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An original solvent free microwave extraction of essential oils from spices

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ABSTRACT: Attention is drawn to the development of a new and green alternative technique for the extraction of essential oils from spices. Solvent-free microwave extraction (SFME) is a combination of dry distillation and microwave heating without added any solvent or water. SFME and hydrodistillation (HD) were compared for the extraction of essential oil from three spices: ajowan (*Carum ajowan*, Apiaceae), cumin (*Cuminum cyminum*, Umbelliferae), star anise (*Illicium anisatum*, Illiciaceae). Better results have been obtained with the proposed method in terms of rapidity (1 h vs. 8 h), efficiency and no solvent used. Furthermore, the SFME procedure yielded essential oils that could be analysed directly without any preliminary clean-up or solvent exchange steps. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS: solvent-free; microwave; dry distillation; essential oil; ajowan (*Carum ajowan*); cumin (*Cuminum cyminum*); star anise (*Illicium anisatum*)

Introduction

Essential oils in spices are complex mixtures of volatile substances, ordinarily terpenes, sesquiterpenes and oxygenated derivatives, generally present at low concentrations. Before such substances can be analysed, they have to be extracted from the matrix. Several extraction processes are developed in order to obtain the best aromatic substance to satisfy the needs of the perfumer and of the flavourist, in accordance with the world-wide legislation governing the use of this product.[1–2]

Recently, an original method for extracting natural products by using microwave energy has been developed in our laboratory. Based on a relatively simple principle, this method involves placing vegetable material in a microwave reactor without any added solvent or water. The internal heating of the *in situ* water within the plant material distends it and makes the glands and oleiferous receptacles burst. This process thus frees essential oil, which is evaporated by the *in situ* water of the plant material by azeotropic distillation. The vapour then passes through a condenser outside the microwave cavity, where it is condensed. The distillate is collected continuously in the receiving flask. The excess of water is refluxed to the extraction vessel. The essential oil is collected directly and dried without any added solvent extraction step. SFME is based on the combination of microwave heating and dry distillation, and is performed at atmospheric pressure, the SFME apparatus is illustrated in detail in Figure 1. SFME is not a modified microwave-assisted solvent extraction (MASE or MAE), which use non-polar or polar solvents, and it is also not a modified hydrodistillation, which use a large quantity of water.[3–4]

To investigate the potential of SFME, comparisons have been made with hydrodistillation for the extraction

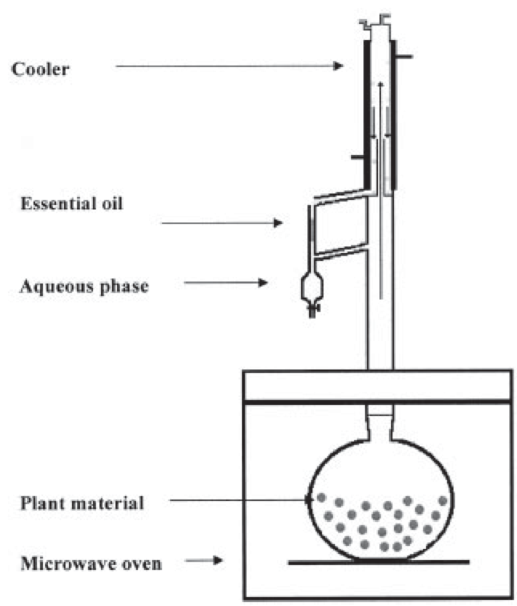

Figure 1. Solvent-free microwave extraction

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of essential oils from three spices; ajowan (*Carum ajowan*, Apiaceae); cumin (*Cuminum cyminum*, Umbelliferae); and star anise (*Illicium anisatum*, Illiciaceae)) commonly used in the food, pharmaceutical and cosmetic industries. We report appropriate comparisons in terms of extraction time, yield and aromatic composition.

Experimental

Spices

Ajowan is the fruit of *Carum ajowan*, a mediterranean herb of the family Apiaceae. Its strong aroma is used to perfume food, essentially in the Indian Ocean regions. It is used also in medicine to treat coughs, throat infections, digestive troubles and fever. Ajowan's flavour is similar to thyme, although stronger and less subtle.[5]

Cumin is the pale green seed of *Cuminum cyminum*, a small herb with small white flowers in the parsley family. The seed is elliptic and deeply furrowed. Cumin is native to the shores of Mediterranean Sea but it is currently grown in many places. Nowadays, cumin seeds form an important part of curry powder in India and are also commonly used in North African cooking. It is actually benefical for digestive problems and distention. Cumin has a distinctive slightly bitter yet warm flavour.[5]

Star anise is the fruit of a Chinese tree, *Illicium anisatum*, from the family Illiciaceae closely related to the Magnioliaceae. The essential oil resides mainly in the pericarp. Star anis is particularly imported in France to prepare the famous liquor called 'pastis'. It is used in medicine to treat digestive troubles and rheumatism and to pacify children. Star anis has a distinctive warm, sweet and aromatic flavour which is reminiscent of aniseed.[5]

SFME Apparatus and Procedure

SFME extractions were performed in a Milestone ETHOS 1600 batch reactor, which is a multimode microwave reactor operating at 2455 MHz with a maximum delivered power of 1000 W, variable in 10 W increments. The dimensions of the PTFE-coated cavity are 35 × 35 × 35 cm. During the experiments, time, temperature, pressure and power were controlled using the 'easy-WAVE' software package. Temperature was monitored with the aid of a shielded thermocouple (ATC-300) inserted directly into the sample container.

In a typical SFME procedure, 250 g of dry seeds were moistened prior to extraction by soaking in water for 1 h, then draining off the excess water. This step is essential to give the seeds the initial moisture. Moistened seeds were next placed in the reactor without any added solvent or water. The essential oil is collected, dried with anhydrous sodium sulphate and stored at 0 °C until used.

HD Apparatus and Procedure

Samples (250 g) of each spice were submitted to hydrodistillation with a Clevenger-type apparatus[6] according to the *European Pharmacopoeia* and extracted with 4 l water for 8 h (until no more essential oil was obtained). The essential oil was collected, dried with anhydrous sodium sulphate and stored at 0 °C until used.

Gas Chromatography–Mass Spectrometry Identification

The essential oils were analysed by GC–MS (Hewlett-Packard computerized system comprising a 5890 gas chromatograph coupled to a 5971A mass spectrometer) using a fused-silica capillary column with an apolar stationary phase SBP5™ (60 m × 0.32 mm i.d., 1 μm film thickness). GC–MS were obtained using the following conditions: carrier gas, He; flow rate, 1 ml/min; split, 1:20; injection volume, 0.1 μl; injection temperature, 250 °C; oven temperature programme, 60–200 °C at 4 °C/min, then held at 200 °C for 30 min; the ionization mode used was electronic impact at 70 eV. Identification of the components was achieved from their retention indices on both columns, determined with reference to a homologous series of alkanes, and by a comparison of their mass spectral fragmentation patterns with those stored in the data bank (Wiley/NBS library) and the literature.

Physical Constants

Essential oils of spices have been analysed according to the standard method of AFNOR. The usual physical constants defining the essential oil have been determined at 20 °C: specific gravity, refractive index, optical rotation and solubility in 80% or 70% ethanol.[7]

Results and Discussion

SFME is an original combination of microwaves and dry distillation. The apparatus is relatively simple. The isolation and concentration of essential oils are performed in a single stage. The obtained solution can be analysed directly without any preliminary clean-up or solvent exchange steps by GC–MS. The extraction time, yield and chemical composition of essential oils from the three spices are shown in Table 1.

One of the advantages of the SFME is rapidity. For HD or SFME, the extraction temperature is equal to water boiling temperature at atmospheric pressure (100 °C). Figure 2 represents the temperature profiles during HD and SFME of the three spices' essential oils. To reach the

Table 1. Composition, and olfactive notes of ajowan, cumin, and star anise essential oils obtained by SFME and HD

RI	Compounds	Ajowan		Cumin		Star anise		Olfactive note
		HD	SFME	HD	SFME	HD	SFME	
1031	α-Pinene	1.3	—	1.6	—	2.1	1.2	Warm, resinous and refreshing
1116	β-Pinene	4.8	1.5	16.2	5.9	—	—	Smell of dry wood, resinous, slightly clinging
1126	Sabinene	—	—	1.1	—	—	—	Warm, wooded-herbaceous, lightly spiced, not very clinging
1157	3-Carene	—	—	—	—	0.8	—	Sweet, diffused, penetrating
1164	β-Myrcene	0.8	—	1.7	0.7	—	—	Sweet, smell of resinous gum, slightly clinging
1194	α-Phellandrene	—	—	0.6	—	—	—	Wooded-pungent, fresh smell of citrus, very light note of mint
1215	Limonene	—	—	0.5	—	11.6	6.6	Fresh, light, perfume of sweet citrus fruit
1235	1,8-Cineole	—	—	—	0.7	1.5	1.5	Fresh, light, freshly camphorated
1258	γ-Terpinene	28.6	16.4	22.3	12.9	—	—	Herbaceous, smell of citrus fruit
1284	*p*-Cymene	29.2	21.2	18.4	12.1	—	—	Citrus fruit note, reminiscent of lemon and bergamot
1558	Linalol	—	—	—	—	1.1	1.7	Fresh and floral with a slight note of citrus
1694	Estragol	—	—	—	—	1.9	3.2	More herbaceous than anethole, but not so sweet
1719	α-Terpineol	—	—	—	—	1.0	—	Delicately floral and sweet
1816	Cumin aldehyde	—	—	22.8	37.4	—	—	Irritant, pungent and herbaceous
1832	α-Terpin-7-enal	—	—	14.4	29.1	—	—	
1854	*p*-Propenyl anisole	—	0.7	—	1.3	—	—	
1858	Anethole (*E*)	—	—	—	—	78.0	81.4	Herbaceous, warm and sweet
2060	Anis aldehyde	—	—	—	—	2.0	3.9	Floral, smell of hay
2205	Thymol	35.4	60.3	—	—	—	—	Strong, herbaceous, and warm, ferly clinging
Extraction time (h)		8	1	8	1	8	1	
Yield (%)		3.34	1.41	1.43	0.63	4.16	1.38	

Compounds listed in order of elution; RI, retention index on SBP5™ column; HD, hydrodistillation (8 h); SFME, solvent-free microwaves extraction (1 h); yields expressed in g essential oil/kg spices.

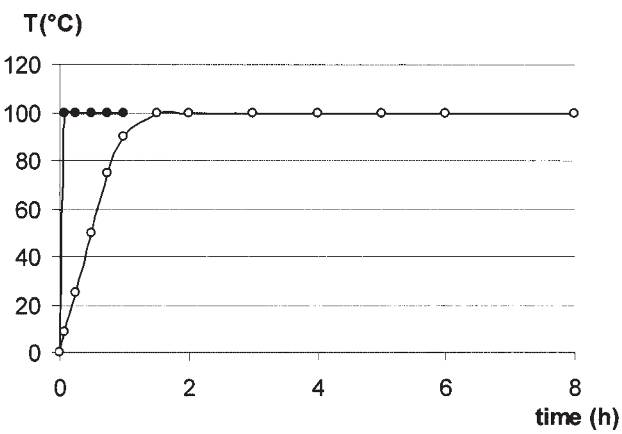

Figure 2. Temperature profiles during HD and SFME of spices essential oil (○, HD; ●, SFME)

extraction temperature (100 °C) and thus obtain the distillation of the first essential oil droplet, it is necessary to heat only 5 min with SFME against 90 min for HD. The quantity of essential oil obtained by SFME after 1 h was sufficient for analytical determinations. It was interesting to compare SFME yields after 1 h with HD yields after 8 h (until no more essential oil was obtained). The SFME method also allowed a substantial saving of energy. HD required heating of approximately 10 kg water and 1 kg spices to the extraction temperature, and evaporating the water and essential oil for 8 h, whereas the SFME method only required heating 1 kg moistened spices and evaporating the *in situ* water and essential oil of the plant material for 1 h.

The yields of essential oils from spices obtained by HD were 3.34% for ajowan, 1.43% for cumin and 4.16% for star anise, and those obtained by SFME were 1.41% for ajowan, 0.63% for cumin and 1.38% for star anise. Regarding the yield ratios between SFME (1 h) and HD (8 h), SFME allows extraction of 33%, 42% and 44%, respectively, of the essential oil present in the treated spices, star anis, ajowan and cumin. It appears that cumin, which gives the smallest yield of essential oil, achieves the highest ratio (44%). Star anise, which gives a very good yield by both HD and SFME, has the lowest ratio. It seems that SFME is a more appropriate extraction method for small seeds such as ajowan and cumin which have similar shape. After a long extraction time (8 h), SFME and HD gives the same yield in essential oils.

However, the composition of essential oils isolated by SFME and HD show a major difference in terms of their aromatic profiles. The star anise essential oil isolated by both HD and SFME is widely dominated by *trans*-anethole (an oxygenated compound), 78% and 81.4%, respectively. Limonene, a monoterpene, which is the second important compound, is only present at 11.6% and 6.6%, respectively, by HD and SFME. The cumin essential oil isolated by either SFME or HD contains the same five dominant compounds but in different amounts: cumin aldehyde (37.4% and 22.8%

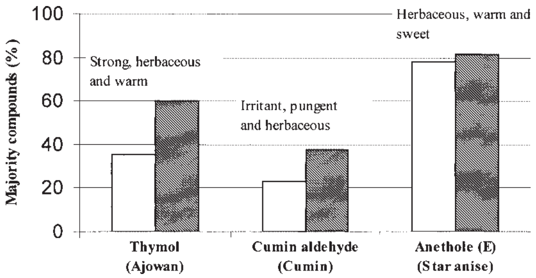

Figure 3. Proportion of the major compounds in the tree essential oils (%) (□, HD; ▧, SFME)

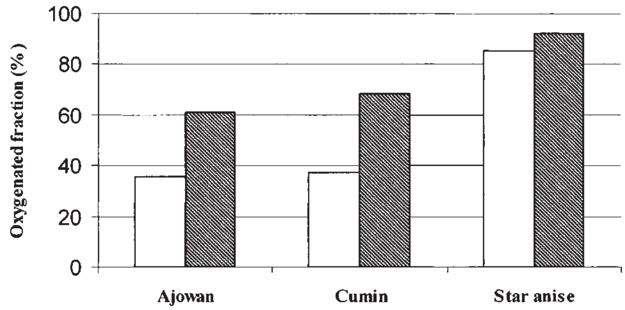

Figure 4. Proportion of the oxygenated fraction in the three essential oils (%) (□, HD; ▧, SFME)

respectively), α-terpin-7-enal (29.1% and 14.4%), γ-terpinene (12.9% and 22.3%), *p*-cymene (12.1% and 18.4%) and β-pinene (5.9% and 16.2%). Ajowan essential oil isolated by SFME is characterized by an important components the oxygenated monoterpene thymol (60.3%), whereas oil extracted by HD is dominated by three compounds in relatively similar amounts: thymol (35.4%), *p*-cymene (29.2%) and γ-terpinene (28.6%). The two latter monoterpenes are also present in the essential oil extracted by SFME, but in lower proportions, 16.4% and 21.2% for γ-terpinene and *p*-cymene respectively. These results are summarized in Figure 3 and Table 1.

The three essential oils isolated from spices by SFME are dominated by the oxygenated fraction (Figure 4). Ajowan and cumin, with similar shape, present the same behaviour: the relative amount of oxygenated fraction in essential oil is less than 40% for HD and more than 60% for SFME extractions. Substantial higher amounts of oxygenated compounds and lower amounts of monoterpenes are present in the SFME extract. Monoterpenes are less valuable than oxygenated compounds as they contribute to the fragrance of the essential oil to a minor extent. Conversely, oxygenated compounds are highly odoriferous and hence are the most valuable. Herbaceous and warm notes characteristic of spices are highlighted by SFME (Table 1). Thymol is responsible for powerful herbaceous and warm notes for ajowan essential oil; cumin aldehyde gives an irritant, pungent and herbaceous note for cumin essential oil; and anethole has an herbaceous, warm and sweet note for star anise essential oil.

There are slightly fewer compounds in the essential oil extracted by SFME compared with that obtained by HD (Table 1). Indeed, some minor compounds are present only in essential oils isolated by HD: α-pinene (1.3%) and β-myrcene (0.8%) for ajowan essential oil; α-pinene (1.6%), sabinene (1.1%), α-phellandrene (0.6%) and limonene (0.5%) for cumin essential oil; and 3-carene (0.8%) and α-terpineol (1%) for star anise essential oil. The loss of some compounds in SFME is not an artefact of the extraction. The reduction of extraction time and the amount of water used in SFME method necessarily reduce the deterioration of principal compounds by thermal and hydrolytic reactions (hydrolysis, *trans*-esterification or oxidation) and the generation of degradation products. Water is a polar solvent that accelerates many reactions, especially reactions via carbocation as intermediates.

Essential oils of spices have been also analysed according to the standard method of AFNOR to determine the usual physical constants defining the essential oil extracted by either SFME or HD: specific gravity, refractive index, optical rotation and solubility in 80% or 70% ethanol at 20 °C (Table 2). There is no significant difference between the physical constants of essential oils obtained by SFME or HD. In comparison with European standards, there is a slight difference between the extracted essential oils and the reference ones.

Table 2. Physical constants of ajowan, cumin and star anise essential oils obtained by HD and SFME at 20 °C

		Ajowan		Cumin		Star anise	
		HD	SFME	HD	SFME	HD	SFME
Specific gravity	d_{20}^{20}	0.923	0.933	0.928	0.950	0.982	0.985
Refractive index	n_D^{20}	1.4972	1.5008	1.5017	1.5096	1.5459	1.5494
Optical rotation	$[\alpha]_D^{20}$	[a]	[a]	3.6°	2.2°	−1.6°	0.1°
Solubility in ethanol (v/v)[b]		1.4 in 1	1.1 in 1	2.0 in 1	1.0 in 1	0.4 in 1	0.5 in 1

[a] Difficult to measure.
[b] Solubility in 80% v/v ethanol to ajowan and cumin essential oil; in 90% v/v ethanol to star anise essential oil.

Conclusion

This original SFME method combining microwave heating and dry distillation provides more valuable essential oils, reduces the extraction time, and allows a substantial saving of energy. After 1 h of SFME extraction, it is possible to collect sufficient essential oil for analytical determinations, whereas HD provides the first essential oil droplet only after 1.5 h. All these advantages make SFME a good alternative for the extraction of essential oil for analytic determinations.

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