Quantitative Analysis of the Essential Oil of *Cinnamomum osmophloeum* Kanehira

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Both bark and leaves of *Cinnamomum osmophloeum* Kanehira from the primary forests of central Taiwan were found to contain high levels of cinnamaldehyde. Twig plantation of this phenotype of trees was accomplished, and genetic stability of the chemical constituents was demonstrated by quantitative analyses.

The essential oil of cassia (*Cinnamomum cassia* Blume) cultivated in the southeastern region of China is widely used as food flavor ingredient. It is believed that the characteristic aroma reminiscent of the main component of cinnamaldehyde gives the slightly pungent flavor of cassia oil (Furia and Bellanca, 1975). Cinnamaldehyde itself is also evaluated as an intensely sweet compound (Hussain et al., 1986). By consideration of the geological relationship, the Taiwan endemic cinnamon tree, *Cinnamomum osmophloeum* Kanehira (Chang, 1976), may have similar constituents as *C. cassia* (ter Heide, 1972; Lawrence, 1978; Thomas, 1980; Yuan et al., 1984; Chen et al., 1985, 1987; Nohara et al., 1985). If this is true, the essential oil of *C. osmophloeum* promises to be a substitute for the cassia oil in the food industry. We thus carried out an extensive and systematic study of the chemical constituents of *C. osmophloeum*.

RESULTS AND DISCUSSION

We began the study in 1978 (stage I). Samples of *C. osmophloeum* were collected from the natural forests located in the central, eastern, and southern regions of Taiwan. The parts of bark and leaves from individual trees were subjected to steam distillations separately to give essential oils (designated as ICb, IC1, IEb, IE1, ISb, and IS1 according to the order of stage, region, and part). Table I outlines the 16 representative constituents of the essential oil. The samples from central Taiwan (ICb and IC1) appeared to have high yields of essential oils, which comprised high contents (~85%) of cinnamaldehyde (Hu et al., 1985). Although the bark portions of samples from the eastern and southern regions also exhibited high levels of cinnamaldehyde, the leaf portions had rather low percentages of this component. Alternatively, linalool is the predominant constituent of the essential oils of IE1 and IS1. Taking account of the yield of essential oil and the component of cinnamaldehyde as a specific flavor compound, the tree of central Taiwan can be considered a good phenotype. In order to know the genetic stability, this phenotype of trees was selected for propagation.

After 5 years, the clonal plantation from cuttings produced vegetatively and the quantitative analyses of these second generation trees were carried out (stage II). A comparison of chemical composition in essential oils of two stages is shown in Table II. The geographic adaption and chemical heredity of *C. osmophloeum* appeared to be excellent. Furthermore, trees of stage II gave even better yields (0.88% of leaf oil and 0.16% of bark oil). Although the essential oil of *C. osmophloeum* is not yet subjected to taste evaluation, it does have chemical composition comparable to that of cassia oil. From the viewpoint of business, leaves seem to be the economical and more accessible source of cinnamon oil instead of isolation from bark.

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Table I. Representative Constituents of the Essential Oils of *C. osmophloeum* Kanehira from Stage I Collections

compound	ICb[a]	IC1[b]	IEb[c]	IE1[d]	ISb[e]	IS1[f]
1,8-cineole	0.15[g]	0.31	3.53	5.11	0.40	0.33
p-cymene	<0.01	0.22	0.07	0.85	<0.01	1.97
benzaldehyde	0.55	1.93	0.30	0.29	0.18	1.08
linalool	0.06	0.70	0.29	50.10	0.24	20.14
bornyl acetate	0.52	0.73	1.97	2.26	0.98	3.04
caryophyllene	2.78	0.57	4.44	5.18	1.80	4.27
α-terpineol	1.62	0.29	10.91	2.92	4.29	2.01
geranial	0.39	0.06	0.72	1.53	0.45	4.45
γ-cadinene	0.58	0.13	0.91	1.73	0.25	1.38
geranyl acetate	0.57	2.33	0.10	0.18	0.07	<0.01
(*Z*)-cinnamaldehyde	1.16	1.01	1.60	0.03	1.69	
caryophyllene oxide	<0.01	0.01	0.52	3.27	0.16	2.68
(*E*)-cinnamaldehyde	85.13	85.27	61.22	0.19	69.10	12.27
cinnamyl acetate	1.24	1.26	0.73	0.16	<0.01	1.51
eugenol	1.26	0.93	0.73	0.35	2.51	2.16
coumarin	0.10	0.42	3.34	0.14	7.60	12.78

[a] Bark oil of two trees collected in the central Taiwan, stage I; 0.13% yield based on the weight of plant material. [b] Leaf oil of 43 trees; 0.74% yield. [c] Bark oil of 12 trees collected in the eastern Taiwan; 0.06% yield. [d] Leaf oil of 14 trees; 0.15% yield. [e] Bark oil of five trees collected in southern Taiwan; 0.05% yield. [f] Leaf oil of 18 trees; 0.06% yield. [g] The number represents average percentage content of the specific compound in the same category of trees.

MATERIALS AND METHODS

Plant Materials. *Stage I.* Samples of *C. osmophloeum* Kanehira (Lauraceae) were collected in 1978 from the primary forests (500–1500-m altitude) of Taiwan. The voucher specimens, identified by Dr. Ta-Wei Hu, have been deposited in the herbarium of the Taiwan Forestry Institute. The leaves (ca. 20 g) or bark (ca. 100 g) of individual tree were separately subjected to steam distillation, and the distillate was continuously extracted with hexane by circulatory apparatus (von Rudloff, 1969) to give the essential oil, which was subsequently analyzed by gas chromatography and other appropriate methods.

Stage II. In 1980, individual trees of central Taiwan (Gu-Kuang and neighboring areas) having high yield of essential oil and high content of cinnamaldehyde were selected for twig plantation in the northern Taiwan (Yang-Ming Shan and Wu-Lai; 800-m altitude). These second-generation trees grew well and reached 5 m in 5 years. Leaves and bark of individuals were then taken to chemical analyses by a procedure similar to that used in stage I.

Instrumentation. Quantitative GC analyses were carried out on a Hewlett-Packard 5710A gas chromatograph equipped with a flame ionization detector. A Hewlett-Packard 3380A reporting integrator was used to determine peak areas without correction for response factors. A fused silica capillary column (25 m × 0.2 mm (i.d.)) coated with a Carbowax 20 M phase was used. The column temperature was programmed from 70 to 210 °C at the rate of 4 °C/min. The essential oil sample (0.5 μL) was injected into the column (12:1 split vent ratio) with N_2 as a carrier gas at a flow rate of 0.2 mL/min. Kovats indices were determined by coinjection of samples and reference compounds with a series

0021-8561/89/1437-0744$01.50/0

Table II. Percentage Composition of the Essential Oils of *C. osmophloeum* Kanehira

peak	Kovats index	compound	ICl	IICb[a]	IICl[b]	identification method[c]
1	1000	α-pinene	0.29	0.24	0.25	RI, GC–MS, PE
2	1003	camphene	0.21	0.22	0.15	RI, GC–MS, PE
3	1022	β-pinene	0.41	0.25	0.35	RI, GC–MS, PE
4	1070	myrcene	0.04	0.05	0.05	RI, GC–MS, PE
5	1090	α-terpinene	0.07	0.12	0.05	RI, GC–MS, PE
6	1101	limonene	0.15	0.28	0.17	RI, GC–MS, PE
7	1109	1,8-cineole	0.31	0.05	0.33	RI, GC–MS, PE
8	1139	ocimene	0.10	0.21	0.06	RI, GC–MS, PE
9	1160	p-cymene	0.22	0.37	0.12	RI, GC–MS, PE
10	1176	terpinolene	0.01	0.02	0.01	RI, GC–MS, PE
11	1380	furfural	0.01	0.03	<0.01	RI, GC–MS, PE
12	1407	*trans*-linalool oxide	0.01	0.01	0.01	RI, GC–MS, PE, NMR
13	1439	benzaldehyde	1.93	0.63	1.69	RI, GC–MS, PE
14	1466	linalool	0.70	<0.01	0.11	RI, GC–MS, PE
15	1483	linalyl acetate	0.03	<0.01	<0.01	RI, GC–MS, PE
16	1502	bornyl acetate	0.73	1.65	0.60	RI, GC–MS, PE, NMR
17	1511	caryophyllene	0.57	1.68	0.53	RI, GC–MS, PE
18	1515	4-terpineol	0.25	0.14	0.13	RI, GC–MS, PE, NMR
19	1531	copacamphene	<0.01	<0.01	<0.01	RI, GC–MS, NMR[d]
20	1552	menthone	0.05	0.04	0.05	RI, GC–MS, PE
21	1562	methyl chavicol	0.80	0.36	0.65	RI, GC–MS, PE
22	1580	γ-muurolene	0.04	<0.01	0.01	RI, GC–MS, PE, NMR
23	1584	citronellyl acetate	0.01	<0.01	<0.01	RI, GC–MS, PE
24	1588	isoborneol	<0.01	<0.01	<0.01	RI, GC–MS, PE, NMR[e], IR
25	1592	neral	0.03	0.13	0.09	RI, GC–MS, PE, NMR
26	1601	α-terpineol	0.29	0.35	0.22	RI, GC–MS, PE, NMR
27	1609	α-terpinyl acetate	0.05	<0.01	0.05	RI, GC–MS, PE, NMR
28	1612	piperitone	0.02	0.05	<0.01	RI, GC–MS, PE
29	1617	γ-humulene	<0.01	<0.01	<0.01	RI, GC–MS, PE, NMR
30	1633	*d*-carvone	<0.01	0.21	0.05	RI, GC–MS, PE, NMR
31	1646	2,6,6-trimethyl-2-vinyl-5-hydroxytetrahydropyran	0.06	0.01	0.06	RI, GC–MS, PE, NMR
32	1648	geranial	0.06	0.20	0.22	RI, GC–MS, PE, NMR
33	1649	γ-cadinene	0.13	0.58	0.13	RI, GC–MS, PE, NMR
34	1691	geranyl acetate	2.33	0.70	1.88	RI, GC–MS, PE, NMR
35	1693	citronellol	<0.01	0.01	0.01	RI, GC–MS, PE, NMR
36	1711	cuminaldehyde	0.02	0.01	0.05	RI, GC–MS, PE, NMR
37	1721	nerol	0.02	0.02	0.01	RI, GC–MS, PE, NMR
38	1725	calacorene	<0.01	<0.01	<0.01	RI, GC–MS, PE
39	1757	safrole	0.01	0.03	0.01	RI, GC–MS, PE
40	1770	2-hydroxy-1,8-cineol	<0.01	<0.01	<0.01	RI, GC–MS, PE, NMR,[e] IR
41	1783	geraniol	0.03	0.39	0.06	RI, GC–MS, PE, NMR, IR
42	1805	(*Z*)-cinnamaldehyde	1.01	0.82	1.02	RI, GC–MS[f]
43	1824	2-phenylethanol	0.02	0.04	0.01	RI, GC–MS, PE
44	1851	*cis*-jasmone	<0.01	<0.01	0.01	RI, GC–MS, PE
45	1884	caryophyllene oxide	0.01	0.02	0.09	RI, GC–MS, PE, NMR, IR
46	1888	phenol	0.15	0.35	0.25	RI, GC–MS, PE
47	1919	methyl eugenol	0.03	<0.01	0.03	RI, GC–MS, PE
48	1920	(*E*)-cinnamaldehyde	85.27	82.25	84.70	RI, GC–MS, PE, NMR, IR
49	1984	elemol	0.02	<0.01	0.02	RI, GC–MS, PE
50	1992	cedrol	0.01	<0.01	<0.01	RI, GC–MS, PE
51	2035	spathulenol	0.01	<0.01	0.03	RI, GC–MS, NMR[g]
52	2047	cinnamyl acetate	1.26	4.66	1.96	RI, GC–MS, PE, NMR, IR
53	2057	eugenol	0.93	0.55	0.79	RI, GC–MS, PE
54	2085	T-cadinol	0.09	0.04	0.24	RI, GC–MS, PE
55	2203	cinnamyl alcohol	0.03	0.79	0.06	RI, GC–MS, PE
56	2234	isoeugenol	0.15	0.13	0.23	RI, GC–MS, PE
57	2237	4,8-dihydroxycarvotanacetone	<0.01	<0.01	0.01	RI, GC–MS, PE, NMR, IR
58	2291	coumarin	0.42	0.09	0.08	RI, GC–MS, PE, NMR
59	2303	1-acetoxy-6,7-dihydroxy-3,7-dimethyloct-2-ene	0.03	0.01	0.01	RI, GC–MS, NMR,[e] IR[h]
60	2438	vanillin	<0.01	0.01	<0.01	RI, GC–MS, PE
61	2486	benzyl benzoate	0.01	0.01	0.01	RI, GC–MS, PE
62	2531	phytol	0.02	<0.01	<0.01	RI, GC–MS, PE
63	*i*	(*E*)-cinnamic acid	<0.01	<0.01	<0.01	MS, PE, NMR, mp
64	*i*	1,6,7-trihydroxy-3,7-dimethyloct-2-ene	<0.01	<0.01	<0.01	MS, NMR,[e] IR[j]

[a] Bark oil of three cultivated trees originally from central Taiwan, stage II; 0.16% yield; 1.06% of constituents unidentified. [b] Leaf oil of 52 cultivated trees; 0.88% yield; 2.27% of constituents were unidentified. [c] Identification methods: RI represents retention index, GC–MS represents on-line gas chromatography–mass spectrometry, PE represents peak enrichment by coinjection with the authentic material, NMR represents proton NMR spectrum, and IR represents infrared spectrum. [d] McMurry, 1970. [e] The ^{13}C NMR spectrum was also recorded. [f] This component was assigned as (*Z*)-cinnamaldehyde as it had a similar mass spectrum as (*E*)-cinnamaldehyde (Bestmann et al., 1982). (*Z*)-Cinnamaldehyde is known to undergo thermal stereoisomerization to the more stable *E* isomer (Klibanov and Giannousis, 1982). [g] Juell et al., 1976. [h] Canonica et al., 1972. [i] The Kovats indices were not determined. [j] Boar and Damps, 1977.

of normal C_8–C_{23} hydrocarbons (Majlat et al., 1974). A Finnigan MAT TSQ 46c quadrupole GC–MS coupled with a SuperIncos data system was used for mass spectrometric analyses. Similar GC conditions as mentioned above were applied except for the carrier gas of He (0.67 mL/min flow rate). The spectra were recorded at an ionization voltage of 70 eV and with a speed of 1 scan/s over a mass range of m/z 40–400. Preparative GC was carried out on a Shimadzu 8A chromatograph using a column (2 m × 3 mm (i.d.)) of 20% Carbowax 20 M supported on Chromosorb W (60/80 mesh). Infrared spectra were run on a Jasco IRA-1 spectrometer or a Perkin-Elmer 983 spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian EM-390 (90 MHz) spectrometer or a Bruker AM-300 WB (300 MHz for ^1H) spectrometer.

ACKNOWLEDGMENT

We thank Dr. Ta-Wei Hu (Department of Forestry, The Chinese Culture University) for identification of plant material. Gratitude is also due to Yi-Jun Chen and Fu-Huei Lin for their technical assistances.

LITERATURE CITED

Bestmann, H. J.; Roth, K.; Ettlinger, M. Eine Stereoselektive Synthesemethode fur (Z)-α,β-Ungesattigte Aldehyde. *Chem. Ber.* **1982**, *115*, 161–171.

Boar, R. B.; Damps, K. Resolution of 2,3-Dihydrosqualene-2,3-diol, 10,11-Dihydro-10,11-dihydroxyfarnesyl Benzoate, and 6,7-Dihydro-6,7-dihydroxygeranyl Benzoate. Synthesis of (3R)- and (3S)-2,3-Epoxy-2,3-dihydrosqualene. *J. Chem. Soc., Perkin Trans. 1* **1977**, 709–712.

Canonica, L.; Rindone, B.; Santaniello, E.; Scolastico, C. A Total Synthesis of Mycophenolic Acid, Some Analogues and Some Biogenetic Intermediates. *Tetrahedron* **1972**, *28*, 4395.

Chang, C. E. Lauraceae. In *Flora of Taiwan*; Li, H. L., et al., Eds.; Epoch: Taipei, Taiwan, 1976; Vol. II, p 417.

Chen, Y.; Li, Z.; Xue, D.; Han, H.; Yang, Y. Analysis of Volatile Constituents of Chinese Medicinal Herbs by Flash Distillation-Capillary Gas Chromatography-Mass Spectrometry. *Gaodeng Xuexiao Huaxue Xuebao* **1985**, *6*, 1075–1079; *Chem. Abstr.* **1986**, *104*, 136143x.

Chen, Y.; Li, Z.; Wang, R.; Xue, D. Identification of Chinese Medical Herbs by Pyrolysis-Capillary Gas Chromatography. *Fenxi Ceshi Tongbao* **1987**, *6*, 12–16; *Chem. Abstr.* **1987**, *107*, 121172u.

Furia, T. E.; Bellanca, N. *Fenaroli's Handbook of Flavor Ingredients*, 2nd ed.; CRC Press: Cleveland, OH, 1975; Vol. I, pp 323–325.

Hu, T. W.; Lin, Y. T.; Ho, C. K. Natural Variation of Chemical Components of Leaf Oil of *Cinnamomum osmophloeum* Kaneh. in Taiwan. In Proceedings of the Annual Meeting of Agricultural Associations of the Republic of China, Taichung, Taiwan, 1985; pp 45–62.

Hussain, R. A.; Kim, J.; Hu, T. W.; Pezzuto, J. M.; Soejarto, D. D.; Kinghorn, A. D. Isolation of a Highly Sweet Constituent from *Cinnamomum osmophloeum* Leaves. *Planta Med.* **1986**, 403–404.

Juell, S. M. K.; Hansen, R.; Jork, H. New Substances isolated from the Essential Oils of Various *Artemisia* Species, Part 1. Spathulenol, an Azulenic Sesquiterpene Alcohol. *Arch. Pharm.* **1976**, *309*, 458–466.

Klibanov, A. M.; Giannousis, P. P. Geometric Specificity of Alcohol Dehydrogenases and Its Potential for Separation of Trans and Cis Isomers of Unsaturated Aldehydes. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3462–3465.

Lawrence, B. M. Progress in Essential Oils. *Perfumer Flavorist* **1978**, *3*, 54–55.

Majlat, P.; Erdos, Z.; Takacs, J. Calculation and Application of the Retention Indices in Programmed-Temperature Gas Chromatography. J. *Chromatogr.* **1974**, *91*, 89–103.

McMurry, J. E. Total Synthesis of Copacamphene. *Tetrahedron Lett.* **1970**, 3731–3734.

Nohara, T.; Kashiwada, Y.; Nishioka, I. Cinncassiol E, a Diterpene from the Bark of *Cinnamomum cassia*. *Phytochemistry* **1985**, *24*, 1849–1850.

ter Heide, R. Qualitative Analysis of the Essential Oil of Cassia (*Cinnamomum cassia* Blume). *J. Agric. Food Chem.* **1972**, *20*, 747–751.

Thomas, A. F. Two New Sesquiterpenoid Ketones from Cassia Oil. *Helv. Chim. Acta* **1980**, *63*, 1615–1618.

von Rudloff, E. Scope and Limitation of Gas Chromatography of Terpenes in Chemosystematic Studies. In *Recent Advances in Phytochemistry*; Seikel, M. K.; Runeckles, V. C. Eds.; Appleton-Century-Crofts: New York, 1969; Vol. II, pp 127–162.

Yuan, A.; Tan, L.; Wei, S.; Kang, S.; Jiang, D. Chemical Constituents of Gui Zhi (*Cinnamomum cassia*), a Traditional Chinese Medicine. *Zhongyao Tongbao* **1984**, *9*, 127–128; *Chem. Abstr.* **1984**, *101*, 60032a.

Received for review September 19, 1988. Accepted December 7, 1988.

Volatiles from Naranjilla Fruit (*Solanum quitoense* Lam.). GC/MS Analysis and Sensory Evaluation Using Sniffing GC

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Aroma volatiles from naranjilla fruit (*Solanum quitoense* Lam.) were concentrated by either a closed-loop stripping or a solvent extraction method. Compounds were identified by capillary GC/MS and sensorially characterized by sniffing GC. The main aroma constituents were esters of butanoic acid and ethyl acetate. Aroma impact compounds could not be found.

Naranjilla or lulo, which looks like a small orange, is the fruit of the tropical nightshade *Solanum quitoense* Lam. It is consumed in Ecuador and northern parts of Brazil either in fresh form or as a drink (Duke, 1970). At present, it is commercially important only in the region of its production. The flavor of naranjilla has been described by several people not accustomed to the fruit as sweet and resembling a mixture of banana, pineapple, and strawberry. Nothing has been published yet about the substances responsible for this interesting aroma. We now communicate the results of our work on the volatile components of naranjilla.

The current goal of aroma analysis is not only to identify components but also to determine their importance to the flavor of the product under investigation. For this reason, we used a gas chromatographic sniffing detector to assess the sensory properties of every separated peak.

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MATERIALS AND METHODS

All solvents used were distilled through a 40-cm Vigreux column. Deionized water was purified through a 30-cm column of activated carbon.

Ripe fruits were obtained by air freight from Ecuador, stored at 4 °C, and used within 7 days of arrival.

0021-8561/89/1437-0746$01.50/0