Volatile Compounds and Odor Characteristics of Carbon Dioxide Extracts of Coriander (*Coriandrum sativum* L.) Fruits

Kaisli Kerrola* and Heikki Kallio

Department of Biochemistry and Food Chemistry, University of Turku, FIN-20500 Turku, Finland

Volatile components of coriander fruits were isolated by supercritical carbon dioxide (SC-CO_2) exctraction at 9 MPa/40 °C and analyzed using GC–MS. The composition of SC-CO_2 extract was compared with liquid CO_2 (LCO_2) extract (5.4 MPa/25 °C). The SC-CO_2 extract resembled the conventional isolates in the relative amounts of monoterpene hydrocarbons. The oxygenated monoterpenes comprised 80% of the SC-CO_2 and 82% of the LCO_2 extract, linalool being the main compound (67%) in both extracts. The sensory characteristics of the aroma of CO_2 extracts were evaluated and compared with those of freshly ground spice. No major differences in the average intensities of any odor attribute could be found between the coriander fruits harvested in 1990 and 1991. The SC-CO_2 extract was evaluated to be more terpenous and less sweet than the reference (coriander 1990). The assessors described the supercritical extract as the most terpenic and spiciest with some pungency. The aroma of LCO_2 extract was characterized as distinctly pomerancelike and sweet, although all odor attributes were evaluated to be less intense than those in freshly ground coriander fruits.

INTRODUCTION

Extraction processes in which liquid or supercritical carbon dioxide has been applied as solvent in the isolation of volatile compounds from fruits, spices, and herbs have gained increasing attention from the food and perfumery industries (Calame and Steiner, 1982; Rizvi et al., 1986; Moyler, 1988; Pellerin, 1991). Use of compressed CO_2 technique offers several advantages over the conventional extraction procedures reviewed by Brogle (1982), Weder (1984), McHugh and Krukonis (1986), and Engelhardt and Gross (1991).

When liquid carbon dioxide (LCO_2) versus supercritical carbon dioxide (SC-CO_2) is discussed, supercritical CO_2 has been stated to be a more versatile solvent than liquid carbon dioxide due to a wider range of extraction conditions. The solvency of SC-CO_2 depends on the density, which is related to temperature and pressure conditions. As a result of the increased efficiency, however, coextraction of high molecular weight substances, e.g., triacylglycerols, waxes, and pigments, becomes substantial (Marentis, 1988). By varying the processing parameters (Zosel, 1978; Temelli et al., 1988) or by introducing a cosolvent (Francis, 1955; Stahl and Gerard, 1985), it is possible to fractionate the total oil into extracts having different compositions. In isolating the odor compounds, only the volatile, low molecular weight substances are of interest. Francis (1954) studied the solubilities of various compounds in LCO_2 and found the solubility to depend on the combined effects of molecular weight and structure. Carbon dioxide is not a universal nonpolar solvent under any condition: LCO_2 expresses selectivity to low-to-medium molecular weight oxygenated and most low molecular weight nonpolar organic compounds (Schultz et al., 1974; Moyler, 1988). The selectivity of LCO_2 combined with the financial advantages in constructing and operating low-pressure equipment makes liquid carbon dioxide processing a preferable choice for recovery of aromatic extracts or essential oils (Sims, 1982; Moyler and Heath, 1988; Bundschuh et al., 1988; Brunke et al., 1991).

* Author to whom correspondence should be addressed (telefax, +358-21-633 6860).

The aroma is the most important factor of the extract when flavor and fragrance products are concerned, and studies on the composition of carbon dioxide extracts of herbs and spices with remarks on sensory quality have been published (Stahl and Quirin, 1984; Bundschuh et al., 1986; Chen et al., 1986; Hirvi et al., 1986; Chen and Ho, 1988; Gopalakrishnan et al., 1990; Nykänen et al., 1990, 1991; Kollmannsberger et al., 1992; Reverchon and Senatore, 1992). At the same time, publications on the sensory evaluation of CO_2 extracts are scarcely available (Stahl and Gerard, 1982, 1983; Moyler and Heath, 1988; Udaya Sankar, 1989; Moyler, 1990). The aim of our study was to compare the volatile composition and the odor characteristics of carbon dioxide extracts of coriander fruits to characterize the flavoring capacity of the extracts.

MATERIALS AND METHODS

Materials. Coriander (*Coriandrum sativum* L. var. LD) of Dutch origin was cultivated at the Agricultural Research Center, South Savo Research Station, in Mikkeli, Finland (61° 40′ N, 27° 15′ E) during the summers of 1990 and 1991. The harvested fruits were dried at 40 °C in a pilot-scale cabinet drier under continuous circulation of air. The material was stored in jute sacks at ambient temperature protected from light until analyzed.

Hydrodistillation. The essential oil was isolated with a Karlsruher apparatus (Stahl, 1953). Twenty grams of coriander fruits was extracted in 100 mL of distilled deionized water for 4 h according to the procedure given by the Dutch Pharmacopoeia (Nederlandse Farmacopee, 1966). The amount of oil was measured on the volumetric scale on the side tube of the apparatus. The oil was dried over anhydrous sodium sulfate and stored at −20 °C in Teflon-sealed screw-cap vials. A 1000-fold dilution of the distillate in *n*-pentane/diethyl ether (1:2 v/v) was made, and internal standards (*n*-tetradecane and *n*-eicosane) were added prior to GC and GC–MS analyses.

Liquid Carbon Dioxide Extraction. A modified J&W high-pressure Soxhlet extraction apparatus (J&W Scientific, Folsom, CA) (Jennings, 1979) was used for the isolation of volatiles by liquid CO_2. Coriander fruits were ground to about 0.2 mm diameter particles with a centrifugal mill (Model ZM 1, Retsch KG, Haan, Germany) under liquid N_2 injection and 3.00 g was weighed into a thimble (Schleicher & Schuell, 19 × 90 mm, Dassel, Germany). The thimble was covered with a cotton–wool plug to keep the material from migrating in the cylinder during the loading of the apparatus (850 cm^3) with liquid CO_2 (AGA, Espoo,

0021-8561/93/1441-0785$04.00/0

Finland). The assembly was immersed up to 5 cm into a water bath at 25 °C, and extraction was carried out for 6 h at 5.4 MPa. These parameters were selected on the basis of our previous experiments with LCO_2 extraction on coriander fruits (Kallio and Kerrola, 1992). At the end of the operation, the apparatus was chilled to 0 °C and carbon dioxide was very slowly discharged to avoid the loss of the most volatile compounds. For gas chromatographic analysis the solvent-free extract was dissolved in 2 mL of *n*-pentane/diethyl ether (1:2 v/v) at the collection vessel, and the internal standards were added. The solution was thereafter transferred to a Teflon-sealed screw-cap vial and stored at −20 °C. A 5-fold dilution of the solution was made prior to GC and GC–MS analyses.

Supercritical Fluid Extraction. Coriander fruits (harvested in 1990) were pulverized in a pin mill under liquid CO_2 injection. Batch procedure was applied using 2 × 10 L autoclave-type extractors at 9 MPa and 40 °C. The volatile substances of 10.0 kg of plant material were extracted with 18 kg of CO_2 in 1 h and separated at 6 MPa and 30 °C. After removal of coextracted water, the pure lipophilic extract was transferred to brown glass bottles and stored at −20 °C until analyzed. A 500-fold dilution of the extract in *n*-pentane/diethyl ether (1:2 v/v) was made, and internal standards were added prior to GC and GC–MS analyses.

Gas Chromatographic and GC–MS Analyses. The gas chromatographic analyses were carried out on a Varian 3300 gas chromatograph (Varian Associates, Walnut Creek, CA) equipped with a flame ionization detector connected to a Shimadzu Chromatopac C-R3A integrator (Shimadzu Corp., Kyoto). Fused silica columns (HNU-Nordion, HNU Systems, Helsinki) (25 m × 0.32 mm i.d.; film thickness, 0.20 μm) coated with NB-351 liquid phase (corresponds to OV-351) were used for the analyses. The oven temperature was programmed as follows: from 40 (isothermal for 5 min) to 150 °C at 4 °C/min and from 150 to 240 °C at 8 °C/min and isothermal period at 240 °C for 12 minutes. The temperature of the injector port and the detector was 240 °C. The split ratio was 1:20, and the flow rate of carrier gas (helium) was 1.6 mL/min. The 70-eV electron impact mass spectra were obtained on a VG Analytical 7070E instrument and VG-11-250 data system (VG, Wythenshawe, Manchester, U.K.). A Dani 3800 HR ch gas chromatograph with the same capillary column and temperature program as in the gas chromatographic analysis was used in GC–MS. Qualitative analysis was based on comparisons of Kováts indices (I_K) and mass spectra of the compounds with indices and spectra reported in the literature (Stenhagen, 1974; TNO, 1979) or found in the NBS 1987 mass spectra library stored in the computer.

Hydrodistillation and liquid carbon dioxide isolation procedures were performed as triplicates, and the relative amounts of compounds are mean values calculated from three gas chromatographic determinations. In this study the supercritical extract is, in fact, a selected fraction, which was analyzed gas chromatographically three times.

Sensory Evaluation. *Assessors.* The five assessors for the selection of the odor attributes to be evaluated in further studies were members of the staff of our department. All were trained in general sensory assessment and had previous experience in descriptive sensory methods. For the evaluations of the samples, 12 assessors (6 men, 6 women) were selected from the staff and graduate students of our department. All were nonsmokers, between 25 and 52 years of age, and five had previous experience in descriptive sensory methods.

Procedure. In the selection of odor attributes the assessors were asked to describe the various sensory characteristics of freshly ground coriander fruits. From the 20 terms listed, 4 were selected (pomerance, terpenelike, gingerlike, and sweet) according to the predominancy of the term in a round-table discussion. The 12 assessors were trained to connect the chosen term to the right attribute by presenting an odor sample for each attribute. The composition of the odor samples and corresponding attributes are presented in Table I. To ensure the similarity of definition for all assessors and all sessions, the odor samples were available throughout the study. For the four odor characteristics, four coriander fruit and/or extract samples (including a "blind control", e.g., the same as reference) were compared with the reference sample and rated for deviation from the reference (R) using a nonnumerical, 100-mm graphic scale. The range was 0 = less than R, 5 = same as R, and 10 = more than R. The scale was converted to numerical values from 0 to 10 for the analysis of the results. Analysis of variance was applied, and the results of five replicate sessions where all 4 samples were presented each time to all 12 assessors were included.

Table I. Odor Samples of the Attributes Evaluated in Sensory Analyses and Their Composition

attribute	composition
pomerance	2 μL of linalool (Fluka, 99%)
terpenelike	5 μL of α-pinene (Oulu turpentine, 99%)
gingerlike	0.02 g of ground ginger
sweet	0.25 g of honey in 10 mL of distilled water

Samples. The samples evaluated were coriander fruits (1990 and 1991), as well as supercritical and liquid carbon dioxide extracts of coriander fruits (1990). The samples for each assessor were prepared simultaneously about 1 h prior to the sessions to allow the headspace to develop in the bottle. The dried fruits were ground with a centrifugal mill (Model ZM 1, Retsch KG, Haan, Germany) equipped with a 1.0-mm sieve under liquid N_2 injection. Freshly prepared coriander flour (0.5 g) was weighed into 35-mL glass bottles wrapped in aluminum paper. The sample was covered with cotton–wool to avoid visual identification and capped with a lid. Twenty microliters of the extracts was applied on a disk of Whatman No. 1 filter paper and covered as described above. All samples were coded with three-digit random numbers and served in randomized order to each assessor in every session. Coriander fruits harvested in 1990 were chosen as the reference and prepared the same way as the samples.

The evaluation of the samples was performed in individual assessment booths at 2 p.m. throughout the whole study. The sessions were held twice a week during five consecutive weeks from the beginning of March till the middle of April 1992.

RESULTS AND DISCUSSION

Chromatographic Analysis. In our previous study (Kallio and Kerrola, 1992) we isolated the essential oil of coriander fruits by conventional methods, i.e., hydrodistillation and solvent extraction, and compared the flavor composition of the isolates with liquid carbon dioxide extracts obtained at various pressures. To evaluate the differences between $SC\text{-}CO_2$ and LCO_2 in isolating the volatiles of coriander, part of the coriander fruits were extracted with commercial-scale supercritical fluid equipment. The pressure and temperature conditions used were selected on the basis of previous experiments with other plants. The aim was to isolate the aroma fraction, which comprises the low molecular weight components, separate from other lipophilic substances. Thus, the yield of the aroma fraction was 0.55%, calculated from the fresh weight of the material. In comparison, isolation with LCO_2 yielded an extract which comprised 0.70% of the fresh plant material and some higher-boiling compounds were assumed to have been coextracted. The composition of the $SC\text{-}CO_2$ extract was analyzed by gas chromatography (Figure 1) and compared with liquid CO_2 extract of the same sample (Table II). The compounds were identified according to their mass spectra and Kováts indices (I_K).

The total monoterpene hydrocarbons represented 19.8% of the supercritical extract, whereas in the liquid CO_2 extract their proportion was only 13.4%. In the hydrodistillate and pentane/ether (1:2 v/v) extract the total amounts of monoterpene hydrocarbons were 20.0 and 24.4%, respectively (Kallio and Kerrola, 1992). Thus, the amount of monoterpene hydrocarbons of $SC\text{-}CO_2$ extract resembled more closely the conventional isolates than the LCO_2 extract. The major terpene compounds were the same in all extracts: α-pinene, D-limonene, and γ-terpinene. The relative amount of α-pinene was clearly larger in supercritical (5.7%) than in liquid carbon dioxide extract (1.7%).

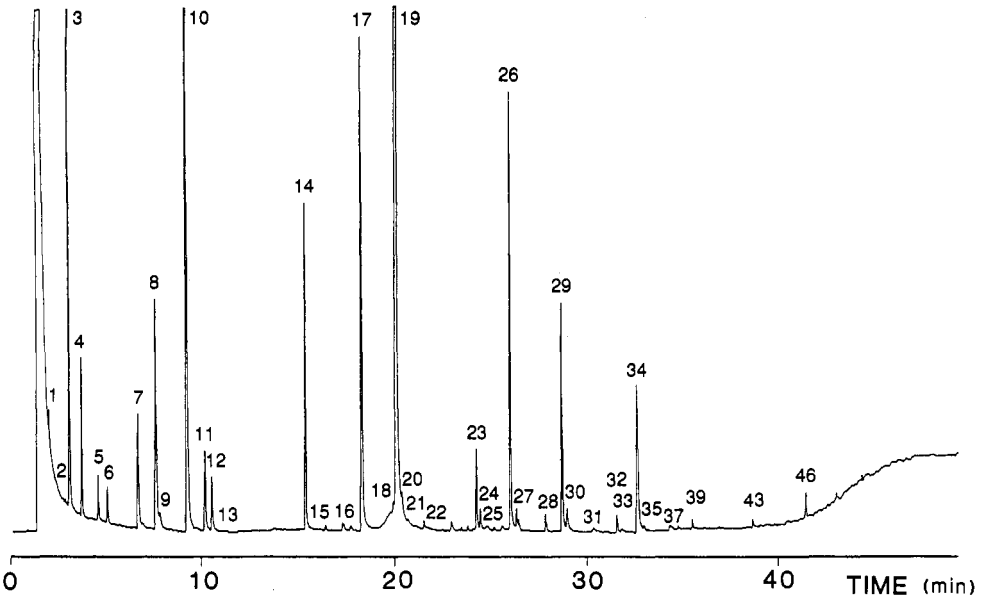

Figure 1. Gas chromatogram of the coriander fruit extract isolated by supercritical carbon dioxide at 9 MPa and 40 °C.

SC-CO_2 extract contained 80% oxygenated monoterpenes, a little less than in LCO_2 extract (81.6%). Linalool was the main compound (67%). The relative amounts of both borneol and geraniol were smaller in the supercritical extract than those in the other isolates.

Our aim of isolating the volatile compounds of the aromatic plant material by selecting suitable operation parameters for the SC-CO_2 extraction was proven successful. Only some of the higher molecular weight compounds were coextracted and in very small quantities. In fact, the amount of these substances was higher in the LCO_2 extract (4.6%). All were not identified, but most of them were fatty acids, their esters, and high molecular weight hydrocarbons, which have minor or no effect on the aroma (Stahl and Gerard, 1983).

Under these conditions, LCO_2 extraction at 5.4 MPa/25 °C and SC-CO_2 extraction at 9 MPa/40 °C, the solubility of monoterpene hydrocarbon moiety was higher in the supercritical than in the liquid carbon dioxide. The higher diffusivity of supercritical CO_2 compared with LCO_2 and the larger amount of CO_2 per kilogram of plant material used in the SC-CO_2 process might account for this. The total amount of oxygen-containing substances was higher in the liquid CO_2 extract, but no trend could be detected when the individual compounds were studied. On the basis of these data, CO_2 at liquid or supercritical fluid state at the vicinity of the critical point expresses similar selectivity toward low molecular weight compounds, both hydrocarbons and oxygenated hydrocarbons.

Sensory Evaluation of the Aroma. Distinct differences in the compositions of the extracts were found, but the importance of these differences for the total aroma of the spice cannot be estimated merely on the basis of chromatographic analysis (von Sydow et al., 1970; Pangborn, 1987). Patton and Josephson (1957) introduced a method to determine the importance of a volatile compound for the flavor of foods. This method combines the chromatographically obtained information on concentration of a compound and the sensorially determined limit of detection, e.g., threshold value, of the compound. The same approach was developed further by Guadagni et al. (1966, 1968) and Teranishi et al. (1990). The flavor impact of a spice or herb consists in most cases of numerous compounds which interact in several ways with each other, i.e., adding, enhancing, or suppressing one another, even causing changes in flavor quality. Models to describe and quantify this phenomenon have been developed, but they provide no indication of the flavor quality of the mixture. Shutte (1985) proposed a model for predicting odor–odor interactions also by using concentrations and threshold values of the compounds. The limitations and special characteristics of the human perception of stimuli have been acknowledged but given no serious attention (Powers, 1981). The major problem encountered is the threshold values of individual compounds, which are determined as pure substances in air or water. The volatiles are usually isolated by solvent extraction or steam distillation. The solubility of the compounds in various solvents is affected by their chemical nature. The ease of release from the matrix and quantitative extraction is often a problem. The matrix also bears a considerable importance for the perception of aroma in sensory evaluations. Sensory studies are laborious and time-consuming, but it is the only way to quantify and characterize the total aroma impact of complex mixtures.

In addition to linalool, several other compounds contribute to the characteristic aroma of coriander fruits, i.e., terpene hydrocarbons and mono- and polyunsaturated fatty aldehydes (Bauer and Garbe, 1985). The sensory characteristics of compressed CO_2 extracted aroma isolates were studied to evaluate the potential of these products and compared with those of freshly ground spice. The results of the descriptive sensory profiling of the odor of coriander fruits cultivated during 2 consecutive years and CO_2 extracts are shown in Figure 2. The coriander fruits of 1990 were evaluated among the samples in each session and, thus, were used as the blind control. The deviation from the reference contrasted with itself gives a measure of reliability (Pangborn, 1984). The means of deviation of coriander (1990) for all odor attributes were small, which reflects good judge reliability. The standard deviations were large, indicating the lack of experience in sensory evaluation, thus affecting the accuracy of the evaluations.

No major differences in the average intensities of any attribute could be found between the coriander fruits harvested in 1990 and 1991. The length of growth period and the effective day degrees were different due to climatic conditions. The growth period in 1991 was exceptionally short, but the effective day degrees were high: 1164 in 1991 vs 1080 in 1990. In fact, the plants suffered frostbite

Table II. Composition of Coriander Fruit Extracts

no.[a]	compound	relative amount, % liquid CO_2 extract	relative amount, % SC-CO_2 extract	I_K NB-351
1	unknown	0.2	0.1	900
2	α-thujene	0.2	tr[b]	945
3	α-pinene	1.7	5.7	1011
4	camphene	0.4	1.0	1051
5	β-pinene	0.2	0.4	1090
6	β-thujene	0.2	0.3	1107
7	β-myrcene	0.5	1.2	1162
8	D-limonene	1.9	2.6	1186
9	β-phellandrene	0.3	tr	1190
10	γ-terpinene	6.7	7.2	1233
11	*m*-cymene	0.7	0.8	1259
12	α-terpinolene	0.4	0.5	1268
13	octanal			1277
14	*n*-tetradecane			1400
15	*cis*-linalool oxide	0.1		1435
16	unknown	0.4	0.1	1465
17	camphor	4.8	4.9	1493
18	unknown	0.1	0.1	1547
19	linalool	67.2	67.0	1551
20	1-octanol	tr	tr	1573
21	terpinen-4-ol	0.1	0.1	1600
22	2-decenal	tr	0.1	1684
23	borneol	1.3	0.7	1690
24	α-terpineol	0.4	0.2	1695
25	unknown	0.7	0.1	1706
26	geranyl acetate	3.4	3.6	1754
27	1-dodecanol	0.3	0.3	1765
28	tridecanal	tr	0.2	1800
29	geraniol	2.4	2.0	1852
30	2-undecenal	0.4	0.3	1900
31	unknown	tr	tr	1935
32	butanoic acid, 3-hexenyl ester	1.0	0.2	1978
33	unknown	0.2	0.1	1988
34	*n*-eicosane			2000
35	unknown	tr	tr	2029
36	tetradecanoic acid, 1-methylethyl ester	0.4		2045
37	octanoic acid	0.4	tr	2091
38	unknown	0.2		2126
39	*cis*-3-hexenyl butanoate	0.8	0.1	2158
40	carvacrol	0.2		2222
41	hexadecanoic acid, methyl ester	0.2		2238
42	decanoic acid	0.6		2278
43	6-methyldocosane	tr	0.1	2300
44	unknown	0.3		2348
45	6-octadecenoic acid, methyl ester	0.3		2383
46	unknown	0.9	0.2	2493

[a] Numbers of the compounds correspond to peaks in Figure 1. [b] tr, in trace amount, ≤0.1%.

in autumn 1991, which eventually caused the maturing of the fruits. The total amount of volatiles isolated by hydrodistillation was higher in the 1991 harvest than in 1990, 0.90 mL/100 g of fresh weight and 0.83 mL/100 g, respectively. Differences in GC–MS analyses (not shown) of these two samples were not significant.

The SC-CO_2 extract was evaluated to be more terpenous and less sweet than the reference, e.g., coriander of 1990. In the round-table discussions the assessors described the supercritical extract as the most terpenic and spiciest with some pungency. The terpenous character was strongly associated with the SC-CO_2 extract in the evaluations and distinguished it from the other samples. All of the odor attributes were perceived to be less intense in the liquid CO_2 extract than in the reference. At the same time the aroma was defined as distinctly pomerancelike and sweet. Moyler (1990) presents the odor profiles of liquid CO_2 extract and steam-distilled oil of coriander fruits. A

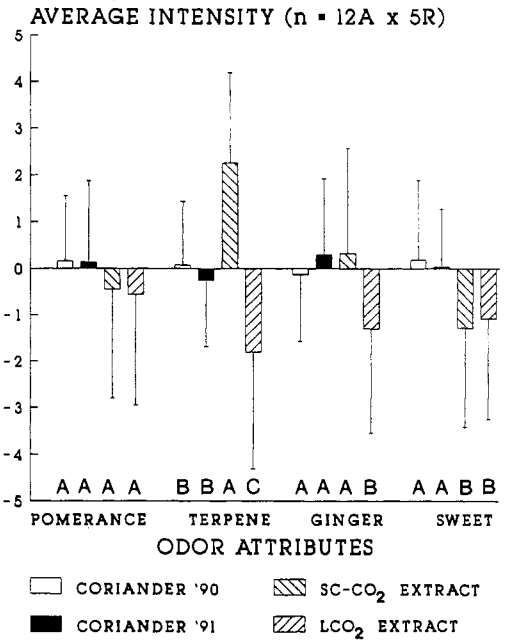

Figure 2. Means and standard deviations for odor attributes of coriander fruits 1990, coriander fruits 1991, supercritical carbon dioxide extract, and liquid carbon dioxide extract. Values show degree of deviation from reference: values less than zero indicate weaker intensity compared with reference (freshly ground coriander fruit 1990), and values higher than zero indicate stronger intensity than reference. Means designated with the same letter did not differ at $p < 0.05$ on the basis of LSD values obtained in analysis of variance.

Table III. *F* Values from Analysis of Variance for the Attributes

source	df	pomerance	terpene	ginger	sweet
assessor	11	2.32*[a]	2.07*	2.09*	4.51***
sample	3	2.66	65.13***	12.99***	11.42***
replication	4	0.72	0.78	0.89	0.70
assessor × sample	33	2.09**	2.74***	2.68***	1.63*
assessor × repl[b]	44	1.83**	2.32**	1.49*	

[a] *, **, ***, significant at $p < 0.05$, 0.01, and 0.001, respectively. [b] Replication.

trained panel was used in assessing the sensory characters, but unfortunately no statistical methods were reported to have been applied. LCO_2-extracted oil was described as sweet candylike and aromatically spicy, when by comparison the distillate was perceived to be less sweet and of slightly terpenic character with later developing spicy and floral notes. The odor of the carbon dioxide extract was evaluated to resemble the aroma of the freshly ground spice much closer than the steam distillate.

One of the characteristics listed in the aroma profiling needs further attention. The assessors reported a cardboardy character, which was present in the ground fruits originating from matrix but not found in the extracts. The matrix was also estimated to moderate the intensities of odor attributes. Carboardlike was chosen as one of the attributes for the evaluations but was later rejected due to diversity in describing the exact response perceived.

The results of analysis of variance for sensory evaluation are presented as *F* values in Table III. Only 5 of the 12 assessors in our panel had previous experience in sensory evaluation procedures, which caused variation in the use of the intensity scale. A few assessors had difficulties in detecting the sweet odor due to the large quantity of linalool in the sample. Laamanen and Jounela-Eriksson (1987) reported inhibition in perceiving minor characteristics when a major characteristic is present. The

samples did not differ in the intensity of pomerancelike odor, which could be explained by the dominance of linalool among the volatiles of coriander fruit (almost 70%). No significant variation among the replicas was found, indicating good reproducibility in sample preparation and presentation resulting in uniform perception of odors throughout the study. Assessor × sample and assessor × replication interactions were significant, reflecting disagreement among assessors most likely caused by insufficient experience and practice in sensory evaluations. Some of the variation undoubtedly originated from the highly volatile nature of the sample, although special consideration was given to the development of full aroma during sample preparation. It is possible that the composition of the headspace changed during the evaluation session, when the lid of the bottle was opened several times, due to the loss of aroma compounds at different rates based on their specific volatilities.

ACKNOWLEDGMENT

We express our gratitude to Bertalan Galambosi for the selection and cultivation of the plant material. Anja Lapveteläinen guided us in planning the sensory evaluations. We thank the sensory panel members for their participation. The research was supported by The Academy of Finland and Aromtech.

LITERATURE CITED

Bauer, K.; Garbe, D. *Common Fragrance and Flavor Materials. Preparation, Properties and Uses*; VCH Publishers: Weinheim, Germany, 1985; pp 147–148.

Brogle, H. CO_2 in solvent extraction. *Chem. Ind.* **1982**, 385–389.

Brunke, E.-J.; Hammerschmidt, F.-J.; Koester, F.-H.; Mair, P. Constituents of dill (*Anethum graveolens* L.) with sensory importance. *J. Essent. Oil Res.* **1991**, *3*, 257–267.

Bundschuh, E.; Tylla, M.; Baumann, G.; Gierschner, K. *Lebensm. Wiss. Technol.* **1986**, *19*, 493–496.

Bundschuh, E.; Baumann, G.; Gierschner, K. *Dtsch. Lebensm. Rundsch.* **1988**, *84*, 205–210.

Calame, J. P.; Steiner, R. CO_2 extraction in the flavour and perfumery industries. *Chem. Ind.* **1982**, 399–402.

Chen, C.-C.; Ho, C.-T. Gas chromatographic analysis of volatile components of ginger oil (*Zingiber officinale* Roscoe) extracted with liquid carbon dioxide. *J. Agric. Food Chem.* **1988**, *36*, 322–328.

Chen, C.-C.; Kuo, M.-C.; Wu, C.-M.; Ho, C.-T. Pungent compounds of ginger (*Zingiber officinale* Roscoe) extracted by liquid carbon dioxide. *J. Agric. Food Chem.* **1986**, *34*, 477–480.

Engelhardt, H.; Gross, A. Supercritical fluid extraction and chromatography: potential and limitations. *Trends Anal. Chem.* **1991**, *10*, 64–70.

Francis, A. W. Ternary systems of liquid carbon dioxide. *J. Phys. Chem.* **1954**, *58*, 1099–1114.

Francis, A. W. Solvent extraction with liquid carbon dioxide. *Ind. Eng. Chem.* **1955**, *47*, 230–233.

Gopalakrishnan, N.; Shanti, P. P. V.; Narayanan, C. S. Composition of clove (*Syzygium aromaticum*) bud oil extracted using carbon dioxide. *J. Sci. Food Agric.* **1990**, *50*, 111–117.

Guadagni, D. G. Requirements for coordination of instrumental and sensory techniques. In *Correlation of Subjective-Objective Methods in the Study of Odors and Taste*; ASTM 440; American Society for Testing and Materials: Philadelphia, PA, 1968; pp 36–48.

Guadagni, D. G.; Buttery, R. G.; Harris, J. Odour intensities of hop oil components. *J. Sci. Food Agric.* **1966**, *17*, 142–144.

Hirvi, T.; Salovaara, I.; Oksanen, H.; Honkanen, E. Volatile constituents of coriander fruit cultivated at different localities and isolated by different methods. In *Progress in Essential Oil Research*; Brunke, E.-J., Ed.; de Gruyter: Berlin, 1986; pp 111–116.

Jennings, W. G. Vapor-phase sampling. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1979**, *2*, 221–224.

Kallio, H.; Kerrola, K. Application of liquid carbon dioxide to the extraction of essential oil of coriander (*Coriandrum sativum* L.) fruits. *Z. Lebensm. Unters. Forsch.* **1992**, *195*, 545–549.

Kollmannsberger, H.; Nitz, S.; Drawert, F. *Z. Lebensm. Unters. Forsch.* **1992**, *194*, 545–551.

Laamanen, M.; Jounela-Eriksson, P. The use of descriptive analysis in the quality control of sweet gale extracts. *Lebensm. Wiss. Technol.* **1987**, *20*, 86–90.

Marentis, R. T. Steps to developing a commerical supercritical carbon dioxide processing plant. In *Supercritical Fluid Extraction and Chromatography: Techniques and Applications*; Charpentier, B. A., Sevenants, M. R., Eds.; ACS Symposium Series 366; American Chemical Society: Washington, DC, 1988; pp 127–143.

McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction. Principles and Practice*; Butterworth: Stoneham, MA, 1986; pp 181–215.

Moyler, D. A. Liquid CO_2 extraction in the flavour and fragrance industries. *Chem. Ind.* **1988**, 660–662.

Moyler, D. A. CO_2 extraction of essential oils: Part III. Pimento berry, coriander and cellery seed oil. In *Flavors and Off-Flavors*; Charalambous, G., Ed.; Elsevier: Amsterdam, 1990; pp 263–280.

Moyler, D. A.; Heath, H. B. Liquid carbon dioxide extraction of essential oils. In *Flavors and Fragrances: A World Perspective*; Lawrence, B. M., Mookherjee, B. D., Willis, B. J., Eds.; Elsevier: Amsterdam, 1988; pp 41–63.

Nederlandse Farmacopee. *Volatile oil content*, 6th ed.; Staatsuitgeverij: s-Gravenhagen, The Netherlands, 1966; pp 72–73.

Nykänen, I.; Nykänen, L.; Alkio, M. The compositions of the flavour of juniper berries isolated by supercritical CO_2 extraction and steam distillation. In *Flavour Science and Technology*; Bessiere, Y., Thomas, A. F., Eds.; Wiley: Chichester, Great Britain, 1990; pp 217–220.

Nykänen, I.; Nykänen, L.; Alkio, M. Composition of angelica root oils obtained by supercritical CO_2 extraction and steam distillation. *J. Essent. Oil Res.* **1991**, *3*, 229–236.

Pangborn, R. M. Sensory analysis as an analytical laboratory tool in food research. In *Modern Methods of Food Analysis*; Stewart, K. K., Whitaker, J. R., Eds.; Avi Publishing: Westport, CT, 1984; pp 265–291.

Pangborn, R. M. Sensory science in flavour research: Achievements, needs and perspectives. In *Flavour Science and Technology*; Martens, M., Dalen, G. A., Russwurm, H., Eds.; Wiley: Chichester, Great Britain, 1987; pp 275–289.

Patton, S.; Josephson, D. V. A method for determining significance of volatile flavor compounds in foods. *Food Res.* **1957**, *22*, 316–318.

Pellerin, P. Supercritical fluid extraction of natural raw materials for the flavor and perfume industry. *Perfum. Flavor.* **1991**, *16*, 37–39.

Powers, J. J. Perception and analysis: A perspective view of attempts to find causal relations between sensory and objective data. In *Flavour '81*; Schreier, P., Ed.; de Gruyter: Berlin, 1981; pp 103–131.

Reverchon, E.; Senatore, F. Isolation of rosemary oil: Comparison between hydrodistillation and supercritical CO_2 extraction. *Flavour Fragrance J.* **1992**, *7*, 227–230.

Rizvi, S. S. H.; Daniels, J. A.; Benado, A. L.; Zollweg, J. A. Supercritical fluid extraction: Operating principles and food applications. *Food Technol.* **1986**, *40*, 57–64.

Schultz, W. G.; Schultz, T. H.; Carlson, R. A.; Hudson, J. S. Pilot-plant extraction with liquid CO_2. *Food Technol.* **1974**, *28*, 32–36, 88.

Shutte, L. A new model for describing interactions in odour mixtures. In *Progress in Flavour Research*; Adda, J., Ed.; Elsevier: Amsterdam, 1985; pp 3–13.

Sims, M. Process uses liquid CO_2 for botanical extraction. *Chem. Eng.* **1982**, 50–51.

Stahl, E. *Microchim. Acta* **1953**, *40*, 367–371.

Stahl, E.; Gerard, D. *Parfum. Kosmet.* **1982**, *63*, 117–125.

Stahl, E.; Gerard, D. *Parfum. Kosmet.* **1983**, *64*, 237–240.

Stahl, E.; Gerard, D. Solubility behaviour and fractionation of essential oils in dense carbon dioxide. *Perfum. Flavor.* **1985**, *10*, 29–37.

Stahl, E.; Quirin, K. W. Extraction of natural substances with dense gases. *Pharm. Res.* **1984**, 189–193.

Stenhagen, E.; Abrahamsson, S. A.; McLafferty, F. W. *Registery of Mass Spectral Data*; Wiley: New York, 1974.

Temelli, F.; Braddock, R. J.; Chen, C. S.; Nagy, S. Supercritical carbon dioxide extraction of terpenes from orange essential oil. In *Supercritical Fluid Extraction and Chromatography: Techniques and Applications*; Charpentier, B. A., Sevenants, M. R., Eds.; ACS Symposium Series 366; American Chemical Society: Washington, DC, 1988; pp 109–126.

Teranishi, R.; Buttery, R. B.; Stern, D. J.; Takeoka, G. Computer assisted correlation of gas chromatographic data with aroma. In *Flavour Science and Technology*; Bessiere, Y., Thomas, A. F., Eds.; Wiley: Chichester, Great Britain, 1990; pp 267–270.

TNO. *Compilation of Mass Spectra of Volatile Compounds in Foods*; ten Noever de Brauw, M. C., Bouwman, J., Tas, A. C., La Vos, G. F., Eds.; Central Institute for Nutrition and Food Research-TNO: Zeist, The Netherlands, 1979.

Udaya Sankar, K. Studies on the physicochemical characteristics of volatile oil from pepper (*Piper nigrum*) extracted by supercritical carbon dioxide. *J. Sci. Food Agric.* **1989**, *48*, 483–493.

von Sydow, E.; Andersson, J.; Anjou, K.; Karlsson, G.; Land, D.; Griffiths, N. The aroma of bilberries (*Vaccinium myrtilus* L.). II. Evaluation of the press juice by sensory methods and by gas chromatography and mass spectrometry. *Lebensm. Wiss. Technol.* **1970**, *3*, 11–17.

Weder, J. K. P. Studies on proteins and amino acids exposed to supercritical carbon dioxide extraction conditions. *Food Chem.* **1984**, *15*, 175–190.

Zosel, K. Separation with supercritical gases: Practical applications. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 702–709.

Received for review October 6, 1992. Revised manuscript received February 11, 1993. Accepted February 18, 1993.