Available online at www.sciencedirect.com
SCIENCE DIRECT®
Analytica Chimica Acta 531 (2005) 97–104
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

Gas chromatography–mass spectrometry analysis of volatile compounds from *Houttuynia cordata Thunb* after extraction by solid-phase microextraction, flash evaporation and steam distillation

Minmin Liang[a,*], Meiling Qi[a], Changbin Zhang[b], Shan Zhou[c], Ruonong Fu[a], Junxiong Huang[b]

[a] *Department of Chemistry, School of Chemical Engineering and Materials Science, Beijing Institute of Technology, Beijing 100081, PR China*
[b] *Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China*
[c] *Beijing Municipal Center for Disease Prevention and Control, Beijing 100020, PR China*

Received 28 August 2004; received in revised form 29 September 2004; accepted 29 September 2004
Available online 22 January 2005

Abstract

Various sampling techniques including flash evaporation (FE), headspace solid-phase microextraction (HS-SPME) and steam distillation (SD) were compared for the gas chromatography–mass spectrometry of volatile constituents present in *Houttuynia cordata Thunb* (HCT). 2-Undecanone (22.21%) and houttuynum (7.23%) were predominant components of HCT samples obtained by HS-SPME whereas those levels were 3.95 and 3.60% in the same samples by FE and 25.93 and 6.60% in those by SD, respectively. SPME with polydimethylsiloxane (PDMS) fibre was more selective and particularly efficient for the isolation of biologically active compounds and afforded a higher yield of total compounds than FE and SD. A total of 60 compounds were detected in SPME extracts. While in FE and SD extracts, the detected compounds were 41 and 51, respectively. The total amount of compounds isolated by SPME was much larger than that isolated by FE or SD. Some minor constituents were isolated by SPME, but not by SD and FE. This carries great significance because of the importance of the oil volatiles to clinical therapy. HS-SPME is a powerful tool for determining the volatile constitutes present in the TCMs.

Keywords: Headspace solid-phase microextraction; Flash evaporation; Stream distillation; Volatile compounds; *Houttuynia cordata Thunb*

1. Introduction

Historically, especially in Asian areas, traditional Chinese medicines (TCMs) have played an important role in clinical therapy. Because of their high pharmacological activity, low toxicity and rare complication [1], more and more interests have been re-attracted in recent years. However, TCMs contain large amount of proteins, sugars, mucilage and tannin in addition to their volatile components, which makes the isolation and measurement of the volatile constituents as well as quality control of crude drugs and their medical preparations extremely difficult. Traditionally, the analysis of volatile compounds from TCMs is usually preceded by the extraction of essential oil by steam distillation, which often requires a large amount of sample and takes several hours to complete. The complex and time-consuming process for the preparation of samples sometimes further complicates the analytical results due to more influencing factors involved. Solid-phase microextraction (SPME) developed by Pawliszyn and coworkers in 1989, is a solventless extraction technique widely used in application of extraction from plants, food, biological and environmental samples [2–6]. SPME has diminished decomposition of plant compounds and cells, minimized activity of enzyme, and decreasing loss of those constituents. SPME techniques offer a useful alternative to conventional techniques. Flash evaporation gas chromatography (FE-GC) is also a rapid way of analyzing volatile compounds in TCMs. The analytical process of FE-GC involves the volatilization of the volatile components in the plant powder in a heater (a PYR-4A pyrolyzer

* Corresponding author. Tel.: +86 10 68941647.
E-mail addresses: minml@sina.com, minmlzcb@hotmail.com (M. Liang).

0003-2670/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2004.09.082

was used in this study) and the entrance into the GC column for the following chromatographic separation. With this method, the ground powder of a TCM material can be directly applied for the analysis and no extraction is required. Furthermore, the amount of sample used is greatly reduced and only a few milligrams of the ground powder of a TCM material are needed, which greatly simplify and shorten the analytical process for volatile compounds from TCMs. FE-GC is of great significance for the rapid identification and quality control of TCMs. The simplicity and the high sensitivity of the two procedures render them the desirable techniques for the analysis of volatile compounds in HCT.

Houttuynia cordata Thunb has been a time-honored traditional Chinese medicine (TCM). It provides a wide range of pharmacological activities including antiviral [7,8], antileukemic [9], antioxidative and antimutagenic effects [10,11]. Medicinal properties claimed for the drug have been attributed to its volatile oil [12,13]. A main component in the essential oil of this medicinal plant, decanoyl acetadehyde, is known to be of pharmacological effects, but it is unstable and easily oxidized (shown in Fig. 1) [14,15] in the process of distillation and during storage. It is often required that the essential oil of this plant should be freshly prepared before analysis and sometimes some stabilizing reagent should be added, which leads to the inconvenience of the analysis. This problem can be addressed perfectly by SPME–GC and FE-GC because they need no solvent extraction. In addition, as this plant exhibits an ample range of biological activity and is widely used in folk medicine, it is very important to extend the study to other volatile constituents present in this TCM.

Some publications are available concerning the essential oil composition of *H. cordata Thunb* by GC–MS [12–17], in which the essential oils were extracted by steam distillation and identified by GC–MS, and 34 compounds from wild *H. cordata Thunb* [16] and 42 compounds from cultivated *H. cordata Thunb* [17] were identified. However, little has been reported concerning the volatile compounds from *H. cordata Thunb* after extraction by solid-phase microextraction and flash evaporation [12–17].

In the present study, we compared three different extraction techniques including HS-SPME, FE and SD for GC–MS of volatile constituents from HCT. The temperature and the particle size of the ground powder of the plant for the FE process and the absorption time, temperature, headspace volume for the HS-PDMS process were optimized. Compounds extracted from HCT were identified according to mass spectra and by comparison with standard substances.

2. Experimental

2.1. Material

Samples of wild HCT were obtained commercially from Jiangxi Province, China. Prior to use, samples were air dried, ground in a high-speed rotary cutting mill, and then screened to give fractions 250, 150, 125 and 75 μm in size.

2.2. Extraction

2.2.1. Steam distillation extraction

The essential oil was prepared as follows: 100 g sample of 125 μm particle size was weighted into a 2000 mL distillation flask, 1000 mL deionised water was added and the mixture was distilled for 4 h. Oil was collected from the condenser and 0.2 mL of oil was diluted with 5 mL of *n*-hexane. Then the extracts were dried with anhydrous sodium sulfate. The particle size of the plant powder is important for steam distillation. In order to compare with FE results, the same particle size of 125 μm was used for steam distillation.

2.2.2. HS-SPME extraction

The manual SPME holder was used with a 100 μm polydimethylsiloxane fibre assembly (Supelco, Bellefonte, USA). Before use, the fibre was conditioned as recommended by the manufacturer. The extraction experiments were carried out in two series. The first was to determine the effect of the absorption temperature and time on extraction efficiency. First, the sample (2.0 g) of 125 μm particle size was hermetically sealed in an 8 mL vial, then SPME fibre was suspended in the HS and equilibrated for nine different time ranges of 5, 10, 15, 20, 25, 30, 40, 50 and 60 min in a thermostatic bath, which was set at the temperature of either 40, 50, 60, 80 or 100 °C. Only that part of the vial with the solid matrix was submerged, to keep the SPME fibre as cool as possible to improve the vapour phase/absorbent fibre coating partition coefficient [18]. The second group of experiments was performed to establish the effect of headspace volume on extraction efficiency. These experiments were performed using 2 g of sample in different size vials, with a headspace volume

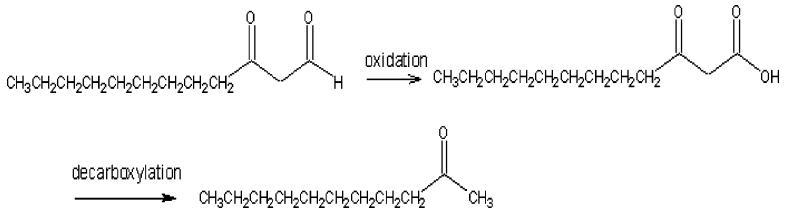

Fig. 1. The houttuynum (decanoyl acetaldehyde) may be converted into 2-undecanone via both oxidation and decarboxylation.