Volatile Compounds Isolated from Edible Korean Fatsia Shoots (*Aralia elata* Seem.)

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Abstract: The volatile concentrate obtained from the edible Korean dureup plant (*Aralia elata* Seem.) by a distillation-extraction system was separated into hydrocarbon and oxygen-containing fractions, and the latter was further separated into nine subfractions by silica gel column chromatography. Gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) were utilized to identify 167 volatile compounds in the fractions. The volatile compounds included 72 hydrocarbons, 31 alcohols, 23 aldehydes, 16 esters, 10 acids, 6 ketons, 3 furans, 2 phenols, 1 indole, 1 oxide, 1 sulfide, and 1 lactone. β -Caryopyllene, a sesquiterpene hydrocarbon, was the most abundant volatile compound identified in Korean dureup (19.53%). Dureup oil was found to possess a woody or herbaceous aroma following sensory evaluation of each fraction and individual volatile component using a GC-sniff apparatus. (Received July 29, 1996; accepted August 22, 1996)

Introduction

Plant, either directly or indirectly, are probably most important to the human being as sources of food and medicine. There are thousands of different types of valuable plants throughout the world that are utilized in the preparation of meals and for medicinal purposes. Plant materials are both volatile and nonvolatile and affect odor and flavor profiles as well as sensory impact. The volatile constituents give a plant its distinctive odor, whereas the nonvolatile compounds are either inert or may be implicated in a diverse number of physiological effects when consumed. They can also serve in many cases as precursors for the formation of volatile flavor compounds. The intensity of the aroma and types of physiological effect show wide variations between plant families and species.

Dureup (*Aralia elata* Seem.) is a deciduous shrub of the Araliaceae family and grows wild in the sunny mountain regions of Korea, North-eastern China, Japan, and Siberia. There are some 800 extant species of 65 genera classified from the Araliaceae family in the world. Of these, 14 extant species of 8 genera are widely distributed in Korea. Young fatsia shoots are gathered through April into May and used in the preparation of traditional Korean dishes. ^{2.3)}

Dried Araliae barks and their cortices have been used

as a folk remedy for stomach ulcer, gastralgia, diabetes, hepatitis, arthritis and nephritis in Korea. The pharmacological activity of the nonvolatile components of dureup have recently become the subject of research in several laboratories throughout the world. Algapanese research group has previously reported the volatile constituents on *Aralia elata* Seemann var. *subinermis* Ohwi botanically related with this plant. However, no attempts have been previously made to characterize the volatile constituents of this plant. The object of the present investigation, then, was to identify and characterize the volatile compounds from fatsia shoots by gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), and GC-sniff sensory analysis.

Material and Methods

Materials

Young fatsia shoots, grown in the Jiri Mountains (Hadong, Korea), were collected in May 1994. Diethyl ether, n-pentane, and anhydrous sodium sulfate were obtained from Wako Pure Chemical Industeries Ltd. (Osaka, Japan).

All authentic chemicals were purchased from reliable commercial sources (Aldrich Chemical Co., Sigma Chemical Co., Fluka Chemika-Biochemica, Soda Perfumary

Key words: Aralia elata, Fatsia shoots, Japanese angelica tree, Volatile compounds, Araliaceae. *Corresponding author

Co. Ltd., and Hasegawa Perfumary Co. Ltd.).

Sample Preparation

The volatile concentrate was prepared with a modified Likens-Nickerson distillation-extraction system (SDE) at atmospheric pressure. 143 A sample flask containing 500 g of crushed fatsia shoots and 1.5 L of distilled water was attached to the lower right joint of the SDE, and a small flask containing 200 ml of redistilled diethyl ether, the extracting solvent, was attached to its left joint. The sample flask was heated to 100°C by an electric heating mantle, and the extracting solvent flask was kept at 38°C by a water bath. The SDE was allowed to proceed for 2 hr, and the extracting solvent was collected. The ether extract was dried over anhydrous sodium sulfate for 12 hr. After removal of sodium sulfate, the extract was concentrated to 1 ml by fractional distillation at 38°C and atmospheric pressure. The above procedure was repeated 10 times utilizing all of the fatsia shoots (5 kg), and the extracts were subsequently combined.

Fractionation of the Volatile Extract

The whole volatile concentrate was fractionated into hydrocarbon and oxygen-containing compound fractions by a silica gel column (1×46 cm). The hydrocarbon and oxygen-containing fractions were eluted with n-pentane (500 ml) and redistilled diethyl ether (500 ml), respectively. Both extracts were concentrated to 0.5 ml, and the diethyl ether eluate was further separated by a similar silica gel column into eight subfractions by the gradient elution of n-pentane and diethyl ether. n-Pentane content in each elution was 98%, 97%, 95%, 93%, 90%, 80%, 50%, and 0%, respectively. Subsequently, the last subfraction was obtained by elution with methanol. The resulting fractions were similarly concentrated to 0.5 ml by fractional distillation. The concentrated extracts were then placed in vials and stored under argon at -4℃ until analysis.

Instrumental Analysis.

A Hewlett-Packard (HP) Model 5890A gas chromatograph equipped with a flame ionization detector (FID) was used for routine analysis. Three different types of fused silica WCOT capillary columns (50 m× 0.25 mm i.d.) coated with HP-101 (dimethylsilicone), HP-20M (carbowax), and HP-FFAP (free fatty acid phase) stationary phases were used. The GC oven temperature of the HP-101 was programmed from 70°C to 200°C, that of the HP-20M from 60°C to 190°C, and that of the HP-FFAP from 60°C to 210°C, all at a ratio of 3°C/min. The injector and detector temperatures were both kept at 230°C. Nitrogen (0.6 ml/min) was used as the carrier gas, and the split ratio was set to 1:100.

A HP Model 5890A GC interfaced to a HP 5970 mass spectrometer was used for MS identification of the GC components using the same columns and oven conditions listed above. Helium (1.0 ml/min) was used as the carrier gas, and the split ratio was set to 1:25. The mass spectra were obtained by the electron impact ionization at 70eV and an ion source temperature of 250°C. The spectral data were recorded on a HP 59970A computer data system. All compounds were identified by comparing the Kovats retention index¹⁵⁾ and MS fragmentation to those of authentic samples. Tentative identifications were made in cases for which an authentic reference standard was not available and identification could only be made on the basis of MS data.

Sensory Evaluation

An aliquot of ether solution from each fraction was adsorbed on a filter paper and air-dried to remove the solvent. The whole volatile concentrate and its subsequent fractions were evaluated by 10 members of the laboratory.

Sensory evaluation of the individual volatile constituents emitted at each peak on the gas chromatogram was accomplished by sniffing at the exit port of a Gasukuro Kogyo Model 350 GC equipped with an effluent splitter and an FID. The GC capillary columns and oven conditions were the same as stated above. Carrier gas was kept at a flow rate of 3.48 ml/min with a split ratio of 1:1.5.

Results and Discussion

All sensory panelists noted that the aroma of the volatile concentrate was very similar to that of fresh fatsia shoots, having an oily herbaceous odor without offflavors. The yields and odor characteristics of the whole volatile concentrate and its fractions/subfractions are summarized in Table 1. The odor of the hydrocarbon fraction (HF) and the oxygen-containing compound fraction (OCCF) was less pleasant than that of the original volatile flavor concentrate. However, the oxygen-containing fraction retained mild fatsia shoot-like odor and was hence considered to be more important in characterizing fatsia shoot aroma. The oxygen-containing compound fraction, then, was further separated into nine subfractions by silica gel column chromatography, and each subfraction was subjected to sensory evaluation. Among the subfractions, some carried floral notes, while others bore more woody and herbaceous odors. The approximate yield of the volatile flavor concentrate obtained from 5 kg of dureup was 0.479 g (0.01%).

Fig. 1 shows the gas chromatogram of the whole volatile concentrate of dureup separated by a HP-FFAP capillary column. One hundred and sixty-seven compounds of approximately 214 peaks on the gas chromatogram were identified in the volatile concentrate by the same technique as mentioned above. These were composed of 72 hydocarbons (71.81%), 31 alcohols (5.56%), 23 al-

Table 1. Yield and Odor Characteristics of the Volatile Flavor Concentrate of Fatsia Shoots and Subsequent Fractions

Fraction	Yield(g) ^a	Odor ^b	Compounds
WVC	0.479	Dureup-like	All volatile components
HF	0.341	Woody or	Hydrocarbons
		herbaceous	
OCCF	0.138	Dureup-like	Oxygen-containing
			compounds
OCCF-1	0.009	Sweet-floral	Aldehydes, ketones, esters,
			furans
OCCF-2	0.004	Herbaceous	Aldehydes, oxide
OCCF-3	0.012	Dried straw-like	Phenols, esters
OCCF-4	0.015	Sweet-floral	Monoterpene alcohols,
			phenols
OCCF-5	0.023	Woody or	Mono and sesquiterpene
		herbaceous	alcohols
OCCF-6	0.008	Woody or	Alkenols, alkanols, lactone
		herbaceous	
OCCF-7	0.018	Sweet-floral	Alkanols, aromatic alcohols
OCCF-8	0.049	Rancidity or sweat	Carboxylic acids
OCCF-9		Medicinal	Not detected

^aYield was obtained from 5 kg of Korean dureup. The yield for each fraction was found by subtracting the solvent peak area from total peak area and dividing by total peak area to obtain a ratio. This value was then multiplied by the weight (g) of the extract. ^bAn aliquot of ether solution from each fraction was adsorbed on a filter paper and air-dried to remove the solvent. The whole volatile concentrate and its subsequent fractions were then evaluated by 10 members of the laboratory. WVC: Whole volatile flavor concentrate, HF: Hydrocarbon fraction, OCCF: Oxygen- contaning compound fraction.

dehydes (2.44%), 16 esters (3.65%), 10 acids (2.02%), 6 ketones (0.24%), 3 furans (0.26%), 2 phenols (0.03%), 1 indole (trace), 1 oxide (0.98%), 1 sulfide (trace), and 1 lactone (3.10%).

These volatile components are listed in Table 2 by elution order from GC with a HP-FFAP capillary column. Table 2 was prepared by the method reported in the previous paper. 16) Some compounds were not positively identified because of the lack of authentic chemical, so Kovats index and mass spectra could not be compared. Percentage contributions of the various classes of compounds were calculated by the GC peak area represented in the whole volatile concentrate chromatogram. Hydrocarbons comprised the majority of the components identified and included 22 alkanes (1.37%), 19 sesquiterpene hydrocarbons (66.78%), 16 monoterpene hydrocarbons (3.68%), and 15 aromatic hydrocarbons (0.04%). The major component of the monoterpene hydrocarbons was β -pinene (1.82%), and that of the sesquiterpene hydrocarbons was β -caryophyllene (19.53%).

Alcohols, the second predominant class of volatiles identified, were composed of 9 alkanols (2.52%), 8 monoterpene alcohols (0.60%), 6 alkenols (0.88%), 5 sesquiterpene alcohols (1.22%), 2 aromatic alcohols (0.49%), and 1 diterpene alcohol (0.05%). Phytol, which is the monounsaturated diterpene alcohol esterified to chlorophyllide a in the chlorophyll molecule, has been thought to be formed by degradation of chlorophyll in plants, and this is similarly proposed for dureup.¹⁷⁾

Aldehydes were composed of 8 alkanals (0.24%), 5 alkenals (0.41%), 4 alkadienals (0.63%), 4 aromatic aldehydes (0.35%), 1 monoterpene aldehyde (0.46%), and 1 sesqui-

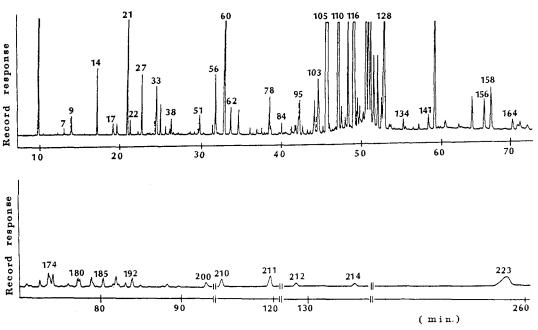


Fig. 1. Gas Chromatogram of Whole Volatile Concentrate of Aralia elata Seem. Obtained by a HP-FFAP Capillary Column.

Table 2. Volatile Compounds Identified in the Extract of Edible Korean Fatsia Shoots (Aralia elata Seem.)

Peak No.	Compound	RI°				GC peak area (%)			
reak No.	Compound	HP-FFAP	HP-20M	HP-101	WVC	HF	OCCF	Subfractions	
2	Ethanal	718	714	418	0.02		0.07	1	
3	Octane	800	800	800	b	1.23			
5	Ethyl formate	835	848	530	b		0.04	1	
7	Nonane	900	900	900	b	b			
7'	Ethyl acetate	900	907	602	0.07		0.24	1	
8	2-Propanol	933	884	500	0.03		0.10	6,7	
9	Ethanol	937	929	485	0.21		0.73	6,7	
9 ′	3-Methylbutanal	937	929	641	b		0.18	1,2	
10	2-Ethylfuran	968	951	694	b		0.02	1	
11	Decane	1000	1000	1000	b	b			
12	Pentanal	1005	958	687	b		b	1,2	
13	α-Thujene	1035	1005	930	b	b			
14	α-Pinene	1042	1034	941	0.63	0.68			
15	Toluene	1068	1042	762	b	0.08			
17	Camphene	1093	1075	957	0.17	0.18			
18	Undecane	1100	1100	1100	b	b			
19	Hexanal	1111	1075	782	0.16		0.56	1,2	
21	β-Pinene	1135	1114	985	1.68	1.82			
22	Sabinene	1144	1123	977	0.15	0.16			
24	Ethylbenzene	1157	1109	859	b	b			
25	(E)-2-Pentenal	1164	1101	707	b		b	1,2	
26	p-Xylene	1166	1116	866	b	b			
26 ´	1-Penten-3-o1	1166	1122	687	0.05		0.17	6	
27	δ-3-Carene	1177	1148	1017	b	b			
27 ′	Myrcene	1177	1161	990	0.63	0.68			
28	α-Phellandrene	1192	1166	1009	0.02	0.02			
30	Dodecane	1200	1200	1200	0.02	0.03			
31	α-Terpinene	1207	1178	1020	0.03	0.03			
32	2-Heptanone	1212 •	1111	815	Ъ		0.02	1	
33	Heptanal	1217	1174	885	b		0.05	1,2	
33 ′	Methyl caproate	1217	1164	907	b		0.02	3	
33 ″	2-Pentanol	1217	1172	732	0.42		1.42	6,7	
33″′	3-Methyl-1-butanol	1217	1172	736	0.39		1.32	6,7	
35	β-Phellandrene	1241	1209	1035	0.10	0.11			
36	(Z)-3-Hexenal	1244	1115	825	b		0.05	2	
37	(Z)-Ocimene	1252	1225	1035	0.09	0.10			
38	(E)-2-Hexenal	1255	1209	836	0.09		0.32	2	
38 ′	2-Pentylfuran	1255	1218	982	0.10		0.35	1	
39	1-Pentanol	1261	1218	763	0.04		0.12	6,7	
41	(E)-Ocimene	1270	1242	1043	0.02	0.02			
42	γ-Terpinene	1274	1238	1058	0.03	0.04			
43	sec-Butylbenzene	1281	1230	1014	b	0.03			
14	Styrene	1296	1234	889	b	b			
45	Tridecane	1300	1300	1300	0.03	0.03			
46	p-Cymene	1303	1261	1025	0.03	0.04			
48	Terpinolene	1314	1275	1089	0.03	0.07			
50	Perillene	1323	1295	1109	0.07	0.08			
51	2-Heptanol	1327	1284	888	0.23		0.81	6,7	
51 ′	(E)-2-Pentenol	1327	1277	762	b		b	6	
52	(Z)-2-Pentenol	1336	1284	775	0.04		0.13	6	
52 ´	m-Diethylbenzene	1336	1278	1070	b	b			
53	p-Diethylbenzene	1345	1286	1080	b	b			
56	1-Hexanol	1364	1318	865	0.82		2.85	6.7	
56 ´	6-Methyl-5-hepten-2-one	1364	1311	971	0.03		0.10	1	
56 ″	o-Diethylbenzene	1364	1305	1099	Ъ	b			
59	p-Methylstyrene	1382	1320	975	b	\boldsymbol{b}			
60	β-Angelica lactone	1389	1314	985	3.10		10.77	6	
61	Tetradecane	1400	1400	1400	b	0.02			

Table 2. continued

Peak No.	Compound	RIª			GC peak area (%)			
Peak No.	Compound	HP-FFAP	HP-20M	HP-101	WVC	HF	OCCF	Subfractions
2	(Z)-3-Hexenol	1402	1357	860	0.39		1.35	6
3	Dipropyldisulfide	1420	1358	1096	b		b	7
1	2,3-Dihydroindene	1426	1346	1031	Ъ	0.06		
l'	(E)-2-Hexenol	1426	1377	870	0.37		1.13	6
1 ″	Nonanal	1426	1372	1091	b		0.17	1,2
7	(E,E)-2,4-Hexadienal	1444	1368	887	0.11		0.37	1,2
7′	Pentylbenzene	1444	1394	1154	ь	0.11		
3	1-Octen-3-ol	1459	1423	981	0.03		0.10	6
0	(E)-2-Octenal	1469	1402	1044	0.09		0.31	1,2
0′	Ethyl octanoate	1469	1416	1183	b		b	3
1	Acetic acid	1473	1405	710	0.03		0.11	8
5	δ-Elemene	1488	1488	1360	0.04	0.21		
6	1,4-Dichlorobenzene	1492	1428	1009	b	0.05		
8 .	Pentadecane	1500	1500	1500	0.50	0.07		
0	2-Furfural	1514	1429	845	b	0.0.	0.05	1,2
3	Decanal	1526	1473	1192	0.06		0.19	1,2
4	α-Copaene	1532	1470	1385	0.16	0.36	0.15	1,2
4 6	(E,E)-2,4-Heptadienal	1532 1542	1470	999	0.16	0.30	0.17	1,2
6 ′	-					0.02	0.17	1,2
	1,2-Dichlorobenzene	1542	1462	1035	b	0.02		
7	Indene	1545	1455	1043	0.04	0.09	0.25	4
0	Linalool	1558	1522	1100	0.10		0.35	4
1	Propanoic acid	1560	1472	790	0.06		0.21	8
2	Benzofuran	1566	1478	1003	0.13		0.44	1
3	1-Octanol	1569	1521	1068	0.15		0.52	6,7
4	(E)-2-Nonenal	1575	1505	1146	0.23		0.81	1,2
5	β-Cubebene	1578	1588	1400	0.49	0.70		
6	Benzaldehyde	1586	1490	983	0.14		0.48	1,2
8	Hexadecane	1600	1600	1600	0.08	0.10		
)1	(E)-α-Bergamotene ^c	1621	1584		0.65	0.73		
)2	2-Undecanone	1626	1584	1278	0.05		0.16	1
)3	Bornyl acetate	1633	1558	1284	1.21		4.20	3
)4	Terpinen-4-ol	1645	1579	1182	b		0.35	4
)4 ′	γ-Elemene	1645	1612	1436	0.10	0.16		
)5	β-Caryophyllene	1660	1594	1438	19.53	21.14		
06	Aromadendrene	1664	1600	1458	0.15	0.35		
10	(E)-β-Farnesene	1692	1658	1452	8.39	12.99		
11	Heptadecane	1700	1700	1700	b	0.13		
 11 ′	Myrtenal	1700	1599	1186	0.46		1.60	1,2
13	Phenylacetaldehyde	1711	1615	1047	0.32		1.11	1,2
13 ′	Alloaromadendrene	1711	1639	1479	b	0.27		_,_
14	(Z,Z)-α-Farnesene ^c	1719	1671	1410	2.25	2.54		
16	α-Humulene	1736	1663	1472	14.23	13.41		
17	α-Terpineol	1740	1659	1197	0.06	10.41	0.21	4,5
18	Dodecanal	1744	1682	1394	b		0.03	1,2
18 ´	(Z,E)-α-Farnesene				0.60	1.94	0.03	1,2
		1744	1690	1483		1.94	0.67	4,5
20	Borneol	1753	1677	1180	0.19	0.00	0.07	4,5
22	Zingiberene	1769	1708	1493	6.90	8.69		
23	(E,E)-α-Farnesene	1775	1717	1500	3.36	2.64		
24	α-Muurolene	1781	1723	1510	2.44	3.27		
25	δ-Cadinene	1789	1735	1523	1.56	3.32		
26	Octadecane	1800	1800	1800	b	b		
26 ´	α-Curcumene	1800	1740	1470	1.22	1.27		
27	β-Sesquiphellandrene	1810	1750	1523	0.49	2.56		
28	Cadina-1,4-diene	1818	1765	1530	4.22	7.32		
29	Nerol	1830	1770	1234	0.09		0.33	4,5
30	Myrtenol	1834	1751	1212	0.09		0.32	4,5
31	Geranyl propionate	1842	1799	1424	0.03		0.10	3
133	Methyl salicylate	1856	1739	1200	0.03		0.10	3

Table 2. continued

Peak No.	Compound -		RIª	GC peak area (%)				
reak No.	Compound	HP-FFAP	HP-20M	HP-101	WVC	HF	OCCF	Subfraction
34	(E,E)-2,4-Decadienal	1867	1779	1300	0.15		0.52	1,2
34	Geraniol	1867	1814	1258	0.02		0.07	4, 5
35	Hexanoic acid	1872	1800	1051	0.07		0.26	8
37	p-Cymen-8-ol	1892	1814	1200	0.05		0.18	
38	Nonadecane	1900	1900	1900	b	0.02		
.40	Geranyl butanoate	1919	1872	1532	b		0.03	3
.41	Benzyl alcohol	1931	1826	1091	0.30		1.03	7
46	2-Phenylethanol	1972	1880	1509	0.19		0.67	7
49	Eicosane	2000	2000	2000	b	b		
.50	β-Ionone	2005	1912	1484	0.10		0.34	1
.51	(E)-2-Hexenoic acid	2009	1910	1106	0.07		0.25	8
.52	(Z)-Jasmone	2015	1914	1382	0.03		0.11	1
55	p-Anisaldehyde	2051	1982	1234	0.03		0.11	1,2
.56	(E)-Nerolidol	2059	2009	1564	0.63		2.19	5
.57	Phenol	2068	1950	1110	b		0.03	3,4
58	Caryophyllene oxide	2078	1962	1600	0.98		3.39	2
59	Biphenyl	2081	1947	1376	b	0.13		
.60	Octanoic acid	2084	2010	1230	b		0.06	8
.62	Heneicosane	2100	2100	2100	b	0.04		
.64	Geranyl hexanoate	2116	2054	1731	0.25		0.86	3
69	Methylcinnamic aldehyde	2125	1992	1309	0.18		0.63	1,2
71	Nonanoic acid	2148	2110	1321	0.12		0.42	8
74	Docosane	2200	2200	2200	0.68	0.03	37.2	-
76	δ-Cadinol	2217	2134	1657	0.02	0.00	0.07	5
70 79	Eugenol	2237	2110	1385	0.03		0.11	3,4
.80	Methyl palmitate	2240	2189	1911	0.27		0.93	3
.81	T-Muurolol	2240	2148	1659	0.22		0.77	5
.85	Ethyl palmitate	2274	2260	1978	0.29		1.01	3
.86	Citronellic acid	2282	2187	1392	0.04		0.13	8
.87	α-Cadinol	2287	2191	1674	0.11		0.39	5
.89	(E,E)-Farnesylacetate	2295	2220	1818	0.10		0.35	3
.90	Tricosane	2300	2300	2300	0.02	0.22	0.00	ŭ
.92	(E,E)-Farnesal	2310	2204	1753	0.35	0.22	1.21	1,2
200	(E,E)-Farnesol	2386	2304	1722	0.24		0.83	5
:01	Tetracosane	2400	2400	2400	0.02	0.08	0.00	J
202	1-Hexadecanol	2405	2329	1864	0.03	0.00	0.11	6,7
302 304	Farnesyl acetone ^c	2403	2357	1004	0.03		0.10	1
07	Pentacosane	2500	2500	2500	0.03	0.23	0.10	•
08	Lauric acid	2506	2427	1593	0.02	0.20	0.30	8
09	Indole	2508	2351	1304	b		0.04	2
				2066	0.42		1.46	3
210 211	Methyl linoleate	2525	2447	2133	0.42		2.06	3
212	Ethyl linoleate Methyl linolenate	2556 2598	2484 2510	2071	0.39		0.68	3
13					b	0.13	0.00	3
13 14	Hexacosane Ethyl linolenate	2600 2614	2600	2600 2137	0.19	0.13	0.67	3
	•		2545				0.07	5
216	Phytol Heptacosane	2636	2571	2111	0.05 b	0.19	0.19	3
18		2700	2700	2700	b b	0.19	0.03	8
219	Myristic acid	2752	2610	1796	b b	0.19	0.03	0
221	Octacosane	2800	2800	2800	b	0.13		
222	Nonacosane Polyvitio poid	2900	2900	2900	b 154	0.04	5.34	o
223	Palmitic acid	2940	2860	2000	90.09	91.08	64.31	8
Known comp	ounds							
Jnknown co	npounds				9.91	8.92	35.69	

^{*}Kovats index were calculated on HP-FFAP, HP-20M and HP-101 capillary columns. *Peak area percent less than 0.02. *Tentatively identified.

Table 3. Organoleptic Characteristics of Each Volatile Component Identified from Edible Korean Dureup (Aralia elata Seem.)

Sensory note	Compounds ^a						
Herbaceous	3-Methylbutanal, (Z)-Ocimene, (E)-Ocimene, γ-Terpinene, 2-Heptanol, β-Angelica lactone, 1-Octen-3-ol, Myrtenal, Dodecanal,α-Muurolene, δ-Cadinene, α-Curcumene, Cadina-1,4-diene, Caryophyllene oxide, Methylcinnamic aldehyde, δ-Cadinol,T-Muurolol, α-Cadinol (18)						
Woody	α -Thujene, α -Pinene, β -Pinene, Sabinene, Myrcene, α -Phellandrene, Styrene, Terpinolene, Perillene, 6-Methyl-5-hepten-2-one, p-Methylstyrene, 2,3-Dihydroindene, δ-Elemene, α -Copaene, Indene, β -Cubebene, (E)- α -Bergamotene, Bornyl acetate, Terpinen-4-ol, γ -Elemene, β -Caryophyllene, Aromadendrene, (E)- β -Farnesene, Alloaromadendrene, (Z,Z)- α -Farnesene, α -Humulene, (Z,E)- α -Farnesene, (E,E)- α -Farnesene, β -Sesquiphellandrene, β -Ionone, (E,E)-Farnesal (31)						
Leafy	(E)-2-Pentenal, Hexanal, 1-Penten-3-ol, (Z)-3-Hexenal, (E)-2-Hexenal, (E)-2-Pentenol, (Z)-2-Pentenol, 1-Hexanol. (Z)-3-Hexenol, (E)-2-Hexenol, (E,E)-2,4-Hexadienal, (E)-2-Octenal, (E,E)-2,4-Heptadienal, Citronellic acid (14)						
Camphoraceous	Camphene, Borneol, Myrtenol (3)						
Fruity	Ethyl acetate, δ -3-Carene, α -Terpinene, Heptanal, Methyl caproate, 2-Pentylfuran, p-Cymene, Ethyloctanoate, Decanal, 1-Octanol, 2-Undecanone, (E,E)-2,4-Decadienal, Benzyl alcohol, Geranyl hexanoate (14)						
Floral	Ethyl formate, Nonanal, Linalool, (E)-2-Nonenal, Phenylacetaldehyde, α-Terpineol, Nerol, Geranyl propionate, Methyl salicylate, Geraniol, p-Cymen-8-ol, Geranyl butanoate, 2-Phenylethanol, p-Anisaldehyde, (E)-Nerolidol, (E,E)-Farnesyl acetate, (E,E)-Farnesyl acetone, Indole, Phytol (20)						
Spicy	2-Ethylfuran, 2-Heptanone, β-Phellandrene, Benzofuran, 2-Furfural, Benzaldehyde, Zingiberene, (Z)-Jasmone, Eugenol (9)						
Winey	Ethanal, 2-Propanol, Ethanol, 2-Pentanol, 3-Methyl-1-butanol, 1-Pentanol (6)						
Sour	Acetic acid, Propionic acid (2)						
Musty	Pentanal, (E)-2-Hexenoic acid (2)						
Sweaty	Hexanoic acid, Octanoic acid, Nonanoic acid (3)						
Oily	Methyl palmitate, Ethyl palmitate, Lauric acid, Methyl linoleate, Ethyl linoleate, Methyl linolenate, Ethyl linolenate, Myristic acid, Palmitic acid (9)						
Medicinal	Phenol, Biphenyl (2)						
Fusel-like	Octane, Nonane, Decane, Toluene, Undecane, Ethyl benzene, p-Xylene, Dodecane, Tridecane, Tetradecane, Pentylbenzene Pentadecane, Hexadecane, Heptadecane, Octadecane, Nonadecane (16)						
Pungent	sec-Butylbenzene, m-Diethylbenzene, p-Diethylbenzene, o-Diethylbenzene, 1,4-Dichlorobenzene, 1,2-Dichlorobenzene (6)						
Odorless	Eicosane, Heneicosane, Docosane, Tricosane, Tetracosane, 1-Hexadecanol, Pentacosane, Hexacosane, Heptacosane, Octacosane, Nonacosane (11)						
Sulfurous	Dipropyl disulfide (1)						

^{*}Overlapping GC peaks were evaluated by injection of authentic compounds.

terpene aldehydes (0.35%). Hexanal, (Z)-3-hexenal, and (E)-2-hexenal were probably formed from the enzyme-induced oxidative breakdown of unsaturated fatty acids including linoleic and linolenic acids. Since leucine had an identical carbon skeleton with that of 3-methylbutanal, this aldehyde may be synthesized from this amino acid in dureup by transamination and decarboxylation. Hethyl-5-hepten-2-one, β -ionone, and farnesyl acetone among the six ketones identified in dureup may arise from the oxidative breakdown of lycopene and β -caro-

tene pigments in the shoots.200

The organoleptic characteristics of each volatile component by GC-sniff evaluation are listed in the Table 3. The results of sniffing the effluents at the exit port of the gas chromatograph revealed the absence of an individual volatile compound solely possessing a characteristic dureup-like aroma. Eighteen of the 167 volatile components identified in dureup had a somewhat herbaceous aroma and were composed of 7 hydrocarbons, 5 alcohols, 4 aldehydes, 1 lactone, and 1 oxide. Thirty-one

compounds possessed a somewhat woody aroma and included 26 hydrocarbons, 2 ketones, 1 ester, 1 alcohol, and 1 aldehyde. Therefore, it is likely that a mixture of the above volatiles invokes the characteristic dureup aroma. These herbaceous and woody aroma compounds would deserve the most attention in an attempt to reconstruct dureup essential oil. Furthermore, several unidentified volatile flavor components probably contribute and may play an important role in the aroma of dureup essential oil.

The most abundant monoterpene hydrocarbons iso-lated in dureup are β -pinene (1.68%), α -pinene (0.63%), and myrcene (0.63%). The biosynthesis of the acyclic monoterpene myrcene undoubtedly arises from the chemical modification of either geranyl pyrophosphate (GPP) or neryl pyrophosphate (NPP). The bicyclic monoterpenes α -pinene and β -pinene, however, are probably only derived from the monocyclic α -terpinyl cation, for the reason that it is structurally possible for linally pyrophosphate (LPP) to cyclize directly. The major sesquiterpene isolated are β -caryophyllene (19.53%), α -humulene (14.23%), (E)- β -farnesene (8.39%), and zingiberene (6.90%), from which they are thought to be derived from the cyclization of various isomers of farnesyl pyrophosphate (FPP).

Although the actual amount of hydrocarbons in dureup essential oil is comparatively large, this essential oil is not utilized for the flavor and perfume industry because of their insolubility in diluted alcohol or depressing the odor and flavor through the fixative effect of these high-boiling components.²³⁾

Characterization of the volatile components of Korean dureup has also provided significant insight into its practical medicinal uses. For example, myrcene, the acyclic monoterpene identified, has been shown to possess potent analgesic activity in rats and at therapeutic doses showes no toxic effects.^{24,25)}

The isolation and identification of volatile aroma compounds from the edible Korean dureup plant (*Aralia elata* Seem.) is a novel endeavor. Characterizing the volatile components and sensory characteristics of dureup essential oil is necessary to begin to study and understand its role in food flavor and its potential applications in the fields of medicine and toxicology. However, to fully understand the significant volatiles implicated in dureup oil aroma and chemistry, further characterization of unidentified oxygen-containing compounds is necessary and is currently in progress.

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두릅의 휘발성 향기성분에 관한 연구

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초록 : 연속수증기증류장치를 이용하여 두룹으로부터 얻어진 휘발성농축물은 탄화수소구분 및 함산소구분으로 분리되었고, 함산소구분은 실리카겔 관 크로마토그래피에 의해서 9개의 계대구분으로 다시 분획하였다. 기체크로마토그래피와 기체크로마토그래피에 질량분석계를 연결시킨 장치는 휘발성성분을 동정하기 위하여 사용하였다. 동정된 167개의 휘발성성분은 72개의 탄화수소, 31개의 알콜, 23개의 알데히드, 16개의 에스테르, 10개의 산, 6개의 케톤, 3개의 푸론, 2개의 페놀, 1개의 인돌, 1개의 산화물, 1개의 설파이드 및 1개의 락톤이었다. Sesquiterpene 탄화수소인 β-caryophyllene은 두릅에서 동정된 휘발성 성분중에서 함량이 가장 높았으며, 19.53%를 차지하였다. 두릅정유는 관능검사용 기체크로마토그래피를 사용하여 각 구분에 함유된 개별 휘발성성분을 평가에 의해서 초목 모양의 향기를 함유하고 있음이 밝혀졌다.

^{*}연락저자