Solvent-Free Microwave Extraction : An Innovative Tool for Rapid Extraction of Essential Oil from Aromatic Herbs and Spices

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A relatively simple apparatus is described for extracting essential oils from aromatic plant material by atmospheric solvent-free microwave extraction (SFME) without the addition of any solvent or water. Isolation and concentration of volatile compounds were performed by a single stage. The product solutions of volatile compounds were directly analyzed by gas chromatography coupled to mass spectrometry (GC-MS). The essential oils from aromatic herbs (basil, crispate mint, thyme) and spices (ajowan, cumin, star anise) extracted by SFME for 30 minutes and 1 hour, were similar to those obtained by conventional hydro-distillation (HD) for (respectively) 4 and 8 hours. Substantially higher amounts of oxygenated compounds and lower amounts of monoterpenes hydrocarbons are present in the essential oils of the aromatic plants extracted by SFME in comparison with HD. Solvent-free microwave extraction is clearly advantageous to conventional distillation in terms of rapidity, efficiency, cleanliness, substantial saving of energy, and is environmentally friendly.

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INTRODUCTION

Essential oils and aromatic extracts have usually been isolated by either hydro-distillation (HD) or solvent extraction. Losses of some volatile compounds, low extraction efficiency, long extraction time, 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 [Pollien et al., 1998; Luque de Castro et al., 1999]. These shortcomings have led to the consideration of the use of new techniques in extraction such as supercritical fluids [Reverchon, 1997], ultrasound [Vinatoru, 2001] and microwave [Craveiro et al., 1989; Chen and Spiro, 1994]. These techniques typically use less solvent and energy [Paré and Bélanger, 1997].

A new alternative for extracting natural products by using microwave energy has been developed in our laboratory. Based on a relatively simple principle, solvent-free microwave extraction (SFME) involves placing plant material in a microwave reactor, without the addition of any solvent or water. The internal heating of the *in situ* water within the plant material distends the material 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. SFME is not a modified microwave assisted extraction (MAE) which uses polar or non polar solvents (such as hexane) and neither is it a modified hydro-distillation which uses a large quantity of water [Tomaniová et al., 1998; Letellier and Budzinski, 1999].

To investigate the potential of the SFME technique, comparisons have been made with hydro-distillation for the extraction of essential oil from three spices : ajowan (*Carum ajowan ; Apiaceae*), cumin (*Cuminum cyminum ; Umbelliferea*), star anise (*Illicium anisatum ; Illiciaceae*), and from three aromatic herbs: basil (*Ocimum basilicum ; Labiaceae*), crispate mint (*Mentha crispa ; Labiaceae*), thyme (*Thymus vulgaris ; Labiaceae*).

Keywords: Essential oil, microwave, solvent-free, extraction, dry-distillation.

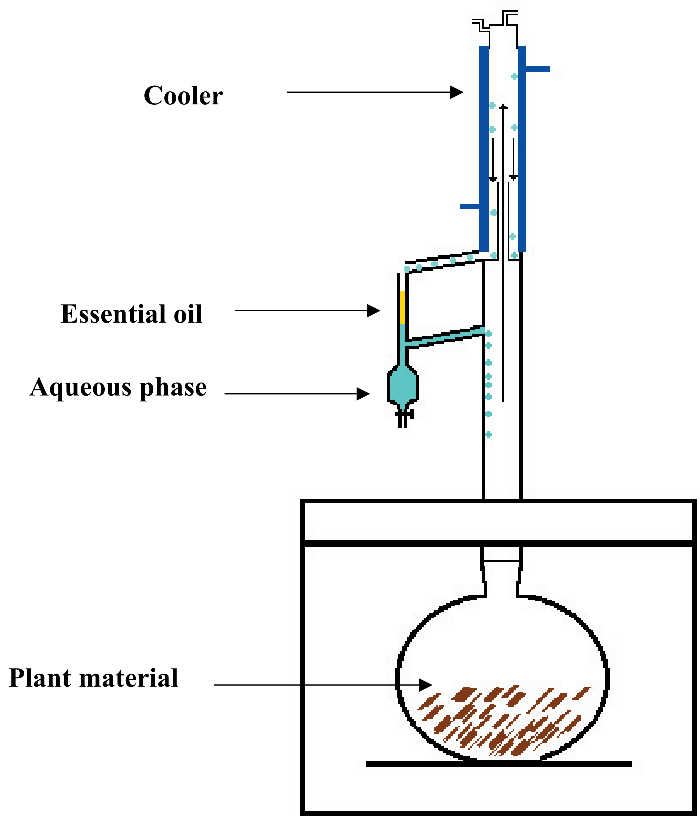

Figure 1 : Solvent-free microwave extraction apparatus

METHODS

SFME was carried out with a Milestone DryDIST® microwave apparatus. The multimode microwave reactor has a twin magnetron (2 × 800 W, 2450 MHz) with a maximum delivered power of 1000 W in 10 W increments. A rotating microwave diffuser ensures homogeneous microwave distribution throughout the plasma coated PTFE cavity (35 cm × 35 cm × 35 cm). The temperature was monitored by a shielded thermocouple (ATC-300) inserted directly into the corresponding container. The SFME apparatus is illustrated in detail in figure 1.

In a typical SFME procedure performed at atmospheric pressure, 250 g of fresh aromatic herbs were heated using a fixed power of 500 Watts for 30 minutes without added any solvent or water. In the case of spice seeds, 250g of dry seeds were moistened prior extraction by soaking in water for 1 hour after which the excess water was drained. This step is essential to give them the initial moisture required to absorb microwaves. Moistened seeds were next placed in the reactor and heated using a fixed power of 500 Watts for 60 minutes. The SFME process thus frees essential oil which is evaporated by the *in situ* water of the plant material. A cooling system outside of the microwave cavity condensed the distillate continuously. The excess water was refluxed to the extraction vessel in order to restore the *in situ* water to the plant material. The extraction was performed at 100°C until no more essential oil was obtained. The essential oil was collected and dried with anhydrous sodium sulphate and stored at 0°C until used.

Hydro-distillation has been performed with a Clevenger-type apparatus [Conseil de l'Europe, 1996]. In a typical procedure, plant material was extracted with 2 to 10 litres of water for 8 hours for spices, and 4 hours for aromatic herbs (until no more essential oil was obtained). The essential oil was collected, dried with anhydrous sodium sulphate and stored at 0°C until used.

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 columns with an apolar stationary phases: SBP5™ (60 m x 0.32 mm x 1 μm film thickness). GC-MS were obtained using the following conditions : carrier gas He ; flow rate 0.7 mL /min ; split 1:20 ; injection volume 0.1 μL ; injection temperature 250°C ; oven

Table 1. Composition, yields, olfactive notes and structure of the major components of essentials oils obtained by SFME and HD

n°	Compound	AROMATIC HERBS						SPICES						Olfactive Note
		Basil		Crispate mint		Thyme		Ajowan		Cumin		Star anise		
		HD	SFME	HD	SFME	HD	SFME	HD	SFME	HD	SFME	HD	SFME	
Terpene Hydrocarbons														
1	β-Pinene	1.1		1.4	0.4			4.8	1.5	16.2	5.9			Smell of dry wood, resinous, slightly clinging
2	p-Cymene					11.1	7.5	29.2	21.2	18.4	12.1			*Citrus* fruit note, reminding lemon and bergamot
3	Limonene			20.2	9.7	0.9	0.6			0.5		11.6	6.6	Fresh, light, perfume of sweet *Citrus* fruit
4	γ-Terpinene	0.2		0.8	0.2	22.8	17.1	28.6	16.4	22.3	12.9			Herbaceous, smell of *Citrus* fruit
Oxygen terpene derivatives														
5	1,8-Cineole	5.8	1.3	0.0	1.5	0.7	0.5				0.7	1.5	1.5	Fresh, light, freshly camphorated
6	Linalol	39.1	25.3	0.4	0.4	4.0	4.6					1.1	1.7	Fresh and floral with a slight note of *Citrus* fruit
7	Carvone			52.3	64.9									Warm-herbaceous, penetrating, spicy
8	Anethole <E>											78.0	81.4	Herbaceous, warm and sweet
9	Thymol			1.9	5.2	40.5	51.0	35.4	60.3					Strong, herbaceous, and warm
10	Eugenol	11.0	43.2	0.2	1.2	0.3	1.5							Powerfull, warm-spicy
Aldehydes														
11	Cumin aldehyde									22.8	37.4			Irritant, pungency and herbaceous
12	α-Terpinen-7-al									14.4	29.1			
Extraction time (min.)		**275**	**30**	**220**	**30**	**260**	**30**	**455**	**60**	**495**	**60**	**460**	**60**	
Yield of essential oil (%)		**0.03**	**0.03**	**0.09**	**0.09**	**0.16**	**0.16**	**3.34**	**1.41**	**1.43**	**0.63**	**4.16**	**1.38**	

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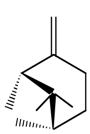

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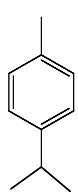

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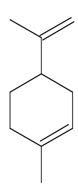

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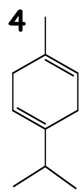

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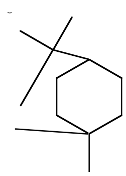

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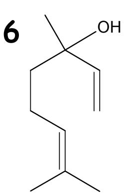

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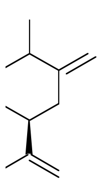

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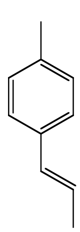

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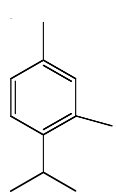

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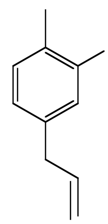

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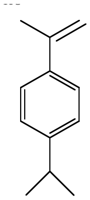

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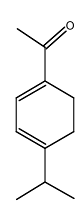

Table 2. Energy consumption of SFME and HD

	SFME		HD	
	Herbs	Spices	Herbs	Spices
Power (W)	500		1000	
Extraction time (h)	0.50	1.00	4.33	7.83
Electric consumption (kWh)	0.25	0.50	4.33	7.83
CO_2 rejected (g)	200	400	3464	6264

temperature progress from 60 to 130°C at 1°C/min, from 130 to 200°C at 2°C/min, from 200 to 250°C at 4°C/min and holding at 250°C for 40 min. ; the ionisation 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 [Arctander, 1994; Adams, 1995].

RESULTS AND DISCUSSION

The yields of essential oil and chemical composition, are reported in Table 1 for the two extraction methods. Solvent-free microwave extraction and hydro-distillation provide extracts with chemical compositions which are qualitatively similar. However, substantially 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 make only a minor contribution to the fragrance of the essential oil. Conversely, the latter are highly odoriferous and, hence, the most valuable. The reduction of the extraction time and the amount of water in the SFME method reduce the deterioration (hydrolysis, trans esterification or oxidation) and the formation of by-products. Generally, SFME essential oils are enriched in major compounds compared to HD.

SFME also allowed substantial saving of time and energy as illustrated in Table 2. The extraction of the first essential oil droplet begins after only 5 min with SFME against 60 to 90 min for HD. Thus, in the case of aromatic herbs, an extraction time of 30 min with SFME provides yields comparable to those obtained after 4 hours by means of HD. Furthermore, hydro-distillation required heating 6 kg of external-water and 500 g of plant material to the extraction temperature, and evaporating water and essential oil for 180 to 360 minutes. The SFME method required only heating plant matter and evaporating *in situ* water and essential oil of the plant material for 25 to 55 minutes. The extraction temperature was equal to water boiling point at atmospheric pressure (100°C).

CONCLUSION

Solvent free microwave extraction has been shown to be feasible with particular interest in avoiding the need for organic solvents or external water in essential oil extraction from plants. The method is thus environmentally friendly, provides a more valuable essential oil and allows substantial saving of time and energy. The SFME method is a green technology and appears as a good alternative for the extraction of essential oils from aromatic plants and spices, of great concern in the food, pharmaceutical, and cosmetic industry.

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