Ultrasonics Sonochemistry 16 (2009) 795–799

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Ultrasound-assisted extraction coupled with under vacuum distillation of flavour compounds from spearmint (carvone-rich) plants: Comparison with conventional hydrodistillation

Carla Da Porto *, Deborha Decorti

Dipartimento di Scienze degli Alimenti, Università di Udine, via Sondrio 2/A, 33100 Udine, Italy

ARTICLE INFO

Article history:
Received 2 February 2009
Received in revised form 28 March 2009
Accepted 28 March 2009
Available online 5 April 2009

Keywords:
Mentha spicata
GC–MS
Essential oil
Ultrasound-assisted extraction
Vacuum distillation

ABSTRACT

Ultrasonically assisted extraction of flavour compounds from different varieties of *Mentha spicata,* using 70% ethanol, have been carried out for 5, 10 and 15 min and coupled with under vacuum distillation. The ultrasound distilled extracts have been analysed by GC–MS and compared with essential oils obtained by hydrodistillation. The results have showed that ultrasonically assisted extraction in combination with under vacuum distillation have provided extracts with higher flavouring strength due to the increased concentration of desirable oxygenated compounds (from 5 to 8 times) compared with hydrodistillation. Extraction yields of flavour volatiles have been calculated giving a range 0.04–0.13% by ultrasound and 0.01–0.02% by hydrodistillation.

1. Introduction

The designation 'spearmint' is commercially applied to several species and varieties of the genus *Mentha* possessing a distinct and characteristic odour profile due to high carvone content.

Native spearmint oil is produced either from the species *Mentha spicata* L. or from the hybrid *Mentha* × *villoso-nervata* Opiz (*Mentha Longifolia* L. × spicata), whereas Scottish spearmint oil is obtained from *Mentha* × *gentilis* L. var *cardiaca* Gray (*Mentha arvensis* L. × *spicata*) [1].

Essential oils are products of the secondary metabolism of plants, and generally are fragrant volatile materials consisting of complex mixtures of mono- and sesqui-terpene hydrocarbons, and oxygenated materials biogenically derived from them. Essential oils are used in flavourings, perfumes, in aromatherapy, as insect and animal repellents, in pharmaceutical preparations, as anti-microbial agents and in many other ways. The recovery of an essential oil from plant is basically by water distillation (hydrodistillation) or steam distillation [2]. These techniques take at least several hours and require the application of heating, which can produce the degradation of thermo labile compounds present in the starting plant material and an incomplete collection of compounds responsible for its fragrance [3].

The spearmint oil market, while smaller than peppermint oil, it is substantial and it is one of the larger essential oil commodities. Spearmint oil is used as a flavouring in sweets, beverages, jellies, salads, soups, cheeses, meats, fish, sauces, gum, ice cream and commercially prepared hygienic products (toothpaste, mouthwash, shampoos and soaps, etc.).

The benefit of using ultrasound in plant extraction has already been demonstrated by bioactive substances [4–7] although few applications are available concerning the extraction of aroma compounds [8–10]. The ultrasonic enhancement of extraction is attributed to disruption of cell walls, particle size reduction and enhanced mass transfer of the cell content via cavitation bubble collapses [4,11].

In this paper, ultrasonically assisted extraction has been coupled with vacuum distillation in order to extract and subsequently concentrate and separate, without excessive heating, the aroma compounds from fresh leaves of two varieties of spearmint (*M. spicata*), plant largely used as flavouring in food preparation, perfumery and medicine. The potential of ultrasonic extraction coupled with under vacuum distillation on flavour compounds recovery has been compared with hydrodistillation.

2. Materials and methods

2.1. Plant material

Fresh leaves of *Mentha* have been harvested at the stage of full bloom at different elevations in two parts of Friuli Venezia Giulia (North–East Italy): Low-Friuli (200 m) and High-Friuli (700 m). Leaves samples have been randomly collected from different parts

* Corresponding author. Tel.: +39 0432 558141; fax: +39 0432 558130.
E-mail address: carla.daporto@uniud.it (C. Da Porto).

1350-4177/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2009.03.010

of plants and have been selected to represent leaves of all ages. The *Mentha* species have been identified by Valentino Casolo, Department of Applied Biology in Plant Protection, University of Udine, Udine (Italy) as *M. spicata*. The vouchers specimen had been deposited at the Herbarium of Natural Science Museum of Udine, Udine, Italy (voucher number MFU 160/66).

2.2. Essential oil hydro-distillation (HD)

An aliquot of 1500 g of fresh leaves of *M. spicata* had been submitted to hydrodistillation with a Clevenger type apparatus according to the standard procedure described in the European Pharmacopoeia [12]. The essential oil had been co-distilled with water for 3 h, collected, dried under anhydrous sodium sulphate and stored at 0 °C until used. Hydro-distillations have been performed at least three times for each sample and the mean values of the extraction yields were reported.

2.3. Ultrasound and vacuum distillation apparatus and procedure (UVD)

Sonochemical experiments have been carried out using an ultrasonic probe (Elettrofor Sonoplus model HD2200 with TT13FZ probe, Bandelin, Berlin; 20-kHz working frequency; 200 W – amplitude setting displayed in % on the scale of 10–100). The probe had been operated at 25% of the scale; this operating condition had been chosen on the good results obtained in a previous work [13]. An aliquot of 50 g of fresh *Mentha* leaves had been added with 100 mL of 70% ethanol v/v (extracting solvent) in a 250 mL conical flask and the probe had been submerged about 2–5 mm under the surface of the mixture. The choice of ethanol–water solution (70% by volume) as extracting solvent had been made based on its polarity relative to the aroma compounds of *Mentha* and its acceptability for practical use. The mixture had been sonicated for 5, 10 and 15 min. The maximum temperature reached at the end of each sonication had been lower than 40 °C. A stirrer had been used to obtain good solvent/plant material contact.

The liquid extract had been separated from the residual plant material by filtration and concentrated under vacuum at 50 °C and 170 mm Hg in a rotary evaporator. Vacuum distillation had been applied to the ultrasound extracts of *M. spicata* in order to separate and concentrate their fragrant volatile compounds that had a high boiling point and might undergo decomposition on heating at atmospheric pressure.

Extractions and consequently solvent distillations had been performed at least three times for each sample UVD5 (5 min sonication), UVD10 (10 min sonication) and UVD15 (15 min sonication).

2.4. GC–MS analysis

The essential oils and ultrasound distilled extracts compositions have been determined by GC. GC–MS analysis which had been performed using a Varian 3400 gas chromatograph coupled to a Varian Saturn ion trap detector. The fused-silica column had been a DB-5 (Supelco, Bellafonte, PA) (30 m × 0.25 mm i.d., film thickness 0.25 m). GC–MS data have been obtained using the following conditions: carrier gas helium (He 99.9995%); flow rate 2.0 ml min^{-1}; the split ratio 1/70 (v/v). An aliquot of 100 mg of essential oils had been diluted with 1 mL *n*-hexane and 1.0 l had been injected into the GC–MS system. The GC analysis of the ultrasound distilled extracts had been carried out on the distilled solvent. It had been ex-

Table 1
Chemical composition and yields of the essential oil (HD) and ultrasound distilled extracts (UVD5, UVD10, UVD15) from fresh leaves of *Mentha spicata* from Low-Friuli.

Compound	Calculated LRI	Ref RI[a]	Ref RI[b]	Sample			
				Hydrodistillation	Ultrasound and vacuum distillation		
				HD Mean[c] ± CV (%)	UVD5 Mean[c] ± CV (%)	UVD10 Mean[c] ± CV (%)	UVD15 Mean[c] ± CV (%)
α-Pinene	938	939		27.5 ± 13.71	–	–	–
Sabinene	977	972		32.4 ± 4.72	–	–	–
β-Pinene	979	981		57.1 ± 3.20	–	–	–
Myrcene	994	999	992	66.1 ± 2.61	–	–	–
3-Octanol	999	992		18.1 ± 6.42	168.5 ± 18.95	255.5 ± 11.12	234.7 ± 11.20
Limonene	1033	1030		963.9 ± 2.58	167.9 ± 20.03	264.1 ± 3.47	
1.8-Cineole	1035	1030		103.7 ± 4.91	2777.4 ± 7.06	2844.2 ± 5.67	3237.7 ± 14.86
trans-β-Ocimene	1044	1043	1050	75.7 ± 4.36	–	–	–
Menthol	1173	1171		10.3 ± 3.68	–	–	–
α-Terpineol	1195	1195		62.8 ± 14.37	110.4 ± 5.32	78.50 ± 11.63	341.0 ± 16.37
DL-Carvone	1253	1253		3302.6 ± 4.65	15227.3 ± 2.38	22481.2 ± 2.12	25345.0 ± 16.26
3-Carvomenthenone	1261			209.7 ± 4.29	962.1 ± 5.38	1983.3 ± 1.85	1920.1 ± 15.77
Piperitenone	1278	1277	1342	246.6 ± 1.72	1097.0 ± 5.30	2579.3 ± 7.08	2887.0 ± 13.88
Menthyl acetate	1297			20.4 ± 2.01	–	–	–
Eucarvone	1349			64.8 ± 3.10	–	109.7 ± 5.65	–
β-Elemene	1394	1393		143.3 ± 3.85	–	–	–
β-Guaiene	1405	1411	1490	16.1 ± 7.20	–	–	–
Isocaryophyllene	1430	1438		275.8 ± 5.31	–	–	–
β-Farnesene	1465	1467	1445	43.5 ± 3.95	–	–	–
Germacrene D	1491	1487		652.1 ± 4.42	450.8 ± 2.66	504.7 ± 5.28	440.4 ± 11.07
Elemicin	1507	1514		38.9 ± 4.56	423.4 ± 1.61	559.4 ± 4.78	472.7 ± 12.97
Viridiflorol	1588	1589	1590	21.0 ± 4.33	–	–	–
Cedrenol	1605	1604		83.9 ± 2.80	81.4 ± 11.41	89.3 ± 4.76	–
α-Cadinol	1668	1676		26.5 ± 4.73	–	–	–
Monoterpene hydrocarbons				1146.9 ± 5.37	167.9 ± 20.02	260.3 ± 3.47	–
Oxygenated monoterpenes				4096.6 ± 4.79	20174.2 ± 5.09	30076.2 ± 5.67	33730.9 ± 15.43
Sesquiterpene hydrocarbons				1130.8 ± 4.94	450.7 ± 2.65	504.6 ± 5.27	440.3 ± 11.06
Oxygenated sesquiterpenes				170.3 ± 4.11	504.7 ± 6.51	648.6 ± 4.77	472.7 ± 12.97
Yield (%)				0.01 ± 4.89	0.04 ± 8.01	0.06 ± 6.23	0.07 ± 5.36

[a] http://www.flavornet.org.
[b] Adams [15].
[c] ug g^{-1} fresh plant.