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Volatile Oil Composition of Boxthorn (*Lycium chinense* M.) Leaves

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ABSTRACT

Volatile components were extracted from leaves of two Boxthorn (*Lycium chinense* M.) cultivars by using simultaneous distillation and extraction, analyzed by gas chromatography-mass spectrometry. Seventy components were identified: 13 acids, 15 alcohols, 18 hydrocarbons, 13 carbonyls, three esters, three ionones, and five others. The principal volatile components (and their peak area percentage) were n-pentanol (11.2~30.2%), phytol (14.5~28.3%), hexadecanoic acid (13.5~17.1%) 2,3-dihydrobenzofuran (1.5~4.2%), benzyl alcohol (1.9~4.8%), phenylacetaldehyde (1.8~3.2%), and octadecadienoic acid (1.7~10.7%). Fresh leaves showed much higher peak area than that of dried leaf in n-pentanol, n-hexanol, cis-2-penten-1-ol, cis-3-hexen-1-ol, benzyl alcohol, and β-phenylethyl alcohol, while dried leaves showed much higher content than that of fresh leaves in 9-hydroxytheaspran A, octadecanoic acid and octadecadienic acid.

Key words: boxthorn, volatile oil, leaves.

The fruit and leaves of boxthorn (*Lycium chinense* Miller), belonging to the family Solanaceae, have been used as foods, tea and medicine in the orient. It is known that boxthorn leaves are capable of abating or reducing the risk of certain diseases such as arteriosclerosis, essential arterial hypertension, diabetes and nightblindness (Soga, 1985). Boxthorn leaves have also been known for improvement of stamina, tranquillizing activity, thirst-quenching and antiaging activity (Soga, 1985).

The effective utilization of boxthorn leaves for tea or as health food ingredients require detailed information on their flavor components. However, this information is limited. Kim et al. (1997) reported only qualitative data on the forty-five volatile flavor components in the boxthorn leaves. Sannai et al. (1984) identified four volatile flavor compounds from *Lycium chinense* leaves. These were 3-hydroxy-β-ionone, and 3-hydroxy-β-ionol etc. No other volatile compounds were identified in the study.

Volatile aroma compounds are the most sensitive components in the process of food drying. The effect of drying on the composition of volatile flavor constituents of various aromatic plants and vegetables has been the subject of numerous studies, which show that the changes in the concentrations of the volatile compounds during drying depend on several factors, such as the drying method and parameters that are characteristic of the product subject to drying (Venskutonis, 1997). Huopalahti et al. (1985) found that the reduction of the flavour extract after drying of dill herb was significant (from 1.7 to 3.9 times in the case of freeze-drying, and from 6.7 to 11.2 times in case of air drying). The oven-dried and freeze-dried green leaves of young raspberry also had a markedly lower total content of volatiles compared with green frozen ones (Kirisi et al, 1989). In another study, the reduction in the total amount of the essential oil of sweet basil, marjoram and oregano during drying at room temperature was found to be 36-45%, 23-33% and 6-17%, respectively (Nykanen & Nykanen, 1987). Only slight quantitative changes of the flavour of laurel (Skrubis, 1982) leaves were determined after drying.

In this paper, the volatile components of boxthorn leaves are identified and compared with that of fresh and dried leaves.

MATERIALS AND METHODS

Two boxthorn cultivars, 'Cheongyang native' and 'Yuseong #2', selected on the basis of uniform leaf size were cultivated at the experimental fields of the Cheonyang Boxthorn Experiment Station in Republic of Korea from 1993 to 1995. The sampled leaves (100 g) which had grown for 2 years were washed with 0.001% acetic acid solution to remove possible pesticide residues and rinsed with water. Fresh leaves were stored in the refrigerator at 4±2℃ before isolation of volatile compounds, and the washed leaves were dried with hot air at 60℃ and ground to pass through a 60 mesh sieve. The ground leaves were flushed with nitrogen and stored at -18℃ until used.

The volatile flavor components from fresh, or an equivalent amount of dried, boxthorn leaf (100g) were isolated using the simultaneous steam distillation and extraction (Schultz et al., 1977).

Freshly distilled n-pentane and diethyl ether (2:1 v/v) used as mix solvent (60 mL) and the extraction was carried out for 2 hrs. The volatile extract was dried over anhydrous sodium sulphate, filtered through a millipore filter and concentrated by passing a slow stream of nitrogen over the extract which was cooled using a bath with solid

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CO_2. Internal standard n-alkanes were purchased from Aldrich Chemical Co., (Milwaukee, USA). Diethyl ether and n-pentane (Sigma Chemical Co., St. Louis, USA) was used as extracting solvent. Other reagents used in the analysis were analytical reagent grade and were used without further purification.

A Hewlett-Packard 5890 gas chromatograph equipped with a SP-2340 fused silica capillary column (30 m×0.25 mm i.d. ; df=0.25 μm, J & W Scientific) and a flame ionization detector was used to analyze the volatile constituents. The operating conditions were as follows : injector temperature, 230℃ and detector temperature, 250℃ ; Helium carrier flow rate, 1 ml/min; temperature program, 50~150℃ at 3℃/min and held at 230℃ for 10 min. Quantitative determinations were carried out by a Hewlett-Packard 5890A integrator without considering response factors. Linear retention indices were calculated against n-paraffin standards (C5-C25 ; Alltech Associates) as references (Majlat et al., 1974). GC-MS analysis was accomplished by using a HP 5890 gas chromatography coupled directly to a 5970B mass spectrometry. The column and temperature program were the same as described above. Mass spectra were obtained by electron ionization at 70 eV and a source temp erature of 250℃ then recorded on Incos data system.

RESULTS AND DISCUSSION

The gas chromatogram of volatile components in boxthorn leaves is shown in Fig. 1 and 2. The volatile components identified in the leaves are shown in Table 1. Seventy volatile flavor components were identified in the leaves. These included 13 acids, 15 alcohols, 18 hydrocarbons, 13 esters, 3 ionones, and others. The principal volatile components and their peak area percentage were n-pentanol (11.2~30.2%), phytol (14.5~28.3%), hexadecanoic acid (13.5~17.1%) 2,3-dihydrobenzofuran (1.5~4.2%), benzyl alcohol (1.9~4.8%), phenylacetaldehyde (1.8~3.2%), and octadecadienoic acid (1.7~10.7%). Thirteen acids in the leaves were identified representing Cheongyang native 22.3% and Yuseong #2 26.4% with fresh leaves, and Cheongyang native 28.8% and Yuseong #2 40.5% with dried leaves of the total volatile, respectively. These were acetic acid, n-butanic acid, n-hexanoic acid, n-heptanoic acid, n-nonanoic acid, n-decanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid and octadecadienoic acid. Of these, hexanoic acid has been reported to have cheese, fatty and rancid odors in strawberry jams (Guichard et al., 1991). Quantitatively, alcohol were the most abundant class of components identified, representing as much as Cheongyang native 57.7% and Yuseong #2 50.6% with fresh leaves, and Cheongyang native 52.5% and Yuseong #2 39.0% with dried leaves. Phytol, which is derived from chlorophyll, contributed from 14.5% to 28.3% of the total volatile components in the leaves. A characteristic mushroom flavor component 1-octene-3-ol (0.2~0.5%) was also

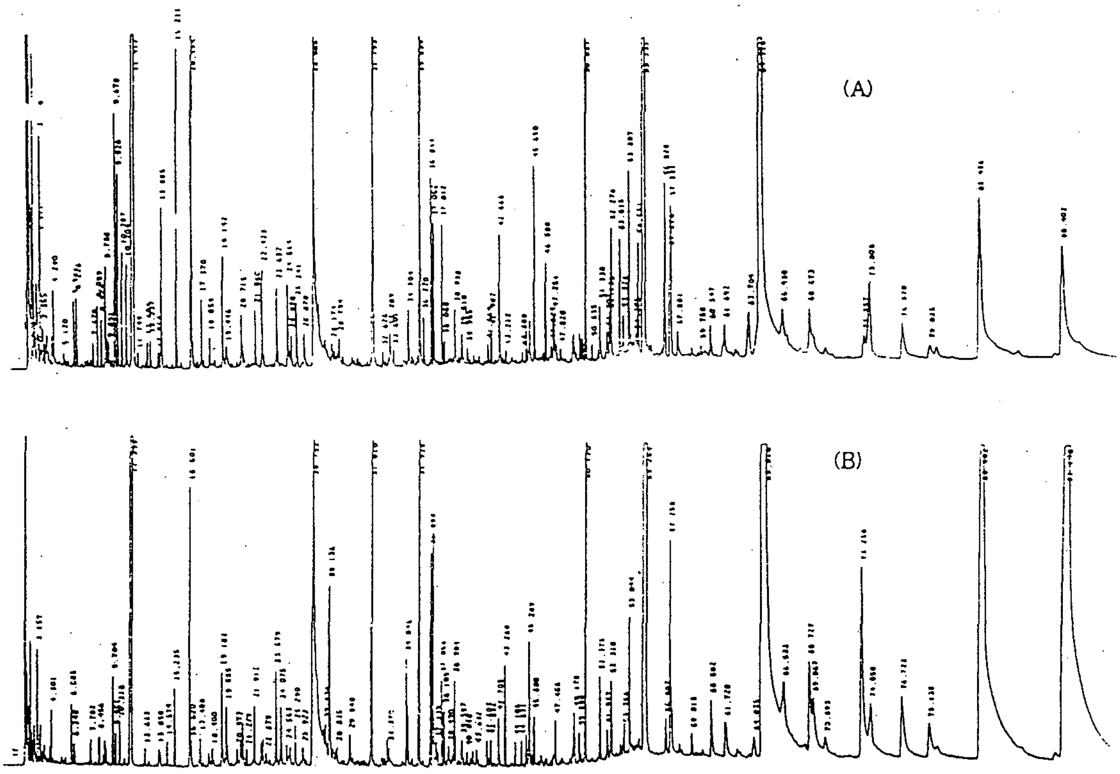

Fig. 1. Gas chromatograms of fresh (A) and dried (B) leaf from *Lycium chinense* cv. Cheongyang Native.

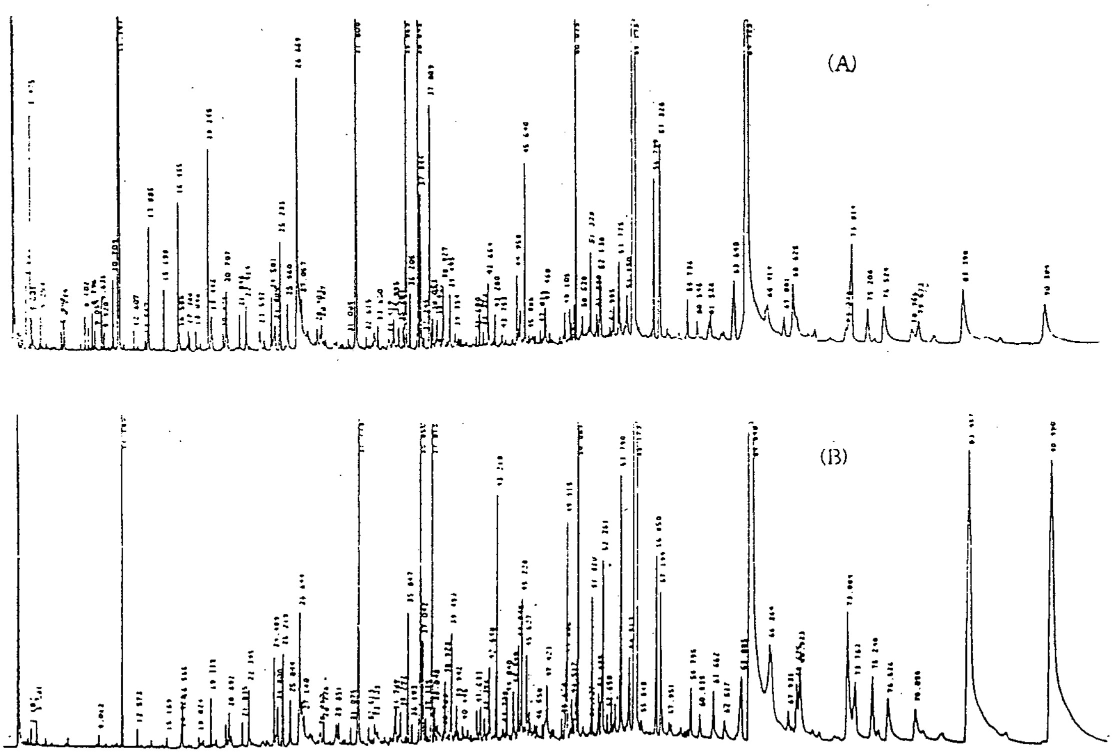

Fig. 2. Gas chromatograms of fresh (A) and dried (B) leaf from Lycium chinense cv. Yuseong #2.

Table 1. Comparison of volatile composition (retention time and peak area percentage of leaves from two boxthorn (*Lycium chinense* M.) cultivars.

Peak No.	Retention time (min)	Compounds	Fresh†		Dried†	
			Cheongyang native	Yuseong #2	Cheongyang native	Yuseong #2
1	3.17	n-Pentanal	0.7	0.2	0.3	0.2
2	4.37	n-Hexanal	0.4	0.3	0.1	0.1
3	8.22	2,6-Dimethyl-4-heptanone	0.2	0.2	0.1	0.1
4	9.17	n-Dodecane	0.1	0.2	0.1	–
5	9.81	3-Methyl-1-butanol	1.1	0.3	0.2	0.2
6	10.87	trans-2-Hexenal	0.4	0.2	0.1	–
7	11.51	n-Pentanol	30.2	11.2	22.0	15.6
8	12.76	n-Tridecane	0.1	–	0.1	0.1
9	14.05	cis-2-Penten-1-ol	0.5	0.4	–	–
10	15.37	n-Hexanol	0.9	0.9	0.1	0.2
11	16.64	cis-3-Hexan-l-ol	3.0	1.4	0.1	0.7
12	17.55	trans-2-Hexen-l-ol	0.2	0.3	0.1	0.1
13	18.27	trans-2-Octenal	0.1	0.1	–	–
14	19.34	l-Octen-3-ol	0.4	0.5	0.2	0.2
15	19.68	Acetic acid	0.1	0.1	–	0.1
16	20.65	trans, trans-2,4-Heptadienal	–	0.2	0.1	0.1
17	20.93	α-Copaene	0.2	0.3	0.2	0.1
18	22.09	Benzaldehyde	0.3	0.2	0.2	0.2
19	22.53	9-Hydroxytheaspran A	–	–	0.2	0.2
20	22.63	n-Octanol	0.3	0.5	0.3	0.1
21	23.91	2,6-Nonadienal	0.3	0.5	–	0.2
22	24.75	β-Caryophyllene	0.2	0.4	–	0.1

Table 1. Continued

Peak No.	Retention Time (min)	Compounds	Fresh†		Dried†	
			Cheongyang native	Yuseong #2	Cheongyang native	Yuseong #2
23	25.01	n-Hexadecane	0.3	0.5	0.2	0.2
24	25.48	2,6-Dimethyl cyclohexanol	0.2	0.6	0.2	0.1
25	26.12	β-Cyclocitral	0.1	0.2	0.3	0.1
26	26.92	Phenylacetaldehyde	2.4	2.8	1.8	3.2
27	27.28	4-(1-Methylethyl)-cyclohexanol	0.1	0.2	–	–
28	28.02	n-Heptadecane	–	–	0.4	0.2
29	28.23	n-Butanoic acid	0.2	0.3	0.2	0.2
30	32.85	n-Octadecane	0.1	–	0.2	–
31	34.66	Geraniol	0.2	0.1	0.3	0.1
32	34.80	n-Hexanoic acid	–	–	0.3	0.1
33	35.07	α-Ionone	0.3	0.3	0.2	0.5
34	36.10	Benzyl alcohol	4.8	4.2	1.9	1.9
35	36.46	n-Nonadecane	0.2	0.3	0.2	0.6
36	37.33	β-Phenylethyl alcohol	1.2	1.5	0.6	0.8
37	38.07	β-Iononeal	0.5	0.9	0.4	0.3
38	38.17	n-Heptanoic acid	–	–	0.2	0.5
39	38.29	n-Dodecanol	0.1	0.2	0.2	0.2
40	39.17	Benzothiazole	0.2	0.4	0.4	0.3
41	39.60	n-Docosane	0.1	0.2	0.1	0.1
42	39.75	β-Ionone epoxide	0.1	0.3	0.2	0.1
43	42.50	n-Heneicosane	0.1	0.2	0.3	0.1
44	43.43	6, 10, 14-Trimethylpentadecanone	0.4	0.2	0.4	0.3
45	44.64	n-Nonanoic acid	–	–	0.1	0.4
46	45.20	n-Docosane	0.1	0.3	0.3	0.3
47	45.71	2,3-Dihydrotrimethyl-3-phenyl-IH-indene	0.2	0.2	0.1	0.1
48	45.88	Methyl hexadecanoate	0.7	1.0	0.6	0.1
49	47.19	n-Decanoic acid	0.1	0.1	0.1	0.3
50	47.70	n-Tricosane	0.2	0.3	0.2	0.1
51	49.38	Farnesylacetone	0.1	0.1	0.1	0.2
52	49.76	Tetrahydrotrimethyl-2(4H)-benzofuranone	0.1	0.2	0.1	0.1
53	50.09	n-Tetracosane	0.1	0.3	–	–
54	50.19	2,3-Dihydrobenzofuran	2.4	1.5	3.6	4.2
55	51.45	Indole	–	–	0.2	0.2
56	51.56	Methyl octadecadienoate	0.2	0.3	0.2	0.2
57	52.14	n-Pentacosane	0.2	0.3	0.2	0.2
58	53.98	Methyl octadecanoate	0.6	1.0	0.3	0.4
59	54.80	n-Hexacosane	0.4	0.8	–	–
60	55.49	Phytol	14.5	28.3	26.3	18.8
61	57.22	n-Heptacosane	0.3	0.9	0.4	0.2
62	57.58	Tetradecanoic acid	0.7	0.6	1.3	0.9
63	60.24	n-Nonacosane	0.2	–	0.3	0.3
64	62.13	Pentadecanoic acid	0.4	0.3	0.3	0.2
65	64.56	n-Triacontane	0.4	0.9	–	–
66	65.40	Hexadecanoic acid	13.5	17.1	13.9	17.1
67	69.18	Heptadecanoic acid	0.9	1.9	0.3	0.7
68	74.80	Octadecanoic acid	1.1	1.7	0.6	1.8
69	84.40	Octadecenoic acid	2.7	2.6	5.2	7.5
70	91.62	Octadecadienoic acid	2.6	1.7	6.3	10.7
		Unknown	4.9	6.8	5.5	7.5

† peak area percentage

found. Benzyl alcohol which gives a "floral" flavor, was also found (1.9~4.2%) and geraniol (orange and rosy odor) were also identified in the leaves.

Three ionones were identified in boxthorn leaves. These were α-ionone, β-ionone, and β-ionone epoxide, representing 0.3%, 0.5%, and 0.1% in fresh Cheongyang native variety leaves, and 0.3, 0.4, and 0.2% in dried Cheongyang native variety leaves, respectively. β-ionone has been known to give a pleasant violet floral flavor to black tea. Sanni et al. (1984) identified four volatile flavor compounds-3 hydroxy-7,8-dehydro-β-ionone, 3-hydroxy-7,8-dehydro-β-ionol, 3-hydroxy-β-ionone, and 3-hydroxy-β-ionol in *Lycium chinense* leaves. However, these components were not identified in the present study.

Contents of n-pentanol and β-phenylethyl alcohol of fresh leaves showed much higher levels than those of dried leaf, while 9-hydroxytheaspran A, octadecanoic acid and octadecadienic acid of dried leaves showed much higher levels than those of fresh leaves.

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