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Assessment of phenolics contents and antioxidant properties in *Cimicifuga dahurica* (Turcz.) Maxim during drying process

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ARTICLE INFO

Chemical compounds studied in this article:
Ferulic acid 4-*O*-*β*-D-glucopyranoside (PubChem CID: 13916049)
Caffeic acid 3-*O*-*β*-D-glucopyranoside (PubChem CID: 5281759)
Caffeic acid (PubChem CID: 689043)
2, 3-Dihydroxy-2-[(4-hydroxyphenyl) methyl]-,4-ethyl ester (PubChem CID: 68793534)
Shomaside A (PubChem CID: 46209783)
Caffeic ester glucoside (PubChem CID: 5281761)
Ferulic acid (PubChem CID: 445858)
Isoferulic acid (PubChem CID: 736186)
Caffeic methl ester (PubChem CID: 689075)
Cimicifugic acid D (PubChem CID: 11742743)
Carboxymethyl isoferulate (PubChem CID: 16729361)
3, 4-Dimethoxycinnamic acid (PubChem CID: 717531)
Cimicifugic acid A (PubChem CID: 6449879)
Cimicifugic acid B (PubChem CID: 6449880)
2-Feruloyl piscidic acid (PubChem CID: 10002902)
2-Isoferuloyl piscidic acid (PubChem CID: 6450179)
Visnagin (PubChem CID: 6716)
(*E*)-3-(3-Methyl-2-butenylidene)-2-indolinone (PubChem CID: 5319526)
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Drying method
Phenolic acids
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ABSTRACT

Cimicifuga dahurica (Turcz.) Maxim is usually used as traditional Chinese medicine and functional tea. In present work, the change of its phenolics profiles and antioxidant activities during drying processes were investigated. Nineteen main bioactive analytes of *C. dahurica* were simultaneously quantified by HPLC-DAD to assess the effect of drying method. Meanwhile, the influence of different drying processes on antioxidant activities were evaluated by DPPH (1,1-diphenyl-2-picrylhydrazyl), ABTS [2,2′-Azino-bis-(3-ethylbenzthiazoline-6-sulphonate)], FRAP (ferric reducing antioxidant power) and hydroxyl radical scavenging method. Results showed that drying method had significant effects on the contents of phenolics and antioxidant properties. The appropriate drying method was oven-dried at 110 °C. Moreover, the content of phenolic acids and antioxidant activity showed significant correlation coefficient. And the most effective constituents contributing to antioxidant activity were isoferulic acid (**8**), cimicifugic acid B (**14**) and 2-isoferuloyl piscidic acid (**16**).

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1. Introduction

The genus *Cimicifuga* is widely distributed in Europe and Asia, which has been used for antipyretic, analgesic, anti-tumor, antioxidant and anti-inflammatory (Sakurai and Nagai, 1996; Yang et al., 2009; Leach and Moore, 2012). Recent researches display that *Cimicifuga* is also a botanical source of physiological activity substance, especially cycloartane-type tetracyclic triterpenoid saponins and phenolic compounds (Hao et al., 2015). Their health-promoting and therapeutic values have been corroborated by long-term use in folk medicine and daily diet (Hao et al., 2013). The most famous plant in this genus is *Cimicifuga racemose* (Black cohosh), the rhizome of which is the most widely used herbal remedy for menopausal syndrome. Various preparations of *C. racemose* have also been proven to help in menopausal disorders and are presently available in Europe and USA as dietary supplements. (He et al., 2012; Wang et al., 2005; Teschke et al., 2009).

Cimicifuga dahurica (Turcz.) Maxim, which is called "Sheng Ma", as well as other *Cimicifuga* species have been widely used in China, Korea and Japan (Inoue et al., 1970). Its rhizome was used as cooling and detoxification agents since ancient times (Zhang, 2011). Meanwhile, it was also listed as health food by Chinese Ministry of Health (China Food and Drug Administration, 2002). In China, it has been applied for making functional tea for thousand years, such as "sheng-ma ge-gen cha" and "sheng-ma cha" (Mao, 1996). In addition, the aerial parts of *C. dahurica* named "Ku Long Ya" is a famous wild edible vegetable in China, which is highly appreciated due to its characteristic flavor and benefits for human body (Zhang et al., 1998). In recent years, with the increase of food market demand, the yields of "Ku Long Ya" (aerial parts) are rising year by year. It's reported that *C. dahurica* has been cultivated in some areas specially for edible vegetable (Rong et al., 2015).

Research have shown that the active constituents of *C. dahurica* are triterpenes and phenolic acids (Zhang et al., 2001; Nian et al., 2012; Iwanaga et al., 2010). Phenolic acids have been proved to possess vital biological activities including anti-cancer (Spilioti et al., 2014; Zhou et al., 2011), antibacterial (Sánchez-Maldonado et al., 2011) and antioxidant (Wang et al., 2016). It's reported that isoferulic acid isolated from *C. dahurica* is an effective natural anti-oxidant agent (Wang et al., 2011). Cimicifugic acid G, which also isolated from *C. dahurica*, displayed significant anti-oxidative activity in DPPH assay (Nuntanakorn et al., 2006). Although, phenolic acids are the very important group of *Cimicifuga* species and played a key role of biological activity, they have not got enough attention. To date, the activity and quality control of *Cimicifuga* species mainly focuses on saponins and the phenolic acids were ignored (Yao et al., 2011).

Drying is the common procedure in the post-harvest process, which could reduce the water content of freshly harvested plants (Tanko et al., 2005; Yuan et al., 2015). In current, researches have shown that drying process could potentiate or reduce the amounts of compounds with potential biological activity (Bruni and Sacchetti, 2009; Yábar et al., 2011). Conventionally, sun-drying and shade drying were the most common technique applied in post-harvest of plants (Booth and Dhiauddin, 1979). However, these processing methods have obvious disadvantages, such as drying conditions could not be controlled and the drying period is slow, which may cause the loss of active ingredients (Zhang et al., 2010; Peng et al., 2006). On the contrary, the advantage of the industrialized oven-dried method is that the drying time was shortened and the consistency of active principle contents could be guaran teed (Martynenko et al., 2006; Zhu et al., 2014). Thus, oven-dried method is widely used in the post-harvest of the plant now. Traditionally, the drying method of *C. dahurica* are mainly sun-drying and shade-drying after harvesting. The drying time under above manner would continue 2 or 3 weeks to reach the standard level of moisture ($\leq$ 13.0%) required by the Chinese Pharmacopoeia (Chinese Pharmacopoeia Committee, 2015). However, sun-drying and shade-drying may result the loss of active ingredients and make it difficult to guarantee the safety, efficacy and consistency. Therefore, it's worth to study the difference between oven-dried method and traditional method on *C. dahurica*.

In our previous research, we found that the content of phenolic acid in *C. dahurica* was much higher than saponins and some phenolic acid in it had significant high nutrition and health function (Hou et al., 2011). Therefore, the drying method investigation of *C. dahurica* should give attention to phenolic acid profiles. Accordingly, the aim of the present study was to study the change of drying process on chemical contents, especially the phenolic acid profiles and antioxidant activity of *C. dahurica*.

2. Materials and methods

2.1. Plant materials

The rhizome of *C. dahurica* were collected from Fengcheng county, Liaoning province of China during the harvest time in September of 2013. In order to keep the sample fresh, the collected materials were stored at −20 °C in a refrigerator until the drying process. The materials were authenticated by Prof. Jincai Lu (School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University). The voucher specimen (No. 20130926001) was kept in Pharmacognosy Laboratory of Shenyang Pharmaceutical University.

2.2. Chemicals and reagents

The nineteen reference compounds including ferulic acid 4-*O*-*β*-D-glucopyranoside (**1**), caffeic acid 3-*O*-*β*-D-glucopyranoside (**2**), caffeic acid (**3**), 2, 3-dihydroxy-2-[(4-hydroxyphenyl)methyl]-,4-ethyl ester (**4**), Shomaside A (**5**), caffeic ester glucoside (**6**), ferulic acid (**7**), isoferulic acid (**8**), caffeic methyl ester (**9**), cimicifugic acid D (**10**), carboxymethyl isoferulate (**11**), 3,4-dimethoxycinnamic acid (**12**), cimicifugic acid A (**13**), cimicifugic acid B (**14**), 2-feruloyl piscidic acid (**15**), 2-isoferuloyl piscidic acid (**16**), visnagin (**17**), (*E*)-3-(3-methyl-2-butenylidene)-2-indolinone (**18**), (*Z*)-3-(3-methyl-2-butenylidene)-2-indolinone (**19**) were isolated and purified from the rhizome of *C. dahurica*. The isolation process was as follows. The rhizome of *Cimicifuga dahurica* was refluxed with 70% (*v/v*) ethanol for 3 times. The concentrated extracts were suspended and partitioned with different polarity solvent. Compounds 1–19 were isolated from the water-soluble extracts. The isolated process was as follows: The water-soluble extract was fractionated by HPD-400 resins eluted with H_2O-EtOH (100:0-10:90, *v/v*) to afford four fractions (F_A–F_D). The four fractions were separated by ODS column chromatography with MeOH and H_2O as the mobile phase (10:00–90:10 *v/v*), respectively. $F_{A\text{-}1}$ was purified by preparative HPLC eluted with CH_3OH-H_2O (20:80, *v/v*) to yield compound **1**, compound **3**, compound **10** and compound **13**. $F_{A\text{-}2}$ was also purified by preparative HPLC eluted with CH_3OH-H_2O (25:75, *v/v*) to yield compound **2** and compound **14** and compound **4**. $F_{A\text{-}3}$ was further purified ODS column chromatography and then $F_{A\text{-}3\text{-}2}$ was subjected to pre-HPLC eluted with CH_3OH-H_2O (30:65, *v/v*) to obtained compounds **17–19**. $F_{B\text{-}1}$ was separated by preparative HPLC eluted with CH_3OH-H_2O (25:75, *v/v*) to yield compound **15** and compound **16**. Subfraction $F_{B\text{-}3}$ was separated by preparative HPLC eluted with CH_3OH-H_2O (45:55, *v/v*) to obtained compound **11**, compound **12** and compound **7**. $F_{C\text{-}3\text{-}1}$was subjected to pre-HPLC eluted with CH_3OH-H_2O (33:65, *v/v*) to obtained compound **6** and compound **8**. $F_{C\text{-}3\text{-}2}$ was separated by preparative HPLC eluted with CH_3OH-H_2O (35:65, *v/v*) to yield compound **5** and compound **9**.

The purity of these compounds were more than 98% by normalization method of HPLC-DAD. Their structures were elucidated by spectroscopic data (1D, 2D NMR) as well as chemical methods.

1, 1-Diphenyl-2-picrylhydrazyl (DPPH), [2,2′-Azinobis-(3-ethylbenzthiazoline-6-sulphonate] (ABTS), tripyridyltriazine (TPTZ), trolox and ascorbic acid were obtained from Sigma-Aldrich Quimica