negatively bring about decrease of the amount of analytes by reason of hydrolysis or other reaction. Otherwise, matrix solid-phase dispersion (MSPD), which was firstly reported by Barker and his partner (Barker, Long, & Short, 1989), required less time and small volumes of solvent as well as less corresponding facility. MSPD, a modified SPE method, is grinding the sample with some solid adsorbent before eluting the target analytes by small volumes of befitting solvent. The analytes extraction, fractionation, purification and filtration were performed simultaneously in one simple

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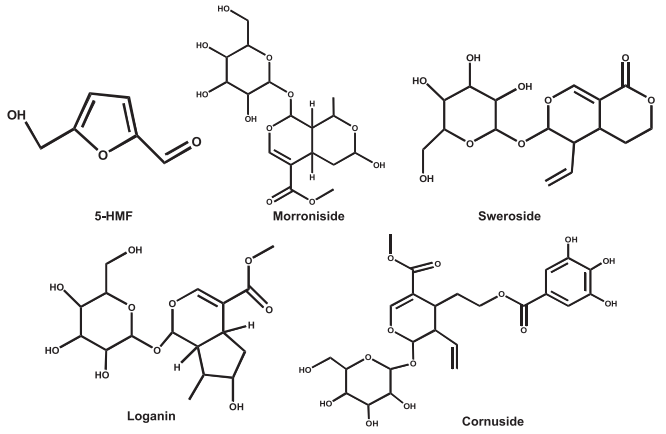

Fig. 1. The structure of 5-HMF and iridoid glycosides.

procedure so that less extraction time and small solvent volume were required (García-López, Canosa, & Rodríguez, 2008). Take advantage of these potential traits, some modified MSPD has been successfully applied to the extraction of some analytes including drugs and pesticides from the complex matrices (Capriotti et al., 2010, 2015).

A vortex-assisted matrix solid-phase dispersion (MSPD) has been established to extract short chain chlorinated paraffins from indoor dust sample (Chen, Chang, & Ding, 2016) and pesticide residues from fish liver and crab hepatopancreas (Souza et al., 2013). It has proved that the vortex-assistant in MSPD procedure instead of vacuum apparatus for eluting is easier than the normal MSPD. In addition, vortex-assisted MSPD can make the analyst be less exposed while the solvent and sample is handled. However, the eluting solvent used was still extremely organic, unfriendly-environmental and toxic. Thus, a green and efficient solvent should be recruited in the elute procedure of vortex-assisted MSPD.

Ionic liquids (ILs), formed by various combinations of organic or inorganic anions and organic cations, have numerous unique properties such as excellent thermal stability, adjustable viscosity, negligible vapor pressure and compatibility with water and organic solvents (Han, Tang, Lee, & Row, 2012). Because of negligible vapor pressure and no ability to produce air waste as ILs' extra character, ILs is often stressed as "green" solvent (El-Hady, Albishri, & Wätzig, 2016). For these reasons, the green ILs is increasingly popular in analytical chemistry (Berthod, Ruiz-Angel, & Carda-Broch, 2008; Buszewski & Studzinska, 2011; Han & Row, 2010; Liu, Jiang, & Jonsson, 2005; Shamsi & Danielson, 2007; Sun & Armstrong, 2010). It has been reported that ILs could interact with analytes by different kinds of mechanism covering π-π, eletrostactic, hydrogen bonding or ion-dipole, and especially inclusion complex (Qiu et al., 2012). These properties enable to make ILs as valid eluent used in vortex-forced MSPD method, which can effectively avoid the use of traditional organic solvents causing serious environmental problems and enhance the analysis sensitivity of analytes in this method.

This investigation was designed to establish a distinctive ionic liquid-based vortex-forced matrix solid phase dispersion (IL-VFMSPD) method for the simultaneous extraction of 5-HMF and iridoid glycosides from crude and processing *Fructus Corni*. Any organic or toxic solvent was not used and less time was required in IL-VFMSPD procedure. The chosen ILs might have particular interaction with the analytes and then sharpened the sensitivity of them. In addition, all target compounds were analyzed in less than nine minutes by ultra-high performance liquid chromatography coupled with ultraviolet detection (UHPLC-UV) in order to simplify the analytical progress. It applied a new method that could be efficiently practiced for the pre-processing of quality control either for crude *Fructus Corni* or for its processing products.

2. Materials and methods

2.1. Chemicals and reagents

Standard substances including morroniside, sweroside, loganin, cornuside and 5-hydroxymethylfurfural (5-HMF) were obtained from Chengdu Must Bio. Sci. and Tec. Co. Ltd. (Chengdu, China). Ultrapure water was provided by a Grindi-Q Academic ultra-pure water system (Grindipore, Milford, MA, USA). C_{18}, AZO, silica, alimina-A, alimina-B, alimina-N, and Florisil PR was supplied from Welchrom. 1-ethyl-3-methylimidazolium bromide ([Emim]Br), 1-Butyl-3-methylimidazolium bromide ([Bmim]Br), 1-Dodecyl-3-methylimidazolium Bromide ([Domim]Br), 1-tetradecyl-3-methylimidazolium bromide ([C_{14}mim]Br), 1-dodecyl-3-methyl chloride imidazole ([Domim]Cl), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim]OTF), 1-dodecyl-3-Methyl-1H-Imidazolium hydrogensulfate ([Domim]HSO_4), 1-dodecyl-3-Methyl-1H-Imidazolium nitrate ([Domim]NO_3), 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim]BF_4), 1-dodecyl-3-methylimidazolium trifluoromethanesulfonate ([Domin]OTF), 1-octyl-3-methylimidazolium tetrafluoroborate ([Omim]BF_4), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate [Omim][PF_6] were offered by Shanghai Chengjie chemical co., Ltd. HPLC grade methanol and formic acid was obtained from Merck (Germany) and Tedia. Other chemicals were of analytical reagent grade. All reagents for ultra-high performance liquid chromatography were filtrated through 0.22 μm nylon syringe filter.

2.2. Herbal plant

Three batches of crude *Fructus Corni* were purchased from Henan Anhui and Shanxi markets, respectively. Other three batches of processing *Fructus Corni* were individually purchased from three different drugstores in Tianjin. The crude *Fructus Corni* dried at 40 degrees and processing *Fructus Corni* were smashed into powder used a pulverizer (Zhongcheng Pharmaceutical Machinery) and passed over 50 meshes, as preparation for later investigation.

2.3. UHPLC analysis

The analyses were performed on an Agilent 1290 series (Agilent, Santa Clara, CA, USA) coupled with ultraviolet detection. The mobile phase included of (A) aqueous acetic acid (0.2%, v/v) and (B) methanol using a gradient elution: 10%–63% B (0–8 min), 63%–10%B (8–8.5 min), then post run 4 min. An ACQUITY UHPLC BEH C_{18} column (2.1 × 100 mm, 1.7 μm) was used to separate at the flow rate of 0.4 mL min^{-1}. The column temperature was hold at 35 °C. The injection volume was 0.5 μL. Determination was demonstrated using an Agilent Technologies 1290. The wavelength UV detection was set at 240 nm. Under the above chromatographic conditions, all the target active compounds, included in standard solution, processing and crude *Fructus Corni*, were separated excellently (Fig. 2), which prepared by the method of ionic liquid-based vortex-forced matrix solid phase dispersion.

2.4. Preparation of standard solutions

2 mg mL^{-1} morroniside, sweroside, loganin, cornuside and 5-HMF solution were individually dissolved in methanol, respectively. Certain amounts of the standards were mixed up to a solution containing 0.3 mg mL^{-1} 5-HMF and 0.2 mg mL^{-1} morroniside, sweroside, loganin and cornuside with methanol. Then a suit of reference stock solution was diluted with methanol and then further diluted with methanol to gain eight different appropriate concentrations for calibration curves. After filtered through the 0.22 μm filter membranes, the solutions were