Chemical Composition of Volatile Oil from *Cinnamomum zeylanicum* Buds

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Cinnamomum zeylanicum, Volatile Oil, GC-MS Analysis

The hydro-distilled volatile oil of the *Cinnamomum zeylanicum* (*C. zeylanicum*) buds was analyzed using GC and GC-MS for the first time. Thirty-four compounds representing ≈ 98% of the oil was characterized. It consists of terpene hydrocarbons (78%) and oxygenated terpenoids (9%). α-Bergamotene (27.38%) and α-copaene (23.05%) are found to be the major compounds. A comparison of the chemical composition of the oil was made with that of flowers and fruits.

Introduction

The genus *Cinnamomum* comprises several hundred species, which occur in Asia and Australia. These are evergreen trees and shrubs and most of the species are aromatic. *C. zeylanicum*, the source of cinnamon bark and leaf oils, is a tree indigenous to Sri Lanka. Many species of cinnamon yield a volatile oil on distillation. The most important cinnamon oils in world trade are those from *C. zeylanicum*, *C. cassia* and *C. camphora.* The other species provide oils, which are utilized as sources for chemical isolates. However, a number of other cinnamon species are distilled on a much smaller scale and the oils used either locally or exported (The Wealth of India, 1992). Major compounds present in stem-bark oil and root-bark oil are cinnamaldehyde (75%) and camphor (56%), respectively (Senanayake *et al.*, 1978). Cinnamon bark oil possesses the delicate aroma of the spice and a sweet and pungent taste. It is employed mainly in the flavouring industry where it is used in meat and fast food seasonings, sauces, pickles, baked goods, confectionery, cola-type drinks, tobacco flavours and in dental and pharmaceutical preparations. Perfumery applications are far less than in flavours because the oil has some skin-sensitizing properties, so it has limited use in some perfumes. Mallavarapu *et al.* (1995) identified 53 constituents along with the major component eugenol (81–84.5%) in cinnamon leaf oil. Cinnamon leaf oil has a warm, spicy, but rather harsh odour, lacking the rich body of the bark oil. Leaf oil has fragrant odor and very pungent taste. Thirty-four compounds have been previously identified in cinnamon fruit oil with *(E)*-cinnamyl acetate (42–54%) and caryophyllene (9–14%) as the major components (Jayaprakasha *et al.*, 1997). Twenty-six compounds constitutes 97% of the volatile oil from cinnamon flowers were characterized with *(E)*-cinnamyl acetate (42%), *trans*-α-bergamotene (8%) and caryophyllene oxide (7%) as the major compounds (Jayaprakasha *et al.*, 2000). The objective of the present study is to determine the chemical composition of the volatile oil from the buds of *C. zeylanicum.* This is the first report on the chemical composition of the buds volatile oil of *C. zeylanicum.*

Materials and Methods

Plant material

The buds of *C. zeylanicum* were collected from Karkala (Coastal Karnataka, India). The species was identified and voucher specimen was deposited at the Manasagangotri herbarium (MGH NO.3A/96/01), Botany Department, University of Mysore, Mysore.

Isolation of volatile components

Fresh buds (100 g) were subjected to hydro-distillation in a Clevenger-type apparatus for 4 h. The yield (v/w) of volatile oil was 0.2%. The volatile oil was dried over anhydrous sodium sulfate and stored at 4° C for analysis.

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GC analysis

The GC analysis was carried out using a Shimadzu GC 15A chromatograph equipped with a FID detector, using a SE-30 column (3 m × 3 mm). The oven temperature was programmed from 60° C for 5 min to 225° C at the rate of 2° C/min at which temperature the column was maintained for 3 min. The injector port temperature was 225° C, the detector temperature was 250° C and nitrogen as carrier gas at a flow rate of 40 ml min^{-1}. Peak areas were computed by a Shimadzu C-R4A chromatopac data processor.

GC-MS analysis

The oil was analyzed using a Shimadzu 17A-GC chromatograph equipped with a QP-5000 (Quadruple) mass spectrometer. The sample was diluted 25 times with acetone, and 1 μl was injected. A fused silica column SPB-1 (30 m × 0.32 mm, film thickness 0.25 μm) coated with polydimethyl siloxane was used. Helium was the carrier gas at a flow rate of 1 ml/min. The injector port temperature was 225° C, the detector temperature was 250° C and the oven temperature was maintained at 60° C for 2 min and then increased to 225° C at the rate of 2° C/min at which temperature the column was maintained for 5 min. The split ratio was 1:25 and the ionization voltage, 70 eV.

Results and Discussion

The volatile oil of buds of *C. zeylanicum* was obtained by hydrodistillation and was analysed by GC and GC-MS. Retention indices for all the compounds were determined according to the Kovats method (Jennings and Shibamoto, 1980) using n-alkanes as standards. The compounds were identified by comparison of Kovats indices with those reported in the literature (Jennings and Shibamoto, 1980; Davies, 1990), wherever possible, by co-injection with an authentic sample and by matching their fragmentation patterns in mass spectra with those stored in NIST library and published mass spectra (Strenhagen *et al.*, 1974; Bravw *et al.*, 1988).

The chemical composition of the bud oil of *C. zeylanicum* is presented in Table I. A total of thirty-four compounds were identified, which constitute ≈ 98% of the volatile oil. Mevalonic acid and shikimic acid metabolites account for ≈ 87% and ≈ 2.4% respectively. Straight chain compounds were present to the extent of ≈ 8%.

Sesquiterpenes were the major compounds (≈ 85%) among the mevalonic acid metabolites. The monoterpene portion was very low (≈ 2%). The major sesquiterpenes were found to be α-bergamotene, α-copaene. Minor compounds were found to be α-humulene, α-muurolene and δ-cadinenes. α-Cadinol and globulol were the major sesquiterpene alcohols. Caryophyllene oxide was the only oxide and present in very low percentage (< 1.0%). Straight-chain compounds represented by two different classes of functional groups *viz* alcohols and acid. Ester *viz. (E)*-cinnamyl acetate was present to an extent of 2.4%.

Comparison of composition of volatile oils from buds, flowers (Jayaprakasha *et al.*, 2000) and fruits (Jayaprakasha *et al.*, 1997) revealed that the oil from buds contain more relative amounts of mevalonic acid derivatives (*viz.*, mono and sesquiterpenes). The character impact compound *i. e.*, *trans*-cinnamyl acetate was found to be the major compound present in the volatile oils of fruits (42–54%) and flower (42%), whereas in buds volatile oil it is present to the extent of 2.4% only. Formation of this compound might have initiated in the buds stage and its further formation could have propagated during the flowering stage and reached a maximum in the fruits stage. Eleven compounds present in the flower volatile oil (Jayaprakasha *et al.*, 2000) are found in the buds oil and constituted to the extent of 66% of the oil. These are α-copaene, α-bergamotene, *trans*-cinnamyl acetate, α-humulene, germacrene-D, 1S-*cis*-calamenene, caryophyllene oxide, globulol, α-cadinol, *epi*-α-bisabolol, and benzyl benzoate. Similarly, twelve compounds present in the fruit volatile oil (Jayaprakasha *et al.*, 1997) are also found in the buds oil and constituted to the extent of 46% of the oil. These are α-pinene, α-copaene, *trans*-cinnamyl acetate, α-humulene, germacrene-D, γ-cadinene, δ-cadinene, β-guaine, caryophyllene oxide, globulol, τ-cadinol, and benzyl benzoate. The amounts of shikimic acid derivatives are increasing during the flowering and fruits stage. It may be concluded that mevalonic acid metabolites formed to a maximum extent during the buds stage and levels increased to some extent during the fruits stage. However, the formation of shikimic acid derivatives initiated dur-

Table I. Chemical composition of the volatile oil of cinnamon buds.

Peak No.	Retention time [min]	Compound	Peak Area [(%]	KI	Identification by
1	3.1	heptanal*	1.09	–	MS
2	4.5	α-pinene	0.87	953	RI, MS,CI
3	9.1	nonanal	1.09	1046	RI, MS
4	9.3	linalool	0.89	1053	RI, MS
5	26.4	α-copaene	23.05	1366	RI, MS, CI
6	28.8	α-bergamotene	27.38	1399	RI, MS
7	29.1	*trans*-cinnamyl acetate	2.41	1430	RI, MS,CI
8	29.3	aromadendrene	1.79	1435	RI, MS
9	29.8	α-cadinene	0.56	1440	RI, MS
10	30.6	α- humulene	6.19	1448	RI, MS
11	32.1	germacrene-D	2.10	1455	RI, MS
12	32.3	valencene	0.66	1458	RI, MS
13	33.2	viridiflorene	3.29	1470	RI, MS
14	33.6	α-muurolene	2.70	1480	RI, MS
15	34.2	γ-cadinene	1.57	1487	RI, MS
16	34.4	1S-*cis*-calamenene	0.92	1492	RI, MS
17	34.9	δ-cadinene	5.97	1509	RI, MS
18	35.3	α-calacorene	0.78	1520	RI, MS
19	35.6	β-guaiene*	0.91	1533	MS
20	35.8	ledol	1.29	1542	RI, MS
21	36.8	spathulenol	2.02	1552	RI, MS
22	37.9	caryophyllene oxide	0.81	1558	RI, MS
23	38.8	globulol	1.67	1569	RI, MS
24	39.9	τ-cadinol	Tr.	1611	RI, MS
25	40.4	τ-murulol	Tr.	1620	RI, MS
26	40.6	torreyol	Tr.	1623	RI, MS
27	40.9	α-cadinol	Tr.	1631	RI, MS
28	42.1	β-bisabolol	1.26	1652	RI, MS
29	42.9	tetradecanol	4.27	1666	RI, MS
30	44.2	epi-α-bisabolol	2.08	1690	RI, MS
31	45.2	benzyl benzoate	Tr.	1707	RI, MS, CI
32	49.0	tetradecanoic acid*	Tr.	1778	MS
33	53.4	hexadecanol	Tr.	1863	RI, MS
34	59.1	hexadecanoic acid*	Tr.	1978	MS

KI: retention Index on SPB-1 column.
MS: mass spectra.
CI: co-injection with authentic sample.
Tr.: less than 0.01%
*: Identified tentatively.

ing buds stage and propagated to the maximum extent during the flowering and fruits stages.

The volatile oil of buds of *C. zeylanicum* contains α-bergamotene (27.4%) and α-copaene (23.1%) as the major compounds. This is different from oils of other parts of *C. zeylanicum* such as leaf, root bark, stem bark, flowers and fruits. But there are some similarities as it contains many other compounds that are present in other oils as well. It has been observed that different type compounds are being present at different stages from buds to fruits through flowers, although some of the compounds are similar.

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