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Effects of drying methods on phytochemical compounds and antioxidant activity of physiologically dropped un-matured citrus fruits☆

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ABSTRACT

Physiologically dropped un-matured citrus fruits have good potential as sources of different bioactive compounds and antioxidants. Drying is a good method to preserve the materials. The effects of three different drying methods (sun-drying, hot air-drying and freeze-drying) on phytochemical compounds and antioxidant activity of physiologically dropped un-matured citrus fruits were investigated. The results showed freeze-drying is good for retaining phenolic compounds, synephrine and antioxidants; hot air-drying is good for retaining flavonoids; and all three methods can be used for retaining limonoids. The results should serve as a guide for the industrial production of high-quality extraction materials for bioactive compounds.

1. Introduction

Physiologically dropped un-matured citrus fruits mean the abscission of young un-matured citrus fruits which are still green and small from stem–branch junction or ovary–stem junction due to physiological reasons (Agricultural dictionary committee, 1998). Physiologically dropped fruit is a normal phenomenon in the maturing process of citrus fruits, which is different from the fruit drop caused by storm, plant diseases or insect pests. Physiologically dropped un-matured citrus fruits usually have two dropping time. The first dropping time occurs in May which can be attributed to imperfect pollination, degeneracy, ovule dysplasia or malnutrition. The second dropping time is in June because of the changes of endogenous hormones caused by early ripening embryo. The quantities of physiologically dropped un-matured citrus fruits are quite considerable (Mao, 2009). In China, only small quantities of physiological fruit drop are collected for use in traditional Chinese medicines (TCM) (Chinese pharmacopoeia edition committee, 2005), and in Japan, most of them are burned as an agricultural waste (Inoue, Tsubaki, Ogawa, Onishi, & Azuma, 2010). However, un-matured citrus fruits usually have higher contents of phytochemical compounds than mature fruits (Barreca, Bellocco, Caristi, Leuzzi, & Gattuso, 2010; Inafuku-Teramoto, Suwa, Fukuzawa, & Kawamitsu, 2011). Thus to make use of them is highly desirable.

Besides citrus juice processing residue, physiologically dropped un-matured citrus fruits will be another attractive source of phytochemical compounds, such as flavonoids, limonoids and adrenergic amines (mainly synephrine). Flavonoids in citrus fruits include two important classes of compounds: flavanone glycosylates (FGs) and polymethoxylated flavones (PMFs). Citrus fruits also contain considerable amounts of phenolic acids, which have attracted recent scientific interest (Robbins, 2003). Flavonoids and phenolic acids have a wide range of biological effects, such as inhibition of key enzymes in mitochondria, protection against coronary heart diseases as well as anti-inflammatory, antitumor and antimicrobial activity (Harborne & Williams, 2000; Morton, Caccetta, Puddey, & Croft, 2000). Synephrine, an amine that was isolated initially as a synthetic product and used pharmacologically as a vasoconstrictor and bronchiectatic agent (Takei, Hirabuki, & Yoshizaki, 1999), is an adrenergic antagonist (Haaz et al., 2006). Limonoids are a prominent group of secondary metabolites in citrus fruit with potential biological activity to improve human health, e.g. anticancer, antimalarial, cholesterol-lowering, and antiviral agents including versus HIV (Manners, 2007).

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In order to preserve and extend their life, the pomace and physiologically dropped un-matured citrus fruits are sold in dry form. Their bioactivity and nutritional value depend mainly on the drying methods (Xiao, 2002). Some novel drying techniques have been used to dry citrus by-products. Senevirathne, Jeon, Ha, & Kim (2009) and Senevirathne et al. (2010) found that far-infrared radiation and high-speed drying gave almost equal total flavonoid contents and antioxidant activity, and shorter drying times compared to freeze-drying. In practice, sun-drying, hot air-drying are the major drying methods which are relatively inexpensive. Drying might cause degradation of phytochemicals in citrus by-products. Garau, Simal, Rosselló, and Femenia (2007) found that dietary fibre components and antioxidant activity of orange pomaces were degraded either when extended drying periods or high drying temperatures are applied during air-drying temperature from 30–90 °C. Wuttipalakorn, Srichumpuang, and Chiewchan (2009) found that limonin of hot air drying treated lime residues had a higher reduction at higher drying temperature. Chen, Yang, and Liu (2011) found the total phenolic and flavonoid contents of drying treated orange peels were decreased by lower drying temperature (50 and 60 °C) and increased by higher drying temperature (70, 80, 90 and 100 °C). So the selection and control of drying methods for physiologically dropped un-matured citrus fruits is a major challenge. To our knowledge, there is no report on drying of physiologically dropped un-matured citrus fruits.

The purpose of this work was to investigate the influence of different drying methods on the content of phenolic compounds, nomilin and limonin, and synephrine in four species of physiologically dropped un-matured citrus fruits as well as on the antioxidant activity. The results should serve as a guide for the industrial production of high-quality extraction materials for bioactive compounds.

2. Materials and methods

2.1. Chemicals

Protocatechuic acid, *p*-hydroxybenzoic acid, vanillic acid, sinapic acid, ferulic acid, caffeic acid, *p*-coumaric acid, narirutin, hesperidin, TPTZ (2,4,6-tris (2-pyridyl)-s-triazine), 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) and Folin–Ciocalteu phenol reagent were purchased from Sigma (St. Louis, MO, USA). Nobiletin and tangeretin were obtained from the National Institute for the Control of Pharmaceutical and Biological Products in China. All other chemicals used in this study were of analytical grade.

2.2. Materials

Physiologically dropped un-matured fruits of four citrus species were collected for the studies described here: Ponkan (*Citrus poonensis* Hort. ex Tanaka Ponkan), the second largest mandarin cultivar in China; Gaocheng (*Citrus gradis* × *Citrus sinensis*), a hybrid grown in the Tanzhou traditional citrus production area; Huyou (*Citrus paradise* Macf. Changshanhuyou), a grapefruit and Foyou (*Citrus grandis* (L.) Osbeck cv Foyoua), a new pummelo cultivar. Physiologically dropped un-matured fruits of Foyou and Huyou were kindly offered by a farm in Quzhou City, Zhejiang Province, June 22–30, 2011. Physiological drop of Ponkan and Gaocheng were collected in the orchard of the Zhejiang Citrus Research Institute in Huangyan City, Zhejiang Province, June 22–30, 2011.

2.3. Sun-drying

Each fruit was cut horizontally into slices 0.5 cm thick and arranged on large bamboo plates to form a layer (0.5 cm thick). The plates were kept in a very large open area that was well ventilated allowing natural air flow to dry the samples at the temperature ranged from 20 to 25 °C and 60% relative humidity for 3 days. After drying, samples were kept in a desiccator for 2 days to allow a homogenous distribution of moisture, the final moisture content was 10g/100 g. The dried fruits were ground with a blade mixer (Wenling Linda machine Co., Wenling, Zhejiang, China) to pass a 0.63 mm sieve (Huakang Experiment Instrument Co., Shangyu, Zhejiang, China) and the size of powder varied from 0 to 0.63 mm. The powders were stored in plastic bags at −20 °C.

2.4. Hot air-drying

The fruits were washed, cut horizontally into slices 0.5 cm thick, and then put on a tray to form a layer 0.5 cm thick and dried in a DHG-9070A hot-acven (Blue Sky Experiment Instrument Co., Hangzhou, Zhejiang, China) at 60 °C, 2 m/s air flow rate and 60% relative humidity for 10 h. The choice of air-drying temperature was based on our pre-experiments, in which the temperature ranged from 30 to 120 °C and it was found that the total phenolic acids increased as the drying temperature increased from 30 °C to 60 °C and decreased at temperatures >60 °C, other bioactive compounds detected in this study were not sensitive to the air-drying temperature. After drying, samples were kept in a desiccator for 2 days to allow a homogenous distribution of moisture, the final moisture content was 10g/100 g. The dried fruits were ground with a blade mixer (Wenling Linda machine Co., Wenling, Zhejiang, China) to pass a 0.63 mm sieve (Huakang Experiment Instrument Co., Shangyu, Zhejiang, China) and the size of powder varied from 0 to 0.63 mm. The powders were stored in plastic bags at −20 °C.

2.5. Freeze-drying

Fruits were washed, cut horizontally into slices 0.5 cm thick, then frozen at −50°C and 12 Pa cavity pressure for ~12 h using Freezone-6 freeze dryer (Labconco Corporation, Kansas City, America). After drying, samples were kept in a desiccator for 2 days to allow a homogenous distribution of moisture, the final moisture content was 10g/100 g. The dried fruit was ground with a blade mixer (Wenling Linda Machine Co., Wenling, Zhejiang, China) to pass a 0.63 mm sieve (Huakang Experiment instrument Co., Shangyu, Zhejiang, China) and the size of powder varied from 0 to 0.63 mm. The powders were stored in plastic bags at −20 °C.

2.6. Extraction of phenolics

A 1 g sample of each cultivar dried fruits drop powder was extracted twice with 20 ml of 80% (v/v) methanol/dimethylsulfoxide/water (4:5:1, by vol.) in an ultrasound bath (150 W) at 25 °C for 30 min. After centrifugation at 1680 × g for 10 min, the supernatants were combined and made to 50 ml for measurement of the total phenolic content (TPC), flavanone glycosides (FGs), polymethoxylated flavones (PMFs) and antioxidant activity (AA).

2.7. Determination of FGs and PMFs

The contents of FGs (narirutin, naringin, hesperidin and neohesperidin) and PMFs (nobiletin and tangeretin) were determined simultaneously by HPLC-photodiode array (PDA). The column used was a Diamonsil C18 column (250 mm × 4.6 mm i.d.). The mobile phase consisted of solution A (methanol) and solution B (4% (v/v) acetic acid). The flow rate was 1.0 ml/min and the column temperature was 40 °C. Gradient elution followed the protocol described (Xu, Ye et al., 2008). Calculation of FG and PMF concentrations (expressed as mg/g dry weight (DW)) was done by an