

Characterization of *Citrus unshiu* (*C. unshiu* Marcov. forma *Miyagawa-wase*) Blossom Aroma by Solid-Phase Microextraction in Conjunction with an Electronic Nose

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The volatile composition of the headspace from *Citrus unshiu* Marcov. forma *Miyagawa-wase* blossom was investigated. The volatile constituents were absorbed by a solid-phase microextraction (SPME) fiber and directly transferred to a GC-MS. Volatile compositional changes of *C. unshiu* blossom prepared via different drying methods (shade, microwave, and freeze-drying methods) were also determined. A total of 96 volatile constituents were confirmed in the headspace from these samples. Monoterpene hydrocarbons were prominent in the headspace volatiles of *C. unshiu* blossom: fresh, 84.1%; shade-dried, 60.0%; microwave-dried, 88.4%; and freeze-dried, 29.9%. *p*-Cymene (23.3%) was the most abundant component in the headspace of fresh *C. unshiu* blossom; γ -terpinene was the most abundant in shade- and microwave-dried samples (26.8 and 31.2%, respectively) and β -caryophyllene (10.5%) in freeze-dried sample. By using an electronic nose consisting of six metal oxide sensors, principal component analysis of the volatile compounds showed a clear aroma discrimination of the fresh and all dried blossom samples.

KEYWORDS: *Citrus unshiu* Marcov. forma *Miyagawa-wase* blossom; headspace aroma; drying method; solid-phase microextraction; electronic nose

INTRODUCTION

Citrus aroma has considerable commercial importance. The rapid growth of the citrus fruit industry in the past few years is due largely to the population increase and growth of the global economy together with the rapid advance of the agricultural science and technology of byproducts (1). *Citrus* belongs to the large family Rutaceae (130 genera), in which the leaves usually possess transparent oil glands and the flowers contain an annular disk and retain rich aroma (1). Most research efforts relating to the flavor of *Citrus* have been concentrated primarily on the fruits (2–4). Although the importance of the blossom aroma of *Citrus* cannot be overlooked, a search for publications relating to aroma components of *Citrus* blossom indicated a relative absence (5).

Due to both economic importance and academic interest, research has been carried out on the identification of volatile flavor compounds of foods on various processing conditions. The effect of drying methods on volatile aroma components is often regarded as a critical factor of food flavor quality. Generally, freeze-drying of aromatic plants is an effective method for producing a product with superior physical and chemical qualities. However, it is considered to be a costly and time-consuming process (6). Air-drying is an effective method

of preservation of aromatic plants; however, hot-air-drying can cause thermal damage to the products (6). An understanding of the aroma quality according to drying methods requires that a relatively complete quantitative and qualitative database be developed.

Solid-phase microextraction (SPME) is a solvent-free extraction technique, which contrasts to conventional extraction methods, and a relatively new method of sample preparation. SPME uses a short length of a narrow-diameter fused-silica optical fiber externally coated with a thin film of polymer as stationary phase [e.g., Carbowax, divinylbenzene (DVB), polyacrylate (PA), polydimethylsiloxane (PDMS)] or a mixture of polymers blended with a porous carbon-based solid material (e.g., PDMS–Carboxen). Some authors have already systematically compared the performance of some of the fibers commercially available for specific applications (7, 8). Bicchietti et al. (8) suggested that the most effective fibers for detecting the volatile flavor from aromatic and medicinal plants were those consisting of two components, that is, a liquid phase (PDMS) and a porous solid (Carboxen or DVB or both).

In recent years, new technology has been introduced to the study of the volatiles by the use of electronic nose, that is, instruments with arrays of conduction polymers and/or metal oxide sensors. These multisensor devices are coupled to statistical data processing packages such as principal component analysis (PCA) and discriminant function analysis (9, 10). There are many reports on food quality control and aroma analysis

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by using electronic nose (11, 12). Natale et al. (11) reported its useful applications for quality analysis on different kinds of foods, such as fish, meat, vegetables, and wine. Hodgins and Simmonds (12) reported that electronic noses can be used to supplement or replace traditional quality control techniques in the food industry.

The objective of this study was to identify the volatile aroma of *Citrus unshiu* blossom and to investigate the changes of aroma effected by various drying methods by using SPME and electronic nose techniques.

MATERIALS AND METHODS

Materials. *C. unshiu* (*C. unshiu* Marcov. forma *Miyagawa-wase*) blossom was harvested at its full bloom stage (May 2001) in Jeju Province of Korea. In all experiments, the whole blossom including petal, pistil, and stamen was used. Authentic chemicals for co-injection in gas chromatography and mass spectrometry were obtained from reliable commercial sources as follows: Aldrich Chemical Co. (Milwaukee, WI); Sigma Chemical Co. (St. Louis, MO); Wako Pure Chemical Industries (Osaka, Japan).

The moisture content of each sample was tested by an air-drying method at 105 °C. *C. unshiu* blossom samples were analyzed colorimetrically in five replications by using a Minolta spectrophotometer CM-508i (Minolta Co., Ltd., Tokyo, Japan). The results were expressed as HunterLab *L* (whiteness/darkness), *a* (red/green), and *b* (yellow/blue).

Drying Method. In this study three different drying methods were adopted in *C. unshiu* blossoms. A sample of the fresh blossom was placed in shady place (~20 °C) that was well-ventilated for 5 days. A fresh *C. unshiu* blossom sample from the same batch was microwave-dried by using a domestic microwave oven (LG Co., Ltd., Seoul, Korea, model ER-646JB) for 5 min at a frequency of 2450 MHz. A third sample of fresh blossom was dried in a freeze-dryer (Ilshin Laboratory Co., Ltd., Seoul, Korea, model FD 5505) at -50 °C and under vacuum (10 mm Torr) overnight.

SPME. In this study, a 100 μ m PDMS fiber (Supelco, Inc., Bellefonte, PA) was used because this particular stationary phase material showed a higher affinity toward volatile compounds than at low concentrations in previous tests. The time the SPME fiber was exposed to the headspace of samples varied from 30 to 70 min to establish the best extraction time, and 60 min was determined to be the optimal extraction time. A 2 g fresh sample and 0.5 g of each dried blossom sample were hermetically sealed in a 10 mL vial from Supelco having a silicone septum and an aluminum cap. The stainless steel needle containing PDMS fiber was inserted through the septum of the sample vial in order to sample the headspace for 60 min by using a Varian 8200 autosampler (Walnut Creek, CA).

GC and GC-MS. After the extraction by the PDMS fiber, the volatile compounds were desorbed for 2 min into the injector of a Varian Saturn 2000R 3800 GC (Walnut Creek, CA) equipped with a CP-Wax 52 CB WCOT fused-silica capillary column (30 m \times 0.25 mm i.d., film thickness = 0.25 μ m, Chromapack, Middelburg, The Netherlands). Helium was the carrier gas at a flow rate of 1.1 mL/min and a linear velocity of 38.7 cm/s. The temperature of the column was maintained at 70 °C for 2 min during desorption and then ramped at 2 °C/min to 230 °C (20 min). The injections were split (1:34) with the injector temperature being held at 230 °C. The GC was interfaced with a Varian Saturn 2000R MS (Walnut Creek, CA) for detection and quantification of the volatile compounds. Kovats retention indices (RIs) were calculated for all volatile components using a homologous series of *n*-alkanes (C₇–C₂₉) under the same GC column and conditions using a Hewlett-Packard 5890 II GC (Hewlett-Packard, Avondale, PA). A nonpolar column was also used for GC analysis, this being a DB-1 fused-silica type (60 m \times 0.25 mm i.d., film thickness = 0.25 μ m, J&W Scientific, Folsom, CA).

Identification of Components. Components were identified by comparing their RIs and matching their mass spectra with those of reference compounds in the data system of the Wiley library and NIST Mass Spectral Search Program (ChemSW Inc., NIST 98 version

database) connected to a Saturn 2000R mass spectrometer. Whenever possible, the volatile flavor components were matched by co-injection with authentic compounds. The results were expressed as the average of triplicate runs.

Statistical Analysis. GC peak area percents of some volatile flavor compounds (α -pinene, β -pinene, myrcene, limonene, γ -terpinene, *p*-cymene, β -caryophyllene, valencene, and farnesene) were subjected to one-way analysis of variance ($p < 0.05$) using the Statistical System (13) software package. Significant differences between means by triplicate tests were determined by Duncan's multiple-range test.

Electronic Nose. *C. unshiu* blossom samples were analyzed by an electronic nose system (Hanbit Instrument, Seoul, Korea) fitted with six metal oxide sensors: TGS 826, TGS 842, TGS 2620, TGS 2610, TGS 2600 (Figaro Engineering Inc., Tokyo, Japan), and 1084CT/24 (Capeur Sensors & Analyzers Ltd., Hants, U.K.). Nitrogen gas (bubbled through aqueous silicon; Shin-Etsu Silicone Korea Co., Ltd., Seoul, Korea) was used as carrier gas at 100 mL/min. A 3 g (fresh) sample and 1 g of each dried sample of minced *C. unshiu* blossoms were placed in a glass jar with gas inlet and outlet tubes fitted through the lid. The jar was equilibrated in a 30 °C air oven prior to use. The jar was kept at a constant temperature (30 °C) to obtain a homogeneous headspace for analysis. The exposure time of sensors to the headspace was 40 s, with a heater cleaning time of 10 s, a purge time of 20 s, and a tuning time limit of 600 s. All analyses were five replications. A test was performed every 15 min. The responses of the sensors are recorded and files were kept in the computer for further analysis. Principal component analysis (PCA) was carried out using the manufacturer-supplied software, a multivariate statistical analysis program (MVSAP, version 3.1).

RESULTS AND DISCUSSION

Volatile Components of Fresh *C. unshiu* Blossom. The initial moisture content of the blossom was 83.1% on a wet weight basis. Hunter *L*, *a*, and *b* values of fresh sample were 90.01, -0.28, and 8.94, respectively. The identified volatile components and their peak area percents are given in **Table 1**. The components are listed in order of their elution on the CP-Wax column. A classification based on functional groups is summarized in **Table 2**. Fifty-one volatile flavor components, constituting 98.5% of the total volatile composition of the headspace, including 30 hydrocarbons (94.2% peak area), 3 aldehydes (0.1%), 8 alcohols (3.7%), 4 ketones (0.2%), 4 esters (0.3%), 1 oxide (trace), and 1 acid (trace), were identified from the fresh *C. unshiu* blossom by the SPME method. Several components were identified tentatively as shown in **Table 1**. Monoterpene hydrocarbons were predominant in fresh blossom aroma (84.1%). *p*-Cymene was the most abundant component (23.3%), followed by γ -terpinene (16.2%), β -pinene (13.0%), α -pinene (8.9%), and limonene (7.8%).

Limonene is the major terpene in most citrus oils, often accounting for nearly 90% of the oil (3, 4). However, limonene was present in only a small quantity in the volatile composition of *C. unshiu* blossom relative to its fruit flavor. Thirteen sesquiterpene hydrocarbons (9.7%) were confirmed in the headspace of fresh *C. unshiu* blossom, and β -caryophyllene (5.1%) was a major component. Monoterpene alcohols were the abundant oxygenated compounds in fresh blossom aroma. 1,8-Cineole was the most predominant alcohol (1.7%), followed by linalool (1.0%), α -terpineol (0.5%), and terpinen-4-ol (0.3%). Other flavor components occurred at low levels.

Volatile Components of Dried *C. unshiu* Blossoms. Volatile compositional changes of *C. unshiu* blossom on the different drying methods [shade-drying (SD), microwave-drying (MD), and freeze-drying (FD) methods] were also investigated. The final moisture content of shade-dried sample was 8%, and the Hunter *L*, *a*, and *b* values were 37.29, 4.59, and 6.53, respectively. The microwave-dried blossom had a moisture

Table 1. Volatile Constituents Identified in the Headspace of *C. unshiu* Blossom

no.	constituent	retention index		peak area %				identification
		CP-Wax	DB-1	fresh	shade-dried	microwave-dried	freeze-dried	
1	ethyl acetate	890		0.1			0.7	RI, ^c MS, ^d Co-GC ^e
2	2-propanol	940		0.2		0.1	1.7	RI, MS
3	α -pinene	1027	940	8.9	2.8	9.3	2.6	RI, MS, Co-GC
4	α -fenchene	1038					tr	RI, MS
5	camphene	1068	955	0.1	tr ^b	0.1	0.1	RI, MS, Co-GC
6	undecane	1082	1105	nq ^a		nq	0.2	RI, MS, Co-GC
7	β -pinene	1107	983	13.0	5.0	12.9	4.2	RI, MS, Co-GC
8	sabinene	1117	1090	3.1	1.4	4.1	1.7	RI, MS, Co-GC
9	δ -3-carene	1122	1017				0.2	RI, MS, Co-GC
10	myrcene	1154	991	3.3	1.5	3.4	0.7	RI, MS, Co-GC
11	α -phellandrene	1161	1006				tr	RI, MS, Co-GC
12	α -terpinene	1174	1013	0.3		0.9	0.2	RI, MS, Co-GC
13	limonene	1193	1039	7.8	6.0	8.4	2.9	RI, MS, Co-GC
14	1,8-cineole	1203	1033	1.7	0.3	1.1	1.5	RI, MS, Co-GC
15	1-(6-methyl-2-piperidyl)propan-2-one ^f	1222			0.1		0.2	RI, MS
16	<i>cis</i> - β -ocimene	1226	1075	0.2	0.2	0.2	0.1	RI, MS, Co-GC
17	cyclononane	1230			0.1		0.1	RI, MS
18	γ -terpinene	1238	1022	16.2	26.8	31.2	10.0	RI, MS, Co-GC
19	<i>trans</i> -ocimene	1243		6.8	9.6	9.6	2.9	RI, MS, Co-GC
20	<i>p</i> -cymene	1263	1021	23.3	6.0	6.4	3.5	RI, MS, Co-GC
21	2-methyl butyrate	1268					0.1	RI, MS
22	α -terpinolene	1274	1086	1.2	0.7	2.1	0.8	RI, MS, Co-GC
23	octanal	1276	1175				0.3	RI, MS, Co-GC
24	heptyl acetate	1278	1111		0.2		0.1	RI, MS, Co-GC
25	tridecane	1289		tr	0.1	tr	0.6	RI, MS, Co-GC
26	6-methyl-5-heptan-2-one ^f	1329		tr			tr	RI, MS
27	tetrahydro-3,6-dimethyl-2H-pyran-2-one ^f	1345		tr			tr	RI, MS
28	thujone	1419	1076				0.5	RI, MS, Co-GC
29	1-methyl-4-isopropenylbenzene ^f	1426		0.3			0.1	RI, MS
30	2-(1-hydrocycloheptyl)furan ^f	1427				0.2		RI, MS
31	2,2,7,7-tetramethyl-3-octen-5-yne ^f	1428				0.1		RI, MS
32	tetradecane	1438	1116	tr				RI, MS, Co-GC
33	tetradec-1-ene	1448		0.1			0.2	RI, MS
34	undecanal	1452	1293		tr	0.1		RI, MS, Co-GC
35	aromadendrene	1452				0.1		RI, MS
36	1-hepten-1-yl acetate	1456		0.1			0.1	RI, MS
37	citronellal	1468	1141	tr		tr		RI, MS, Co-GC
38	α -copaene	1475	1387	0.2	1.1	0.1	0.4	RI, MS, Co-GC
39	pentadecane	1478			tr	tr	tr	RI, MS, Co-GC
40	decanal	1479	1191		tr	tr	tr	RI, MS, Co-GC
41	α -cubebene	1482	1360	nq	tr	tr	0.1	RI, MS, Co-GC
42	borneol	1509	1131	tr		tr		RI, MS, Co-GC
43	β -cubebene	1521		0.2	0.8	0.1	tr	RI, MS, Co-GC,
44	sabinene hydrate	1536		0.1		tr		RI, MS
45	linalool	1542	1092	1.0		0.5	2.0	RI, MS, Co-GC
46	β -elemene	1563		0.1	tr	0.1	0.4	RI, MS, Co-GC
47	β -caryophyllene	1573	1429	5.1	17.0	3.9	10.5	RI, MS, Co-GC
48	undecanal	1581					tr	RI, MS, Co-GC
49	terpinen-4-ol	1587	1176	0.3	0.1	0.1	0.1	RI, MS, Co-GC
50	γ -elemene	1593					0.1	RI, MS
51	α -humulene	1642		0.6	1.7	0.5	1.5	RI, MS, Co-GC
52	δ -muurolene	1650		tr	0.1	tr	0.1	RI, MS
53	decyl acetate	1650	1398		tr		0.1	RI, MS, Co-GC
54	terpinyl acetate	1662	1342		tr		0.1	RI, MS, Co-GC
55	(<i>E</i>)-11-tetradecenol	1673		tr	0.1	tr	tr	RI, MS
56	cyclopentadecanone	1676		nq	tr	nq	0.1	RI, MS
57	neral	1676	1223		tr			RI, MS, Co-GC
58	germacrene D	1679		0.2	tr		0.9	RI, MS
59	bicyclosesquiphellandrene	1680		0.3	1.1	0.3	0.6	RI, MS
60	α -terpineol	1682	1184	0.5	0.1	0.1	0.5	RI, MS, Co-GC
61	linalyl propionate	1683			0.2		0.1	RI, MS
62	dodecanal	1687	1393	tr	tr	tr	0.1	RI, MS, Co-GC
63	germacrene B	1703		0.1	0.3	0.2	tr	RI, MS
64	δ -selinene	1717		tr	tr	tr	0.1	RI, MS
65	valencene	1732	1497	1.3	3.3	1.2	3.3	RI, MS, Co-GC
66	neryl acetate	1732	1352		0.2		tr	RI, MS, Co-GC
67	farnesene	1738	1456	1.6	8.2	1.2	8.5	RI, MS, Co-GC
68	carvone	1744	122				tr	RI, MS, Co-GC
69	citronellol	1757	1220	tr	tr	tr	tr	RI, MS, Co-GC
70	sesquiphellandrene	1760					0.1	RI, MS
71	tridecanal	1772	1497	tr	tr		0.1	RI, MS, Co-GC
72	geranyl acetate	1772	1340		0.1		tr	RI, MS, Co-GC

Table 1. (Continued)

no.	constituent	retention index		peak area %				identification
		CP-Wax	DB-1	fresh	shade-dried	microwave-dried	freeze-dried	
73	terpinyl propionate	1774	1431		0.1		tr	RI, MS, Co-GC
74	cumin aldehyde	1775					0.1	RI, MS
75	perill aldehyde	1787	1257				tr	RI, MS, Co-GC
76	octadecane	1794					0.1	RI, MS, Co-GC
77	phenylethyl acetoacetate	1796				0.1	0.2	RI, MS
78	cadinene	1799			0.1		0.1	RI, MS
79	<i>p</i> -mentha-1-en-9-yl acetate	1800			0.1		0.1	RI, MS
80	<i>exo</i> -2-hydroxycineol acetate ^f	1841				tr	0.1	RI, MS
81	carveol	1846	1207				0.4	RI, MS, Co-GC
82	nerol	1847	1219				0.5	RI, MS, Co-GC
83	geraniol	1848	1241				0.2	RI, MS, Co-GC
84	limonene-10-yl acetate	1883		0.1		nq		RI, MS
85	dodecyl acetate	1900			1.1		2.0	RI, MS
86	tetradecanal	1902					1.5	RI, MS
87	<i>cis</i> -jasmone	1922		0.1			0.1	RI, MS
88	caryophyllene oxide	1950		tr				RI, MS, Co-GC
89	cinnamic acid	1957		tr				RI, MS
90	dehydrocarveol	1923					tr	RI, MS
91	cinnamyl alcohol	2168	1280				3.4	RI, MS, Co-GC
92	<i>p</i> -mentha-1,8-dien-10-ol ^f	2173					tr	RI, MS
93	cedryl acetate	2186	1871				0.2	RI, MS, Co-GC
94	bisabolol	2201	1675				0.1	RI, MS, Co-GC
95	sinensal	2207					0.1	RI, MS, Co-GC
96	eudesmol	2214	1646				0.2	RI, MS, Co-GC

^a nq, not quantified. ^b Trace, <0.05% (peak area percent). ^c RI, identification based on retention index. ^d MS, identification based on comparison of mass spectra. ^e Co-GC, identification based on co-injection with authentic compounds. ^f Tentatively identified.

Table 2. Constitution of Functional Groups in the Headspace of *C. unshiu* Blossom

functional group	fresh		shady-dried		microwave-dried		freeze-dried	
	total no.	peak area %	total no.	peak area %	total no.	peak area %	total no.	peak area %
hydrocarbons								
aliphatics	5	0.4	2	0.1	4	0.1	6	1.2
monoterpenes	12	84.1	11	60.0	12	88.4	15	29.9
sesquiterpenes	13	9.7	14	33.8	13	7.7	16	26.7
aldehydes								
aliphatics	2	0.1	4	0.1	3	0.1	6	2.0
terpenes	1	tr ^a	1	tr	1	tr	3	0.2
alcohols								
aliphatics	2	0.2	1	0.1	2	0.1	2	1.7
monoterpenes	6	3.5	4	0.5	6	1.8	11	8.8
sesquiterpenes							3	0.4
ketones	4	0.2	3	0.2	1	tr	7	0.7
esters	4	0.3	9	2.0	4	0.1	15	3.8
oxides	1	tr						
acids	1	tr						
miscellaneous					1	0.2		
total	51	98.5	49	96.8	47	98.5	84	75.4

^a Trace, <0.05% (peak area percent).

content of 9%, and the Hunter *L*, *a*, and *b* values were 42.33, 2.60, and 7.73, respectively. Moisture content of the freeze-dried blossom was 8%, and Hunter *L*, *a*, and *b* values were 57.42, -0.52, and 13.14, respectively. Comparison of the volatile flavor profiles of the fresh and dried blossom samples revealed distinct qualitative and quantitative differences (Tables 1 and 2). The headspace of dried *C. unshiu* blossoms was composed of hydrocarbons (SD, 93.9%; MD, 96.2%; and FD, 57.8%), aldehydes (SD, 0.1%; MD, 0.1%; and FD, 2.2%), alcohols (SD, 0.6%; MD, 1.9%; and FD, 10.9%), ketones (SD, 0.2%; MD, trace; and FD, 0.7%), esters (SD, 2.0%; MD, 0.1%; and FD, 3.8%), and trace amounts of miscellaneous compounds.

Monoterpene hydrocarbons were prominent in the headspace aroma of shade-, microwave-, and freeze-dried samples (60.0, 88.4, and 29.9%, respectively). γ -Terpinene was the most

abundant volatile component in the headspace of shade-, and microwave-dried *C. unshiu* blossoms (26.8 and 31.2%, respectively), and β -caryophyllene (10.5%) in freeze-dried sample, although its content was much higher in the shade-dried sample (17.0%). *p*-Cymene showed the greatest percent difference of all the volatile constituents from four *C. unshiu* blossom samples. The oxygenated compounds are important contributors to citrus flavor (3, 4). α -Terpineol is a desirable flavor in many fruits, whereas in others it is perceived as an off-flavor described as terpine-like, camphoraceous, stale, musty, and pungent (14, 15). It is a degradation product of essential oil components in some fruit juice. It occurs in aged orange juice (16). Therefore, it has been proposed as a quality indicator of essential oil components in some fruit juices (17). α -Terpineol content was the highest in the freeze-dried sample (0.5%), followed by

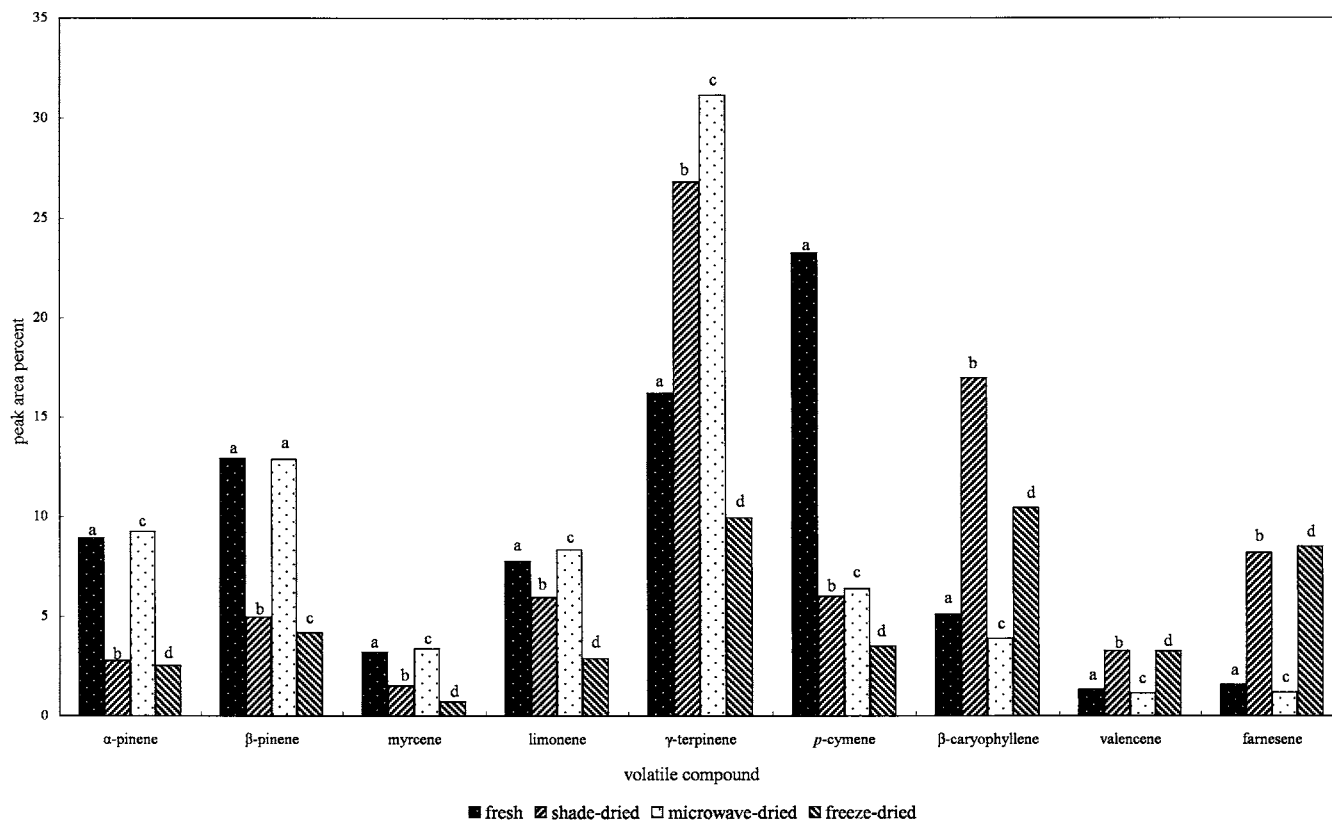


Figure 1. Effect of drying method on relative abundance of α -pinene, β -pinene, myrcene, limonene, γ -terpinene, *p*-cymene, β -caryophyllene, valencene, and farnesene in the headspace of *C. unshiu* blossom. For each compound, different letters above the bars indicate a significant difference ($p < 0.05$).

fresh (0.5%), microwave-dried (0.1%), and shade-dried (0.1%) samples. The content of sesquiterpene hydrocarbons was highest in the shade-dried sample, whereas alcohols showed the opposite predominance.

The use of a microwave to heat foods is widely popular. The convenience and quickness of preparation have instigated a range of food products for microwave heating. The mechanisms for heating food in the microwave are different from those in the conventional oven and can cause differences in the flavor of the prepared food. There is significant water and aroma migration to the surface and into the air because of a 100 °C maximal temperature, and these losses can cause microwaved food materials to have less desirable flavor (18). The newly identified compounds in microwave-dried sample in comparison with a fresh sample were 2-(1-hydrocycloheptyl)furan, 2,2,7,7-tetramethyl-3-octen-5-yne, undecanal, aromadendrene, penta-decane, decanal, phenylethyl acetoacetate, and *exo*-2-hydroxycineol acetate.

Freeze-dried *C. unshiu* blossom had the greatest total number of volatile flavor compounds. Twenty-three volatile components were not detected in fresh or shade- and microwave-dried samples, but small amounts of these components were detected in the freeze-dried sample. The freeze-dried sample had a low hydrocarbon content, especially monoterpene, as compared with other sample groups, and had high alcohol content.

Figure 1 shows the effect of the drying method on the abundance of the nine volatile compounds of *C. unshiu* blossom. Concentrations of α -pinene, β -pinene, myrcene, limonene, γ -terpinene, *p*-cymene, β -caryophyllene, valencene, and farnesene showed significantly different patterns depending on the method used to dry the blossom. However, the level of β -pinene in microwave-dried sample was not significantly different from level found in the fresh sample. Fresh blossom aroma of *C.*

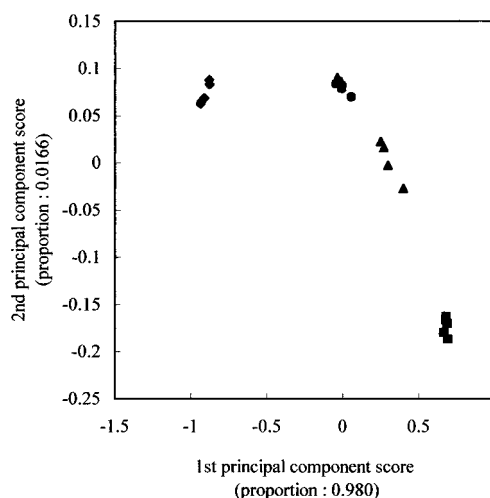


Figure 2. PCA of ratio of resistance by the electronic nose to volatile components from *C. unshiu* blossoms prepared by different drying methods (◆, fresh; ■, shade-dried; ●, microwave-dried; ▲, freeze-dried).

unshiu was characterized by its high content of *p*-cymene (23.3%). *p*-Cymene concentration in fresh sample was significantly reduced upon drying by all three methods. The amounts of α -pinene, β -pinene, myrcene, and limonene were decreased in shade- or freeze-dried samples, but not in the microwave-dried sample. However, β -caryophyllene, valencene, and farnesene contents were significantly increased when the samples were dried by SD or FD methods. The significant increase of γ -terpinene concentration in the MD sample is noteworthy.

Electronic Nose. An electronic nose consisting of six metal oxide sensors was used to recognize volatile aroma in the headspace of *C. unshiu* blossom. **Figure 2** shows the PCA result of the six sensors toward four samples. PCA of volatile

compounds allowed a clear discrimination of four differently prepared blossom samples through their volatile fractions, even for blossoms prepared by some different drying methods that had very similar organoleptic characteristics. In fresh sample, the PCA plot showed a high negative value of the first principal component and a high positive value of the second principal component, whereas the opposite phenomenon was shown in the shade-dried sample. From the PCA plot, it can be seen that the electronic nose was able to distinguish the fresh and each dried sample. The ability to distinguish effluent from differently treated samples creates the possibility of using the electronic nose as an end-point quality control sensor toward volatile aromas.

From these experiments it is concluded that the headspace aroma of *C. unshiu* blossom was found to be a rich source of monoterpene hydrocarbons. *p*-Cymene, γ -terpinene, α -pinene, β -pinene, and limonene were the most abundant components. β -Caryophyllene was a major sesquiterpene component. Comparing the volatile components of the fresh and three differently dried samples showed distinct qualitative and quantitative differences. γ -Terpinene was the most abundant volatile component in the headspace of shade- and microwave-dried *C. unshiu* blossoms and β -caryophyllene in the freeze-dried sample. *p*-Cymene showed the greatest percent difference of all the volatile constituents from four *C. unshiu* blossom samples. The PCA data by electronic nose supported the clear aroma differences of the fresh and each dried *C. unshiu* blossom sample. An organoleptic comparison of the volatile flavor components from fresh and dried samples will provide more detailed information about the odor-active compounds of these blossom samples.

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