

## Volatile Components and Key Odorants of Fennel (*Foeniculum vulgare* Mill.) and Thyme (*Thymus vulgaris* L.) Oil Extracts Obtained by Simultaneous Distillation–Extraction and Supercritical Fluid Extraction

M. CONSUELO DÍAZ-MAROTO,<sup>\*,†</sup> IGNACIO JAVIER DÍAZ-MAROTO HIDALGO,<sup>‡</sup>  
 EVA SÁNCHEZ-PALOMO,<sup>†</sup> AND M. SOLEDAD PÉREZ-COELLO<sup>†</sup>

Área de Tecnología de los Alimentos, Facultad de Ciencias Químicas, Campus Universitario, 10, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain, and Departamento de Ingeniería Agroforestal, Escuela Politécnica Superior, Campus Universitario s/n, Universidad de Santiago de Compostela, 27002 Lugo, Spain

Volatile oil extracts of fennel seeds (*Foeniculum vulgare* Mill.) and thyme leaves (*Thymus vulgaris* L.) were obtained by simultaneous distillation–extraction (SDE) and supercritical fluid extraction (SFE) and analyzed by gas chromatography–mass spectrometry (GC-MS). In general, fennel oil extracted by SDE and SFE showed similar compositions, with *trans*-anethole, estragole, and fenchone as the main components. In contrast, thymol and *p*-cymene, the most abundant compounds in thyme leaves, showed big differences, with generally higher amounts of monoterpenes obtained by SDE. However, in this case, the differences between the extracts were higher. Key odorants of fennel seeds determined by gas chromatography–olfactometry (GC-O) showed similar patterns when applying SDE and SFE. *trans*-Anethole (anise, licorice), estragole (anise, licorice, sweet), fenchone (mint, camphor, warm), and 1-octen-3-ol (mushroom) were the most intense odor compounds detected in fennel extracts. Thymol and carvacrol, with oregano, thyme, and spicy notes, were identified as key compounds contributing to the aroma of thyme leaves.

**KEYWORDS:** *Foeniculum vulgare* Mill.; *Thymus vulgaris* L.; *trans*-anethole; estragole; fenchone; thymol; carvacrol; GC-O; key odorants

### INTRODUCTION

Spices play a central role in the diet of Mediterranean countries. A large variety of spices are grown in these countries, such as fennel and thyme. Fennel (*Foeniculum vulgare* Mill.; botanical family: *Apiaceae*) can be an annual, biennial, or perennial aromatic plant, depending on the variety, that presents two subspecies (*piperitum* and *capillaceum*). Subspecies *capillaceum* includes three varieties (*vulgare*, *dulce*, and *azoricum*). The sweet (*dulce*) and bitter (*vulgare*) varieties grow wild in Mediterranean countries; however, it is the sweet fennel that is cultivated and most widely used mainly because of its relatively delicate flavor. Its seeds are aniselike in aroma and are used as flavorings in baked goods, meat and fish dishes, ice cream, alcoholic beverages, and herb mixtures (1, 2). The major components of fennel seed essential oils are *trans*-anethole, fenchone, and estragole (methyl chavicol) (3–6). The ratio of these compounds varies considerably depending on the phenological state and origin of the seeds (3–6).

Thyme (*Thymus vulgaris* L.; botanical family: *Lamiaceae*) is a perennial aromatic plant of the Mediterranean flora. Seven thyme chemotypes have been described whose principal volatile components are 1,8-cineole, linalool,  $\alpha$ -terpineol, geraniol, *trans*-thujan-4-ol and terpinen-4-ol, thymol, and carvacrol (7–9). The odor of thyme has been described as herbaceous, slightly sweet, and with pungent notes reminiscent of mint. It is highly suitable as a flavoring for a wide variety of dishes, including sauces, vegetables, legumes, meats, and even desserts (2).

The commercial importance of both spices in Mediterranean countries has led to several studies with regard to their chemical composition (3–12). However, there are no studies about the odor active compounds of these spices. In the past 10 years, gas chromatography-olfactometry (GC-O) has been widely applied as a useful technique to determine the most potent odorants in fruits, herbs, and spices, such as dill, parsley, rambutan (tropical fruit), lime, clementines (mandarin oranges), or bay leaves (13–19).

The volatile fraction of the aromatic plants is designated the “volatile or essential oil”. Before such substances can be analyzed by GC, they have to be extracted and concentrated, and a number of different methods can be used for that purpose,

\* To whom correspondence should be addressed. Tel: 00-34-926-295300 ext. 3424. Fax: 00-34-926-295318. E-mail: MariaConsuelo.Diaz@uclm.es.

<sup>†</sup> Universidad de Castilla-La Mancha.

<sup>‡</sup> Universidad de Santiago de Compostela.

e.g., hydrodistillation, steam distillation, Soxhlet extraction, simultaneous distillation–extraction (SDE), headspace techniques, and supercritical fluid extraction (SFE). The majority of these extraction techniques are used to obtain volatile oil extracts at an analytical scale (2, 20–26). Only hydrodistillation, steam distillation, and SFE are used to produce essential oils industrially. The choice of a suitable process will be determined by the intended use of the plant extract.

The aim of this study was to establish the differences, from a quantitative standpoint, in the composition of the volatile oil extracts from fennel and thyme, obtained by SDE and SFE. To determine the best extraction method to preserve the natural character of the plant, the contribution of each one of the extracted volatile compounds in the overall aroma of these aromatic plants was investigated by GC-O.

## MATERIALS AND METHODS

**Plant Materials.** Dried whole fennel seeds and ground thyme leaves were acquired at a Spanish market, homogenized, and kept in the dark prior to analysis. The moisture content, which was determined (in duplicate) using a laboratory oven at 105 °C, was 7.1% for fennel and 9.9% for thyme.

**SDE Extraction.** A microscale SDE apparatus (Chrompack, Mid-delburg, The Netherlands) was used as previously described (23, 27). One gram of sample (dried fennel seeds or dried thyme leaves) in 60 mL of Milli-Q water with 100  $\mu$ L of internal standard [1-phenylethanol in absolute ethanol (1.048 g/L) for fennel and ethyl caprate in absolute ethanol (1.078 g/L) for thyme] was extracted under atmospheric conditions for 2 h using dichloromethane as solvent. The recovery of this method was previously tested and checked (23). The volatile oil extracts (1 mL) were frozen prior to analysis. Three replications of each extraction were performed.

**SFE Extraction.** Supercritical CO<sub>2</sub> extractions were performed in a Hewlett-Packard 7680A (Hewlett-Packard, Palo Alto, CA) extraction module equipped with a 7 mL thick-walled stainless steel thimble and a variable restrictor, allowing instant depressurization of the supercritical fluid and the control of the pressure independently of the supercritical flow rate.

An amount of 0.5 g of spice and 100  $\mu$ L of internal standard [1-phenylethanol in absolute ethanol (1.048 g/L) for fennel and ethyl caprate in absolute ethanol (1.078 g/L) for thyme] was placed in the thimble and extracted during 25 min, at a temperature of 40 °C and a CO<sub>2</sub> density of 0.72 g/mL (pressure: 120 bar). The SFE extract was collected on an octadecylsilane trap held at –5 °C. The extracts (1 mL) were recovered with dichloromethane and kept frozen until their analysis by GC–mass spectrometry (MS). Sampling conditions were previously optimized (23). Three replications of each extraction were performed.

**GC-MS.** A Hewlett-Packard G 1800 B GCD System (Hewlett-Packard), equipped with a gas chromatograph and a quadrupole mass detector in electron impact mode at 70 eV, was used to carry out the GC-MS analysis of the SDE and SFE extracts. An amount of 1  $\mu$ L was injected in splitless mode during 0.1 min (split ratio of 1:20) on a SPB-1 (Supelco) methyl silicone column (50 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m film thickness). The oven temperature was set at 70 °C for 3 min, then the temperature was programmed to increase at 4 °C/min to 120 °C, and then at 8 °C/min to 250 °C. Inlet and detector temperatures were 250 and 280 °C, respectively. Mass detector conditions were as follows: source temperature, 178 °C; scanning rate, 1 scan/s; and mass acquisition range, *m/z* 40–450.

**GC-O.** GC-O was carried out on a Hewlett-Packard (Hewlett-Packard) gas chromatograph equipped with a FID and a sniffing port (ODO-1 from SGE). An amount of 1  $\mu$ L was injected in splitless mode during 0.6 min (split ratio of 1:20) on a SPB-1 (Supelco) methyl silicone column (50 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m film thickness). The oven temperature program was 70 °C (3 min), raised at 4 °C/min to 120 °C, and then raised at 8 °C/min to 250 °C. The injector temperature was constant at 250 °C. The carrier gas was helium at a flow rate of 0.8 mL/min. Six experienced judges participated in the study. Each volatile oil extract was analyzed in duplicate. Judges evaluated the odor intensity

**Table 1.** Chemical Composition (%) of Fennel Seed Volatile Oil Extracts Obtained by SDE and SFE

compound	RI	SDE		SFE	
		mean ( <i>n</i> = 3)	RSD (%)	mean ( <i>n</i> = 3)	RSD (%)
$\alpha$ -pinene <sup>a</sup>	933	0.62	7.3	0.31	12.6
camphene <sup>a</sup>	946	0.07	6.2	Tr	
sabinene <sup>a</sup>	968	0.04	6.9	Tr	
$\beta$ -pinene <sup>a</sup>	973	0.04	6.7	Tr	
$\beta$ -myrcene <sup>a</sup>	983	0.17	9.2	0.13	18.0
$\alpha$ -phellandrene <sup>a</sup>	1000	0.09	5.8	0.07	12.0
$\alpha$ -terpinene <sup>a</sup>	1012	0.01	5.2	Tr	
<i>p</i> -cymene <sup>a</sup>	1015	0.18	6.9	0.05	10.9
1,8-cineole <sup>a</sup> + limonene <sup>a</sup>	1024	1.01	2.8	0.87	16.4
$\gamma$ -terpinene <sup>a</sup>	1051	0.12	6.1	0.23	10.9
<i>trans</i> -sabinene hydrate <sup>a</sup>	1056	0.08	12.6	Tr	
fenchone <sup>a</sup>	1071	19.33	4.4	12.71	9.1
$\alpha$ -terpinolene <sup>a</sup>	1081	0.06	7.1	0.05	15.0
linalool <sup>a</sup>	1086	0.04	13.9	0.03	14.4
[154] <sup>+</sup> (2%), 99 (100%), 71 (65%), 93 (60%), 121 (25%), 136 (15%)	1109	0.07	16.5	Tr	
camphor <sup>a</sup>	1125	0.49	9.3	0.32	11.5
4-terpineol <sup>b</sup>	1167	0.04	3.3	0.02	9.7
estragole <sup>a</sup>	1184	25.84	3.3	20.33	6.2
<i>p</i> -anisaldehyde <sup>a</sup>	1220	1.90	2.9	0.99	6.8
<i>cis</i> -anethole <sup>b</sup>	1233	0.12	12.0	0.10	17.1
<i>trans</i> -anethole <sup>a</sup>	1275	49.71	0.3	63.80	3.9

<sup>a</sup> Identification based on coincidence of GC retention indices and MS data with those of authentic standards from Sigma-Aldrich. <sup>b</sup> Tentatively identified. Tr, traces; RI, retention indices (SPB-1, 0.25  $\mu$ m); and RSD, relative standard deviation.

of each compound placing a mark in unstructured 5 cm line scales anchored at the ends with the terms “not perceptible” and “strongly perceptible”.

Identification of the volatile components was performed comparing their GC retention indices, mass spectra, and odors with those of authentic standards from Sigma-Aldrich. The tentative identification of compounds for which it was not possible to find reference volatiles was carried out by comparison of their mass spectra with spectral data from the Wiley G 1035 A library. It was confirmed by using the Kovats retention indices on the SPB-1 column, calculated using *n*-paraffins (C<sub>5</sub>–C<sub>25</sub>) as external references, and on the basis of Kovats retention indices published in the literature (28–30). The semiquantitative procedure was based on the comparison of peak areas.

## RESULTS AND DISCUSSION

**Volatile Components of Fennel Seeds and Thyme Leaves.** Tables 1 and 2 present the composition (peak area %) of essential oil volatiles identified in fennel seeds and thyme leaves, isolated by SDE and SFE. The chromatographic profiles obtained with both extraction techniques were similar in the two studied spices. Nevertheless, differences in the proportion of the diverse groups of compounds in the volatile oil extracts of these aromatic plants were found.

*trans*-Anethole was the main compound of fennel, and it was extracted in major proportion by SFE (63.80 vs 49.71% by SDE). Other important compounds, from the quantitative point of view, were estragole and fenchone, which appeared in high amounts in volatile oil extracts obtained by SDE. Although *p*-anisaldehyde and *cis*-anethole were detected in low quantities, these compounds play a key role in the overall aroma of fennel, mainly in SFE extracts. Sesquiterpenes were not detected in any of the extracts by GC-MS. With the results obtained and based on recent literature (4–6), the analyzed fennel seeds may belong to the *F. vulgare* L. species, *capillaceum* subspecies, variety *vulgare*, and anethole chemotype, characterized by a

**Table 2.** Chemical Composition (%) of Thyme Leaf Volatile Oil Extracts Obtained by SDE and SFE<sup>a</sup>

compound	RI	SDE		SFE	
		mean (n = 3)	RSD (%)	mean (n = 3)	RSD (%)
$\alpha$ -thujene <sup>b</sup>	925	0.51	7.9	Tr	
$\alpha$ -pinene <sup>a</sup>	933	2.13	8.2	0.20	6.6
camphene <sup>a</sup>	946	1.49	4.6	0.13	11.4
verbenene <sup>b</sup>	949	0.07	9.1		
1-octen-3-ol <sup>a</sup>	963	0.23	10.2	0.11	12.8
1-octen-3-one <sup>a</sup>	966	0.11	8.3		
sabinene <sup>a</sup>	968	0.08	16.7		
$\beta$ -pinene <sup>a</sup>	973	0.24	5.7		
$\beta$ -myrcene <sup>a</sup>	983	0.53	7.7	Tr	
$\alpha$ -phellandrene <sup>a</sup>	1000	0.07	6.1		
$\delta$ -3-carene <sup>a</sup>	1008	0.04	11.5		
$\alpha$ -terpinene <sup>a</sup>	1012	0.79	11.2	0.18	20.6
<i>p</i> -cymene <sup>a</sup>	1015	33.00	3.7	8.49	13.9
1,8-cineole <sup>a</sup> + limonene <sup>a</sup>	1024	2.75	2.3	2.26	11.3
<i>trans</i> -ocimene <sup>b</sup>	1039	0.03	12.4		
$\gamma$ -terpinene <sup>a</sup>	1051	4.75	3.1	1.60	20.5
<i>trans</i> -sabinene hydrate <sup>a</sup>	1056	0.96	17.2	0.62	16.1
<i>cis</i> -linalool oxide <sup>b</sup>	1060	0.08	8.3	Tr	
<i>trans</i> -linalool oxide <sup>b</sup> + isopropenyl-4-methylbenzene <sup>b</sup>	1074	0.16	5.3	Tr	
$\alpha$ -terpinolene <sup>a</sup>	1081	0.06	5.9	Tr	
linalool <sup>a</sup>	1086	3.57	4.7	3.29	1.8
camphor <sup>a</sup>	1125	0.70	9.5	1.38	12.8
<i>trans</i> -verbenol <sup>b</sup>	1133	0.47	9.3	0.16	14.2
<i>endo</i> -borneol <sup>a</sup>	1153	3.55	3.6	3.95	11.7
<i>p</i> -cymen-8-ol <sup>b</sup>	1165	0.31	5.6	0.20	20.8
4-terpineol <sup>b</sup>	1167	1.00	8.7	1.08	8.7
$\alpha$ -terpineol <sup>a</sup>	1177	0.86	3.6	0.98	9.2
verbenone <sup>b</sup>	1185	1.67	2.0	1.43	13.9
methyl thymyl ether <sup>b</sup>	1218	0.67	11.9	0.36	10.1
[164] <sup>+</sup> (100%), 121 (70%), 93 (60%), 136 (50%)	1221	0.32	13.3	0.50	19.4
methyl thymyl ether (isomer) <sup>b</sup>	1230	0.58	10.1	0.38	11.7
linalyl acetate <sup>a</sup>	1244	0.20	11.8	1.03	8.2
[150] <sup>+</sup> (30%), 135 (100%), 115 (15%), 91 (15%)	1265	0.18	6.9	0.12	16.6
thymol <sup>a</sup>	1274	31.06	2.5	60.91	2.1
carvacrol <sup>a</sup>	1281	5.18	2.6	8.90	3.3
<i>trans</i> -caryophyllene <sup>a</sup>	1428	0.51	6.4	0.85	7.5
calarene <sup>b</sup>	1478	0.02	13.1	Tr	
$\gamma$ -cadinene <sup>b</sup>	1516	0.04	12.6	Tr	
[202] <sup>+</sup> (10%), 159 (100%), 160 (15%), 129 (10%)	1519	0.03	5.6	Tr	
$\delta$ -cadinene <sup>b</sup>	1523	0.04	15.3	0.08	16.8
caryophyllene oxide <sup>a</sup>	1584	0.61	6.2	0.54	5.8
<i>trans</i> -cadinol <sup>b</sup>	1638	0.12	14.2	0.08	20.9

<sup>a</sup> See footnotes in Table 1.

high anethole and a middle fenchone and estragole content (in our case, *trans*-anethole, 49.71–63.80%; estragole, 20.33–25.84%; and fenchone, 12.71–19.33%).

In the case of thyme, larger differences were found between the two extraction techniques. Thymol was the major compound in the volatile oil extracts obtained by SFE. However, SDE produced extracts with equal quantities of thymol and *p*-cymene. The volatile oil extracts obtained by SDE showed higher amounts of monoterpene hydrocarbons than those obtained by SFE (46.48 vs 12.86%). SFE samples were richer in oxygenated terpenes, due to the high amount of thymol extracted by this technique. The sesquiterpene content was similar in both extracts.

Thyme chemotypes can be classified by their main volatile components as 1,8-cineole, linalool,  $\alpha$ -terpineol, geraniol, *trans*-thujan-4-ol and terpinen-4-ol, thymol, and carvacrol (7–9). Thyme leaves analyzed may belong to the thymol chemotype, characterized by a high thymol content.

**Table 3.** Odor Active Compounds Found in Fennel Seed Volatile Oil Extracts Obtained by SDE and SFE

compound	RI <sup>a</sup>	odor description	SDE <sup>e</sup>	SFE <sup>e</sup>
methyl butanoate <sup>c</sup>	748	fruity	3.1	
<i>cis</i> -3-hexenal <sup>c</sup>	777	fresh, green grasslike	2.0 (5)	
not identified	818	salted fish	1.7 (2)	
not identified	832	sweet, fruity	2.5	
methylbutyric acid <sup>c</sup>	847	medicinal, rancid	4.7	2.2
not identified	850	roasted nut	4.2 (2)	1.7 (1)
not identified	861	cheese, lactic	4.2 (2)	1.7 (1)
methional <sup>c</sup>	865	baked potato	4.4	
not identified	890	roasted nut	4.7	1.7 (1)
$\alpha$ -pinene <sup>b</sup>	933	pine, fresh	2.8	1.7
1-octen-3-ol <sup>c</sup>	963	mushroom	5.0	2.5
$\alpha$ -terpinene <sup>b</sup>	1012	lemon, flowery	4.2 (4)	1.7 (2)
<i>p</i> -cymene <sup>b</sup>	1015	fuel		1.7 (2)
1,8-cineole <sup>b</sup>	1024	minty	3.8 (4)	2.5
limonene <sup>b</sup>	1024	sweet, citrus	3.3 (4)	1.7
<i>trans</i> -sabinene hydrate <sup>b</sup>	1056	wood, dry	1.7	1.9
fenchone <sup>b</sup>	1071	mint, camphor, warm	5.0	5.0
linalool <sup>b</sup>	1086	flowery	1.7 (4)	1.7 (1)
camphor <sup>b</sup>	1125	camphor, rancid, oily	2.5	4.2
estragole <sup>b</sup>	1184	anise, licorice, sweet	5.0	4.4
<i>p</i> -anisaldehyde <sup>b</sup>	1220	herbaceous, infusion, anise	3.1	4.4
<i>cis</i> -anethole <sup>d</sup>	1233	herbaceous	3.9	3.6
<i>trans</i> -anethole <sup>b</sup>	1275	anise, licorice	5.0	5.0
1-(4-methoxyphenyl)- 2-propanone <sup>d</sup>	1337	fruity, sweet, clove	2.5 (2)	3.6
not identified	1354	flowery	2.9 (4)	
1-(4-methoxyphenyl)- 1-propanone <sup>d</sup>	1372	fruity	3.0 (5)	3.7 (5)
<i>trans</i> -caryophyllene <sup>c</sup>	1428	wood, oak	1.7 (2)	3.3 (1)

<sup>a</sup> RI, retention indices (SPB-1, 0.25  $\mu$ m). <sup>b</sup> Identification based on coincidence of GC retention indices and MS data with those of authentic standards from Sigma-Aldrich. <sup>c</sup> Identification based on coincidence of GC retention indices and similarity of odors with those of authentic standards from Sigma-Aldrich. Because of the low concentration, the compound was not detected by GC-MS. <sup>d</sup> Tentatively identified. <sup>e</sup> Mean odor intensity (0–5 scale, six assessors). In case compounds were not detected by all assessors, the number of those who positively identified the compound is indicated in parentheses.

In conclusion, volatile oil extracts obtained by SFE were rich in oxygenated terpenes, with a small proportion of hydrocarbon monoterpenes. These last compounds were better extracted by SDE, since during the depressurization of the CO<sub>2</sub>, losses of the most volatile compounds can take place (31).

Because of their high content in oxygenated terpenes, which present typical odor notes of aromatic plants, the volatile oil extracts obtained by SFE faithfully represent the aroma of the natural plant. For this reason, SFE is widely used to obtain plant volatile oil extracts at analytical scale, as well as to obtain essential oils industrially in replacement of conventional techniques such as hydrodistillation and steam distillation.

**Odor Active Compounds of Fennel Seeds and Thyme Leaves.** Odor active compounds identified in fennel seeds and thyme leaves are presented in Tables 3 and 4 together with their odor descriptions and retention indices. A comparison of both SDE and SFE extracts has been carried out.

*trans*-Anethole, estragole, fenchone, and 1-octen-3-ol were the most intense odor compounds detected in fennel extracts. *trans*-Anethole and estragole represented the characteristic anise, sweet, and licorice notes of this spice. Another aroma impact compound contributing to the anise aroma of fennel was *p*-anisaldehyde, which although contained in a low proportion, it obtained a high result in both extracts. Other spices such as anise, caraway, cummin, and dill, all members of the same family, share the aniselike aroma of fennel (2). Fenchone was described as minty, camphoraceous, and warm. The camphoraceous note



**Table 4.** Odor Active Compounds Found in Thyme Leaf Volatile Oil Extracts Obtained by SDE and SFE<sup>a</sup>

compound	RI	odor description	SDE <sup>e</sup>	SFE <sup>e</sup>
methyl butanoate <sup>c</sup>	748	sweet, fruity, apricot	2.9	
cis-3-hexenal <sup>c</sup>	777	fresh green, herb	1.7	
methylbutyric acid <sup>c</sup>	847	medicinal, rancid, cheese	3.8	2.2 (5)
methional <sup>c</sup>	865	baked potato	4.2	
not identified	872	dry herb	3.3 (2)	1.7(2)
not identified	890	roasted nut	5.0	
α-pinene <sup>b</sup>	933	pine, fragrant, fresh	2.5 (2)	1.7 (3)
1-octen-3-ol <sup>b</sup>	963	mushroom	4.2	2.8
1-octen-3-one <sup>b</sup>	966	mushroom	4.2	2.2
β-myrcene <sup>b</sup>	983	balsamic	1.7 (3)	
α-terpinene <sup>b</sup>	1012	lemon	2.1	1.7 (3)
p-cymene <sup>b</sup>	1015	fuel	3.8	1.7 (4)
1,8-cineole <sup>b</sup>	1024	eucalyptus, minty, balsamic	4.6	2.5 (4)
limonene <sup>b</sup>	1024	sweet, citrus	3.8	2.1 (4)
trans-ocimene <sup>d</sup>	1039	herb	2.5	2.2 (3)
γ-terpinene <sup>b</sup>	1051	turpentine, plastic	2.9	2.1 (4)
trans-sabinene hydrate <sup>b</sup>	1056	wood, dry	2.2 (3)	3.3
cis-linalool oxide <sup>d</sup>	1060	flowery	1.7 (1)	
trans-linalool oxide <sup>d</sup>	1074	flowery	1.7 (2)	1.7
linalool <sup>b</sup>	1086	flowery, lavender	4.6	3.6
camphor <sup>b</sup>	1125	camphor	3.3	2.2
trans-verbenol <sup>d</sup>	1133	herb	2.9	2.5
endo-borneol <sup>b</sup>	1153	camphor	4.4 (3)	3.3
p-cymen-8-ol <sup>d</sup>	1165	musty, humidity	3.8	3.9
methyl thymyl ether <sup>d</sup>	1218	rosemary, incense	2.5 (2)	3.1
methyl thymyl ether (isomer) <sup>d</sup>	1230	herb, anise	4.2	3.3
linalyl acetate <sup>b</sup>	1244	flowery, carnation	2.5 (2)	1.7 (2)
thymol <sup>b</sup>	1274	oregano, thyme, spicy	5.0	5.0
carvacrol <sup>b</sup>	1281	oregano, thyme, spicy	5.0	5.0
not identified	1324	clove		1.7 (1)
not identified	1341	fruity, sweet, vegetable-like	2.9	3.6
trans-caryophyllene <sup>b</sup>	1428	wood, dry, oak	2.5	3.3
not identified	1452	sweet, fruity		3.3 (5)
calarene <sup>d</sup>	1478	aromatic plant	2.5 (2)	2.5
γ-cadinene <sup>d</sup>	1516	wood, fragrant, flowery	1.7	2.7 (5)
δ-cadinene <sup>d</sup>	1523	wood	1.7	2.1 (4)
caryophyllene oxide <sup>b</sup>	1584	spicy, fragrant, incense	1.7	2.2
trans-cadinol <sup>d</sup>	1638	wood	1.7	2.2

<sup>a</sup> See footnotes in Table 3.

was also given by camphor, mainly in SFE extracts. 1-Octen-3-ol with a mushroom odor showed high intensity in SDE extracts. It has been reported as one of the aroma compounds of rocket salad (32). This compound was not identified by GC-MS. However, it was clearly detected by GC-O, due to its low odor threshold, 1.0 ppb in water solution (33).

For the green/grassy odor note of fennel seeds, cis-3-hexenal was identified in SDE extracts. p-Anisaldehyde and cis-anethole were described as herbaceous in both volatile oil extracts. However, they did not present fresh green notes. Methional (baked potato) was only detected in SDE extracts. This aldehyde presents a low odor threshold, 0.2 ppb in water solution (33). It has also been identified in bay extracts obtained by solvent extraction (19) and in omija (*Schizandra chinensis*) leaf extracts obtained by SDE (34).

Less volatile compounds, such as 1-(4-methoxyphenyl)-2-propanone, 1-(4-methoxyphenyl)-1-propanone, trans-caryophyllene, and an unidentified compound (flowery), were detected by GC-O, but it was impossible to quantify them by GC-MS. 1-(4-Methoxyphenyl)-2-propanone and 1-(4-methoxyphenyl)-1-propanone are products of trans-anethole oxidation (3) and present fruity notes. Besides, 1-(4-methoxyphenyl)-2-propanone had a characteristic sweet and clove odor.

Other compounds that contributed to the overall aroma of fennel seeds were α-pinene (pine, fresh), α-terpinene (lemon,

flowery), and 1,8-cineole (minty) that eluted together with limonene (sweet, citrus).

Thymol and carvacrol were identified as key compounds contributing to the aroma of thyme leaves, with the highest intensities in SDE and SFE extracts. Both compounds showed an oregano, thyme, and spicylike aroma. Other components with similar odor descriptions were methyl thymyl ether isomers, which to a lesser extent also contributed to the characteristic aroma of thyme.

An unidentified compound, with a strong roasted nut aroma, was detected in SDE extracts; however, it could not be identified by GC-MS. As in fennel, methional (baked potato) appeared in thyme SDE extracts. 1-Octen-3-ol and 1-octen-3-one, with a strong mushroom odor, were found in both volatile oil extracts. These compounds could be generated via fatty acid oxidation and have been previously reported as aroma compounds of several aromatic plants and fruits (14, 18, 19, 32, 35).

Floral notes were mainly presented by linalool and slightly by its derivatives, cis- and trans-linalool oxide. Linalool has been identified as a key compound responsible for the aroma of clementine peel oil (18). 1,8-Cineole had a strong and balsamic minty odor, while camphor and endo-borneol were responsible for the camphoraceous aroma impression.

It is worth noting, mainly in thyme and to a lesser extent in fennel, that the most volatile compounds were largely detected in SDE extracts, whereas the less volatile compounds showed higher intensities in SFE extracts. The less volatile compounds present typical odor notes of aromatic plants, such as fruity, fragrant, flowery, spicy, and woody notes. However, the most volatile compounds gave odor notes that are not representative of the overall aroma of these spices. That might be the reason the volatile oil extracts obtained by SFE faithfully reproduced the aroma of the raw material.

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