Journal of Chromatography A, 1217 (2010) 7345–7350

Contents lists available at ScienceDirect

Journal of Chromatography A

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

A surprising method for green extraction of essential oil from dry spices: Microwave dry-diffusion and gravity

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ARTICLE INFO

Article history:
Received 27 July 2010
Received in revised form
23 September 2010
Accepted 24 September 2010
Available online 1 October 2010

Keywords:
Microwave
Extraction
Dry-diffusion
Earth gravity
Essential oil
Spices

ABSTRACT

Without adding any solvent or water, we proposed a novel and green approach for the extraction of secondary metabolites from dried plant materials. This "solvent, water and vapor free" approach based on a simple principle involves the application of microwave irradiation and earth gravity to extract the essential oil from dried caraway seeds. Microwave dry-diffusion and gravity (MDG) has been compared with a conventional technique, hydrodistillation (HD), for the extraction of essential oil from dried caraway seeds. Essential oils isolated by MDG were quantitatively (yield) and qualitatively (aromatic profile) similar to those obtained by HD, but MDG was better than HD in terms of rapidity (45 min versus 300 min), energy saving, and cleanliness. The present apparatus permits fast and efficient extraction, reduces waste, avoids water and solvent consumption, and allows substantial energy savings.

1. Introduction

An analytical procedure for essential oil and aromas from herbs or spices comprises two steps: distillation or extraction which takes at least several hours and analysis which is finished after 15 min. Distillation or extraction is frequently done by a prolonged heating and stirring in water or solvent using Clevenger, Dean–Stark or Likens–Nikerson apparatus. This distillation consumes more than 70% of total process energy and time with high consumption of solvent [1–3]. Thus, other techniques should evolve with the aim of reducing this sample preparation step. Furthermore, with the development of the "Green Chemistry" concept "green extraction techniques" are becoming more and more attractive. Much attention has been devoted to the application of microwave dielectric heating for the extraction of essential oil such as compressed air microwave distillation (CAMD) [4], vacuum microwave hydrodistillation (VMHD) [5], microwave hydrodistillation (MWHD) [6], solvent free microwave extraction (SFME) [7], microwave-accelerated steam distillation (MASD) [8], microwave steam distillation [9] and microwave hydrodiffusion and gravity (MHG) [10]. Now, the extraction of essential oil under microwave irradiation without adding of any organic solvent or water is one of the upcoming extraction techniques that can offer high reproducibility in shorter times, simplified manipulation, reduced solvent consumption and lower energy input. There have been two reported articles in the current literature regarding "green microwave" extraction techniques of essential oil [10,11]. Microwave hydrodiffusion and gravity (MHG) have been reported by Chemat and co-workers as an efficient, economical and environmental friendly approach [10,12,13]. MHG was conceived for the extraction of volatile compounds from fresh plant materials with a minimum 60% of initial moisture [13]. It works without using any solvent or water, when microwave energy is applied, the natural water within the plant tissue heats up, distorting the plant cells, causing them to rupture and dropping by earth gravity. Also, Chemat and co-workers [11] have been recently developed another type of green microwave design: microwave steam diffusion (MSDf). It was also designed and constructed as a cleaner and eco-friendly process for the extraction of essential oil from dry plant materials. MSDf was applied for the extraction of dry lavender flowers which were submitted to a combined process of microwave irradiation and saturated steam diffusion. Microwaves distend the plant cells and the steam carrying the essential oil and drop by earth gravity outside the microwave reactor. Certainly, the most remarkable benefit of the both processes (MHG and MSDf) was their rapidity and energy saving. However, these both systems needed the presence of water, as "in situ" water in the case of MHG and saturated steam in the case of MSDf, to release the essential

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doi:10.1016/j.chroma.2010.09.062

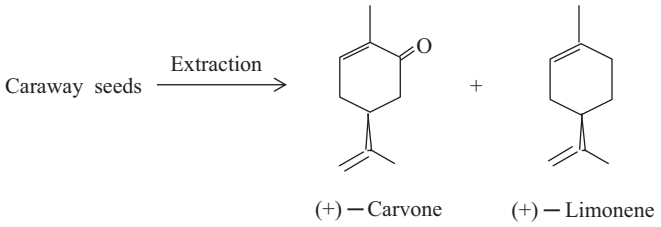

Fig. 1. Extraction of carvone and limonene from caraway seeds.

from the plant materials. To simplify these both processes, we are surprise that it can be possible to extract essential oil from dried plant materials without the addition of any solvent or water. This new and original technique has been applied to the extraction of essential oils from dried caraway seeds without any added solvent or water.

Caraway (*Carum carvi L.*) essential oil has been used as a fragrance component in cosmetic preparations including liquors, perfumes and toothpaste, while the seeds have been used as a spice and food flavouring agent [14]. Carvone and limonene are the main components (Fig. 1) with carveol, pinene, and camphene [15,16]. Recently carvone has been introduced as an effective inhibitor against sprouting, mainly in stored onions and potatoes, whereas limonene is being investigated as a raw material to produce carvone [17–19]. In practice, steam-distillation, hydrodistillation and organic solvent extraction are the most widely used procedures for the extraction of essential oil from caraway seeds. Losses of some volatile compounds, low extraction efficiency, degradation of unsaturated or ester compounds through thermal or hydrolytic effects and toxic solvent residue in the extract may be encountered using these extraction methods. Up to now, several new extraction processes have been reported for the extraction of caraway essential oil such as supercritical fluid extraction, ultrasound assisted extraction, microwave-assisted extraction and hydrodistillation by direct induction heating assisted by magnetic field (Table 1) [20–23]. The aim behind the development of these new extraction technologies was the extraction of caraway essential oil and possible improvement of its yield. Losses of some volatile compounds, low extraction efficiency, degradation of unsaturated or ester compounds through thermal or hydrolytic effects and high energy consumption solvent may be encountered using these extraction methods.

This present study has been planned with the aim to design and optimize a new and green technique for the extraction of essential oils from dried caraway seeds without any added solvent or water, just under the influence of microwave-heating and earth gravity, namely Microwave dry-diffusion and gravity (MDG) (Fig. 2). The results obtained by the optimized MDG were compared with those achieved using a conventional hydrodistillation method. We intend to make appropriate comparison in terms of extraction time, yield, aromatic composition, energy used and environmental impact. Finally, extraction mechanism was proposed to understand the action of MDG.

2. Experimental

2.1. Plants material

Caraway seeds (*Carum. carvi* L.) were purchased from a market in Avignon (France). The initial moisture content of dried caraway seeds was 7.75%. Only the dry plant material was employed in all extractions.

2.2. Microwave dry diffusion apparatus and procedure

Microwave dry-diffusion and gravity (MDG) has been performed in a Milestone NEOS microwave laboratory illustrated in Fig. 2. This is a multimode microwave reactor 2.45 GHz with a maximum delivered power of 900 W variable in 10 W increments. The extraction vessels are made from Pyrex and have a capacity of 1500 ml. Time, temperature, pressure and power can be controlled with the "easy-WAVE" software package. During experiments temperature was monitored by temperature sensor optic fibers which were inserted in the centre and outer layer of sample and also in the sample reactor. Temperature variations in different parts of plant material and reactor were measured continuously and data was saved automatically. This feedback helped in controlling the temperature by microwave power regulator.

In a typical MDG procedure at atmospheric pressure, batch of 200 g of dried caraway seeds were packed and heated into a multimode microwave reactor without added solvent or water. The direct interaction of microwaves with dried plant material favours the release of essential oils trapped inside the cells of plant tissues. The essential oil thus moves naturally downwards by earth gravity on a spiral condenser outside the microwave cavity where it condensed. The essential oil is collected, dried with anhydrous sodium sulphate and stored at 4 °C until analyzed. Extractions were performed at least three times, and the mean values were reported.

2.3. Hydrodistillation apparatus and procedure

For comparison, 200 g of dried caraway seeds was submitted to hydrodistillation (HD) with a Clevenger-type apparatus according to the European Pharmacopoeia and extracted with 1 L of water until no more essential oil was obtained [24]. The essential oil was collected, dried under anhydrous sodium sulphate and stored at 4 °C until use. Extractions were performed at least three times, and the mean values were reported.

2.4. Gas chromatography–mass spectrometry

The essential oils were analyzed by gas chromatography coupled to mass spectrometry (GC–MS) (Hewlett-Packard computerized system comprising a 6890 gas chromatograph coupled to a 5973A

Table 1
Recent publications on the extraction of caraway essential oil.

Method	Solvent	Comments	Year/reference
Supercritical fluid extraction (SFE)	CO_2	SFE (t = 45 min) compared with Soxhlet extraction ensures increase in yield of carvone with shorter extraction time.	1999 [20]
Ultrasound-assisted extraction (UAE)	n-hexane	UAE (t = 60 min) was more rapid and better in term of carvone yield than conventional system.	2004 [21]
Microwave-assisted extraction (MAE)	Hexane	MAE (t = 60 min) gives more rapid extraction and yield than conventional system.	2005 [22]
Hydrodistillation by direct induction heating assisted by a magnetic field (DIHMF)	Water	DIHMF (t = 7 h) was found more efficient than conventional hydrodistillation, with better quality of carvone/limonene.	2006 [23]