

Studies on the Storage Quality of CO₂-Extracted Cardamom and Clove Bud Oils

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Studies on the storage quality of supercritical carbon dioxide extracted cardamom (*Elettaria cardamomum* Maton) and clove (*Syzygium aromaticum* L.) bud oils were carried out and the results compared with the quality of commercially steam distilled oils. It was observed that chemical composition of the oils changed during 90 days of storage. Compositional variations were remarkable in the CO₂-extracted oils. Changes in the clove bud oil composition were comparatively less prominent than in the cardamom oil. The class of components that underwent quantitative reduction was the terpene hydrocarbons in both oils, whereas the other components showed varying responses at low and ambient temperatures of storage.

INTRODUCTION

Detailed studies have been reported on the quality and compositional aspects of spice oils and oleoresins extracted using liquid or supercritical CO₂ (Moyler, 1984; Moyler and Heath, 1986). In many of the research papers published during the past two decades, merits of the CO₂ extraction have been highlighted, giving special reference to the natural fine aroma and flavor of the extracts (Rizvi *et al.*, 1986). Predictions were also made in which CO₂ was touted as the solvent of the future (Blenford, 1983). Even though in-depth studies prove that the CO₂ extracts have many merits, no systematic study has been carried out on the storage quality of the CO₂ extracts. Since CO₂ extracts have not been subjected to heat, vacuum, hydrodistillation, etc. and compositionally they contain nonvolatiles and colorants also, they differ from the corresponding hydrodistilled oils and solvent-extracted oleoresins. Hence, their storage study is important, especially when we consider the fact that the time duration between oil production and utilization generally varies from 3 to 6 months (M. Venkatesh, Synthite Industrial Chemicals Ltd., Kerala, 1991, personal communication). In this paper we report a study carried out on the compositional changes of extracts obtained by CO₂ extraction of two major spices, cardamom (*Elettaria cardamomum*) and clove buds (*Syzygium aromaticum*) during storage.

MATERIALS AND METHODS

Cardamom and Clove Bud Oils. Cardamom and clove buds were procured from the local market, cleaned, ground, and extracted using CO₂ at 100 bar of pressure, 25 °C, and 30 min contact time as described in our earlier publications (Gopalakrishnan *et al.*, 1990b; Gopalakrishnan and Narayanan, 1991). Freshly prepared steam-distilled commercial cardamom and clove bud oils were purchased from the producing center and used as references.

Storage of Oils. Two milliliters each of cardamom and clove bud oils was taken in three sets of airtight 5-mL glass vials with Teflon screw caps. One set of carbon dioxide extracts was stored in a freezer at 0 ± 1 °C. One set of CO₂ extracts and the steam-distilled oils were stored at ambient conditions, 28 ± 3 °C temperature.

GLC Analyses. Compositional analyses of the fresh and stored samples were carried out on a Hewlett-Packard Model 5840 A GLC unit using an OV-17 packed column (10% OV-17 in Chromosorb WHP 100-120 mesh). The column temperature was programmed between 80 and 160 °C, at the rate of 5 °C/min.

Injection port and detectors were maintained at 250 and 300 °C, respectively. Component peaks were identified using a standard reference and quantified using an electronic integrator.

RESULTS

Commercially distilled cardamom oil and clove bud oil were colorless. The CO₂ extract of cardamom was pale yellow and that of clove buds was brown in color. Both extracts had an appreciable quantity of nonvolatiles (Gopalakrishnan *et al.*, 1990b; Gopalakrishnan and Narayanan, 1991). The CO₂ extracts had a natural aroma of the original spice which was better than that of the distilled oils. The commercial oils had the distilled "note" of the corresponding spice.

Changes in Cardamom Oil. β -Pinene, sabinene, and δ -limonene were the major terpene hydrocarbons and underwent remarkable changes during storage (Table I). These hydrocarbons showed 35-50% reduction during 90 days of storage at 0 ± 1 °C, in CO₂-extracted oil. β -Pinene and sabinene together were reduced from 7.1 to 0.4% at ambient condition. Similarly, δ -limonene was reduced from 2.3 to 0.5% during the same period of storage. The above hydrocarbons were reduced from 14.4 to 6.8% in the commercial oil stored at ambient condition. Cineole contents were decreased in the 0 ± 1 °C stored sample from 27.0 to 21.8% and in the ambient temperature stored samples from 27.0 to 14.7% and from 38.8 to 27.8% in commercial oil. Reductions in percentage proportion of these values are, respectively, 19, 45, and 28%. Changes also took place in the terpene alcohols but were not prominent. In the CO₂ extract stored at 0 ± 1 °C and distilled oil, the terpenyl acetate content increased during 90 days of storage. In other samples, a remarkable increase of this ester content was noted in 45 days and thereafter it reduced to the original level. The two minor esters, geranyl acetate and linalyl acetate, also underwent minor changes in their content in all of the samples during storage.

The minor components, each of which accounted for more than 0.1% in the oil, also underwent important and quality-affecting changes. The minor components eluting before terpenyl acetate in the GLC [termed in this text as more volatile minor components (MVMC)] increased quantitatively and changed qualitatively. A similar observation was made for the minor components eluting after terpenyl acetate in the GLC [termed as less volatile minor components (LVMC)]. In the fresh CO₂ extract of cardamom, four MVMCs and six LVMCs accounted for,

Table I. Changes in Cardamom Oil during Storage

component	days of storage								
	carbon dioxide extracted oil					commercial distilled oil			
	0	45 ^a	90 ^a	45	90	0	45	90	
α -pinene	0.7	1.1	0.5	0.7	0.2	2.3	1.5	0.6	
β -pinene	4.3	3.0	2.0	1.7	0.3	6.2	4.0	2.5	
sabinene	2.8	2.0	1.4	1.2	0.1	4.2	2.6	1.6	
δ -limonene	2.3	1.8	1.5	1.6	0.5	4.0	3.7	2.7	
cineole	27.0	24.7	21.8	22.9	14.7	38.8	30.2	27.8	
linalol	3.9	4.0	3.3	3.8	2.2	5.7	5.4	5.3	
terpen-4-ol	2.0	1.6	2.1	2.0	2.0	2.0	2.9	3.2	
α -terpeneol	5.9	5.8	5.5	5.5	4.4	3.4	3.0	3.3	
linalyl acetate	1.5	1.6	1.7	1.0	0.8	1.0	1.5	1.7	
geraniol	0.4	0.5	0.5	0.4	0.8	0.2	0.2	0.3	
terpenyl acetate	40.9	46.6	49.4	53.1	40.3	24.6	40.3	43.3	
geranyl acetate	0.6	0.6	1.1	0.5	0.8	0.8	1.9	1.3	
nerolidol	1.5	2.1	1.5	1.0	1.6	tr	tr	0.5	
MVMC ^b	1.7 (4) ^c	1.8 (3)	3.8 (7)	2.8 (7)	5.8 (12)	0.5 (4)	2.3 (6)	0.9 (3)	
LVMC ^b	1.8 (6)	2.2 (4)	3.5 (7)	1.0 (4)	25.4 (14)	0.2 (2)	0.2 (2)	2.1 (6)	

^a At 0 \pm 1 °C. ^b MVMC, more volatile minor components; LVMC, less volatile minor components. ^c Figure in parentheses is number of components <0.1%.

Table II. Changes in Clove Bud Oil during Storage

component	days of storage								
	carbon dioxide extracted oil					commercial distilled oil			
	0	45 ^a	90 ^a	45	90	0	45	90	
α -cubebene	1.5	1.1	1.3	1.2	1.2	0.7	0.7	0.6	
α -copaene	1.7	1.4	1.5	1.4	1.4	1.0	1.0	1.0	
caryophyllene	16.6	15.0	14.7	15.1	13.6	10.8	10.5	9.4	
eugenol	62.2	61.4	64.8	61.3	65.7	71.0	70.1	72.6	
isoeugenol	0.9	0.9	0.8	0.8	0.6	0.6	0.6	0.5	
nerolidol	1.2	1.2	1.2	1.2	1.2	0.4	1.2	1.1	
eugenol acetate	14.3	13.8	13.6	14.6	13.6	12.1	13.4	12.3	
farnesol	0.1	0.3	0.3	0.4	0.3	0.2	0.3	0.4	
MVMC ^b	0.2 (1) ^c	0.1 (1)	0.3 (1)	0.1 (1)	0.2 (1)	0.1 (1)		0.1 (1)	
LVMC ^b	1.1 (2)	2.7 (8)	1.4 (4)	3.6 (9)	2.2 (5)	2.2 (6)	2.3 (7)	1.8 (4)	

^a At 0 \pm 1 °C. ^b MVMC, more volatile minor components; LVMC, less volatile minor components. ^c Figure in parentheses gives number of components <0.1%.

respectively, 1.7 and 1.8%, and their number increased to seven each and their quantity increased from to 3.8 and 3.5%, respectively, in the 0 \pm 1 °C stored oil. At the same time the numbers of MVMCs and LVMCs were 12 and 14 and their proportions were 5.8 and 25.4%, respectively, in the samples stored at ambient condition. The changes in LVMCs and MVMCs were minor in the distilled oil.

Changes in Clove Bud Oil. The major components of clove bud oil were caryophyllene, eugenol, and eugenol acetate (Table II). Reductions in caryophyllene content during 90 days of storage were 11, 18, and 13%, respectively, in 0 \pm 1 °C and ambient condition stored samples and commercial oil. Eugenol content remained fairly constant in all samples, whereas eugenol acetate underwent changes which were prominent in the CO₂-extracted clove bud oil. Changes in the number and quantity of the minor components were less remarkable in all three samples during storage.

DISCUSSION

Chemical changes in terpenoid compounds are known to occur due to light, oxygen, catalyst, moisture, heat, etc. (Thomas, 1971), resulting in the formation of new compounds or polymerization (Verghese, 1982). The cardamom oil and clove bud oil are mixtures of a number of terpenoids, and the changes taking place in each component may also affect or initiate changes in other components of the oil. Unlike the commercial steam-distilled oils, the CO₂ extracts also contain a high quantity of nonvolatiles and coloring materials (Gopalakrishnan *et*

al., 1990b). The majority of these nonvolatiles are lipids containing polyunsaturated fatty acids (Gopalakrishnan *et al.*, 1990a). These fatty acids undergo autoxidation very easily and can initiate the chemical changes in the terpenes also (Lillard, 1978). The presence of chlorophyll and carotenoids might also affect the storage life of oils.

When CO₂ extracts of cardamom and clove buds were stored at 0 \pm 1 °C, the effect of temperature was minimal, but at ambient conditions it was significant. Therefore, a higher levels of degradation or chemical changes were noted in those samples than in those stored at low temperature. This was very prominent in β -pinene, sabinene, δ -limonene, cineole, etc., in the 90-days-stored CO₂-extracted cardamom oil. However, the esters were more stable than other components, and hence a proportional increase corresponding almost to the reduction of other components was noted. A remarkable reduction at the later stage of storage in the ester content was noted when samples were stored at ambient conditions with a concurrent increase of LVMCs. This shows chemical changes other than hydrolysis had taken place, resulting in the formation of compounds having higher molecular weight including polymerized compounds. A high quantity of LVMCs may also be formed due to the decomposition of polymerized compounds at the elevated temperature in the GLC column during analysis. However, the corresponding changes were not as significant in the distilled oil when stored at the similar conditions. This shows the nonvolatile components play a deleterious role, especially at ambient conditions, in the quality aspects of

CO₂-extracted cardamom oil, resulting in compositional variation which directly affected its fine aroma and flavor.

In the clove bud oil, less significant changes, except for caryophyllene, took place. This may be due to the antioxidant properties and highly stable phenolic nature of eugenol and related components (Nakatani, 1988) which together were present more than three-fourths in the oil. Even in the presence of these components, changes in the terpenoid hydrocarbons of CO₂-extracted oil were significant, emphasizing the effect of nonvolatiles in the quality aspects of clove bud extract when stored at ambient condition.

CONCLUSION

From these observations it can be concluded that during storage CO₂-extracted cardamom and clove bud oils, even though they have better quality if used as fresh, deteriorate in quality faster than the distilled commercial oils. A variety of chemical changes taking place during storage result in changes of the fine composition and the loss of even natural aroma of the oils obtained by CO₂ extraction. The presence of an effective antioxidant or preservatives and storage at very low temperature may be opted for to minimize the rate of chemical changes in these extracts during storage.

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