Supercritical Carbon Dioxide Extraction of Chamomile Essential Oil and Its Analysis by Gas Chromatography–Mass Spectrometry

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The essential oil of chamomile flowerheads was extracted by supercritical CO_2, producing the fractional separation of the extract to enhance the process selectivity. The extract fractions were analyzed by GC–MS and SFC to assess the presence of undesirable compounds and to obtain the detailed oil composition. The best oil was obtained by extracting at p = 90 bar and T = 40 °C and fractionating the product in two separators in series operating at p = 90 bar, T = 0 °C, and p = 30 bar, T = −5 °C, respectively. All undesired compounds were precipitated in the first separator. The oil did not suffer thermal degradation: matricine was not converted to chamazulene. The other chamomile oil characteristic compounds (bisabolol oxides, α-bisabolol, and bisabolone oxide) contributed more than 75% and dicycloethers contributed about 13% to the oil composition. Organoleptic analysis confirmed the high quality of the product.

INTRODUCTION

Supercritical fluid extraction (SCFE) is receiving great attention in the agrochemical field. It can be used as an analytical method to prepare samples from complex natural products, but it can also be applied as an industrial process to obtain new or improved-quality products from vegetable matter.

CO_2 is the most widely used among the possible solvents in SCFE because it is cheap, simple to use, and shows a great affinity to lipophilic compounds to be extracted. Nevertheless, some attempts to use other solvents such as nitrous oxide (Stahl and Schütz, 1978; Brunner, 1984) have been performed. Cosolvent addition to CO_2 has been studied too (Vidal and Richard, 1987; Raghuram Rao et al., 1992).

Essential oil production is one of the industrial processes that can be improved by the adoption of SCFE. In fact, the traditional techniques can produce thermal degradation of the product (steam distillation) or its pollution by organic solvents (solvent extraction).

SCFE of essential oils has been attempted by several authors [see the reviews from Stahl et al. (1986) and Reverchon et al. (1993a)], but the products obtained usually show a waxy consistency due to the simultaneous extraction of the oil, cuticular waxes, and other undesirable compounds.

It has been recently assessed that cuticular waxes can be eliminated by fractional separation of the supercritical extracts by using two or more separators operating in series at adequate process conditions (Reverchon and Senatore, 1992; Reverchon et al., 1993b). Fatty acids and their derivatives can be completely eliminated in the extract by adopting adequate SCFE process conditions, i.e., low solvent densities.

The essential oil of chamomile flowerheads is an example of a difficult to reproduce natural product. The presence of thermally labile compounds such as matricine produces an essential oil that is quite different in composition and aroma from the starting material. Typically, a blue viscous liquid with distinct off-notes is obtained by steam distillation.

The SCFE of chamomile flowerheads was investigated by Stahl and Schutz (1978), who explored the pressure range from 72 to 500 bar and temperatures between 31 and 80 °C. They found that the main constituents of this essential oil are easily soluble in supercritical CO_2. The chamomile oil was easily dissolved by supercritical N_2O, but some undesirable compounds were also coextracted. They used thin-layer chromatography and spectroscopy to isolate terpenes, bisabolol, matricine, and dicycloethers.

Vuorela et al. (1990) tried to isolate chamomile essential oil at 200 bar and 40 °C, but the extract contained only "about 20% of volatile oil". These authors identified β-farnesene, bisabolol oxides A and B, α-bisabolol, and matricine as chamazulene by GC–MS. They found only traces of matricine (chamazulene), though they used a chamomile chemotype containing high quantities of this compound. They showed the enrichment of active compounds in SCFE products with respect to conventionally extracted products.

These two studies attempt to characterize supercritical fluid chamomile extracts: in one case the extract was obtained in one condition only (Vuorela et al., 1990), and in both cases single-step separation was used.

The objective of this study was to obtain a high-quality chamomile essential oil by assessing the supercritical CO_2 (SC-CO_2) parameters that optimize the process performance and the extract quality. To achieve this objective, the separation of the extracts by stepwise fractionation was adopted and the procedure was developed for a potential industrial production. At optimum extraction conditions, the compounds that constitute the essential oil and the waxes were identified.

MATERIALS AND METHODS

SCFE Apparatus. The apparatus used in SCFE experiments is schematically represented in Figure 1. It mainly consists of a high-pressure pump (Milton Roy, Pont Saint Pierre, France, Model Milroyal B) capable of a maximum pressure of 500 bar and a maximum CO_2 flow rate of about 4 kg/h; an extraction vessel (internal volume 400 cm^3, p_{max} = 700 bar), and three

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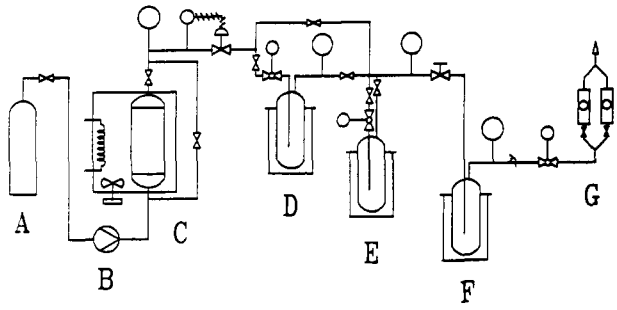

Figure 1. Schematic representation of the SCFE apparatus: (A) CO_2 tank; (B) pump; (C) thermostated oven; (D, E, F) separators; (G) flow rate measurement.

separators in series used to fractionate the extract and capable of operating at temperatures from −10 to 60 °C and at pressures up to 300 bar. In this study the process disposition with two separators has been adopted to precipitate the cuticular waxes in the first separator and the chamomile essential oil in the second one. Further details on the apparatus and its operation have been published elsewhere (Reverchon, 1992; Reverchon and Senatore, 1992). Experiments referred to in this study were performed under the following general operating conditions: CO_2 flow rate, 0.8 kg/h; chamomile flowerheads charged in the extractor, 110 ± 0.5 g; extraction duration, 150 min.

Materials. Chamomile flowerheads [*Chamomilla recutita* (L.) Rausch.], air-dried in the shade and chopped, were supplied by Betulla srl, Italy. They had a moisture content of 10.5% on dry basis.

Analytical Procedures. *a. Gas Chromatography–Mass Spectrometry.* GC–MS data were obtained on a Varian Model 3400 gas chromatograph, interfaced with a Finnigan Mat Magnum ion trap detector (ITS 40, Finnigan MAT, San Jose, CA) operated in electron ionization mode at 70 eV. Mass spectra were also obtained by a Hewlett-Packard 5890 gas chromatograph coupled with a mass detector (Hewlett-Packard, Palo Alto, CA, Model MSD 5970 HP). The column used for oil separation was a fused silica DB-5 column (J&W, Folsom, CA), 30 m × 0.25 mm i.d., film thickness 0.25 μm.

GC conditions for essential oil separation were as follows: oven temperature, 50 °C for 5 min, programmed to increase from 50 to 250 °C at a rate of 2 °C/min, and subsequently isothermal at 250 °C. The column used for cuticular wax identification was an HP-1, 25 m × 0.20 mm i.d., film thickness 0.33 μm. GC conditions for cuticular wax separation were as follows: oven temperature 120 °C for 1 min, programmed to increase to 210 °C at 5 °C/min, followed by a second ramp from 210 to 290 °C at 3 °C/min and then isothermal. All samples were injected twice using the split technique.

The percentage composition of the essential oil and of the cuticular wax compounds was computed from GC peak areas without using correction factors.

The identification of compounds was based on the comparison of the retention times and of the mass spectra with the corresponding data of components of reference oils and pure compounds whenever possible. Mass spectra were compared with those of mass spectra libraries (NIST, U.S. National Institute of Standards and Technology, and WILEY5).

b. Supercritical Fluid Chromatography. Cuticular waxes were also analyzed by supercritical fluid chromatography (SFC). SFC data were obtained on a Fisons (Danvers, MA) Model SFC 3000 chromatograph equipped with a flame ionization detector. A fused silica SE 52 (Mega) capillary column, 10 m long × 0.100 mm i.d., film thickness 0.4 μm, was used for these separations. The adopted SFC conditions were: oven temperature, 120 °C; injector temperature, 50 °C.; injection time, 200 ms; pressure programming, 0.4 bar/min departing from 130 bar.

Pressure increases of 2 bar/min or more and different oven temperature can produce shorter retention times (maximum 30 min) if compared to those adopted in the present study (Reverchon et al., 1993a). However, the described procedure allowed an accurate separation of all compounds contained in the cuticular waxes of chamomile.

c. Thin-Layer Chromatography. The supercritical extracted chamomile oil was also analyzed by thin-layer chromatography (TLC) according to the method described by Stahl and Schutz (1978): support, Kieselgel 60, F254; thickness, 0.25 mm; eluent, chloroform–benzene 75 + 25.

RESULTS AND DISCUSSION

Preliminary supercritical extraction tests were conducted at p = 100, 150, and 200 bar and temperature from 35 to 50 °C, using the single-step SCFE separation technique, i.e., single-stage depressurization of the supercritical solution. These experiments confirmed that at none of the operative conditions was it possible to obtain the pure essential oil, since large quantities of cuticular waxes were present in the supercritical extract. This experimental evidence was anticipated in the Introduction and can be explained if one takes into account that cuticular waxes are located on the surface of the plant, while essential oil compounds are located in the internal part of the leaf. Therefore, cuticular waxes are extracted by simple leaching at all extraction conditions, while the internal mass-transfer resistance has to be overcome to extract the essential oil (Reverchon, 1992). Other undesirable compounds were coextracted at higher CO_2 densities (p > 120 bar, T < 40 °C). They were detected by GC–MS: their mass spectra demonstrated that they were mainly constituted by fatty acid methyl esters. We did not attempt the detailed identification of these undesirable compounds. These tests established that the chamomile used in the present study belonged to the bisabolol oxide chemotype and contained small quantities of matricine and α-bisabolol.

Successive tests were performed using the extract fractionation technique. In the first separator operative conditions were set so that cuticular wax solubility was very low, thus resulting in their supersaturation and precipitation. The best conditions to perform this task were found at p = 90 bar and T = 0 °C, but temperatures between 30 and −5°C were explored. This separation was extremely efficient as one can deduce from the analysis of the optimized chamomile oil proposed in Table 1: no paraffins, coming from the wax fraction, were detected.

In the second separator p = 30 bar and T = −5 °C were fixed to minimize oil compound solubility in the gaseous CO_2 and consequently the quantity of volatile compounds that were lost in the exit stream. The fluid dynamics in this separator was also accurately studied to avoid the entrainment of the volatile compounds in the gaseous stream at the exit of the apparatus. GC–MS analysis performed on the exhaust gas confirmed the efficiency of these procedures.

The relative percentage of fatty acid methyl esters was evaluated from the areas on the GC chromatograms of the oil produced at different extraction conditions. The minimization of their content was obtained by operating the extraction at moderate supercritical CO_2 densities, i.e., densities lower than about 0.5 g/cm^3.

The search for optimum extraction conditions was conducted in the pressure range from 80 to 120 bar and for temperatures from 35 to 50 °C. These ranges are narrower than those explored by Stahl and Schutz (1978) because it is now well-known that at higher densities (for example, 40 °C and pressures higher than 200 bar) supercritical CO_2 shows a strong solvent power but selectivity decreases (Stahl et al., 1986; Reverchon et al., 1993a). In fact, these authors reported that at higher solvent densities the increase of extraction yield was mainly due to the increase in cuticular wax and other undesirable compound content. The optimization procedure was

Table 1. Composition of the Chamomile Essential Oil Obtained by SCFE at 90 bar, 40 °C

compound	Rt[a] (min)	area %[b]
6 methyl-5-hepten-2-one	20.02	0.07
ocimene	25.33	0.11
linalool	28.26	0.57
isoborneol	33.07	0.10
menthol	33.43	tr[c]
4-terpineol	34.02	0.07
α-terpineol	35.00	0.09
n. id. $C_{10}H_{16}O$	38.25	0.11
nerol	39.58	0.65
geraniol	41.07	0.24
menthyl acetate	45.13	0.17
n. id. $C_{12}H_{22}O_2$	48.10	0.17
β-elemene	49.17	tr
β-caryophyllene	51.01	0.13
β-farnesene	53.33	1.53
trans-nerolidol	60.07	0.42
spathulenol	60.53	0.65
caryophyllene oxide	63.18	0.17
n. id. $C_{15}H_{26}O$	64.03	0.39
T-cadinol	64.39	0.36
bisabolol oxide B	65.38	16.88
α-bisabolol	66.14	0.35
bisabolone oxide	67.09	7.76
matricine (chamazulene)	69.39	3.52
bisabolol oxide A	70.53	50.42
n. id. $C_{15}H_{26}O$	71.43	0.34
n. id.	72.09	0.56
n. id. $C_{15}H_{26}O$	74.07	0.18
cis-dicycloether MW 200	77.46	9.64
trans-dicycloether MW 200	78.23	3.33
trans-farnesol	79.02	0.32
cis,trans-farnesol	79.55	0.42
cis-dicycloether MW 214	79.92	tr
trans-dicycloether MW 214	81.18	tr

[a] Rt, retention time on DB5 GC column. [b] GC peak area percentage. [c] tr, peak areas smaller than 0.05%.

iterative. After each supercritical extraction test, the products were analyzed by GC–MS. Comparison among successive chromatograms indicated the relative trends of the undesired compounds. This procedure was described in detail in a previous work (Reverchon, 1992).

Extraction conditions of 90 bar and 40 °C gave the optimum yield and composition. A white odorless mass, i.e., the cuticular waxes, and a pale yellow liquid with a strong chamomile odor were collected in the first and second separator, respectively.

The yields, expressed as weight of extract divided by the weight of the starting material, were 1.18% for essential oil and 0.8% for cuticular waxes. Nonnegligible quantities of water (0.4%) were also recovered in the second separator and eliminated by centrifugation.

GC–MS analyses of these products were reported in Tables 1 and 2. The GC chromatogram of the essential oil is presented in Figure 2. The SFC chromatogram of the cuticular waxes is given in Figure 3. The SFC chromatogram shows some minor compounds that were not resolved by GC; perhaps they are paraffin isomers. On the contrary, lighter olefins identified by GC (see Table 2) were not detected by SFC at the adopted operating conditions.

As a rule, essential oils are mixtures of hydrocarbon terpenes, oxygenated terpenes, and sesquiterpenes. These compound families are present in SC-CO_2 extracts but in different relative proportions than in some previously examined essential oils (Reverchon and Senatore, 1992; Reverchon, 1992; Reverchon et al., 1993b). The analysis of GC results given in Table 1 shows that hydrocarbon terpenes contribute very little to the chamomile essential oil composition (0.20%). Sesquiterpenes (1.66%) are

Table 2. Cuticular Waxes Obtained by Fractional Separation of SC-CO_2 of Chamomile Flowerheads

compound	Rt[a] (min)	area %[b]
hexadecene	13.12	0.44
octadecene	17.43	2.17
docosene	26.82	0.83
tricosane	29.59	1.64
tetracosane	32.09	0.31
pentacosane	34.65	10.50
hexacosane	36.98	1.52
methylhexacosane	38.73	0.26
heptacosane	39.74	17.56
octacosane	41.78	2.74
methylheptacosane	43.07	0.85
nonacosane	43.94	24.12
triacontane	45.54	2.86
entriacontane	47.73	19.71
methyltriacontane	49.24	1.26
dotriacontane	49.80	1.54
methylentriacontane	51.39	1.16
tritriacontane	52.57	9.46
methyldotriacontane	54.70	1.13

[a] Rt, retention time on HP-1 capillary column. [b] GC peak area percentage.

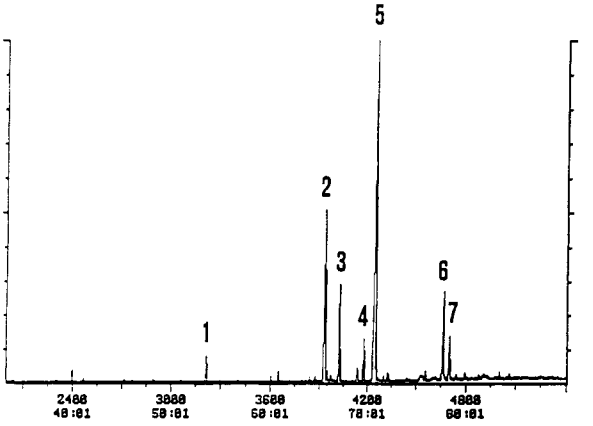

Figure 2. GC chromatogram of the chamomile essential oil obtained by fractional separation of the SCF extract (extraction performed at $p = 90$ bar, $T = 40$ °C): (1) β-farnesene; (2) bisabolol oxide B; (3) bisabolone oxide; (4) matricine (as chamazulene); (5) bisabolol oxide A; (6) *cis*-dicycloether MW 200; (7) *trans*-dicycloether MW 200.

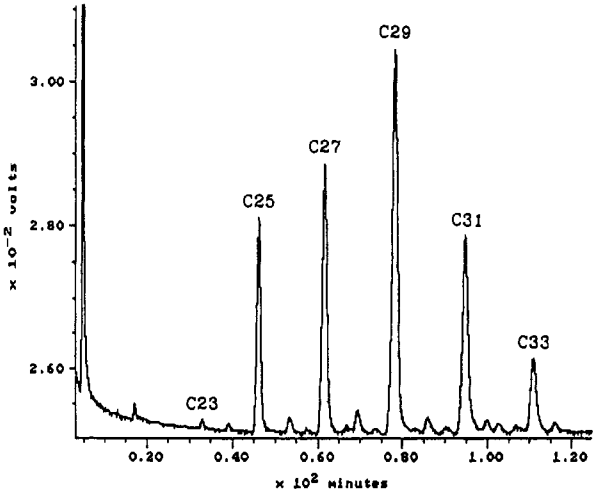

Figure 3. SFC chromatogram of the chamomile cuticular waxes collected in the first separator (extraction performed at $p = 90$ bar, $T = 40$ °C).

mainly represented by β-farnesene (1.53%), which in some cases has been found in very high percentages in chamomile oils (17.9%) (Vuorela et al., 1990). Oxygenated compounds

are considered to be the main constituents of the aroma of many essential oils. In the chamomile oil obtained in this study oxygenated terpenes contribute only 1.83% to the total area. The major contribution comes from oxygenated sesquiterpenes, which represent 78.48% of the oil composition. Oxygenated sesquiterpenes contain the most characteristic chamomile essential oil compounds, namely, bisabolol oxide B (16.88%), α-bisabolol (0.35%), bisabolone oxide (7.76%), and bisabolol oxide A (50.42%).

Matricine (evaluated as chamazulene) represents 3.52% and dicycloethers contribute more than 12.97% to the total area. The thermal transformation from matricine to chamazulene has been previously discussed in this work and was extensively treated by Vuorela et al. (1989). The chamomile oil produced by SCFE has a yellow color because this extraction process does not produce any thermal transformation. We also separated matricine by TLC according to the method proposed by Stahl and Schutz (1978) and briefly described under Materials and Methods. Matricine shows an UV absorption spectrum with a maximum at 255 nm.

Jakovlev et al. (1983) demonstrated that chamazulene shows significantly less activity than matricine from the antiphlogistic point of view. Thus, the chamomile essential oil in which the conversion from matricine to chamazulene has not taken place can exhibit more valuable pharmacological properties.

The GC chromatogram of the essential oil gave two peaks with 200 amu as the base peak in the mass spectrum (see Table 1) and a fractionation that we hypothesized should be that of a dicycloether, whose presence in the chamomile oil was demonstrated by Bohlmann et al. (1961). We performed a TLC of the extract according to the method described by Stahl and Schutz (1978). The fraction that should contain dicycloethers was scraped from the TLC plate and analyzed by GC–MS, which gave two peaks at retention times of 77.46 and 78.23 min, using the GC procedure described under Materials and Methods. These peaks showed similar fragmentation patterns, however, with different intensities of the various fragments. Their spectra, compared with those reported in the literature (Duffield et al., 1965; Katritzky and Rees, 1984) for compounds with a tetrahydrofuran ring, suggested the identifications as *cis*-2-[hexadiyn-(2,4)-ylidene]-1,6-dioxaspiro[4.4]nonene-(3) [Rt 77.46 min, *m/e* 200 (100), 199 (25), 185 (19), 172 (12), 171 (26), 170 (26), 169 (19), 158 (15), 115 (56), 76 (36), 63 (12)] and *trans*-2-[hexadiyn-(2,4)-ylidene]-1,6-dioxaspiro[4.4]nonene-(3) [Rt 78.23 min, *m/e* 200 (100), 199 (25), 185 (18), 172 (12), 171 (21), 170 (26), 169 (19), 158 (16), 115 (54), 76 (35), 63 (11)].

Moreover, a further couple of peaks were detected, though in a very small amount, at Rt 79.92 and 81.18 min that showed a base peak at 214 amu. Comparing the mass spectra of these compounds with those reported in the literature (Isser et al., 1968; Katritzky and Rees, 1984) for tetrahydrofuran compounds, we hypothesized that they could be another couple of dicycloethers. The structures could be *cis*-2-[hexadiyn-(2,4)-ylidene]-1,6-dioxaspiro-[4,5]decene-(3) [Rt 79.92 min, *m/e* 214 (100), 213 (19), 199 (19), 186 (17), 185 (33), 169 (24), 159 (15), 156 (53), 115 (34), 76 (29), 63 (7), 57 (21), 55 (42)] and the *trans* analogous structure [Rt 81.18 min, *m/e* 214 (100), 213 (20), 199 (9), 186 (16), 185 (34), 169 (26), 159 (13), 156 (55), 115 (37), 76 (30), 63 (8), 57 (14), 55 (41)]. Limited quantites of the material available from extraction and TLC did not allow an HPLC separation of these compounds to obtain their NMR spectra. This analysis will be performed in the future when extraction products will be obtained using a pilot SCFE plant (Reverchon et al., 1993c).

Breinlich and Scharnagel (1968) demonstrated that dicycloethers contained in chamomile flowerheads contribute to pharmacological properties of chamomile extracts mainly exhibiting an anti-inflammatory and spasmolytic activity. Thus, these compounds have to be regarded as valuable constituents of the chamomile essential oil.

Organoleptic analyses were performed using the standard panel testing (IFT, 1981); 15 panelists were used, and tests were replicated twice. The optimum SCFE product showed an odor not distinguishable from that of the starting vegetable material. Two commercial chamomile oils obtained by steam distillation were also tested. They possessed distinct off-notes that were evaluated as sweet and harsh by testers.

The SC-CO_2 essential oil of chamomile has also a very different appearance with respect to the steam distillation products. Matricine was not converted to chamazulene as demonstrated by the pale yellow color of this extract. Moreover, viscosity was lower, since paraffins were practically absent.

Gas chromatographic analysis of steam-distilled products was not performed. However, this kind of comparison has been previously reported by some authors for other plant matter (Stahl et al., 1986; Reverchon and Senatore, 1992) and partly by Vuorela et al. (1990) for chamomile itself.

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