

THE ESSENTIAL OILS OF *CINNAMOMUM MOLLISSIMUM* AS NATURAL SOURCES OF SAFROLE AND BENZYL BENZOATE

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IBRAHIM JANTAN & GOH, S.H. 1990. The essential oils of *Cinnamomum mollissimum* as natural sources of safrole and benzyl benzoate. The leaf, bark and wood oils of *Cinnamomum mollissimum* were isolated in 2.65, 1.97 and 0.40% yields, respectively by water-distillation. The components of the oils were identified by co-chromatography with authentic samples on three different capillary columns, capillary GC/MS and nuclear magnetic resonance (¹H-NMR).

The main components of the leaf oil were benzyl benzoate and benzyl alcohol which comprised 77.69 and 10.71% of the oil, respectively. The components of the bark and wood oils were very similar to each other except for small differences in the contents of the minor components. The bark and wood oils were almost entirely made up of safrole (93.36 and 98.96%, respectively). The major components of the oils, benzyl benzoate and safrole were isolated by column chromatography on silica gel impregnated with silver nitrate.

Key words: *Cinnamomum mollissimum* - gas chromatography - benzyl benzoate - safrole

Introduction

Cinnamomum mollissimum (family Lauraceae) is one of the 21 species of *Cinnamomum* in Peninsular Malaysia (Kochummen 1989). It is a tree of 3 to 4 m in height, and is distributed mainly on the western side of the Peninsular (Burkill 1935). The bark of this tree is used by the Malays as a spice in betel quid which they believe can serve as a tonic (Burkill 1935). The barks from other *Cinnamomum* species, namely, *C. zeylanicum*, *C. loureirii* and *C. cassia* are the source of cinnamon bark which has been an item of trade since ancient time. The major chemical component of the spice is cinnamaldehyde (Guenther 1975).

The essential oil distilled from the bark of *C. zeylanicum* is used as flavouring in food and drinks and employed in oriental type perfumes (Guenther 1975). It is also used as a carminative and a preservative (Wade 1978). The leaves of *C. cassia* and other species of *Cinnamomum* produce essential oils with a high percentage of eugenol which is the starting material for conversion into vanillin (Guenther 1975).

As part of the survey of the essential oils of *Cinnamomum* species in Peninsular Malaysia for chemicals to be used as raw materials in food, pharmaceutical and technical products, this study describes the constituents of leaf, bark and wood oils of *C. mollissimum*.

Materials and methods

Collection of materials

The leaf, wood and bark of *C. mollissimum* were collected at Jengka Forest Reserve, Pahang, in the month of June. The plant materials were air dried under shade at room temperature for two days. A voucher specimen has been deposited at the herbarium of Forest Research Institute Malaysia, Kepong.

Quantitative extraction of the essential oils

The ground plant materials (200 g) (mesh size 40 - 60) were water-distilled for 8 h. The aqueous layer from the distillate was extracted with ether. The ether layer was dehydrated with anhydrous sodium sulfate and the solvent was evaporated at a low temperature to recover the dissolved oil. The yields were averaged over two experiments and calculated on dry weight.

Isolation of pure components from the essential oils

The clear yellow oils were dried over anhydrous sodium sulfate overnight. Four grams of each oil was chromatographed on silica gel coated with silver nitrate which was eluted with 600 ml of petroleum ether. The column was prepared by dissolving 10 g silver nitrate in a small amount of water and adding 100 g silica gel (230 - 400 mesh) and an amount of water sufficient to form a fluid paste. The product was dried at 40°C overnight.

The separations were monitored by TLC and GC. The components on TLC plates were located by heating the developed plates after spraying with 3% vanillin in 0.5% concentrated sulfuric acid in methanol. From the results of TLC and GC, fractions containing pure benzyl benzoate and safrole were combined separately. From the leaf oil, 2.80 g (70%) of benzyl benzoate (colourless oil) were isolated while from the bark and wood oils, 3.52 g (88%) and 3.68 g (92%) of safrole (colourless oil) were obtained, respectively.

The identity of the components were assigned by comparing their GC retention indices with those of authentic samples on columns of different polarities, namely OV 101, CP Sil 8 and OV 351. The components were also identified by GC/MS and comparison of the spectra thus obtained with authentic spectral data. The isolated compounds, safrole and benzyl benzoate were also identified by their $^1\text{H-NMR}$ spectra.

Analysis of the essential oils

GC analysis was carried out on a Shimadzu gas chromatograph model GC 9A equipped with FID detector and a CR 3A chromatopac data processor using silicon OV 101 capillary column (25 m \times 0.2 mm I.D.) and HP chromatographs model 5840 A and 5880 A equipped with FID detector using silicon CP Sil 8 and silicon OV 351 (both 25 m \times 0.2 mm I.D.) capillary columns respectively.

The programmes of the gas chromatographs were as follows:

- a) Shimadzu model GC-9A with silicon OV 101 capillary column (100% methyl, fluid) using nitrogen gas at 1 - 2 ml min⁻¹, initial temperature 60°C for 10 min, then 3°C min⁻¹ to 230°C;
- b) HP model 5840 A with silicon CP Sil 8 (5% phenyl, 95% methyl) using helium as carrier gas at 1 - 2 ml min⁻¹, initial temperature 80°C for 10 min, then 3°C min⁻¹ to 230°C;
- c) HP model 5880 A with silicon OV 351 capillary column (carbowax 20 M/nitro terephthalic acid) using helium as carrier gas at 1 - 2 ml min⁻¹, initial temperature 60°C for 10 min, then 3°C min⁻¹ to 230°C.

The GC/MS data were obtained with a Finnigan 4500 mass spectrometer (4500 A) (70 eV direct inlet) using CP Sil 8 capillary column (25 m \times 0.2 mm I.D.); initially at 100°C for 1 min, then 10°C min⁻¹ to 250°C for 20 min with helium as carrier gas. $^1\text{H-NMR}$ analysis was performed on a Joel Fx 90.

Kovats retention indices

Kovats indices were obtained from the gas chromatogram by a logarithmic interpolation between bracketing alkanes. The homologous series of C₈ - C₂₄ n-alkane were used as standards (Kovats 1965).

Results and discussion

Yields of essential oils

Water distillation of the ground fresh materials yielded 2.65, 1.97 and 0.40% of essential oils from the leaf, bark and wood of *C. mollissimum* respectively.

Compared to other aromatic forest trees such as *Eucalyptus globulus* and *Pogostemon cablin* distilled commercially in other countries (Wijesekera 1986), the yields of oils obtained from the leaf and bark may be considered satisfactory. The essential oils were pale yellow in colour. The leaf oil possessed a strong spicy odour, while the bark and wood oils had odour that resembled closely that of saffras oil.

Analyses and isolation of components from the essential oils

Safrole was isolated at 88 and 92% concentration from the bark and wood oils of *C. mollissimum*, respectively. Seventy percent of benzyl benzoate was isolated from the leaf oil. Figures 1, 2 and 3 show the chromatograms of the leaf, bark and wood oils respectively. The names of the components of the oils and their peak area percentages are listed in Table 1. Capillary GC analyses showed the presence of 58 components in the leaf oil of which 30 were identified; of the 30 components in the bark oil 16 were identified; of the 18 components in the wood oil 11 were identified.

Chemical constituents of the essential oils

The leaf oil of *C. mollissimum*

The main components of the leaf oil of *C. mollissimum* were benzyl benzoate and benzyl alcohol which comprised 77.69 and 10.71% of the oil, respectively. The other nonterpenes which were present in small quantities were benzyl salicylate, benzaldehyde, safrole, myristic aldehyde, eugenol, benzoic acid and benzyl acetate, arranged in decreasing order of percent concentration. Monoterpenoids and sesquiterpenoids were minors and represented only 2.66 and 2.95% of the leaf oil, respectively (Table 1). The main monoterpene was α -terpineol which constituted 1.08% of the oil. The other monoterpenoids were p-cymene, linalool, carvacrol, α -phellandrene, sabinol and terpinen-4-ol. The major sesquiterpenoid of the oil was α -caryophyllene (1.18%). Other sesquiterpenoids present were zingiberene, α -cadinol, T-cadinol, B-bisabolene, α -farnesene, spathulenol, B-farnesene, α -selinene, B-maaliene, nerolidol, d-cadinene and viridiflorol.

The leaf oil could be a natural source of benzyl benzoate which is medicinally used in 10 to 30% lotion or emulsion to treat scabies and pediculosis and as an insect repellent. It is also used as a fixative in perfumery (Windholz *et al.* 1983). The presence of significant amount of benzyl alcohol and other minor components exerted a profound influence on the aroma of the oil and made it a potential perfumery material.

Table 1. Composition and Kovat indices of the leaf, bark and wood oils of *Cinnamomum mollicissimum* on CP Sil 8 column

Peak number	Compound	CP Sil 8 *KI	Plant parts			Identification
			Leaf	Bark	Wood	
Nonterpenes						
1	2-butoxyethanol	899	-	-	trace	b
2	safrole	1293	0.15	93.36	98.96	a, b & c
3	eugenol	1358	trace	1.65	0.46	a & b
4	hexanoic acid	964	-	trace	-	a & b
5	benzyl alcohol	1039	10.71	-	trace	a & b
6	benzaldehyde	965	0.22	-	trace	a & b
7	benzoic acid	-	trace	-	-	a & b
8	benzyl acetate	1169	trace	-	-	a & b
9	benzyl benzoate	1777	77.69	-	-	a, b & c
10	benzyl salicylate	1886	0.88	-	-	a & b
11	myristic aldehyde	1579	0.10	-	-	b
Monoterpenes						
12	α -pinene	941	-	trace	-	a & b
13	β -pinene	983	-	trace	-	a & b
14	α -phellandrene	1007	0.17	0.35	-	a & b
15	cineole	1041	-	2.23	trace	a & b
16	terpinen-4-ol	1182	0.07	0.27	-	a & b
17	α -terpineol	1193	1.08	0.44	trace	a & b
18	limonene	1037	-	0.91	-	a & b
19	p-cymene	1036	0.73	-	-	a & b
20	linalool	1102	0.24	0.20	0.05	a & b
21	sabinol	1204	0.13	-	-	a & b
22	carvacrol	1301	0.24	-	-	a & b
Sesquiterpenes						
23	copaene	1381	-	trace	-	a & b
24	B-elemene	1396	-	trace	-	b
25	γ -farnesene	1420	0.18	-	-	b
26	B-farnesene	1494	0.11	-	-	b
27	B-maaliene	1418	0.10	-	0.18	b
28	γ -muurolene	1531	-	0.16	0.11	b
29	zingiberene	1393	0.27	-	-	b
30	B-caryophyllene 1429	-	0.10	trace	-	a & b
31	α -caryophyllene	1462	1.18	trace	-	a & b
32	α -selinene	1529	0.11	-	-	b
33	B-bisabolene	1512	0.19	-	-	b
34	d-cadinene	1550	trace	-	-	b
35	nerolidol	1569	0.10	-	0.11	a & b
36	spathulenol	1589	0.17	-	-	a & b
37	viridiflorol	1603	trace	-	-	a & b
38	α -cadinol	1657	0.22	-	-	a & b
39	T-cadinol	1671	0.22	-	-	a & b

(a - coinjection with authentic sample, b - mass fragmentation, c - $^1\text{H-NMR}$, * KI of compounds on OV 101 and OV 351 columns were also determined)

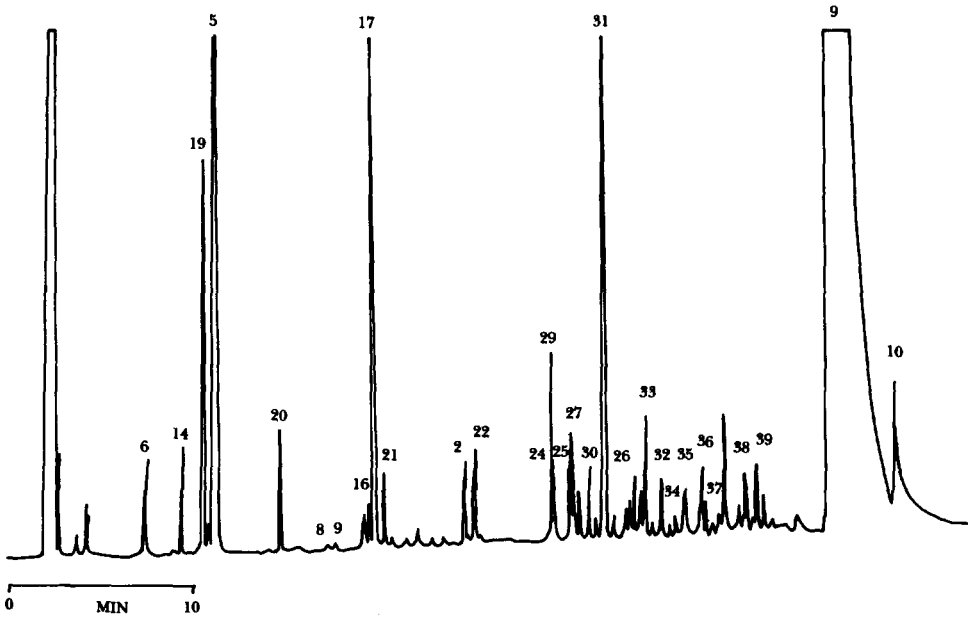


Figure 1. Gas chromatogram obtained with capillary CP Sil 8 column for the leaf oil of *Cinnamomum mollissimum*; for identity of peaks, see Table 1

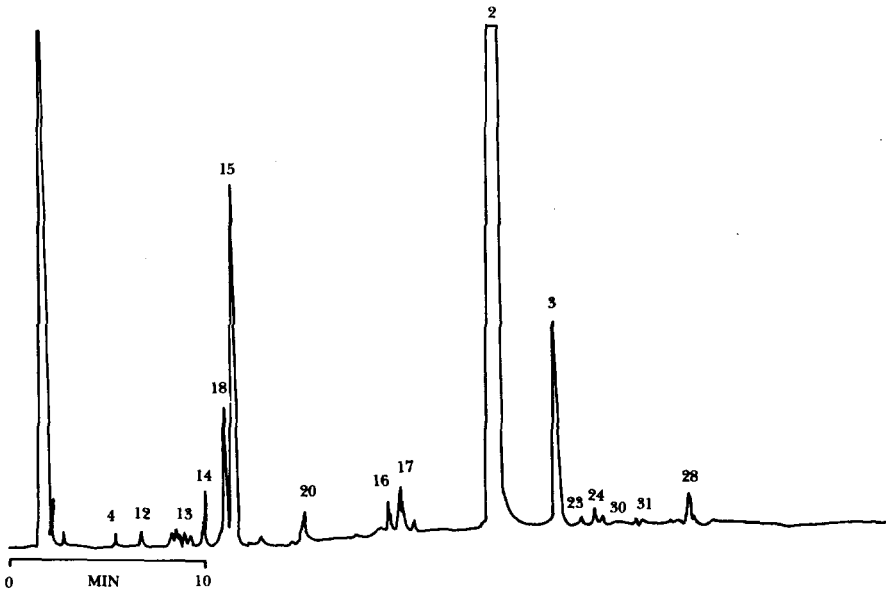


Figure 2. Gas chromatogram obtained with capillary CP Sil 8 column for the bark oil of *Cinnamomum mollissimum*; for identity of peaks, see Table 1

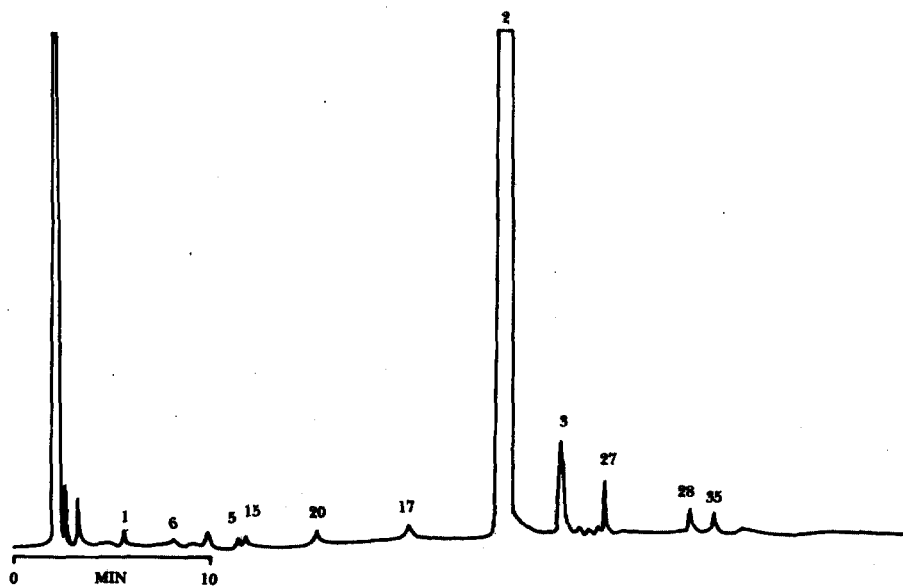


Figure 3. Gas chromatogram obtained with capillary CP Sil 8 column for the wood oil of *Cinnamomum mollissimum*; for identity of peaks, see Table 1

The bark and wood oils of *C. mollissimum*

The components of the bark oil of *C. mollissimum* were very similar to that of their wood except for small differences in the contents of the minor components (Table 2). Hexanoic acid, pinenes, α -phellandrene, terpinen-4-ol, limonene, copaene, β -elemene and caryophyllenes were only present in the former, while 2-butoxyethanol, benzyl alcohol, benzaldehyde, β -maaliene and nerolidol were only found in the latter. The bark and wood oils were almost entirely made up of safrole (93.36 and 98.96% respectively) and very similar in composition to sassafras oil. In fact the former contained higher percentage of the compound than the latter which is made up of about 80% safrole. Thus the bark and wood oils could be a natural source of safrole and substitute sassafras oil which is used in flavour, perfumery and as a topical anti-infective, pediculicide and carminative in medicine (Windholz *et al.* 1983).

Conclusion

The quantitative and qualitative analyses of the components in the leaf, wood and bark oils of *C. mollissimum* indicated that this species can be a natural source for benzyl benzoate and safrole which are commercially important chemicals for flavour, fragrance and medicine. The distribution and accumulation of the components in different parts of the plant may contribute to the

identification of this *Cinnamomum* species.

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