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Effect of microwaves on the *in situ* hydrodistillation of four different Lamiaceae

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ABSTRACT

The development of alternative techniques to classic hydrodistillation (HD) has been prompted because of the drawbacks of the more traditional technique. These drawbacks include: partial thermal degradation, high energy consumption and the fact that it is a time-consuming process. *In situ* microwave-generated hydrodistillation (MGH) and microwave hydrodiffusion and gravity (MHG) are suitable methods which may improve the preparation of essential oils. In this work, we report a comparison study of HD, MGH and MHG used in the extraction of four plant species cultivated in Piedmont (Italy): lavender, oregano, basil and sage. Both microwave-assisted procedures gave excellent results; in particular the essential oils obtained under MHG were very similar to those obtained with HD. In MGH, the polarity and the physico-chemical properties of the extracted compounds caused bigger differences in essential oil composition.

1. Introduction

The use of essential oils (EO) in the food and pharmaceutical industries has a long history. EO are a complex mixture of secondary metabolites, including terpenes, phenolics and alcohols. Although alternative processes are known, the vast majority of EO are produced by hydrodistillation under vapor steam. Hydrodistillation (HD) is a simple form of steam distillation, which is often used to isolate non-water soluble, high boiling point and natural products. In HD, botanicals are fully submerged in water, producing a "soup", whose steam contains the aromatic compounds. The EO of the distillate are then extracted and analyzed. This is the most ancient method of distillation and the most versatile. The long treatment time and local overheating may cause partial degradation or hydrolysis resulting in EO with a burnt note and the loss of more volatile compounds [1]. HD seems to work best for powders (i.e., spice powders, ground wood, etc.) and very tough materials like roots, wood or nuts.

Over the last few years, more laboratories have successfully applied microwave-assisted extraction (MAE) [2,3] and *in situ* microwave-generated hydrodistillation (MGH) [4], which are both now well recognized as innovative green and efficient techniques [5]. Dielectric heating is a non-classical energy source that is capable of reducing extraction times because of its selective volumetric heating that also gives excellent product quality [6,7]. In MGH, molecular motion within polar or ionic components causes heating. The rapid delivery of energy to the sample allows the temperature to rise rapidly in the plant cell and, after cell membrane collapse, the essential oil is released and carried away by the water vapor; the condensation and collection of the product, followed by EO isolation conclude the extractive operation [8]. Another green technique for EO extraction, microwave hydrodiffusion and gravity (MHG) developed by Chemat et al. [9,10], combines microwave heating and earth's gravity at

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atmospheric pressure. Thanks to hydrodiffusion and earth's gravity, the extract can drip out from the microwave reactor, falling through a perforated Pyrex disc and is cooled by a cooling system; water and essential oils are collected and easily separated into a suitable vessel, traditionally called the "Florentine flask".

The present work deals with Lamiaceae, cosmopolitan plants containing about 236 genera and 6900 to 7200 species. These plants are frequently aromatic in all parts and also are widely cultivated for decorative foliage or food use. Lavender, Greek oregano, sweet basil and sage contain fine essential oils used in cosmetics, food and pharmaceuticals, and were thus chosen for this study. In a previous work [11], we reported the results obtained with HD and MGH in the extraction of fresh and dry mint leaves. We herein report the results of a new comparison study on the effectiveness of MGH and MHG on four different genotypes (dry material): *Lavandula angustifolia* Mill. (lavender), *Origanum vulgare* L. ssp. *hirtum* (Link) Ietswaart (Greek oregano), *Ocimum basilicum* L. (sweet basil), *Salvia officinalis* L. ssp. *Lavandulifolia* (sage). Yields and the chemical profiles of the main components are described and commented on.

2. Results and discussion

2.1. Extraction yield and time

The percentage of dry plant material (% DM) is reported in Table 1. Oregano and basil leaves had lower dry matter levels than the leaves of the other genotypes tested, probably because *Origanum vulgare* and *Ocimum basilicum* have more tender leaves than the other species; in particular, oregano DM was twice as high as in previous experiments when leaves were harvested from much older plants [12]. *Salvia officinalis* L. ssp. *Lavandulifolia* plants were harvested at pre-blossoming stage and their DM were in line with previous experiments [13].

HD, MGH and MHG EO yields are listed in Table 2. No striking differences in the three methods were found in oil yield for *Ocimum basilicum*. HD and MHG of *Origanum vulgare* and *Salvia officinalis* gave the best results, while MGH gave a better yield for *Lavandula angustifolia* distillation, probably due to the presence of the flowers. Considering the extraction times, MHG seems to be more efficient than HD, which is the reference method in EO extraction.

2.2. Composition of essential oils

The EO extracted by MGH, MHG and HD are all rather similar in their composition. In general, a similar number of volatile secondary metabolites was found in the essential oils techniques, but there are some differences in their relative amounts.

In the case of *Lavandula angustifolia* Mill. (Table 3), the compounds extracted via the three methods are roughly the same. A higher oxygenated monoterpene content was found under MHG. These include borneol (13.72%), linalool (8.14%), carvone (3.91%), cryptone (3.56%), camphor (3.55%) and 4-terpineol (1.57%), whereas HD mainly leads to higher quantities of α-cadinol (3.95%), α-terpineol (2.14%), carvacrol (1.54) and phellandral (0.69%). MGH extracts highlight a high yield in coumarin (16.59%), 7-methoxycoumarin (11.81%) and caryophyllene oxide (4.26%). Borneol is the most abundant compound found in the MHG profile, while coumarin is the most abundant in HD and MGH.

Linalool, carvacrol and 4-terpineol are the major components in *Origanum vulgare* L. ssp. *hirtum* (Link) Ietswaart dried leaves (Table 4), but their abundance is different in HD, MGH and MHG essential oils. While linalool is the main compound in MHG (26.66%), carvacrol appears to be the most abundant in MGH and HD (35.01% and 26.70% respectively), and the quantity of 4-terpineol is significantly more abundant in MGH (18.05%) than in HD (7.44%) and MHG (4.99).

Table 1
Dry matter percentage (DM).

	DM
Lavandula angustifolia Mill. (leaves + flowers)	24.85
Origanum vulgare L. ssp. *hirtum* (Link) Ietswaart (leaves)	12.65
Ocimum basilicum L. (leaves)	14.43
Salvia officinalis L. ssp. *lavandulifolia* (leaves)	22.50

Table 2
HD *vs* MGH *vs* MHG EO yield ($^w/_w$% dry weight).

	HD[a]	MGH[b]	MHG[b]
Lavandula angustifolia Mill. (leaves + flowers)	0.05	0.13	0.05
Origanum vulgare L. ssp. *hirtum* (Link) Ietswaart (leaves)	0.75	0.08	0.73
Ocimum basilicum L. (leaves)	0.06	0.01	0.06
Salvia officinalis L. ssp. *lavandulifolia* (leaves)	1.36	0.02	1.32

[a] Extraction time: 45 min.
[b] Extraction time: 20 min.

Table 3
Main components of *Lavandula angustifolia* Mill. L. dried material EO.

Compound	HD (%)	MGH (%)	MHG (%)
1,8-Cineole	t	1.22	1.35
Linalool	5.11	3.59	8.14
Camphor	1.42	1.69	3.55
Borneol	9.68	7.14	13.72
4-Terpineol	0.99	0.49	1.57
Cryptone	2.71	1.39	3.56
α-Terpineol	2.14	0.74	1.86
trans-Carveol	0.56	t	0.66
Cuminic aldehyde	0.78	0.61	0.96
Carvone	2.03	2.11	3.91
Phellandral	0.69	0.39	0.57
Carvacrol	1.54	0.76	1.11
Piperitenone	0.47	0.28	0.43
β-Caryophyllene	0.43	1.29	0.33
Coumarin	10.52	16.59	9.41
trans-β-Farnesene	0.21	0.25	0.15
β-Ionone	0.59	0.45	0.52
Dihydroactinidiolide	1.10	0.94	0.44
Caryophyllene oxide	2.48	4.26	2.90
α-Cadinol	3.95	3.68	3.01
7-Methoxycoumarin	2.93	11.81	1.66