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Volatile components extracted from hawthorn by supercritical carbon dioxide extraction as affected by polarities of co-solvents

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RESEARCH PAPER

Abstract

Hawthorn fruit is highly valuable to be used as functional food and traditional medicine. It is important to extract and identify volatile components from hawthorn. The aim of this study was to investigate the volatile components from hawthorn. The volatile components of hawthorn were extracted by supercritical carbon dioxide fluid extraction method combined with different polar co-solvents and identified by gas chromatography coupled with mass spectrometry (GC-MS). Thirty-nine, twenty-nine, thirty-three, twenty-two and seventeen volatile chemical compounds were extracted with co-solvent methanol, 95% ethanol, anhydrous ethanol, ethyl acetate and without co-solvent, respectively, and indentified by GC-MS. This study will provide a scientific basis for potential application of hawthorn in food and pharmaceutical industry.

Keywords: co-solvent, hawthorn, polarity, supercritical fluid extraction, volatile components

1. Introduction

Crataegus pinnatifida, part of a large genus of shrubs and trees in the family Rosaceae, is also known as English hawthorn. Hawthorn originates from continental Europe. It is gentle and safe for long-term use with no toxic side-effects. Hawthorn fruit is highly valuable to be used as functional food and traditional medicine. Hawthorn fruit had been shown to have many health benefits including cardiovascular protective, hypotensive and hypocholesterolemic effects (Zhang *et al.*, 2001). Moreover, hawthorn has a unique sweet and sour flavour, and can produce hawthorn flavour. Volatile component from natural products has a great interest to food, pharmaceutical, and cosmetic industries. To better explore the main volatile components of hawthorn, it is important to develop an effective extraction method. In recent years, the volatile components of hawthorn have attracted a little attention. It was reported that 32 volatile compounds of hawthorn fruit were extracted with simultaneous distillation method and identified by gas chromatography-mass spectrometry (GC-MS) (Chen *et al.*, 1997; Xie *et al.*, 1997). Ding and Li (1999) investigated the flavour compounds in hawthorn fruit with simultaneous distillation-extraction and GC-MS. However, there are no reports about hawthorn volatile components with supercritical fluid extraction (SFE). The SFE presents an alternative to conventional methods of steam distillation and solvent extraction. The supercritical carbon dioxide (CO_2) has good solvent properties for extraction of non-polar compounds such as hydrocarbons (Liang and Wai, 2001) and its polarity can be changed by some polar co-solvents to improve the extraction of more hydrophilic compounds (Talansier *et al.*, 2008). The aim of this present work was to investigate the effect of co-solvents with different polarities on volatile components in hawthorn extracted by SFE. The volatile components were identified using GC-MS. This study will provide a scientific basis for potential application of hawthorn in food or pharmaceutical industry and lay a chemical foundation for searching the active components in hawthorn.

2. Materials and methods

Materials

Matured hawthorn fruits (*C. pinnatifida* var. major) were collected from the Hawthorn Garden of Hebei Normal University of Science and Technology (Qinhuangdao, Hebei Province, China). The seeds were removed and the fruits were dried and milled by a knife mill.

Volatile components extraction

The extraction was carried out in a Speed SFE system (model SF-2; Applied Separations, Allentown, PA, USA) with a 50 ml extraction column. The raw material packed bed was prepared by manual packing of the ground particles into extraction column and a glass wool plug was placed at both sides of the column in order to avoid the drag of small particles by solvents. The powdered hawthorn fruit (10 g) were extracted both using supercritical CO_2 alone and supercritical CO_2 with addition of organic solvents at flow rate 1 ml/min. Methanol, 95% ethanol, anhydrous ethanol and ethyl acetate were used as co-solvents. The extractions with supercritical CO_2 were performed at a temperature of 50 °C and at pressure of 25 MPa. The extracts passed through dewatering procedure over anhydrous sodium sulfate, passed through a 0.45 μm filter, and was stored at 4 °C prior to GC-MS analysis (Liu and Xu, 2012).

GC-MS analysis

GC-MS analysis was performed on an HP6890 gas chromatography instrument (Agilent Technologies Co., Ltd., Santa Clara, CA, USA) coupled with an HP5973A Saturn mass spectrometer (Agilent Technologies Co., Ltd.). The analytes were separated on a SilHP-5 cross-linked polymethyl siloxane capillary column (15 m × 0.25 mm, 0.25 μm film thickness; Agilent Technologies Co., Ltd.). The oven temperature was maintained at 40 °C for 2 min and then programmed at 2 °C/min to 215 °C and held at 215 °C for 2 min. The injector temperature was set at 230 °C. Helium (99.99%) was used as carrier gas at a flow rate of 1.2 ml/min. The mass spectrometer was operated in electron impact mode with ionisation energy of 70 ev. The mass range was scanned from *m/z* 35 to 400 amu. The temperatures of the transfer line and ionisation source were set at 230 °C.

3. Results and discussion

The GC-MS chromatogram of volatile components from SFE revealed the presences of 39, 29, 33, 22 and 17 compounds with co-solvent methanol, 95% ethyl alcohol, anhydrous ethanol, ethyl acetate and without co-solvent, respectively. These compounds were identified by comparing the fragmentation patterns of resulting mass spectra with those published in literature and using the National Institute of Standards and Technology Mass Spectral Database of gas chromatograph-mass spectrometer (Agilent Technologies Co., Ltd.). The detailed chromatographic and chemical information of the volatile components were shown in Supplementary Table S1 while the chromatograms were shown in Figure 1. The hawthorn volatile components with different co-solvents were not exactly same. However, eicosane, heptadecane and n-hexadecanoic acid were the same compounds with different co-solvents. Alkanes, fatty acids, esters, alcohols, ketones and aldehydes are important components of the hawthorn volatile components. The data were partially identical with those in previous studies by Chen *et al.* (1997) and Xie *et al.* (1997), who reported that 32 volatile components from hawthorn contained alcohols, aldehydes, esters, alkanes and ketones.

Several authors used ethanol or methanol as co-solvent for supercritical carbon dioxide extraction. Among them, Badalyan *et al.* (1998) studied the extraction of ginger oleoresin using ethanol as co-solvent; under subcritical conditions, an addition of 2% of ethanol increased the yield to approximately 10%. Wang *et al.* (2001) studied SFE of ginseng roots and proved that ethanol increased the yield. The greater polarity of co-solvent has, the higher content of extracted compounds yield, such as methanol and anhydrous ethanol. Ramandi *et al.* (2011) optimised the experimental parameters of SFE to extract fatty acids from the flowers of *Borago officinalis* L. using a central composite design. The optimum conditions of SFE were obtained at a pressure of 350 atm, a temperature of 65 °C, a methanol modifier volume of 100 μl, and a static and dynamic extraction time of 10 min. Extraction yields based on SFE varied in the range of 0.02 to 1.96% (w/w). Xiao *et al.* (2007) obtained the essential oil of *Marchantia convoluta* by SFE using methanol as a modifier. Maximum yields were obtained using the following conditions: extraction temperature, 35 °C; dynamic time, 35 min; pressure, 15 Mpa and modifier volume, 40 ml. In the present study, most compounds (39) were identified using methanol as co-solvent. These volatile components contained 16 esters, eight acids, six alkanes, three alcohols and other chemical compounds. 29 and 33 compounds were extracted with SFE using 95% ethanol and anhydrous ethanol, respectively. Only 22 volatile components were extracted using less polar ethyl acetate as co-solvent. The number of compounds reflect the different characteristics of taste, therefore, the characteristic taste of hawthorn fruit is not embodied by one or several compounds, but coordinated by a variety of components, including esters, alkanes, alcohols and so on.

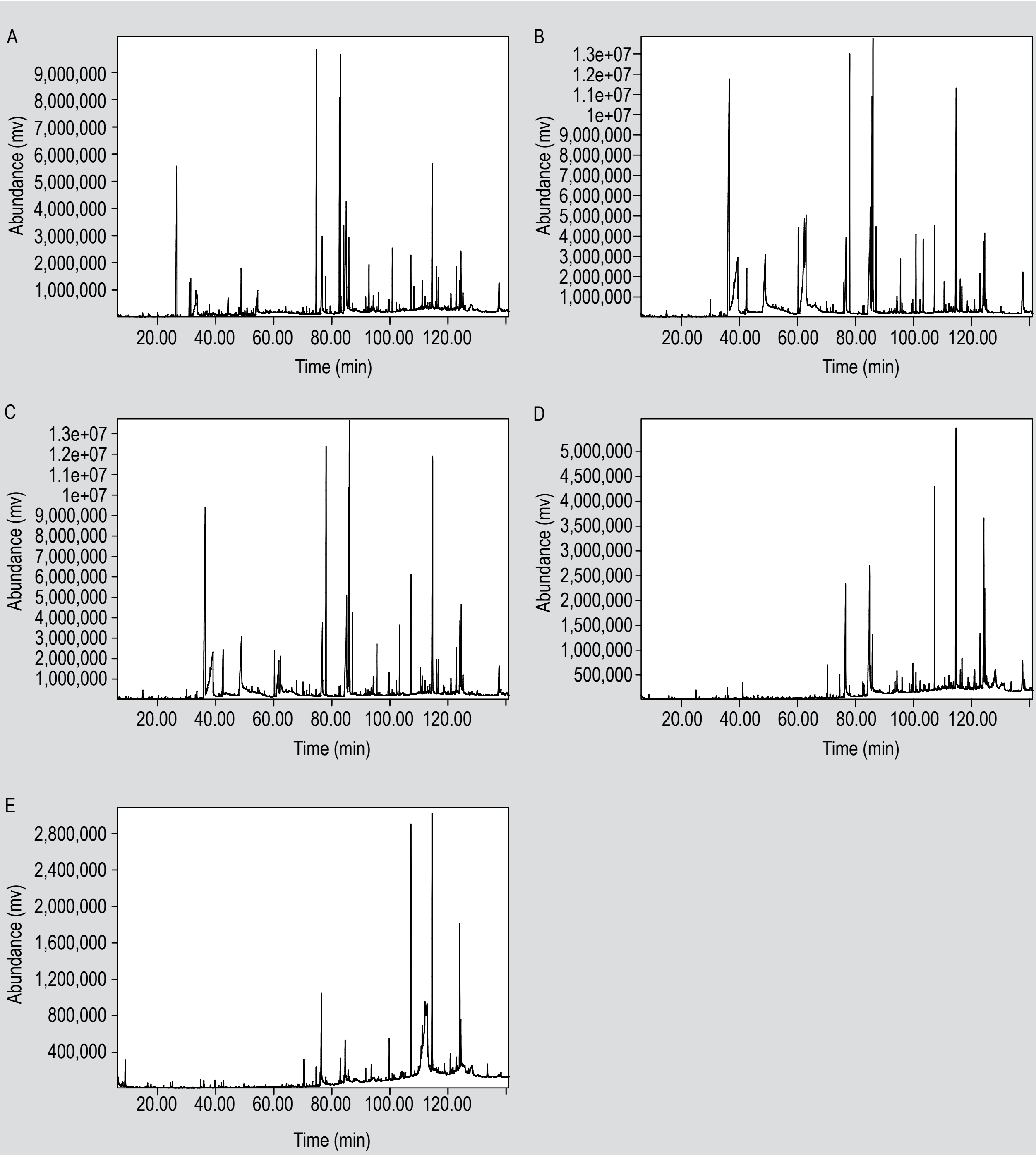

Figure 1. Total ion chromatograms of volatile components from hawthorn with different co-solvents: (A) methanol; (B) 95% ethanol; (C) anhydrous ethanol; (D) ethyl acetate; (E) without co-solvent.

4. Conclusions

The composition profile of hawthorn extracts obtained by SFE was similar to the one obtained by hydrodistillation, but SFE with greater polar co-solvents extracts extracted more hydrophilic compounds than conventional extraction methodology. Based on the co-solvent comparison study, it appears that several co-solvents are available other than supercritical CO_2 for the effective extraction of volatile components in hawthorn. The greater polarity the co-solvents has, the higher content the extracted volatile components yield. 39 compounds were extracted with SFE using methanol as co-solvent and identified by GC-MS. The current study will provide a broader use and application of the SFE technology to cosmetic, pharmaceutical and food industries.

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Supplementary material

Supplementary material can be found online at http://dx.doi.org/10.3920/QAS2012.0214.

Table S1. Gas chromatography-mass spectrometry identification of volatile components from hawthorn and relative contents with different co-solvents.

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