Supercritical Carbon Dioxide Extraction of Cardamom

Narayanan Gopalakrishnan* and Cadavallur S. Narayanan

Regional Research Laboratory (CSIR), Trivandrum 695019, Kerala, India

Cardamom (*Eletteria cardamomum* Maton) seeds were extracted with supercritical carbon dioxide at different conditions of pressure, temperature, contact time, and moisture content to estimate the yield and compositional variations. The yield of cardamom extract was found to be fairly constant at different conditions of extraction, but the nonvolatiles and chlorophyll contents varied in the extract with extraction parameters. The proportion of minor and major components also showed variations under different conditions of extraction.

INTRODUCTION

Cardamom (*Eletteria cardamomum* Maton) is one of the most commonly used spices. The cardamom flavor is incorporated in processed foods, mainly by using the hydrodistilled cardamom oil and, to some extent, by adding the solvent-extracted cardamom oleoresin (Lewis, 1984).

Both the hydrodistilled oil and the oleoresin have a different aroma from that of the natural cardamom. This is due to the heat and water based changes taking place during distillation in the oil and the solvent residue, removal of more volatiles, etc. in the oleoresin. To get cardamom oil devoid of the above limitations, carbon dioxide extraction of cardamom was found to be ideal (Gopalakrishnan and Narayanan, 1988). Carbon dioxide as a solvent has advantages: it is a colorless, odorless, tasteless, noncorrosive, chemically inert gas which retains no solvent residue in the extract, and it can be compressed to liquid or supercritical (SC) state (Grimmett, 1981). The solvation property of the carbon dioxide can also be modified by adjusting pressure, temperature, moisture contents, etc. (Rizvi et al., 1986) through density and dielectric constant changes (Stahl et al., 1978).

Natural products like cardamom oil contain various components, mainly oxygenated and nonoxygenated terpenes. Each of these components plays a definite but unknown role in the solubility of the oil in supercritical carbon dioxide, other than the influence of extraction parameters. In this paper we report the influence of the extraction parameters on yield and composition of the cardamom oil obtained with carbon dioxide extraction.

MATERIALS AND METHODS

The NOVA SWISS (Switzerland) liquid and supercritical carbon dioxide extraction unit was used for the study. The unit was equipped with a compressor, extractor, separator, and heating arrangements for the extractor and separator. Temperature and pressure were measured at all stages by thermocouple-based digital indicating system and pressure transducers. Carbon dioxide gas, in cylinders at 30–80 kg/cm^2 pressure, was the source of the solvent.

Freshly ground cardamom seeds (40–60 mesh) were filled in the extractor, and carbon dioxide was pumped into it up to the required pressure. Temperature was maintained by circulating warm water through the jacket of the extract. When the required pressure was attained in the extractor, the inlet was closed and the contact time was measured. The supercritical carbon dioxide containing the dissolved cardamom oil was released to the separator, where the extract was deposited and the solvent flash evaporated through the exhaust. The effect of the change in one of the parameters was studied by keeping the other parameters of extraction constant. Nonvolatile materials were estimated by hydrodistillation of known amounts of the extract. The oil in the residue after carbon dioxide extraction and the chlorophyll in the extract were estimated according to an AOAC method and calculated on weight basis (AOAC, 1984).

The cardamom extract volatile composition was analyzed using a Hewlett-Packard 5840A gas chromatograph fitted with a stainless steel column (6 ft × $^1/_8$ in.) packed with OV-17 on Chromosorb. The column temperature was programmed at 80–200 °C, at the rate of 5 °C/min. Injector and detector temperatures were maintained at 250 °C. N_2 at the rate of 20 mL/min was used as carrier gas. The components were identified using standard references obtained from Fluka Switzerland and BASF AG Germany.

RESULTS AND DISCUSSION

The yield of cardamom extract by carbon dioxide extraction accounted for 85–95% of that obtained with petroleum ether extraction (Mathew, 1985). This shows the solubility of cardamom oil in supercritical carbon dioxide is fairly high, so a maximum amount of extract is obtained from cardamom seeds even by a single extraction. The residue after carbon dioxide extraction contained only 0.4–0.8% oil. The yield of extract at pressures ranging from 100 to 600 bar was fairly constant. At the same time, the nonvolatile content in the extract varied, with a minimum of 4.5% in that obtained at 100 bar and a maximum of 9.5% at 500 bar. This may be due to better solubility of the nonvolatiles at higher pressure but at the expense of the volatiles. The nonvolatile content of petroleum ether extracted cardamom oleoresin was as high as 30–40% (Mathew, 1985).

The extract obtained with carbon dioxide was light green to green in color when the pressure of extraction increased. The corresponding increase in the chlorophyll contents was from 18 to 93 ppm in the extract (Table I). Coloring materials like chlorophylls are known to be insoluble in the carbon dioxide (Grimmett, 1981). However, we found that colorants are being extracted with cardamom oil due to the entrainer effect of cardamom oil constituents in carbon dioxide (Bruner, 1983). Addition of moisture or organic solvents is suggested for improving the solubility of oils in carbon dioxide, but increase in the moisture contents of the cardamom seeds did not affect the yield. The essential oil solubility was found to decrease in carbon dioxide when a high level of moisture is present in the tobacco (Roselius et al., 1972). The yield of cardamom extract was 7.6% at half an hour of contact time, which also remained fairly constant when contact time was increased to 3 h. By organic solvents an optimum time duration of 5 h is reported for cardamom oil extraction

* Author to whom correspondence should be addressed.

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Table I. Yield and Characteristics of Cardamom Extract Obtained by SC CO_2

	pressure[a]						temp[b]			time[c]				moisture[d]		
	100 bar	200 bar	300 bar	400 bar	500 bar	600 bar	40 °C	50 °C	60 °C	0.5 h	1 h	2 h	3 h	10%	20%	30%
yield of oil, %	7.6	7.5	7.9	7.5	7.8	7.6	7.8	7.8	7.8	7.6	7.6	7.7	7.8	7.8	7.6	7.6
residual oil, %	0.6	0.8	0.6	0.6	0.5	0.6	0.5	0.7	0.4	0.5	0.6	0.6	0.5	0.6	0.7	0.7
nonvolatiles, %	4.5	5.4	7.0	8.8	9.5	9.4	9.5	8.8	9.2	9.3	9.5	9.5	9.5	9.5	9.4	10.0
chlorophyll, ppm	18	29	38	53	90	93	90	85	85	40	90	90	90	90	90	81

[a] Temperature 40 °C, contact time 3 h, and moisture 10%. [b] Pressure 500 bar, contact time 3 h, and moisture 10%. [c] Pressure 500 bar, temperature 40 °C, and moisture 10%. [d] Pressure 500 bar, temperature 40 °C, and contact time 3 h (average of three trials).

Table II. Composition of Cardamom Extract Volatiles Obtained by SC CO_2 at Different Pressures

	pressure					
compound	100 bar	200 bar	300 bar	400 bar	500 bar	600 bar
α-pinene	1.6	1.5	1.5	1.4	1.6	1.7
sabinene	4.1	3.8	4.0	4.0	4.2	4.5
β-pinene	2.8	2.8	2.6	2.4	2.6	2.6
δ-limonene	2.4	2.4	2.5	2.3	2.4	2.6
1,8-cineole	29.7	29.9	29.2	27.3	30.0	30.8
linalool	2.6	2.5	2.7	2.7	2.6	2.6
terpinen-4-ol	1.3	1.3	1.5	1.5	1.3	1.3
α-terpineol	4.6	4.5	4.5	4.6	4.5	4.4
linalyl acetate	1.6	1.6	1.9	1.9	1.7	1.6
geraniol	0.6	0.6	0.8	0.7	0.6	0.5
nerol	0.4	0.4	0.4	0.5	0.4	0.3
terpinyl acetate	37.0	38.8	37.0	37.2	36.7	38.2
geranyl acetate	0.7	0.7	1.0	1.0	0.8	0.7
nerolidol	1.6	1.8	1.3	1.3	1.4	1.2

(Mathew, 1985). The lower time duration for carbon dioxide extraction is due to the high diffusivity at supercritical state in the seed particles (Blenford, 1983). At half an hour of contact time the chlorophyll content was considerably low in the extract and hence the color also. The temperature of extraction did not affect significantly the yield, nonvolatiles, or chlorophyll content in the 40–60 °C range at 500 bar.

Effect of Extraction Parameters on Volatile Oil Composition. *Effect of Pressure.* The major volatile components of the cardamom extract obtained at different pressure are given in Table II. Variation in the pressure of extraction did not seem to have a significant impact on the composition of the major volatile components of cardamom extract. This could be due to the presence of components with varying molecular weight and polarity which might influence almost uniformly the solvation property of supercritical carbon dioxide, and hence the same patterns of extraction at pressures between 100 and 600 bar are obtained.

The 1,8-cineole and terpinyl acetate together, comprising two-thirds of the total volatiles, remained almost at the same level at all pressures of extraction. There were about 12 minor components, each ranging from 0.05% to 0.5% eluted in GLC at low temperatures before the elution of terpinyl acetate, which are termed here more volatile minor components (MVMC), the total of which increased from 2.2% at 100 bar to 3.5% at 500 bar. These components together comprised less than 1.9% in distilled cardamom oil. Similarly, about 13 less volatile minor components (LVMC) eluted after terpinyl acetate in GLC, present at a 2.2% level in the distilled oil, were present 4.0–6.0% in the extract obtained at different pressures. In many spices and aromatic plants these minor components play a very important role in imparting the natural aroma (Stahl and Gerard, 1985). It was also noteworthy that many of these minor components were absent in the distilled oil. This may be one of the reasons for the better and natural aroma of cardamom extracts obtained by carbon dioxide.

Table III. Composition of Cardamom Extract Volatiles Obtained by SC CO_2 at Different Temperatures

	temp		
compound	40 °C	50 °C	60 °C
α-pinene	1.6	1.6	1.5
sabinene	4.2	4.2	3.9
β-pinene	2.6	2.4	2.2
δ-limonene	2.4	2.4	2.3
1,8-cineole	30.0	28.7	27.5
linalool	2.6	2.5	2.3
terpinen-4-ol	1.3	1.2	1.3
α-terpineol	4.5	4.7	4.5
linalyl acetate	1.7	1.6	1.7
geraniol	0.6	0.5	0.7
nerol	0.4	0.3	0.9
terpinyl acetate	36.7	37.3	35.7
geranyl acetate	0.8	0.8	0.9
nerolidol	1.4	1.7	1.3

Table IV. Composition of Cardamom Extract Volatiles Obtained by SC CO_2 at Different Contact Times

	contact time			
compound	0.5 h	1 h	2 h	3 h
α-pinene	1.8	1.3	1.5	1.6
sabinene	4.2	3.7	3.9	4.2
β-pinene	2.5	2.4	2.4	2.6
δ-limonene	2.6	2.5	2.3	2.4
1,8-cineaole	29.1	28.3	27.0	30.0
linalool	3.1	3.0	2.7	2.6
terpinen-4-ol	1.5	1.6	1.5	1.3
α-terpineol	4.5	4.9	4.4	4.5
linalyl acetate	1.8	1.8	1.8	1.7
geraniol	0.5	0.5	0.7	0.6
nerol	0.4	0.3	0.4	0.4
terpinyl acetate	39.0	42.5	35.5	36.7
geranyl acetate	0.8	0.9	0.9	0.8
nerolidol	1.6	1.5	1.3	1.4

Effect of Temperature. The major effect noted when the extraction temperature was increased from 40 to 60 °C was a general reduction in the major components, especially more volatiles (Table III). MVMC decreased from 3.3% to 2.1% and LVMC increased from 5.0% to 8.0% when the extraction temperature was increased. It was due to the loss of more volatiles with carbon dioxide during the flash evaporation at high temperature. Stahl and Gerard (1985) have shown that a general reduction in the solubility of volatile compounds in carbon dioxide at elevated temperature takes place, but this was not true in cardamom oil extraction with supercritical carbon dioxide, probably due to the presence of a number of components with varying polarity.

Effect of Contact Time. The 1,8-cineole content first decreased and then increased with contact time, whereas terpinyl acetate recorded a maximum at 1 h of contact time and then decreased (Table IV). The proportions of MVMC and LVMC were, respectively, 2.6% and 2.0% at half an hour of contact time, which increased to 3.3% and 5.0% at 3 h, showing an increased solubility of minor components with increase in contact time.

Table V. Composition of Cardamom Extract Volatiles Obtained by SC CO_2 at Different Moisture Contents

compound	moisture 10%	20%	30%
α-pinene	1.6	0.9	1.3
sabinene	4.2	2.8	3.7
β-pinene	2.6	1.8	2.2
δ-limonene	2.4	1.9	2.3
1,8-cineole	30.0	22.3	27.8
linalool	2.6	2.7	2.7
terpinen-4-ol	1.3	1.5	1.4
α-terpineol	4.5	4.9	4.8
linalyl acetate	1.7	2.0	1.8
geraniol	0.6	0.8	0.6
nerol	0.4	0.5	0.4
terpinyl acetate	36.7	37.6	42.6
geranyl acetate	0.8	1.1	0.8
nerolidol	1.4	1.7	1.6

Effect of Moisture Content. The use of water as entrainer for increasing the solubility property of carbon dioxide is a subject of much interest (Brunner, 1983). The contents of terpene hydrocarbons and 1,8-cineole decreased with the increase in moisture level from 10% to 20% by added water, whereas further increase to 30% moisture level gave an opposite pattern of changes (Table V). Minor increases were also noted in the contents of terpinyl acetate, nerolidol, geraniol, terpineol, and terpinen-4-ol, which are all polar in nature, when the moisture level increased to 20%. To this level it appears, even in a mixture, the solubilities of polar components improve in carbon dioxide, which was similar to the observations made with individual polar compounds (Stahl and Gerard, 1985).

Conclusion. In conclusion, the cardamom extract obtained at different conditions of extraction with supercritical carbon dioxide has shown that the product in good yield and required quality can be obtained even at 100 bar, 40 °C, and shorter contact time without added moisture from the ground cardamom seeds. This product was light green in color, had fewer nonvolatiles, and had a natural aroma different from that of the hydrodistilled product and petroleum extract of cardamom. These parameters of extraction are also milder than the other sets of carbon dioxide extraction conditions and hence adaptable.

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Registry No. CO_2, 124-38-9; α-pinene, 80-56-8; sabinene, 3387-41-5; β-pinene, 127-91-3; δ-limonene, 5989-27-5; 1,8-cineole, 470-82-6; linalool, 78-70-6; terpinen-4-ol, 562-74-3; α-terpineol, 98-55-5; linalyl acetate, 115-95-7; geraniol, 106-24-1; nerol, 106-25-2; terpinyl acetate, 8007-35-0; geranyl acetate, 105-87-3; nerolidol, 142-50-7.