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Volatile Constituents of Cinnamon (*Cinnamomum zeylanicum*) Oils

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Analysis of *Cinnamomum zeylanicum* leaf, stem bark, and root bark oils indicated 72 compounds, of which 32 have not been reported before in cinnamon oils. All three oils had a similar array of compounds but in varying proportions. Of the new compounds reported there were 11 monoterpenes, 4 sesquiterpenes, 2 aliphatic, and 15 aromatic compounds.

Cinnamomum zeylanicum, the cinnamon of commerce, provides various types of oils depending on which part of the plant is utilized. Oils derived from the leaf, stem bark, and root bark have commercial usage. The most complete studies available on the volatile constituents of cinnamon oils are those by Angmor et al. (1972) and Wijesekera et al. (1974). A total of 41 compounds have been identified with the major component of cinnamon leaf oil being eugenol (about 70% of total volatiles) and cinnamaldehyde the major component of stem bark oil (about 75% of total).

In this paper we examined cinnamon oils in more detail by subfractionation of each oil and GC analysis of the fractions on a SCOT column and report the presence of a substantial number of additional compounds.

EXPERIMENTAL SECTION

Isolation of Volatiles. Samples of commercial cinnamon leaf and bark oils were obtained from Bush Boake and Allen Ltd, London. Oil was also obtained by steam distillation of cinnamon leaf, stem bark, and root bark (30-g lots) in a specially designed all-glass apparatus (Senanayake et al., 1978). The volatiles were trapped in a layer of pentane–ether (0.5 mL), dried over anhydrous sodium sulfate, and concentrated over a gentle stream of nitrogen. In order to facilitate the separation and identification of the minor constituents, the major compounds of leaf oil (eugenol) and stem bark oil (cinnamaldehyde) were removed. Cinnamon root bark oil was analyzed without fractionation.

To remove eugenol, leaf oil (2 mL) was dissolved in diethyl either (5 mL) and shaken with 10% potassium hydroxide solution (3 × 5 mL). The ether layer was removed, washed with distilled water (5 mL), and dried over anhydrous sodium sulfate. Excess ether was evaporated with nitrogen gas. The noneugenol fraction was separated into hydrocarbon and oxygenated fractions by column chromatography, as described by Stahl and Jork (1969) with minor modifications. A sample was loaded onto a column of deactivated silica gel (12.0 × 1.0 cm) and eluted with *n*-pentane to remove the hydrocarbons, followed by diethyl ether to remove oxygenated compounds (Hedin et al., 1975).

To remove cinnamaldehyde, stem bark oil (1 mL) was shaken with *n*-pentane (1 mL). Two layers formed, with cinnamaldehyde the bottom layer. The top layer of pentane was relatively free of cinnamaldehyde, but contained the other constituents of stem bark oil. Chromatograms of the bottom layer showed mainly cinnamaldehyde and traces of other major peaks. The pentane layer was treated as described for the noneugenol fraction of cinnamon leaf oil, to separate the hydrocarbon and oxygenated fractions.

Gas Chromatography. Oil samples (1 μL) were analyzed by flame ionization gas chromatography using a high-performance glass SCOT column (70 m × 0.5 mm i.d.) with Carbowax 20M (S.G.E., Melbourne) fitted with a pre-column stream splitter (30:1). The operating conditions were: high-purity nitrogen, 3 mL/min; hydrogen, 25 mL/min; and air, 300 mL/min; injector temperature, 200 °C; detector temperature, 235 °C. The relative abundance of each compound in the oils was calculated by a digital integrator. Substantial preliminary analyses of the oils were made on 3 m × 3.2 mm o.d. stainless steel columns packed with either 10% Carbowax 20M, 15% LAC-2R-446 or 10% SE-30 on 80–100 mesh Chromosorb W.

For preparative analyses, a glass column (3 m × 6.4 mm o.d.) packed with 20% Carbowax 20M on 60–80 mesh Gas Chrom Q was used. The emergence of each compound from the column was monitored in a trial run, and in a subsequent run fractions were collected for infrared analysis according to the method of Edwards and Fagerson (1965), where the fractions were trapped in 3.8-cm long hypodermic needles cooled by dry ice. The trapped fractions were transferred to an ultra-microcavity cell (type D, 0.5 mm path, Research and Industrial Instruments, London) in carbon tetrachloride with a syringe. All spectra were recorded with a Hilger and Watt Infrascan IR

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Table I. Volatile Constituents Identified in Commercial Cinnamon Leaf, Stem Bark, and Root Bark Oils of 2.5-Year-Old Plant[a]

Peak			Relative %			
No.	Retention time, min	Compound	Leaf oil	Stem bark oil	Root bark oil	Identified by
1	9.0	α-Pinene	1.0	0.6	4.3	RD, PE, IR
2	9.4	Unknown	Tr	Tr	0.1	
3	9.8	Camphene	0.4	0.2	1.9	RD, PE, IR
4	10.7	β-Pinene	0.3	0.1	2.2	RD, PE, IR
5†	11.7	Sabinene	Tr	0.02	0.8	RD, PE
6†	11.8	Δ^3-Carene	0.1	0.03	Tr	RD, PE
7*†	12.0	Myrcene	0.1	0.1	2.2	RD, PE
8	12.3	α-Phellandrene	0.1	0.6	0.2	RD, PE, IR
9	12.7	α-Terpinene	0.1	0.4	0.2	RD, PE, IR
10	13.3	Limonene	0.4	0.5	3.1	RD, PE, IR
11	13.7	1:8-Cineole	0.6	2.0	11.7	RD, PE, IR
12*†	14.3	*cis*-Ocimene	0.02	0.03	0.6	RD, PE
13†	15.0	γ-Terpinene	0.1	0.03	0.2	RD, PE
14*†	15.1	*trans*-Ocimene	0.02	Tr	0.2	RD, PE
15	15.9	*p*-Cymene	1.2	1.1	1.4	RD, PE, IR
16*	16.4	Terpinolene	0.1	0.1	0.3	RD, PE, IR
17*†	18.3	*n*-Hexanol	Tr	Tr	ND	RD, PE
18*†	21.6	Fenchone	Tr	Tr	0.02	RD, PE
19†	24.3	Furfural	0.02	0.03	0.02	RD, PE
20*†	25.0	*trans*-Linalool oxide furanoid form	0.1	0.1	0.1	RD, PE
21	26.8	α-Ylangene	1.0	0.3	ND	RD, PE, IR
22*†	27.0	Nonanal	Tr	ND	ND	RD, PE
23*	27.4	Benzaldehyde	0.7	0.3	ND	RD, PE, IR
24	27.8	Camphor	Tr	Tr	56.2	RD, PE, IR
25	28.7	Linalool	3.4	2.4	0.9	RD, PE, IR
26*†	29.4	Linalool acetate	Tr	Tr	0.3	RD, PE
27*†	30.7	Bornyl acetate	Tr	0.1	0.03	RD, PE
28	31.7	Terpinen-4-ol	0.1	0.4	2.7	RD, PE, IR
29	32.3	Caryophyllene	5.8	3.3	0.5	RD, PE, IR
30*†	33.4	2-Phenylacetaldehyde	Tr	Tr	0.04	RD, PE
31*†	34.6	Borneol	Tr	0.02	0.1	RD, PE
32*	35.0	Methyl chavicol	Tr	Tr	0.4	RD, PE, IR
33	35.8	α-Humulene	0.9	0.6	0.2	RD, PE, IR
34	36.4	α-Terpineol	0.4	0.7	6.9	RD, PE, IR
35*†	37.2	β-Selanene	Tr	Tr	ND	RD
36*†	37.9	γ-Cadenene	0.01	ND	0.5	RD, PE
37*†	38.1	Geranial	0.02	Tr	ND	RD
38	38.5	Piperitone	0.04	0.1	0.9	RD, PE, IR
39*†	38.7	Geranyl acetate	ND	Tr	ND	RD, PE
40	39.0	Cuminaldehyde	0.1	0.04	0.1	RD, PE
41*	39.6	Hydrocinnamaldehyde	0.2	0.4	Tr	RD, PE, IR
42*†	40.3	Phenylethyl acetate	0.03	0.1	Tr	RD, PE
43†	41.4	Nerol	Tr	Tr	ND	RD
44	44.1	Geraniol	0.04	0.1	0.7	RD, PE, IR
45*†	44.8	Benzyl alcohol	Tr	Tr	Tr	RD, PE
46	45.7	Safrole	2.3	Tr	0.3	RD, PE, IR
47*	46.8	2-Phenylethyl alcohol	Tr	0.4	Tr	RD, PE, IR
48	48.1	Unknown	ND	ND	Tr	
49*	49.2	2-Phenylpropyl acetate	1.0	0.1	Tr	RD, PE, IR
50	50.4	Unknown	Tr	Tr	ND	
51*†	51.8	Phenol	0.02	Tr	Tr	RD, PE
52*	52.5	Caryophyllene oxide	0.5	Tr	0.2	RD, PE, IR
53*†	52.9	Methyleugenol	0.01	Tr	ND	RD, PE
54	53.5	Cinnamaldehyde	2.0	75.0	0.7	RD, PE, IR
55†	54.5	Methyl cinnamate	0.03	Tr	Tr	RD, PE
56	55.1	Unknown	Tr	ND	Tr	
57*†	56.3	Methylisoeugenol	Tr	ND	Tr	RD, PE
58	56.9	Unknown	ND	ND	ND	
59†	58.8	Ethyl cinnamate	0.02	ND	Tr	RD, PE
60	60.1	Cinnamyl acetate	1.7	5.0	Tr	RD, PE, IR
61	60.6	Eugenol	70.1	2.2	0.5	RD, PE, IR
62	62.9	Unknown	Tr	ND	ND	
63	63.8	Acetyleugenol	2.5	0.2	0.1	RD, PE, IR
64	64.5	Unknown	Tr	Tr	ND	
65	65.2	Cinnamyl alcohol	0.4	0.3	0.1	RD, PE, IR
66*†	67.1	Farnesol	0.1	0.03	ND	RD, PE
67†	68.8	Isoeugenol	0.1	0.02	ND	RD, PE
68*†	69.2	2-Vinylphenol	Tr	0.03	ND	RD
69*	71.3	Coumarin	Tr	0.7	ND	RD, PE, IR
70*†	72.8	Vanillin	ND	Tr	ND	RD, PE
71	79.2	Benzylbenzoate	3.5	0.7	0.3	RD, PE, IR
72*†	83.1	2-Phenylethyl benzoate	Tr	Tr	ND	RD

[a] ND, not detected; *, new compound; †, tentative identification; RD, retention data; PE, peak enhancement; IR, infrared spectrum.

spectrometer and compared with the spectra derived from authentic compounds or with published spectra.

RESULTS AND DISCUSSION

The compounds isolated and their relative abundance in cinnamon leaf, stem bark, and root bark oils are shown in Table I. Of the compounds identified, eight have not previously been reported in cinnamon oils. The new compounds were the monoterpene, terpinolene, the sesquiterpene, caryophyllene oxide, and six aromatic compounds (benzaldehyde, methyl chavicol, hydrocinnamaldehyde, 2-phenylethyl alcohol, 2-phenylpropyl acetate, and coumarin). A further 24 compounds that have not been previously found in cinnamon oils were tentatively identified and included ten monoterpenes (myrcene, *cis*-ocimene, *trans*-ocimene, fenchone, *trans*-linalool oxide furanoid form, linalyl acetate, bornyl acetate, borneol, geraniol, and geranyl acetate), three sesquiterpenes (β-selanene, γ-cadenene, and farnesol), two aliphatic compounds (hexanol and nonanal), and nine aromatic compounds (2-phenylacetaldehyde, 2-phenylethyl acetate, benzyl alcohol, phenol, methyleugenol, methylisoeugenol, 2-vinylphenol, vanillin, and 2-phenylethyl benzoate). Final identification of these volatiles awaits mass spectral analysis.

Most compounds were found in all three oils but the composition of the oils was quite different. The major component in leaf oil was eugenol (~70%) with caryophyllene, linalool, and benzyl benzoate also of some quantitative importance. Cinnamaldehyde (75%) was the major component in stem bark oil with a contribution also from cinnamyl acetate and caryophyllene, while camphor (56%) was the major component of root bark oil with cineole, α-terpineol, α-pinene, and limonene also of importance.

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Comparative Study of Ashing Techniques for the Digestion of Horticultural Plant Samples

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Three methods of digestion of plant material involving two dry ashing techniques and a wet ashing technique using $H_2SO_4 + H_2O_2$ were compared to a $HNO_3 + HClO_4$ method for the determination of Fe, Mn, Zn, Cu, Ca, and Mg by atomic absorption and K by flame emission in seven horticultural crops. The results obtained led to further determinations of these elements using a dry ashing method and the $HNO_3 + HClO_4$ method for a further eight horticultural crops. For all crops and elements investigated, the dry ashing procedure involving 0.5-h treatment of ashed material with HCl gave comparable results to both the $HNO_3 + HClO_4$ digestion and to the dry ash treatment involving a lengthy steam bath treatment of the ash. The $H_2SO_4 + H_2O_2$ method gave a high percentage of unsatisfactory Fe values and occasional unsatisfactory Ca and Zn values.

There is a great deal of controversy regarding the suitability of dry ashing vs. wet ashing techniques for the digestion of plant material prior to the determination of nutrients (Jones and Steyn, 1973; Koirtyohann and Pickett, 1975). Wet ashing of plant samples using $HNO_3 + HClO_4$ has proved satisfactory for the determination of micronutrients (Gorsuch, 1959, 1970; Isaac and Johnson, 1975; Koirtyohann and Pickett, 1975) and macronutrients (Gorsuch, 1970; Isaac and Johnson, 1975), while with dry ashing lower values have occasionally been reported for some micronutrients due to incomplete recovery (Basson and Böhmer, 1972; Gorsuch, 1970). Nevertheless, the dry ashing technique is widely used because of convenience and because the wet digestion method using perchloric acid can be hazardous. The choice of the dry ashing technique should, however, be dictated by the type of plants and elements to be determined, and it would be unwise to generalize regarding its suitability for all types of plants (Gorsuch, 1970). Recently, a wet ashing technique using $H_2SO_4 + H_2O_2$ has been found suitable for the determination of macronutrients (including N) and micronutrients in plant material associated with ecological studies (Parkinson and Allen, 1975). The objective of this investigation was, therefore, to assess two dry ashing techniques and the wet ashing technique using $H_2SO_4 + H_2O_2$ for the determination of macro- and micronutrients in a wide range of horticultural plant samples differing considerably in nutrient levels. These techniques were compared with the $HNO_3 + HClO_4$ wet digestion technique which we have used as a "standard" method since it receives universal application and is accepted as giving satisfactory results.

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MATERIALS AND METHODS

Plant Samples. Leaf samples of carrot cv. Topweight, freesia (Diploid), lettuce cv. Yateslake, peach cv. Golden Queen, rhododendron cv. Tallyho, and strawberry cv. Tioga and asparagus spear cv. Mary Washington were ashed by two dry ashing techniques, by a wet ashing technique, and by the standard $HNO_3 + HClO_4$ digestion technique. One of the dry ashing techniques was again

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