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Comparison of hydrodistillation and supercritical fluid extraction for the determination of essential oils in aromatic plants

Steven B. Hawthorne*

Energy and Environmental Research Center, University of North Dakota, Box 8213, Grand Forks, ND 58202 (USA)

Marja-Liisa Riekkola and Katariina Serenius

Department of Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki (Finland)

Yvonne Holm and Raimo Hiltunen

Department of Pharmacy, Pharmacognosy Division, University of Helsinki, Fabianinkatu 35, SF-001 70 Helsinki (Finland)

Kari Hartonen

Department of Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki (Finland)

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ABSTRACT

Supercritical fluid extraction (SFE) and hydrodistillation were compared as methods to extract essential oils from savory, peppermint and dragonhead. Despite the high solubilities of essential oil components in supercritical CO,, the extraction rates were relatively slow with pure CO, (*ca. 80%* recovery after 90 min). However, a 15-min static extraction with methylene chloride as modifier followed by a 15-min dynamic extraction with pure CO, yielded high recoveries which agreed well with the results of hydrodistillation performed for 4 h. Spike recovery studies demonstrated that compounds as volatile as monoterpenes can be quantitatively (>90%) collected off-line from the SFE effluent. SFE recovered some organic compounds from each of the samples that were not extracted by hydrodistillation, most notably C,,, C,,, C,,, and C_{33} n-alkanes.

INTRODUCTION

Supercritical fluids are receiving increasing attention for performing analytical-scale extractions of samples ranging from environmental matrices to food products because of the potential to perform rapid (often <30 min) extractions, to reduce the use of hazardous solvents, and to couple the extraction step with gas, liquid or supercritical fluid chromatography [1–3]. Recently, supercritical fluid extraction (SFE) has been applied to the determination of essential oil components using both off-line SFE and SFE coupled with GC [4–8]. While the majority of reports have focussed on qualitative analysis, SFE and SFE-GC have been demonstrated to yield reasonable recoveries of spiked essential oil compounds and reproducible recoveries of native (not spiked) compounds [6,9]. However, high

* Corresponding author.

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recoveries of spiked compounds from aromatic plants do not necessarily indicate high recoveries of native compounds, since spiked compounds are likely only associated with surface sites on the plant matrix, while the native essential oils are distributed throughout the plant material.

To further investigate the ability of SFE to yield quantitative extractions of native essential oil compounds, SFE recoveries from three aromatic plants, savory [9], peppermint [10] and dragonhead [11,12], were compared to those obtained using hydrodistillation [13–15]. Both the absolute quantities of each major essential oil component (as mg extracted per gram of plant tissue) and the distribution of the individual compounds (as % composition of the extracted essential oil) are compared in the SFE and hydrodistillation extracts using capillary GC. The use of organically modified CO_2 to increase SFE rates is also described.

EXPERIMENTAL

Sample extractions

Three aromatic plants, savory (***Satureja hortensis*** **L.**), dragonhead (*Dracocephalum moldavica* L.) and peppermint (*Mentha x piperita* L.), were used as received (air dried and coarsely ground). All hydrodistillations were performed using triplicate 25-g portions of each sample for 4 h using 500 ml of water per extraction as previously described [13–15]. Following hydrodistillation, the extracted essential oils were quantitatively transferred into a volumetric flask using several rinses of methylene chloride and diluted as appropriate for gas chromatographic analysis.

SFE was performed on replicate portions of each sample using "SFEgrade" CO_2 (Scott Specialty Gases, Plumsteadville, PA, USA) supplied to an ISCO SIX-210 extraction unit by a Model 260D syringe pump (ISCO, Lincoln, NE, USA). All extractions were performed at 400 atm (1 atm = 101 325 Pa) and a temperature of 70°C. Stainless-steel extraction cells (2.5 ml) supplied with the extraction unit were filled with each sample (500 mg) for all SFE studies. SFE flow-rates were maintained at *ca.* 0.7 ml/min (measured as liquid CO_2 at the pump) using outlet restrictors made from 12 cm lengths of 32 μm I.D. fused-silica tubing (Polymicro Technologies, Phoenix, AZ, USA) which were attached to the extractor using a short (*ca.* 2 cm) length of 1/16 in. (1 in. = 2.54 cm) O.D. stainless-steel tubing and a "Swagelok" tubing union. Since preliminary studies demonstrated that unheated restrictors frequently plugged (both from water freezing at the restrictor outlet and from extracted organic material at the restrictor inlet), the restrictor heater previously described by Burford *et al.* [16] was used at 100°C for all extractions reported here. (The restrictor heater sold with the ISCO unit was not available for this study.) Except as otherwise noted, extracted analytes were collected into 4 ml methylene chloride placed in an 7-ml glass screw-top vial.

All extractions with pure CO_2 were performed in the dynamic (continual flow) mode. The extraction rates of individual compounds were determined by collecting fractions at specific time intervals during SFE, and analyzing in a manner identical to that used for the other extracts. All of the extractions performed with the addition of organic modifier (either pesticide-grade hexane, acetone or methylene chloride) were performed by adding 0.5 ml of the modifier to the sample in the 2.5 ml extraction cell and immediately inserting the cell into the SFE unit and pressurizing to 400 atm. The extraction was then performed in the static mode for 15 min (*i.e.,* the outlet valve on the SFE unit was left closed when the inlet valve was opened), then the outlet valve was opened and the cell was swept for an additional 15 min with CO_2 in the dynamic mode. For the modifier experiments, the extracted analytes were collected in 4 ml of the same solvent as was used for the modifier.

Gas chromatographic analysis

All GC analyses were performed using a 12.5 m HP Ultra 1 column having a 0.2 mm I.D. and a 0.33 μm film thickness (Hewlett-Packard, Avondale, PA, USA). GC-flame ionization detection (FID) analyses were performed using a Hewlett-Packard Model 5890 gas chromatograph in the split mode with a temperature program of 50°C (hold for 2 min) followed by a temperature ramp at 8°C min to 300°C. Quantitations were based on the addition of dodecane as the internal

TABLE I

CONCENTRATIONS OF ESSENTIAL OIL COMPONENTS IN SAVORY BASED ON HYDRODISTILLATION AND SFE

Species	Peak no.[a]	Hydrodistillation		SFE, set 1		SFE, set 2	
		mg/g (%R.S.D.)[b]	Composition (%)	mg/g (%R.S.D.)[b]	Composition (%)	mg/g (%R.S.D.)[b]	Composition (%)[c]
$C_{10}H_{16}$ [d]	1	0.13 (10)	0.8 ± 0.1	0.15 (7)	0.7 ± 0.0	0.13 (7)	0.6 ± 0.0
a-Pinene'	2	0.19 (9)	1.1 ± 0.1	0.21 (6)	1.0 ± 0.1	0.19 (8)	0.9 ± 0.1
β-Pinene[e]	3	0.09 (10)	0.5 ± 0.0	0.11 (8)	0.5 ± 0.0	0.10 (7)	0.4 ± 0.0
$C_{10}H_{16}$ [d]	4	0.28 (7)	1.6 ± 0.1	0.33 (7)	1.5 ± 0.1	0.29 (7)	1.3 ± 0.1
$C_{10}H_{16}$ [d]	5	0.46 (8)	2.6 ± 0.1	0.48 (14)	1.8 ± 0.3	0.41 (5)	1.9 ± 0.1
ρ-Cymene[e]	6	1.25 (7)	7.0 ± 0.2	1.46 (3)	6.6 ± 0.2	1.31 (8)	5.9 ± 0.5
y-Terpinene'	7	4.40 (8)	24.6 ± 1.1	5.08 (6)	22.9 ± 1.1	4.46 (8)	28.3 ± 1.6
$C_{10}H_{12}O_2$ [d]	8	0.06 (51)	0.3 ± 0.1	1.15 (7)	4.5 ± 0.4	1.30 (8)	5.2 ± 0.4
Carvacrol'	9	12.14 (4)	59.5 ± 1.5	14.31 (1)	55.9 ± 1.0	14.85 (0.2)	59.3 ± 0.9
$C_{15}H_{24}$ [d]	10	0.21 (9)	1.0 ± 0.1	0.30 (5)	1.2 ± 0.1	0.31 (4)	1.2 ± 0.0
$C_{15}H_{24}$ [d]	11	0.22 (4)	1.1 ± 0.2	0.42 (3)	1.6 ± 0.1	0.44 (3)	1.7 ± 0.0
$C_{10}H_{14}O_2$ [d]	12	0.01 (7)	0.1 ± 0.0	0.49 (12)	1.9 ± 0.2	0.48 (9)	1.9 ± 0.2
Total		19.44	100	24.41	100	24.27	100

[a] Peak numbers refer to the chromatogram in Fig. 1.
[b] Concentrations and percent relative standard deviations (%R.S.D.) were based on triplicate hydrodistillations performed on the same day, and two triplicate sets of SFE extractions performed on two different days.
[c] Compositions of each component were calculated for each individual extract, as the % (w/w) of the species listed in the table.
[d] Tentative identification based on MS.
[e] Identification based on comparison of mass spectra and chromatographic retention times with those of standard compounds.

TABLE II

CONCENTRATIONS OF ESSENTIAL OIL COMPONENTS IN PEPPERMINT BASED ON HYDRODISTILLATION AND SFE

Species	Peak no.[a]	Hydrodistillation		SFE, set 1		SFE, set 2	
		mg/g (%R.S.D.)[b]	Composition (%)	mg/g (%R.S.D.)[b]	Composition (%)[c]	mg/g (%R.S.D.)[b]	Composition (%)
a-Pinene'	1	0.04 (4)	0.7 ± 0.0	0.04 (8)	0.7 ± 0.1	0.04 (4)	0.8 ± 0.0
β-Pinene[e]	2	0.09 (7)	1.4 ± 0.0	0.07 (18)	1.3 ± 0.2	0.08 (18)	1.4 ± 0.2
1 ,8-Cineole[d]	3	0.53 (12)	7.3 ± 0.2	0.46 (4)	7.9 ± 0.3	0.49 (8)	7.9 ± 0.3
cis-Sabinenehydrate[d]	4	0.15 (18)	2.1 ± 0.2	0.23 (6)	3.9 ± 0.2	0.26 (12)	4.1 ± 0.2
Menthone[d]	5	2.07 (5)	28.7 ± 1.5	1.60 (6)	27.5 ± 1.2	1.70 (5)	27.4 ± 1.4
Menthol'	6	3.33 (12)	46.0 ± 1.5	2.59 (2)	44.7 ± 0.9	2.76 (8)	44.4 ± 1.1
Menthylacetate'	7	0.31 (3)	4.3 ± 0.3	0.27 (11)	4.3 ± 0.3	0.28 (5)	4.5 ± 0.5
β-Carophyllene[e]	8	0.29 (10)	4.0 ± 0.1	0.22 (12)	3.8 ± 0.5	0.24 (10)	3.9 ± 0.1
$C_{15}H_{24}$ [d]	9	0.26 (11)	3.6 ± 0.1	0.23 (4)	3.9 ± 0.2	0.26 (16)	4.2 ± 0.4
$C_{15}H_{24}$ [d]	10	0.14 (13)	1.9 ± 0.1	0.10 (14)	1.7 ± 0.2	0.11 (23)	1.8 ± 0.3
Total		7.21	100	5.81	100	6.22	100

[a] Peak numbers refer to the chromatogram in Fig. 2.
[b] Concentrations and percent relative standard deviations (%R.S.D.) were based on triplicate hydrodistillations performed on the same day, and two triplicate sets of SFE extractions performed on two different days.
[c] Compositions of each component were calculated for each individual extract, as the % (w/w) of the species listed in the table.
[d] Tentative identification based on MS.
[e] Identification based on comparison of mass spectra and chromatographic retention times with those of standard compounds.

TABLE III

CONCENTRATIONS OF ESSENTIAL OIL COMPONENTS IN DRAGONHEAD BASED ON HYDRODISTILLATION AND SFE

Species	Peak no.*	Hydrodistillation		SFE	
		mg/g (%R.S.D.)[b]	Composition (%)	mg/g (%R.S.D.)[b]	Composition (%)
Neral'	1	0.015 (46)	2.9 ± 0.3	0.024 (2)	2.7 ± 0.3
Geraniol'	2	0.014 (40)	2.5 ± 0.1	0.030 (11)	3.3 ± 0.1
Geranial[e]	3	0.021 (39)	3.8 ± 0.4	0.063 (4)	7.1 ± 0.8
Thymol'	4	0.038 (40)	7.0 ± 0.6	0.091 (11)	10.2 ± 2.0
Carvacrol[e]	5	0.081 (48)	14.9 ± 1.6	0.123 (8)	13.7 ± 2.0
Neryl acetate[d]	6	0.017 (34)	3.1 ± 0.3	0.062 (5)	6.9 ± 0.6
Geranylacetate'	7	0.360 (45)	65.8 ± 1.1	0.511 (22)	56.1 ± 5.6
Total		0.75	100	1.27	100

[a] Peak numbers refer to the chromatogram in Fig. 3.
[b] Concentrations and percent relative standard deviations (%R.S.D.) were based on triplicate hydrodistillations and triplicate SFE extractions.
[c] Compositions of each component were calculated for each individual extract, as the % (w/w) of the species listed in the table.
[d] Tentative identification based on MS.
[e] Identification based on comparison of mass spectra and chromatographic retention times with those of standard compounds.

standard to each extract and on standard curves generated from the pure standard compounds. [When the pure compounds were not available (as indicated in Tables I-III), the FID relative response factors were estimated based on the FID responses of the pure standards having the same molecular formula.] GC-MS analyses were performed using identical GC conditions on a Hewlett-Packard Model 5989A GC-MS system. Except as otherwise noted, all identifications were based on comparisons of the mass spectra and retention times of the pure standards with those of the sample species.

RESULTS AND DISCUSSION

As noted above, the initial supercritical fluid extractions were hampered by plugging of the outlet restrictor which occurred intermittently during SFE of each of the three samples. However, when the restrictor heater [16] was used to heat the restrictor to 100°C, plugging from matrix components was eliminated, although it was important to ensure that the inlet end of the restrictor (and not just the middle portion of the restrictor) was heated. This arrangement heated all of the restrictor except the outlet end of the restrictor (*ca.* 4 cm) that was inserted into the collection vial. Plugging at the restrictor outlet (presumably from extracted water freezing at the end of the restrictor) also occasionally occurred as the solvent temperature dropped below 0°C from the cooling effect of the expanding CO,. This was easily avoided by simply placing the collection solvent vial in a small beaker containing *ca.* 15 ml of room temperature water at the beginning of the extraction.

The GC-FID chromatograms of the SFE and hydrodistillation extracts from savory, peppermint, and dragonhead are shown in Figs. 1-3 (peak identities are given in Tables I-III) and, in general, show the same major components as would be expected from earlier reports [9–12]. Qualitatively, the chromatograms of the SFE extracts were very similar to those from the hydrodistillation extracts for all three samples, although SFE did extract some additional species from each of the samples (none of which were present in SFE blanks). Most notably, all of the SFE extracts contained plant wax odd-numbered n-alkanes (primarily C_{27}, C_{29}, C_{31} and C,,), while none of these alkanes were detected in significant quantities in any of the hydrodistillation extracts. (The presence of n-alkanes in the

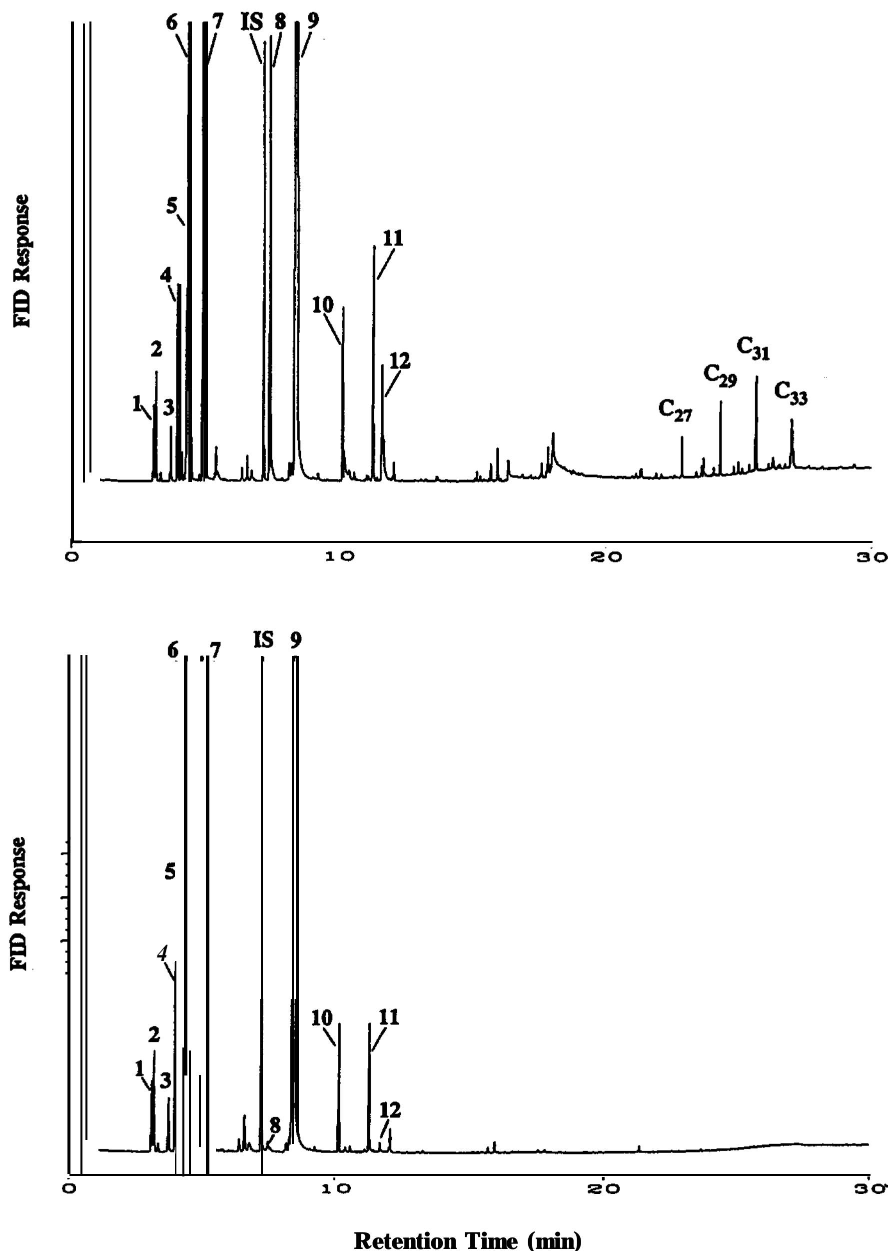

Fig. 1. GC-FID chromatograms of the SFE (top) and hydrodistillation (bottom) extracts of savory. Individual peaks are identified in Table I (IS designates the internal standard). Chromatographic conditions are given in the text.

SFE extracts was also confirmed by the presence of n-alkanes in liquid methylene chloride extracts of the same plant materials.) While nearly all of the additional species extracted by SFE were relatively non-volatile and eluted much later than the primary essential oil components (i.e., several minutes after the sesquiterpenes), the SFE extract from savory contained significant concentrations of two species (peaks 8 and 12 in Fig. 1) which eluted with the primary essential oil components (discussed later in the text).

Extraction with pure CO_2

Preliminary development of the SFE condi-

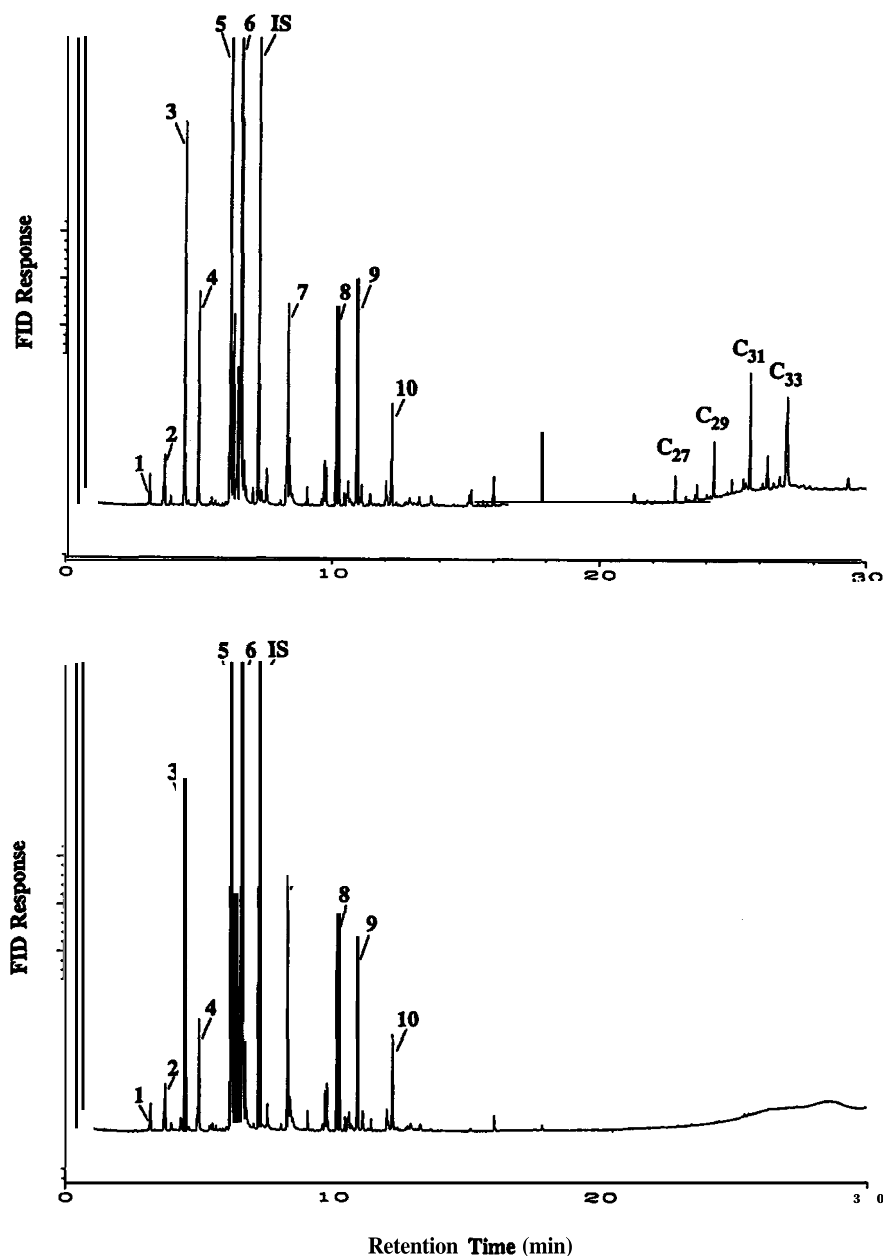

Fig. 2. GC-FID chromatograms of the SFE (top) and hydrodistillation (bottom) extracts of peppermint. Individual peaks are identified in Table II (IS designates the internal standard). Chromatographic conditions are given in the text.

tions were performed using savory, with the goal of obtaining quantitative (>95%) extraction of the essential oils with an extraction time of 30 minutes. Since individual essential oil components typically have high solubilities in supercritical CO_2 under the conditions used in this study, it was hoped that pure CO_2 could be used for quantitative SFE extractions. However, as shown in Fig. 4 by the extraction rates of carvacrol and γ-terpinene, SFE with pure CO_2 at 400 atm for 30 min only recovered ca. 75% of the total extractable essential oil components.

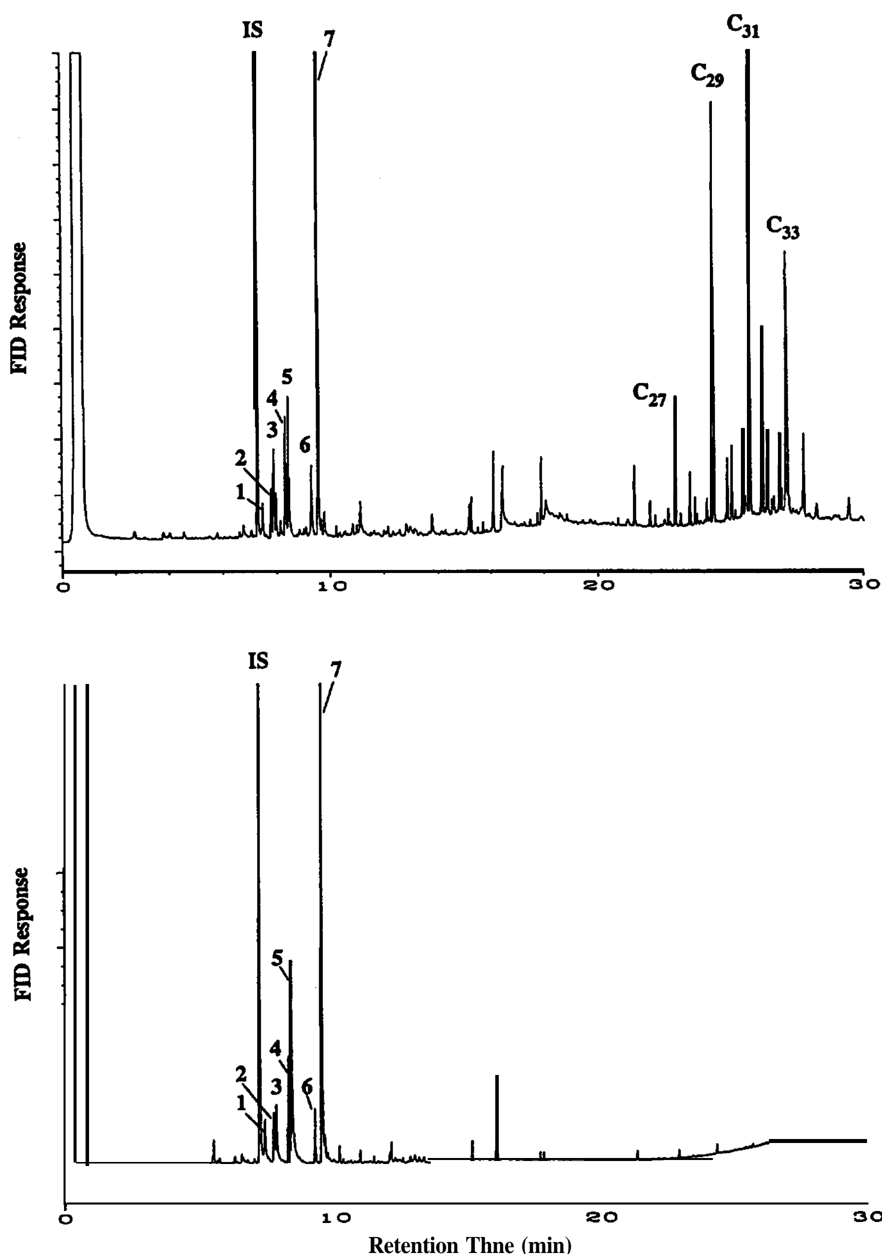

Fig. 3. GC-FID chromatograms of the SFE (top) and hydrodistillation (bottom) extracts of dragonhead. Individual peaks are identified in Table III (IS designates the internal standard). Chromatographic conditions are given in the text.

Even after 90 min of extraction with pure CO,, cu. 15% of additional extractable components remained in the savory matrix. Since the solubility of individual essential oil components is very high (typically several %, w/w, ref. 17) and since a 30-min extraction would utilize cu. 20 ml of the supercritical CO,, the extraction rates appear to be kinetically limited (rather than solubility limited) in a manner similar to that previously described by a diffusion model for SFE [18]. (Note that while the extraction rates are described by the mathematics of the diffusion

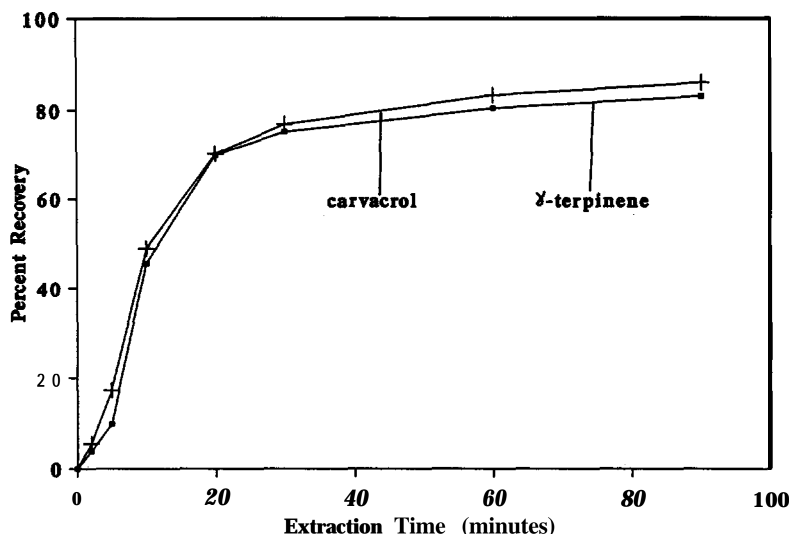

Fig. 4. Extraction rates of carvacrol and γ-terpinene using pure CO_2. Quantitative recovery (100%) was defined as the total quantities of each component extracted by a combination of SFE for 90 min with pure CO_2 followed by an additional extraction with methylene chloride modified CO_2 (15 min static followed by 15 min dynamic as described in the text).

model, matrix-analyte interactions and the related kinetics of the desorption process are likely to fit the same mathematics, and appear more likely to control SFE rates than diffusion of the analytes in the matrix alone.) Because a primary goal of the extraction method was to achieve quantitative recovery with an extraction time of no more than 30 min, the addition of organic modifiers to the CO_2 was therefore evaluated.

Comparison of organic modifiers

The addition of organic modifiers to CO_2 can be achieved either by utilizing a dual pumping system, or by purchasing the modified CO_2 as a pre-mixed fluid. A much simpler (and less expensive) alternative is to simply add a measured volume (0.5 ml in this study) of the modifier directly to the extraction cell, an approach that only requires one pump filled with pure CO_2. To ensure that the modifier was not rapidly swept out of the extraction cell upon pressurization, the initial extraction was performed in the static mode (no flow out of the cell) after pressurization with the CO_2 pump. After the 15-min static extraction step, the outlet valve of the extractor was opened and the extracted analytes were then swept out of the cell with pure CO_2 for an additional 15-min dynamic extraction (performed in a manner identical to that used for the pure CO_2 extractions discussed above).

While selection criteria for SFE modifiers are not clear [3], we hoped to obtain high extraction efficiencies using a modifier that has good characteristics for subsequent GC injections, as well as for efficient collection of the SFE-extracted analytes (19). Therefore, three modifiers (hexane, acetone and methylene chloride) were chosen for the initial modifier survey. To avoid any potential GC injection problems that might occur with mixed solvent systems, the SFE extracts from the modifier survey were collected in the same solvent as that used for the modifier. Replicate samples of savory were sequentially extracted three times with each modifier.

The relative extraction efficiencies (compared to the yields from triplicate hydrodistillation extractions) obtained after one and after three sequential extractions with the three modifiers are shown in Fig. 5. A single extraction with hexane-modified CO_2 yielded poor recoveries (*ca.* 40 to 60%), although three sequential extractions (a total extraction time of 90 min) yielded recoveries similar to those obtained from four hours of hydrodistillation. While the recoveries with acetone modifier were superior to

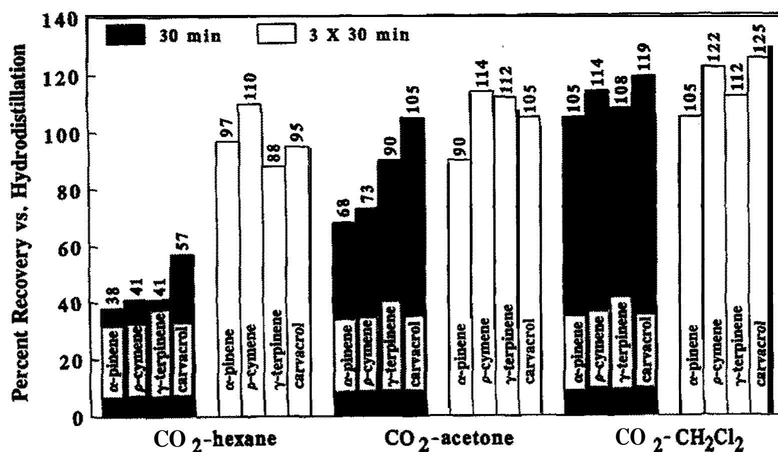

Fig. 5. Relative extraction efficiencies of representative essential oil components from savory using hexane, acetone and methylene chloride modifiers in CO,. Three sequential extractions were performed with each modifier of replicate savory samples. The bars indicate the quantity of the components extracted after one 15 min static/15 min dynamic extraction ("30 min") and after three sequential 15115 min extractions ("3 x 30 min"). Extraction efficiencies are based on the amounts extracted using hydrodistillation of triplicate samples.

the hexane modifier, three sequential extractions were still required to obtain extraction efficiencies similar to those achieved using hydrodistillation. However, a single 30-min extraction (15 min static/l5 min dynamic) with the methylene chloride-modified CO, was sufficient to obtain extraction efficiencies even higher than those obtained using hydrodistillation. In addition, three sequential extractions with methylene chloride modifier failed to yield any significant increase in the amounts of the essential oil components that were extracted (Fig. 5). Since a single extraction with methylene chloride-modified CO, yielded essentially quantitative extraction efficiencies with a total extraction time of only 30 min, this method was used for all subsequent extractions.

Collection efficiencies of volatile compounds

Many of the more volatile flavor and fragrance compounds (e.g., monoterpenes) of interest in this study have previously been shown to be lost during off-line SFE when the extracted organics are collected in liquid solvents, although with careful choice of collection solvent conditions the collection efficiencies of species such as a-pinene have been increased to 90% [19]. If such losses occurred during the dynamic SFE step because of poor collection efficiencies, the resultant low recoveries could mistakenly be blamed on poor extraction (rather than poor collection) efficiencies. Therefore, the recoveries of spiked organics (*i.e.,* added to the sample rather than a native component) using the methylene chloride-modified CO, procedure were measured to determine if the extracted analytes were efficiently removed from the extraction cell and efficiently trapped in the collection solvent. Approximately 25 to 30 μg each of several representative flavor compounds were spiked onto a savory sample that had previously been exhaustively extracted (Le., no detectable analytes remaining in the SFE? extracts) using four sequential methylene chloride modified CO, extractions, The spiked samples were then immediately extracted using methylene chloride-modified CO, in the same manner as that used for the normal samples (15 min static followed by 15 min dynamic SFE). The average recoveries from three spiked samples were α-pinene (92%), y-terpinene (97%) thymol (98%), eugenol (102%), geranyl acetate (97%) and β-caryophyllene (102%), which demonstrates that collection in 4 ml of methylene chloride was sufficient for the compounds of interest in this study.

Comparison of SFE and hydrodtitillation extracts

Although the focus of this study was to develop SFE conditions for essential oil components, some interesting differences in the SFE versus the **hydrodistillation** extracts were readily apparent. First, the **hydrodistillation** extracts were light yellow, while the **SFE** extracts were dark green indicating the extraction of chlorophyll along with the essential oils (this was not the case when using pure CO,, as the dark green extracts only resulted from the modified CO, extractions). Examination of the GC-FID **chromatograms** also showed the presence of **odd**-numbered plant wax n-alkanes in the SFE extracts that were not detected in the **hydrodistillation** extracts (Figs. 1-3). The **concentrations** found for these alkanes from the three test samples are shown in Table IV, and are generally lower than the major essential oil components of savory and peppermint, however the n-alkanes have concentrations similar to the most concentrated flavor compound (geranial acetate) from dragonhead (Table III). Kinetic plots similar to those shown in Fig. 4 demonstrate that these alkanes are extracted more rapidly with pure CO, than the essential oil components, which might be expected since plant waxes are found on the tissue surface. While these alkanes do not interfere with the determination of the essential oil components by GC-FID, their presence in the SFE extracts requires that higher final **chromatographic** temperatures be used to ensure their removal from the GC column.

TABLE IV

CONCENTRATIONS OF n-ALKANES EXTRACTED BY **SFE** FROM SAVORY, PEPPERMINT AND **DRAGONHEAD**

	Concentration (mg/g plant tissue)		
	Savory	Peppermint	Dragonhead
Heptacosane (C,,)	0.09	0.05	0.13
Nonacosane (C,,)	0.17	0.11	0.48
Untriacontane (C,,)	0.33	0.22	0.77
Tritriacontane (C,,)	0.35	0.32	0.61

The quantities of each of the major flavor and fragrance compounds extracted using **hydrodistillation** and **SFE** are shown in Tables I-III. The quantitative reproducibilities of the two extraction techniques were similar for savory and peppermint (Tables I and II), however, **SFE** yielded much better **quantitative reproducibilities** for the dragonhead sample. (It must be noted that the relative standard deviations shown in Tables I-III are based on the **mg/g** tissue of each extracted species, and not on the percent composition data. **RSDs** based on the percent composition for each extract are typically lower, e.g., 2 to 11% for the hydrodistillation extracts of dragonhead compared to ***ca. 40%*** for the **mg/g** data.) **Initially** there was concern that the relatively small samples used for SFE (0.5 g) might not be representative of the bulk sample. However, the **RSDs** obtained using SFE clearly demonstrate that the 0.5-g samples were sufficiently large to be representative of the bulk sample, since SFE obtained similar (or better) reproducibilities than hydrodistillation performed using 20-g samples. In addition, since the **RSDs** obtained from replicate GC analyses of single extracts were typically **<2%,** these results demonstrate that the quantitative variations shown in Tables I-III result from the extraction processes, and are not a result of sample **in**homogeneity or the GC analysis.

SFE extracted slightly higher quantities of all of the species from savory than hydrodistillation (Table I), while SFE extracted **slightly** lower quantities from **peppermint** (Table II). The average amounts of the essential oil components extracted from dragonhead were much higher using SFE. However, the total quantity of essential oils available in dragonhead for extraction is much lower (***ca.*** 1 **mg/g** tissue) than those available from savory and peppermint (***ca.*** 20 and 6 **mg/g,** respectively), which makes quantitative recovery of the extracted oils from the hydrodistillation apparatus difficult. **Although** care was taken to recover all of the oil from the hydrodistillation (using solvent washes), it is likely that the lower apparent recoveries (and the poorer quantitative reproducibility based on the **mg/g** data) shown for the hydrodistillation of dragonhead is a result of an inability to **quantita-**

tively recover the relatively small amounts of essential oil from the hydrodistillation apparatus.

When the extraction results are compared based on percent composition of the extracted essential oil, all three samples showed good agreement between the SFE and hydrodistillation extracts (Tables I-III), with the exception of some very low concentration species (e.g., <0.1 mg/g) such as geranial and neryl acetate (from dragonhead, Table III) which showed cu. two times higher concentrations in the SFE extracts. The most significant difference found between the SFE and hydrodistillation extracts from all three samples used in this study was the relative concentrations of peaks 8 and 12 in the savory extracts [tentatively identified by MS as a hydroxy- and methoxy-substituted phenyl propene isomer, $C_{10}H_{12}O_2$ ($M_r = 164$), and a $C_{10}H_{14}O_2$ (M_r = 166) isomer, respectively]. Both of these species were found at concentrations 15 to 20 times higher in the SFE extracts than in the hydrodistillation extracts (Table I), possibly because hydrodistillation was not effective for their extraction (as was the case for the *n*-alkanes). Alternatively, hydrodistillation has been shown to cause degradation of some essential oil components from exposure to high temperatures and atmospheric oxygen [13] resulting in poor recoveries. To determine whether these two species were poorly extracted or degraded during hydrodistillation, a 0.5-g portion of the savory residue (after hydrodistillation) was extracted by SFE. The SFE extract contained both species (as well as small amounts of carvacrol and the two sesquiterpenes, and all of the n-alkanes). However, the quantities of the two species that were recovered were $<1/3$ of those expected based on SEE of the original savory samples, indicating that some degradation of those species during hydrodistillation may have occurred.

The similarity in composition seen for the more volatile compounds (e.g., monoterpenes) in Tables I-III was particularly interesting since it was initially suspected that the hydrodistillation technique could result in significant losses of such volatile species during the four hour extraction. However, since the spike recovery study discussed above demonstrated the ability of SFE to quantitatively collect monoterpenes, and since the SFE and hydrodistillation extracts showed very similar distributions of the volatile components, the results of this study suggest that hydrodistillation does not result in significant losses of the more volatile essential oil components .

CONCLUSIONS

SFE provides a rapid and quantitative method for extracting essential oils from aromatic plants that compares favorably with the results of hydrodistillation. While essential oil components generally have high solubility in pure supercritical CO,, the addition of an organic modifier (methylene chloride) greatly increased the extraction rates indicating that matrix-analyte interactions are more important than bulk solubility for controlling SEE extraction rates and recoveries.

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