Thesis for Degree of Master of Science

Comparison of Effective Volatile Components of ***Angelica gigas*** *Nakai and* ***A. autiloba*** *Kitagawa*

by

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Advisor Prof. Song, Ki-Dong, Ph.D.

Department of Alternative Medicine

Major : Immunity and Food Therapy

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Kim, Kyong-Su

has met the thesis requirements of Chosun Uniuversity

Committee Chairperson _____

Moon, Kyung-Rye M.D.

Committee Member _____

Suh, Chae-Hong M.D.

Committee Member _____

Song, Ki-Dong Ph.D.

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ABSTRACT

Comparative analysis of effective volatile components of Angelica gigas Nakai and Angelica acutiloba Kitagawa

Kim, Kyong-Su
Advisors: Prof. Song, Ki-Dong, Ph.D
Department of Alternative Medicine
Chosun University Graduate School of Health Sciences

The effective volatile compounds of *Angelica gigas* Nakai and *Angelica acutiloba* Kitagawa were extracted by simultaneous steam distillation and extraction (SDE) method and identified with gas chromatograph/mass spectrometry (GC/MS) analysis. A total of 116 and 77 compounds were identified and quantified from A. gigas and A. acutiloba, including hydrocarbons 40 and 23, alcohols 36 and 19, esters 15 and 6, aldehydes 12 and 13, ketones 8 and 10, and miscellaneous 5 and 6, respectively. The major compounds of *A. gigas* were identified *α*-pinene, 2,4,6-trimethyl heptane, camphene, *α*-limonene, *β*-eudesmol, vervenol, *α*-murrolene and sphatulenol. Among them, *α*-pinene (30.89%) and 2,4,6-trimethyl heptane (13.39%) were found as the predominantly abundant components of *A. gigas*. *γ*-Terpinene (26.98%) and *ρ*-cymene (12.05%) were identified the major compounds of *A. acutiloba*, and butylidenephthalide, 3-ethoxyphthalide, (Z)-β-ocimene, tetra-decanol and hexadecanol were identified in considerable amount. As a result, profile of the volatile components was highly different in between both

species. The amount of volatile oils in *A. gigas* (0.313%) was obtained above three times than *A. acutiloba* (0.091%). The essential oil contained in *A. gigas* was 1.37 folds higher than essential oil contained in A. *acutiloba*. Consequently, the effective volatile oils of *A. gigas* Nakai and *A. acutiloba* Kitagawa could usefully be used in fragrance, flavor and pharmaceutical industries and aromatherapy, and the volatile oils of *A. gigas* Nakai is considered to be more useful by its composition.

INTRODUCTION

Essential oils of plants and other products from secondary their metabolism are commonly used in folk medicine, food flavoring, and the pharmaceutical industry (1,2). Some biological activities of essential oils have been known for long time (3,4). Interest in the use of essential oils from aromatic medicinal plants is growing in the food and pharmaceutical industries, and analysis of the volatile components (including essential oils) from the *Angelica* genus is important due to its increasing demand in functional foods and pharmaceutical industries. Recently its effects on immunostimulation, inhibition of blood platelet cohesion and acetylcholinesterase activity, anticancer and other health promoting activities have been proved beneficial (5-7).

Angelica radix belongs to the family of *Umbelliferae*, genus *Angelica*. In Asia, *Angelica* is predominantly regarded as a "female" remedy, (also known as "female ginseng"), and is used to treat dysmenorrhea (painful menstruation), amenorrhea (absence of menstruation), metrorrhagia (abnormal menstruation), menopausal symptoms (especially hot flashes), and to assure a healthy pregnancy and easy delivery. *Angelica* has also been used to treat abdominal pain, anemia, injuries, arthritis, migraine headache, and other conditions (8-10). Among the members of the *Angelica* genus, only three species are used in medicine, Korean, Chinese, and Japanese pharmacopoeia prescribe *A. gigas* Nakai, *A. sinensis* Diels, and *A. acutiloba* Kitagawa, respectively, as *Angelica* radix. A great quantity of *A. gigas* Nakai and *A. acutiloba* Kitagawa is cultivated in Korea, *A. gigas* is mainly used for Chinese medicine within Korea, and *A. acutiloba* is exported.

Angelica gigas Nakai (Danggui, in Korean) is a well-known therapeutic herb used as a sedative and anodyne, as well as in the treatment of gynecological diseases, and anemia (9,10). It is also a common ingredient of herbal tea, medicinal alcoholic drinks and tonic agents because of its unique innocuousness (5). The major active components of *A. gigas* Nakai are coumarins such as decursin, decursinol, nodakenetin, umbelliferone, nodakenin, and β-sitosterol and essential oil such as α-pinene, limonene, β-eudesmol, and elemol (11,12). Many studies have been carried out on the physiological activity such as anti-amnestic activity of decursin, inhibition of AChE by decursinol angelate, and isolation and structural determination of coumarin derivatives (13-17).

The root of *Angelica acutiloba* Kitagwa (Yamato-Tohki, in Japanese) is a well-known herb used in the treatment of gynecological diseases and arthritis (18). The major components are phthalides such as ligustilide, butylidene-phthalide, butylphthalide, polyacetylene derivatives such as falcarinol, flacrindiol, and flacarinolone, and essential oils such as α-terpinene and ρ-cymene (19,20). The complex pectic arabinogalactan, AGIIb-1, isolated from the roots of *A. acutiloba* Kitagawa, showed anticomplementary activity (21,22).

The major components and medicinal effects of *A. gigas* and *A. acutiloba* are obviously different. Therefore, prior to use of essential oils from these plants, the characteristics of their essential oils and effective volatile components should be assessed. Apart from one study on the antibiotic resistance inhibitor of volatile compounds of *A. gigas*, analyses of the volatile components of *A. gigas* are lacking (23). In 1988, Chi *et al.* reported the essential oils of *A. gigas* Nakai, as part of the studies on essential oils in plants of the *Angelica* genus in Korea, and recently Cho *et al.* (12,24)

published a comparative study of the volatile compounds of *A. gigas* Nakai and *A. acutiloba* Kitagawa. Some of the work on the essential oils of *A. gigas* was carried out using the fresh roots, but there is no adequate research for the essential oils of commercial dried products.

In the present investigation, we analyzed the volatile organic compounds of *Angelica gigas* Nakai and *Angelica acutiloba* Kitagawa, and evaluated characteristics of their essential oils and effective volatile components.

MATERIALS AND METHODS

A. Materials and analytic apparatus

1. Materials

Angelica gigas Nakai (Todanggui) and *Angelica acutiloba* Kitagawa (Ildanggui) at the presterilization stage were purchased from a local retail shop. This sample was stored at -18℃ until required for the experiments.

2. Reagents

The reagents used in the experiments were purchased from Sigma Co. (USA) and Fisher Scientific (USA). Organic solvents used for the extraction and chromatography were redistilled using a wire spiral packed double distilling apparatus (Normschliff Geratebau, Wertheim, Germany) and Milli-Q water that was generated with a water purification system (Millepore Corporation, Bedford, USA).

3. Analytic apparatus

a. Distilling apparatus : Wire spiral packed double distilling apparatus (Normschliff Geratebau, Germany)

b. Simultaneous steam distillation and extraction (SDE) : Likens & Nickerson type simultaneous steam distillation and extraction apparatus (Normschliff, Wertheim, Germany)

c. Blender : Multi mixer (Braun MR 550 CA, Braun, Spain)

d. pH meter : pH/ION meter (DMS, Korea)

e. Concentration column : Vigreux column (250 ㎖, Normschliff, Wertheim, Germany)

f. Gas chromatography/mass spectrometer : Shimadzu GC/MS QP-5000 equipped with mass spectrum library WILEY 139, NIST 62 (Shimadzu, Japan)

g. Capillary column : DB-Wax (60 m×0.25 mm i.d., 0.25 μm film thickness, J&W, USA)

B. Methods

1. Extraction of volatile compounds from Angelica gigas Nakai

Fifty gram samples were taken each time and homogenized in a blender (MR 350CA, Braun, Spain) and mixed with 1 L distilled water. By maintaining the pH at 6.5, the resultant slurry was used for the quantitative analysis with 1μl of n-butyl benzene added as an internal standard. The essential oils were extracted for 2 hours with 200 mL redistilled n-pentane/ diethyl ether (1:1, v/v) mixture using a simultaneous steam distillation and extraction (SDE, Likens & Nickerson type) apparatus as modified by Schultz et al. (25,26) under atmospheric pressure. The extract was dehydrated for 12 hours over anhydrous sodium sulfate and concentrated to final volume approximately 1.5 ml using a Vigreux column. This sample was finally used for the GC/MS analysis.

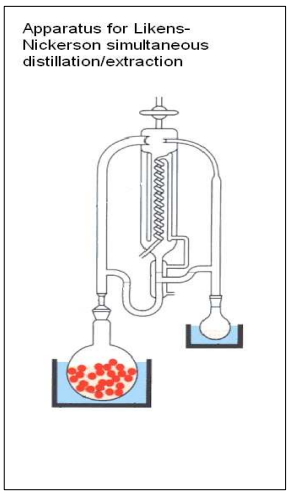

Figure 1. Diagram of simultaneous steam distillation extraction apparatus (SDE) according to Likens-Nickerson.

2. *Establishment of retention index*

Kovats (27) suggested RI (retention index or Kovats index) as suitable indication rule for retention indication which was indicated by a same spice or compound to retention time for standard alkane.

Retention index as parameter used for checking of a solute from chromatogram by comparing the retention time of both alkane that appeared the above and below of the solute.

$$RI_i = 100\ Z + 100\ \{ \frac{\text{Log } V_{R(i)} - \text{Log } V_{R(Z)}}{\text{Log } V_{R(Z+1)} - \text{Log } V_{R(Z)}} \}$$

RI_i : Retention index of compound i

$V_{R(i)}$, $V_{R(Z)}$, $V_{R(Z+1)}$: Each space revision time of alkane of compound I, carbon each number Z, Z+1

According to definition, retention time of alkane has the value as multiply of carbon number that the compound has to be unrelated with column solid phase, the temperature of separation and requirements of other chromatography. Therefore, n-alkane was indicated as standard index for CH_4 (RI=100), C_2H_6 (RI=200) ⋯ C_nH_{2n+2} (RI=100n), and even anything in analysis column (28).

For retention index, the dilution mixture of n-alkane; I (C_7～C_{17}) and II (C_{13} ～ C_{23}), was used as internal standard. 1μL mixture was analysed to find out the retention time of internal standard by GC-FID under the condition of Table 1. RI of each peak was established by a basic program that substituted the RT of each peak of n-alkane confirmed at GC chromatogram.

3. Analysis and identification of volatile compounds by GC/MS

Shimadzu GC/MS QP-5000 (Kyoto, Japan) in the EI (electron impact) mode was used for the quantitative analysis. The ionization voltage and temperature of injector and ion source were 70 eV, 250℃ and 230℃ respectively. The mass spectrometer scanned from 41 to 350 m/z. A DB-WAX capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W, USA) was used for the separation. The oven temperature was programed as : 40℃ (isothermal for 3 min) which was ramped to 150℃ at 2℃/min and then to 200℃ at 4℃/min (isothermal for 30 min). Helium was used as the carrier gas at a flow rate of 1.0 ml/min with an injector volume of 1 μl using a 1:20 split ratio.

Mass spectra of volatile organic compounds were identified with the aid of our own mass spectral data and those contained within the WILEY 139, NIST 62 and NIST 12 libraries and mass spectral data books (29,30) as well as by the comparison of retention indices to reference data (31,32). The quantitative analysis was carried out with the help of peak area percent of internal standard (n-butyl benzene) by using following formula :

$$\text{Component Content (mg/kg)} = \frac{C\% \times 1000\ g}{A\% \times B\ g}$$

- A% : Peak area% of each sample of internal standard
- B g : Amount of sample
- C% : Peak area% of each component in sample

Table 1. GC/MS conditions for identification of volatile components

Column	DB-W (60 m × 0.25 mm i.d., 0.25 μm filmthickness)
Carrier gas	Helium (1.0 mL/min)
Temp. program	40℃ (3 min) -2℃/min-150℃-4℃/min-200℃ (30 min)
Injector	250℃, split ratio 1 : 20 (0～2 min splitless)
Temperature	Ion source and interface 230℃
Ionization	Electron impact ionization (EI)
Ionization voltage	70 eV
Mass range(*m/z*)	40～350
Injection volume	1 μL
Split ratio	1:20

RESULTS AND DISCUSSION

A. Retention index of n-alkanes

The standard value of retention index was determined by two different mixture of n-alkanes, mixture I (C_7～C_{17}), mixture II (C_{13}～ C_{23}) considering as an internal standard. 1μL mixture was analysed to find out the retention time of internal standard by GC-MS (Figure 2). RI of each peak was established by a basic program that substituted the RT of each peak of n-alkane confirmed at GC chromatogram (Table 2).

Table 2. Retention time of n-alkane mixture for gas chromatographic retention index

Alkanes	Rention time	Alkanes	Rention time	Alkanes	Rention time
$C_{7:0}$	5.153	$C_{13:0}$	30.446	$C_{19:0}$	66.439
$C_{8:0}$	6.141	$C_{14:0}$	37.341	$C_{20:0}$	70.156
$C_{9:0}$	8.194	$C_{15:0}$	44.079	$C_{21:0}$	73.446
$C_{10:0}$	11.828	$C_{16:0}$	50.509	$C_{22:0}$	76.548
$C_{11:0}$	17.136	$C_{17:0}$	56.629	$C_{23:0}$	79.183
$C_{12:0}$	23.57	$C_{18:0}$	62.005		

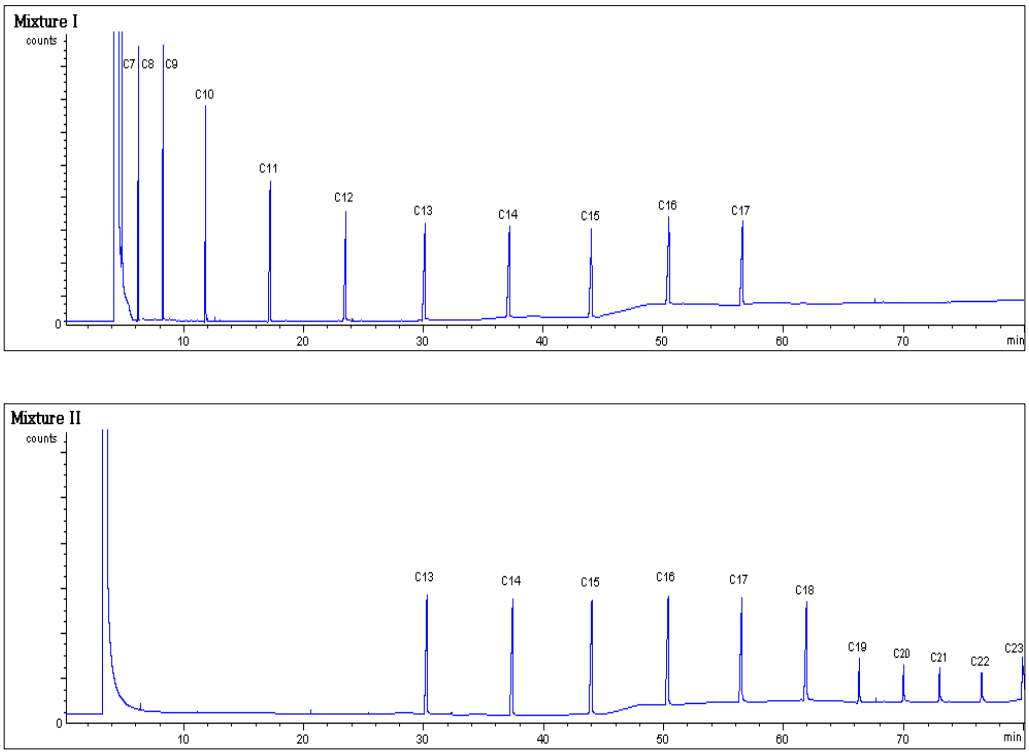

Figure 2. GC chromatograms of n-alkane standard mixture Ⅰ *and* Ⅱ.

B. Effective volatile components of Angelica gigas Nakai

The volatile compounds were extracted from *Angelica gigas* Nakai using SDE method and then detected and identified by GC/MS. The GC/MS chromatogram is shown in Figure 3, and the identified volatile components from GC/MS analysis and their relative peak area percentage are shown in Table 3.

A total of 116 compounds were identified and quantified from *Angelica gigas* Nakai, including 40 hydrocarbons, 36 alcohols, 15 esters, 12 aldehydes, 8 ketones, and 5 miscellaneous. The amount of volatile oils in *A. gigas* was obtained 0.313% yield.

Hydrocarbons (66.58%) were detected as the main functional group in the volatile compounds of *A. gigas* Nakai. The major hydrocarbons were *α*-pinene (30.89%), 2,4,6-trimethyl heptane (13.39%), *α*-limonene (4.29%), camphene (4.10%) and 2-methyl octane (3.27%). 33 of the 40 hydrocarbons were monoterpenes and sesquiterpenes. Alkane hydrocarbons were minor components of the volatile compounds.

Alcohols (23.39%) were the second most abundant functional group in the above sample. *β*-Eudesmol (5.01%) was the most abundant compounds, and vervenol (2.15%), *α*-eudesmol (1.90%), sphatulenol (1.85%) and pinocarveol (1.22%) were also detected. All of these are terpene alcohols. Aliphatic alcohols such as 3-methyl-2-butenol, 4-tetradecanol, pentadecanol and hexadecanol, made up less than 0.5% of the volatiles.

Ketones constituted 3.65% of the volatile organic compounds, with 2-hydroxycyclopentadecanone (1.56%) and verbenone (1.44%) as the main components. We also detected 6-methyl-5-hepten-2-one, which is thought to be an auto-oxidative product of *α*-farnesene (33). This result suggests that *α*-farnesene is a volatile component of *A. gigas* and is consistent with the findings of Cho *et al.,* who detected *α*-farnesene in both of the stem and root of *A. gigas* (24). However, *α*-farnesene was not directly detected in our study.

The total percentage of esters was 3.38%. Guaiyl acetate (0.52%), myrtanyl acetate (0.46%) and bornyl acetate (0.39%) were the main esters. These compounds are important in the formulation of imitation flavor (34). Aldehydes (1.92%) were minor compounds in the volatile components of *A. gigas,* and pinene oxide, limonene oxide, and 2-pentyl furan were also detected.

α-Pinene (30.89%) was the dominant volatile compound, followed by 2,4,6-trimethyl heptane (13.39%), *β*-eudesmol (5.01%), *α*-limonene (4.29%), camphene (4.10%), verbenol (2.15%), sphatulenol (1.85%), 2-hydroxycyclopentadecanone (1.56%), and *α*-murrolene (1.52%). Terpenoids were relatively generally more abundant than other compounds. This result was consistent with a previous study on the volatile compounds of *Angelica gigas* Nakai and *A. acutiloba* Kitagawa (24). Other minor components were (E)-*ρ*-2-menthen-1-ol, pinocarveol, verbenone, cuminol and *α*-eudesmol, which have the flavor characteristics of wood, pine, turpentine, and flower (35).

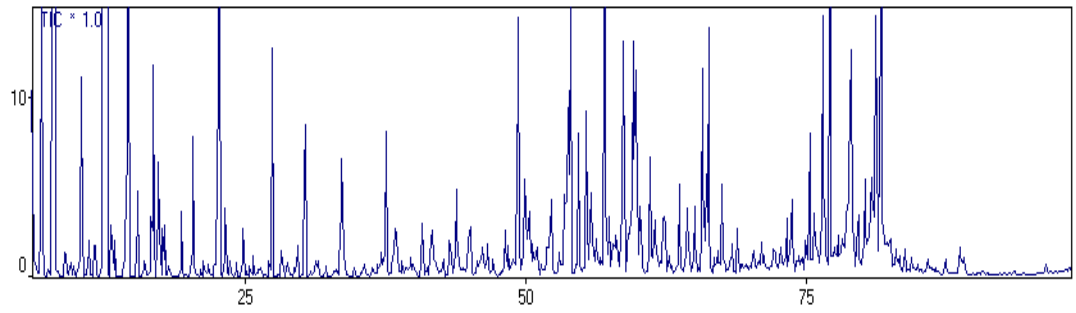

Figure 3. GC/MS chromatogram of volatile components of ***Angelica gigas*** *Nakai.*

Table 3. Volatile components identified from ***Angelica gigas Nakai***

NO.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg	Area%
1	6.828	836	2-Methyl octane	C_9H_{20}	128	102.487	3.27
2	7.456	865	Ethyl acetate	$C_4H_8O_2$	88	0.973	0.03
3	7.982	888	2,4,6-Trimethyl heptane	$C_{10}H_{22}$	142	419.415	13.39
4	8.269	899	3-Methyl butanal	$C_5H_{10}O$	86	0.634	0.02
5	8.934	924	Ethanol	C_2H_6O	46	1.608	0.05
6	9.718	951	2-Methyl nonane	$C_{10}H_{22}$	142	0.926	0.03
7	10.089	963	3-Methyl nonane	$C_{10}H_{22}$	142	0.766	0.02
8	10.367	972	*(Z)*-2-Nonen-4-yne	C_9H_{14}	122	30.985	0.99
9	11.012	991	*(E)*-2-Nonen-4-yne	C_9H_{14}	122	6.245	0.20
10	11.570	1006	Tricyclene	$C_{10}H_{16}$	136	5.994	0.19
11	12.625	1029	*α*-Pinene	$C_{10}H_{16}$	136	967.750	30.89
12	13.019	1037	4-Methyl-1-penten-3-one	$C_6H_{15}O$	98	7.991	0.26
13	13.317	1043	2-Methyl-3-buten-2-ol	$C_5H_{10}O$	86	3.963	0.13
14	14.207	1061	2-Methyl decane	$C_{11}H_{24}$	156	3.581	0.11
15	14.559	1067	Camphene	$C_{10}H_{16}$	136	128.498	4.10
16	15.354	1081	Hexanal	$C_6H_{12}O$	100	10.339	0.33
17	15.920	1091	2-Methyl-2-butenal	C_5H_9O	84	1.772	0.06
18	16.025	1092	2-Methyl-propanol	$C_4H_{10}O$	74	1.411	0.05
19	16.547	1101	Undecane	$C_{11}H_{24}$	156	8.138	0.26
20	16.764	1105	*β*-Pinene	$C_{10}H_{16}$	136	31.148	0.99
21	17.179	1113	Alloocimene	$C_{10}H_{16}$	136	15.238	0.49
22	17.300	1115	*α*-Myrcene	$C_{10}H_{16}$	136	5.216	0.17
23	17.562	1119	Sabinene	$C_{10}H_{16}$	136	6.180	0.20
24	18.157	1130	2-Carene	$C_{10}H_{16}$	136	1.298	0.04
25	19.265	1148	*δ*-3-carene	$C_{10}H_{16}$	136	8.384	0.27
26	20.058	1160	2-Methylpropyl isobutyrate	$C_8H_{16}O_2$	144	0.899	0.03
27	20.302	1164	*β*-Myrcene	$C_{10}H_{16}$	136	18.055	0.58
28	20.575	1168	*α*-Fenchene	$C_{10}H_{16}$	136	0.931	0.03
29	20.970	1174	*α*-Phellandrene	$C_{10}H_{16}$	136	0.902	0.03
30	21.223	1178	*α*-Terpinene	$C_{10}H_{16}$	136	2.345	0.07

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 3. Continued

NO.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg	Area%
31	21.483	1181	2-Heptanone	$C_7H_{14}O$	114	0.925	0.03
32	21.638	1184	Heptanal	$C_7H_{14}O$	114	1.433	0.05
33	21.825	1186	Methyl hexanoate	$C_7H_{14}O_2$	130	0.679	0.02
34	22.154	1191	2,3-dehydro-1,8-cineole	$C_{10}H_{16}O$	152	1.372	0.04
35	22.703	1198	*α*-Limonene	$C_{10}H_{16}$	136	134.339	4.29
36	23.144	1205	*β*-Phellandrene	$C_{10}H_{16}$	136	8.874	0.28
37	23.630	1213	1,3,8-Menthatriene	$C_{10}H_{12}$	134	2.020	0.06
38	24.167	1222	Isopulegone	$C_{10}H_{16}O$	152	2.040	0.07
39	24.739	1231	2-Pentyl furan	$C_9H_{14}O$	138	5.825	0.19
40	24.995	1235	*(Z)*-*β*-Ocimene	$C_{10}H_{16}$	136	1.951	0.06
41	25.675	1245	*γ*-Terpinene	$C_{10}H_{16}$	136	2.639	0.08
42	26.090	1251	*(E)*-*β*-Ocimene	$C_{10}H_{16}$	136	0.923	0.03
43	26.310	1254	Pentanol	$C_5H_{12}O$	88	1.318	0.04
44	27.060	1265	Hexyl acetate	$C_8H_{16}O_2$	144	2.299	0.07
45	27.354	1269	*ρ*-Cymene	$C_{10}H_{14}$	134	33.553	1.07
46	28.212	1281	Terpinolene	$C_{10}H_{16}$	136	3.713	0.12
47	28.703	1288	Octanal	$C_8H_{16}O$	128	1.718	0.05
48	29.654	1300	Tridecane	$C_{13}H_{28}$	184	4.322	0.14
I.S.	30.305	1311	*Butylbenzene*	*$C_{10}H_{14}$*	*134*	0.000	0.00
49	30.743	1318	4-Methyl pentanol	$C_6H_{14}O$	102	0.567	0.02
50	31.159	1324	3-Methyl-2-butenol	$C_5H_{10}O$	86	3.852	0.12
51	32.028	1337	6-Methyl-5-hepten-2-one	$C_8H_{14}O$	126	1.485	0.05
52	33.065	1353	Propyl tiglate	$C_8H_{14}O_2$	142	1.832	0.06
53	33.265	1356	Isopropyl hexanoate	$C_9H_{18}O_2$	158	23.875	0.76
54	34.250	1370	Butyl hexanoate	$C_9H_{18}O_2$	158	1.496	0.05
55	35.437	1389	2-Nonanone	$C_9H_{18}O$	142	1.719	0.05
56	36.542	1404	Myrtanol	$C_{10}H_{18}O$	154	24.782	0.79
57	37.369	1415	Pentyl isohexanoate	$C_{11}H_{22}O_2$	186	11.044	0.35
58	37.662	1419	Butyl heptanoate	$C_{11}H_{22}O_2$	186	3.027	0.10
59	38.290	1429	*(E)*-2-Octenal	$C_8C_{14}O$	126	1.007	0.03
60	38.691	1436	3,5-Dimethyl styrene	$C_{10}H_{12}$	132	3.035	0.10

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 3. Continued

NO.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg	Area%
61	40.299	1460	Limonene oxide	$C_{10}H_{16}O$	152	6.268	0.20
62	40.412	1462	2-Methylbutyl hexanoate	$C_{11}H_{22}O_2$	186	7.996	0.26
63	41.882	1484	Cyclosativene	$C_{15}H_{24}$	204	11.232	0.36
64	42.335	1490	*α*-Campholene aldehyde	$C_{10}H_{16}O$	152	13.112	0.42
65	42.535	1493	*α*-Copaene	$C_{15}H_{24}$	204	5.763	0.18
66	44.464	1523	*(E)*-*ρ*-Mentha-2,8-dien-1ol	$C_{10}H_{16}O$	152	4.029	0.13
67	45.316	1537	*(E)*-2-Nonenal	$C_9H_{16}O$	140	3.161	0.10
68	46.206	1551	Linalool	$C_{10}H_{18}O$	154	5.452	0.17
69	46.546	1556	Butyl octanoate	$C_{12}H_{24}O_2$	200	4.707	0.15
70	47.389	1569	*(E)*-*ρ*-2-Menthen-1-ol	$C_{10}H_{18}O$	154	36.665	1.17
71	48.345	1583	Bornyl acetate	$C_{12}H_{20}O_2$	196	12.212	0.39
72	48.775	1590	Aromadendrene	$C_{15}H_{24}$	204	5.512	0.18
73	49.765	1605	4-Terpineol	$C_{10}H_{18}O$	154	6.465	0.21
74	50.881	1624	Thujopsene	$C_{15}H_{24}$	204	5.616	0.18
75	51.281	1631	Myrtenal	$C_{10}H_{14}O$	150	13.803	0.44
76	53.081	1661	Pinocarveol	$C_{10}H_{16}O$	152	38.156	1.22
77	53.458	1667	*α*-Phellandren-8-ol	$C_{10}H_{16}O$	152	13.537	0.43
78	54.639	1686	Vervenol	$C_{10}H_{16}O$	152	67.265	2.15
79	54.963	1691	*(E)*-*β*-Caryophyllene	$C_{15}H_{24}$	204	7.009	0.22
80	55.564	1700	*α*-Terpineol	$C_{10}H_{18}O$	154	7.049	0.22
81	56.295	1714	Verbenone	$C_{10}H_{14}O$	150	45.118	1.44
82	57.107	1729	*α*-Murrolene	$C_{15}H_{24}$	204	47.597	1.52
83	57.269	1732	*β*-Phellandren-8-ol	$C_{10}H_{16}O$	152	29.785	0.95
84	57.696	1739	*r*-Elemene	$C_{15}H_{24}$	204	21.348	0.68
85	58.462	1753	*cis*-Piperitol	$C_{10}H_{18}O$	154	13.545	0.43
86	58.595	1756	Myrtanyl acetate	$C_{12}H_{20}O_2$	196	14.400	0.46
87	58.944	1762	*δ*-Cadinene	$C_{15}H_{24}$	204	10.759	0.34
88	59.300	1768	*(E,Z)*-2,4-Decadienal	$C_{10}H_{16}O$	152	2.052	0.07
89	59.493	1772	*β*-Citronellol	$C_{10}H_{20}O$	156	6.997	0.22
90	60.170	1783	3-Isopropylbenzaldehyde	$C_{10}H_{12}O$	148	3.037	0.10

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 3. Continued

NO.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg	Area%
91	60.984	1798	Myrtenol	$C_{10}H_{16}O$	152	12.291	0.39
92	61.680	1813	*(E,E)*-2,4-Decadienal	$C_{10}H_{16}O$	152	7.979	0.25
93	62.349	1828	Cuparene	$C_{15}H_{22}$	202	11.606	0.37
94	62.958	1842	*cis*-Carveol	$C_{10}H_{16}O$	152	29.343	0.94
95	63.251	1848	*p*-Cymen-8-ol	$C_{10}H_{14}O$	150	16.878	0.54
96	63.497	1854	Cuminol	$C_{10}H_{14}O$	150	33.660	1.07
97	64.277	1871	*trans*-Carveol	$C_{10}H_{16}O$	152	4.851	0.15
98	64.674	1880	Pinene oxide	$C_{10}H_{16}O$	152	16.723	0.53
99	65.980	1911	*p*-Meth-1-en-9-ol	$C_{10}H_{16}O$	152	5.003	0.16
100	69.213	1998	*β*-Caryophyllene oxide	$C_{15}H_{24}O$	220	2.901	0.09
101	70.324	2029	Globulol	$C_{15}H_{26}O$	222	7.744	0.25
102	70.833	2043	4-Tetradecanol	$C_{14}H_{30}O$	214	12.166	0.39
103	71.369	2058	Octanoic acid	$C_8H_{16}O_2$	144	2.071	0.07
104	72.356	2086	Elemol	$C_{15}H_{26}O$	222	20.669	0.66
105	72.751	2096	Guaiol	$C_{15}H_{26}O$	222	10.897	0.35
106	73.738	2124	Cyclopentadecanone	$C_{15}H_{28}O$	224	6.027	0.19
107	74.172	2136	Sphatulenol	$C_{15}H_{24}O$	220	58.080	1.85
108	75.629	2176	Tetradecanol	$C_{14}H_{30}O$	214	7.193	0.23
109	76.109	2189	2-Hydroxycyclopentadecanone	$C_{15}H_{28}O_2$	240	48.968	1.56
110	77.276	2217	Guaiyl acetate	$C_{17}H_{28}O_2$	264	16.180	0.52
111	77.424	2220	Methyl hexadecanoate	$C_{17}H_{34}O_2$	270	3.991	0.13
112	77.670	2226	Bulnesol	$C_{15}H_{26}O$	222	6.703	0.21
113	77.871	2230	Agarospirol	$C_{15}H_{26}O$	222	19.382	0.62
114	78.244	2238	*α*-Eudesmol	$C_{15}H_{26}O$	222	59.476	1.90
115	78.760	2250	*β*-Eudesmol	$C_{15}H_{26}O$	222	156.832	5.01
116	85.672	2377	Hexadecanol	$C_{16}H_{34}O$	242	3.930	0.13
			Total			3132.926	100

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 4. Relative content of functional groups in identified volatile components of ***Angelica gigas*** *Nakai*

Functional groups	Number	Relative area%
Alcohols	36	23.39
Aldehydes	12	1.92
Esters	15	3.38
Hydrocarbons	40	66.58
Ketones	8	3.65
Miscellaneous	5	1.08
Total	116	100

C. Characteristics of essential oils in Angelica gigas Nakai

The percentage composition of essential oils provides the most important parameter for characterizing each respective plant (36). To allow a comparison, the essential oil groups of volatile organic compounds identified by GC/MS are reported in Table 3 and summarized in Table 5.

Monoterpene hydrocarbons (57.48%) represented the largest fraction of the *Angelica gigas* Nakai root oil constituents. 24 kinds of monoterpene hydrocarbons including α-pinene, 2,4,6-trimethyl heptane, α-limonene, camphene, ρ-cymene, β-pinene, β-myrcene, and alloocimene, were confirmed. The α-pinene (30.89%) was the main component. Depending upon the reaction conditions, α-pinene can be converted to 1,8-cineole, used in the pharmaceuticals and perfumeries, α-terpineol, used as a fragrance and a disinfectant, and camhpor used in the production of celluloid, as a softener for cellulose esters, and in pharmaceutical preparations (37). It has also been reported that α-pinene strongly inhibits acetylcholinesterase (AChE) (38). Therefore, the volatile compounds of *Angelica gigas* Nakai could potentially be used in food, pharmaceuticals, and cosmetics. α-Limonene was the second main component (4.29%) among monoterpene hydrocarbons.

It is well known that variations are due to species differences as well as to geographical origin, harvesting time and growing conditions (39). Also, differences in the odor of the root oils can be attributed to the compositional differences of the volatiles, especially in the relative amounts of various monoterpene hydrocarbons (40). A large number of different monoterpene compounds produce a high quality of oil aroma (41).

Sesquiterpene hydrocarbons represented 4.03% of the volatiles compounds in *Angelica gigas* Nakai. Nine kinds of sesquiterpenes were confirmed, and *a* -murrolene, *y*-elemene, and *δ*-cadinene were identified as main components. These molecules contribute to a wide range of biological activities, including regulation of plant growth, and insecticidal, antifungal, and antibacterial properties of plants (42-44).

Oxygenated terpene hydrocarbons confer special characteristics to the *Angelica gigas* Nakai root oil, such as particular odor notes and stability of the oil against alteration (45). The percentage of oxygenated terpenes was 29.01% (monoterpenes 15.75%, sesquiterpenes 13.26%). *β*-Eudesmol, an oxygenated sesquiterpene, was the major compound in this group, and verbenol, sphatulenol, *a*-eudesmol, 2-hydroxycyclopentadecanone, and verbenone were also detected in large amounts. *a*, *β*-Eudesmol and sphatulenol have antioxidant activity, and verbenol and verbenone inhibit AChE (38,46). 2-Hydroxycyclopentadecanone is a macrocyclic compound. Macrocyclic compounds occur in animals as ketones, alcohols and esters are recognized as attractants. These compounds have been used for centuries as pharmaceutical ingredients and as odorants (37). 2-Hydroxycyclopentadecanone has not been reported in previous investigations of the volatile compounds of *A. gigas*. However, our result is supported by the finding of Kerschbaum that the principal odor of *Angelica archangelica* L. was 15-pentadecanoide (Exaltolide) (37). It is thought that 2-hydroxycyclopentadecanone plays an important role as an attractant for woman.

Table 5. Relative concentration by terpenoid groups in volatile component of ***Angelica gigas*** *Nakai*

Terpenoid groups	Number	Relative area%	
Monoterpenes (C_{10})	Monoterpenes	24	57.48
	Oxygenated monoterpens	30	15.75
Sesquiterpenes (C_{15})	Sesquiterpenes	9	4.03
	Oxygenated sesquiterpenes	13	13.45
Total		76	90.71

D. Effective volatile compounds of ***Angelica acutiloba*** *Kitagawa*

77 compounds were identified and quantified from *Angelica acutiloba* Kitagawa, and the list of effective volatile components is shown in Table 6. The GC/MS chromatogram of volatile components identified from the sample is shown in Figure 4. The volatile components contained 23 hydrocarbons (55.96%), 19 alcohols (14.85%), 13 aldehydes (5.65%), 10 ketones (16.21%), 6 esters (4.97%) and 6 miscellaneous components (2.36%) (Table 7).

The major hydrocarbons were γ-terpinene and ρ-cymene, and their relative contents were 26.98% and 12.05%, respectively. *(Z)*-*β*-Ocimene (4.84%), *β*-myrecene (2.62%) and *α*-limonene (1.28%) were also detected as major compounds. Other hydrocarbons such as α-pinene, camphene, sabienene, and caryophyllene were present at less than 1%. Twenty of hydrocarbons were monoterpenes and sesquiterpenes, and alkane hydrocarbons were minor constituents, as in the essential oils of *A. gigas*.

Alcohols were primarily aliphatic: tetradecanol (6.19%), hexadecanol (3.42%), and dodecanol (1.50%), etc. In contrast to *A. gigas*, terpene alcohols (linalool, 4-terpineol, cuminol, and nerolidol) were detected as minor components.

Butanal (1.32%) and hexanal (1.08%) were the main aldehydes. The aldehydes with lower molecular weight are characterized by their unpleasant and pungent odors and irritant effect in the nose. As the molecular weight increases, the odor profile gradually changes to a more pleasant fruity character. Especially, aldehydes C_8 to C_{10} have a very attractive floral odor (34). In our analysis, aldehydes having lower and higher molecular weight were detected at 3.48% and 2.17%, respectively.

Ketones constituted the second most abundant functional group in *A. acutiloba* oils, with butylidenephthalide (7.81%) and 3-ethoxyphthalide (4.43%) being the most prominent. These phthalides have diverse pharmacological effects (e.g. antitumor, anticonvulsant, anaesthesia prolongation, and $PGF_{2\alpha}$ inhibitor) and they are important marker coumpounds used for assessing danggui quality (47-50).

Esters with high molecular weight such as dodecyl acetate (1.64%) and hexadecyl acetate (1.34%) were identified. Tri- and tetramethyl pyrazine were also detected.

Some terpenoids such as γ-terpinene (26.98%), ρ-cymene (12.05%) and butylidenephthalide (7.81%) were relatively more abundant than other components. Cho *et al.* reported that the major volatile components in *A. acutiloba* were γ-terpinene (15%) and butylphthalide (70%) (24). However, according to studies by Lu *et al.*, Japanese Danggui contains lower ligustildes (48). The total amount of volatile oils in *A. acutiloba* was yielded 0.091%.

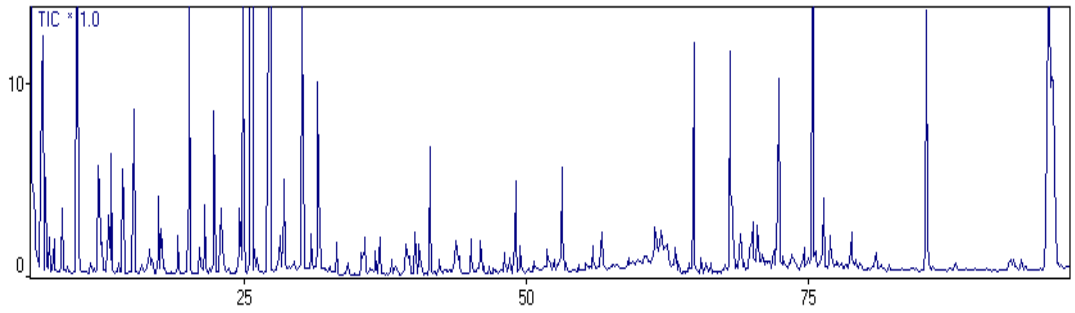

Figure 4. GC/MS chromatogram of volatile components of ***Angelica acutiloba*** *Kitagawa*

Table 6. Volatile components identified from ***Angelica acutiloba*** *Kitagawa*

NO.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg	Area%
1	6.165	802	Ethyl formate	$C_3H_6O_2$	74	7.822	0.86
2	7.144	851	Butanal	C_4H_8O	72	12.038	1.32
3	7.411	863	Ethyl acetate	$C_4H_8O_2$	88	5.226	0.57
4	7.743	878	2-Butanone	C_4H_8O	72	1.595	0.18
5	8.094	892	2-Methyl butanal	$C_5H_{10}O$	86	0.471	0.05
6	8.214	897	3-Methyl butanal	$C_5H_{10}O$	86	1.602	0.18
7	8.887	923	Ethanol	C_2H_6O	46	3.449	0.38
8	10.198	968	2,3-Butanedione	$C_4H_6O_2$	86	24.266	2.67
9	10.292	971	2-Pentanone	$C_5H_{10}O$	86	3.119	0.34
10	12.130	1020	*α*-Pinene	$C_{10}H_{16}$	136	6.477	0.71
11	12.369	1025	*α*-Thujene	$C_{10}H_{16}$	136	1.626	0.18
12	12.958	1037	2-Butenal	C_4H_6O	70	3.307	0.36
13	13.220	1043	2-Methyl-3-buten-2-ol	$C_5H_{10}O$	86	6.626	0.73
14	13.936	1057	2,3-Pentanedione	$C_5H_8O_2$	100	0.567	0.06
15	14.287	1063	Camphene	$C_{10}H_{16}$	136	7.488	0.82
16	15.227	1080	Hexanal	$C_6H_{12}O$	100	9.822	1.08
17	15.917	1092	2-Methyl propanol	$C_4H_{10}O$	74	0.441	0.05
18	16.375	1099	Undecane	$C_{11}H_{24}$	156	0.550	0.06
19	16.604	1103	*β*-Pinene	$C_{10}H_{16}$	136	1.585	0.17
20	16.905	1109	3-Pentanol	$C_5H_{12}O$	88	0.513	0.06
21	17.430	1118	Sabinene	$C_{10}H_{16}$	136	5.112	0.56
22	17.698	1123	2-Pentanol	$C_5H_{12}O$	88	2.863	0.31
23	19.140	1147	Butanol	$C_4H_{10}O$	74	2.638	0.29
24	20.170	1163	*β*-Myrcene	$C_{10}H_{16}$	136	23.840	2.62
25	21.103	1177	*α*-Terpinene	$C_{10}H_{16}$	136	1.767	0.19
26	21.527	1183	Heptanal	$C_7H_{14}O$	114	4.472	0.49
27	22.362	1195	*α*-Limonene	$C_{10}H_{16}$	136	11.620	1.28
28	22.957	1203	*β*-Phellandrene	$C_{10}H_{16}$	136	4.695	0.52
29	24.597	1230	2-Pentyl furan	$C_9H_{14}O$	138	4.481	0.49
30	24.939	1235	*(Z)*-*β*-Ocimene	$C_{10}H_{16}$	136	44.976	4.94

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 6. Continued

NO.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg	Area%
31	25.743	1247	*r*-Terpinene	$C_{10}H_{16}$	136	245.559	26.98
32	25.995	1251	*(E)*-*β*-Ocimene	$C_{10}H_{16}$	136	1.443	0.16
33	26.189	1254	Pentanol	$C_5H_{12}O$	88	0.645	0.07
34	27.278	1269	*p*-Cymene	$C_{10}H_{14}$	134	109.650	12.05
35	28.085	1281	*a*-Terpinolene	$C_{10}H_{16}$	136	0.647	0.07
36	28.197	1282	3-Hydroxy-2-butanone	$C_4H_8O_2$	88	2.666	0.29
37	28.569	1287	Octanal	$C_8H_{16}O$	128	6.533	0.72
I.S.	30.138	1309	***Butylbenzene***	***$C_{10}H_{14}$***	***134***	-	-
38	30.991	1323	3-Methyl-2-butenol	$C_5H_{10}O$	86	3.236	0.36
39	31.584	1332	*(E)*-5-Undecen-3-yne	$C_{11}H_{18}$	150	14.156	1.55
40	33.245	1357	Hexanol	$C_6H_{14}O$	102	2.046	0.22
41	35.333	1386	2-Ethyl-5-methyl pyrazine	$C_7H_{10}N_2$	122	0.538	0.06
42	35.457	1388	2-Nonanone	$C_9H_{18}O$	142	1.904	0.21
43	36.688	1405	Trimethyl pyrazine	$C_7H_{10}N_2$	122	1.721	0.19
44	37.058	1411	Pentylbenzene	$C_{11}H_{16}$	148	2.442	0.27
45	38.120	1428	*(E)*-2-Octenal	$C_8C_{14}O$	126	0.816	0.09
46	39.436	1449	Acetic acid	$C_2H_4O_2$	60	3.225	0.35
47	39.725	1453	1-Octen-3-ol	$C_8H_{16}O$	128	1.507	0.17
48	40.165	1460	Furfural	$C_5H_4O_2$	96	3.555	0.39
49	40.541	1466	2,6-Diethyl pyrazine	$C_8H_{12}N_2$	136	1.825	0.20
50	41.497	1480	Tetramethyl pyrazine	$C_8H_{12}N_2$	136	9.735	1.07
51	42.383	1493	2-Ethyl hexanol	$C_8H_{18}O$	130	0.715	0.08
52	44.133	1520	Benzaldehyde	C_7H_6O	106	1.336	0.15
53	45.134	1536	*(E)*-2-Nonenal	$C_9H_{16}O$	140	2.731	0.30
54	46.002	1550	Linalool	$C_{10}H_{18}O$	154	2.082	0.23
55	48.113	1582	Bornyl acetate	$C_{12}H_{20}O_2$	196	1.703	0.19
56	48.618	1589	*β*-Elemene	$C_{15}H_{24}$	204	1.275	0.14
57	49.111	1596	*(E)*-*β*-Caryophyllene	$C_{15}H_{24}$	204	8.606	0.95
58	49.553	1603	4-Terpineol	$C_{10}H_{18}O$	154	2.336	0.26
59	51.938	1644	*(E)*-2-Decenal	$C_{10}H_{18}O$	154	2.361	0.26
60	53.219	1665	*(Z)*-β-Farnesene	$C_{15}H_{24}$	204	7.811	0.86

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 6. Continued

NO.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg	Area%
61	55.951	1710	Germacrene D	$C_{15}H_{24}$	204	2.038	0.22
62	56.779	1725	*(E,E)*-α-Farnesene	$C_{15}H_{24}$	204	3.410	0.37
63	61.504	1811	*(E,E)*-2,4-Decadienal	$C_{10}H_{16}O$	152	2.324	0.26
64	63.309	1852	Cuminol	$C_{10}H_{14}O$	150	1.652	0.18
65	64.928	1888	Dodecyl acetate	$C_{14}H_{28}O_2$	228	14.953	1.64
66	65.581	1903	Pentanophenone	$C_{11}H_{14}O$	162	0.895	0.10
67	66.025	1915	Phenethyl alcohol	$C_8H_{10}O$	122	0.714	0.08
68	68.148	1972	Dodecanol	$C_{12}H_{26}O$	186	13.684	1.50
69	69.096	1997	Patchulane	$C_{15}H_{26}$	206	2.620	0.29
70	70.593	2039	(E)-Nerolidol	$C_{15}H_{26}O$	222	2.452	0.27
71	72.441	2090	Hexadecyl acetate	$C_{18}H_{36}O_2$	284	12.173	1.34
72	74.720	2154	ɣ-Decalactone	$C_{10}H_{18}O_2$	170	1.129	0.12
73	75.485	2175	Tetradecanol	$C_{14}H_{30}O$	214	56.380	6.19
74	78.944	2256	Ethyl hexadecanoate	$C_{18}H_{36}O_2$	284	3.375	0.37
75	85.621	2378	Hexadecanol	$C_{16}H_{34}O$	242	31.086	3.42
76	96.472	2529	Butylidenephtalide	$C_{12}H_{12}O_2$	188	71.061	7.81
77	96.764	2534	3-Ethoxyphtalide	$C_{10}H_{10}O_3$	178	40.276	4.43
			Total			910.081	100

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 7. Relative content of functional groups in identified volatile components of ***Angelica acutiloba*** *Kitagawa*

Functional groups	Number	Relative area%
Alcohols	19	14.85
Aldehydes	13	5.65
Esters	6	4.97
Hydrocarbons	23	55.96
Ketones	10	16.21
Miscellaneous	6	2.36
Total	77	100

E. Characteristics of essential oils in ***Angelica acutiloba*** *Kitagawa*

The essential oil groups of volatile components identified from *A. acutiloba* are summarized in Table 8.

Monoterpene hydrocarbons (51.25%) contributed the largest fraction of the *A. acutiloba* Kitagawa root oil constituents. There were 14 compounds, including γ-terpinene, ρ-cymene, *(Z)*-β-ocimene, β-myrcene, and α-limonene. γ-Terpinene and α-limonene have a ρ-menthane skeleton, which appears to represent the most stable monoterpene structure. Six dines having a ρ-menthane skeleton occur in nature, these being limonene, α-terpinolene, γ-terpinene, α-phellandrene and β-phellandrene. It can be assumed that the high content of these monoterpene compounds indicates the stability of essential oils in *A. acutiloba* (51).

Sesquiterpene hydrocarbons represented 2.83% of the volatiles. *(E)*-β-Caryophyllene (0.95%) and *(E,E)*-farnesene were present in appreciable amounts, the others being present in trace amounts (below 0.4%). Germacrene-D (2.038 mg/kg, 0.22%) was detected in the sample and is known for its biogenetic significance because it can be photoisomerized to α- and β-bourbonenes together with β-copaene (52).

The percentage of oxygenated terpenes was 13.62% (monoterpenes 13.35%, sesquiterpenes 0.27%). Butylidenephthalide (7.881%) and 3-ethoxyphthalide (4.43%) were the main compounds in oxygenated form. These alkylphthalide derivatives are specific for *A. acutiloba* and other *Apiaceae* plants. Phthalides, which are components of the essential oil, are volatile and unique constituents. The characteristic odor of *Apiaceae* plants is often due to

phthalide derivatives. Various phthalides were isolated, and their biological effects include antianginal, antispasmodic, smooth muscle relaxant, anticholinergic, and acaricidal activities (53-55). Similarly, the essential oil of *Angelica tenuissima* Nakai, in which 3-butylidenephtahalide and 3-butylidene-4,5-dehydrophthalide were found to be major components, has been used as a medicine to stop pain and provide relief from female diseases (56). Miyazawa *et al.* also reported an insecticidal effect of phthalides from *A. acutiloba* (57).

The analytical results indicate that ligustilide is not found in the root of *A. giaas* Nakai, although it belongs to the same genus as *A. acutiloba* Kitagawa. Our results agree with a previous study by Lu *et al.* (34).

Table 8. Relative concentration by terpenoid groups in volatile components of Angelica acutiloba Kitagawa

Terpenoid groups	Number	Relative area%	
Monoterpenes (C_{10})	Monoterpenes	14	51.25
	Oxygenated monoterpens	8	13.35
Sesquiterpenes (C_{15})	Sesquiterpenes	6	1.38
	Oxygenated sesquiterpenes	1	0.27
Total		29	66.25

*F. Comparison of effective volatile components from **Angelica gigas** Nakai and **Angelica acutiloba** Kitagawa*

A total of 116 and 77 compounds were identified and quantified from *A. gigas* and *A. acutiloba*, including hydrocarbons 40 and 23, alcohols 36 and 19, esters 15 and 6, aldehydes 12 and 13, ketones 8 and 10, and miscellaneous 5 and 6, respectively (Figure 5). The amount of essential oil from *A. gigas* and *A. acutiloba* was 3132.926 mg/kg and 910.081 mg/kg, respectively. 34 kinds of volatile components including *α*-pinene, camphene, *β*-myrecene, *α*-terpinene, *γ*-terpinene, and ρ-cymene were detected in both samples, but the amounts of each compound differed (Table 8). *α*-Pinene was the major component of *A. gigas* Nakai, but a minor component in *A. acutiloba* Kitagawa. The percentage of this compound in *A. gigas* (967.750 mg/kg) was about 150 times higher than in *A. acutiloba* (6.477 mg/kg). The other hand, *γ*-terpinene was present in *A. acutiloba* at 93 times its amount in *A. gigas*. Fifteen volatile components, including *γ*-terpinene, *ρ*-cymene, *(Z)*-*β*-ocimene, tetradecanol, and hexadecanol, were higher in *A. acutiloba* than in *A. gigas*. As a result, the volatile components profiles from these two species are very different. The many of compounds was contained in *A. gigas*, and the amount of volatile oils was higher than *A. acutiloba*. From this research, *A. gigas* Nakai yielded more effective volatile components than *A. acutiloba* Kitagawa.

Cyclopentadecanone and 2-hydroxycyclopentadecanone were present in *A. gigas* Nakai but not *A. acutiloba* Kitagawa. Likewise, butylidenephthalide and 3-ethoxyphthalide were present in A. acutiloba Kitagawa but no A. gigas Nakai. Therefore, these four compounds can be used as indicator compounds to determine the type and origin of these plants.

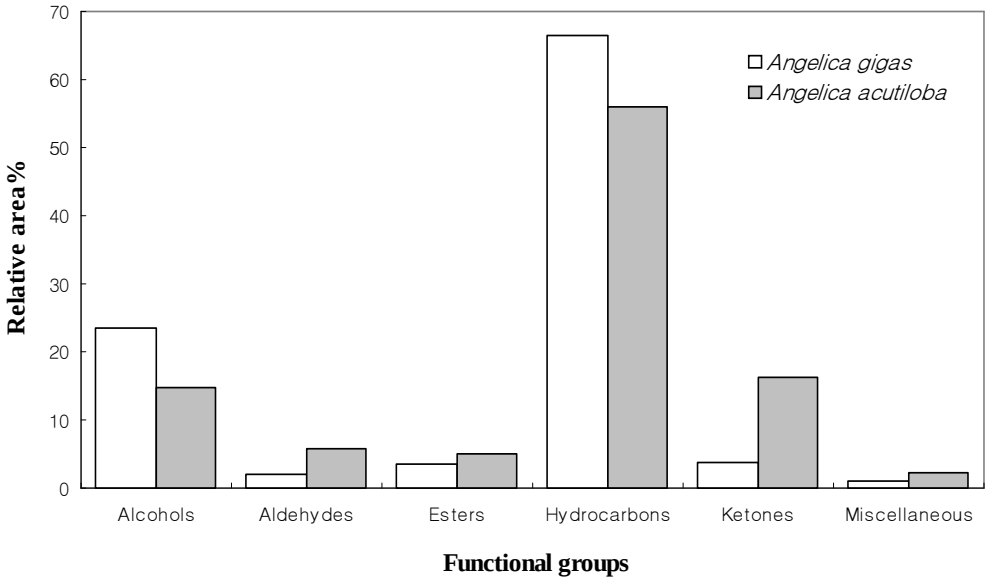

Figure 5. Comparison of relative concentration of functional groups in identified volatile components of ***Agnelica*** *species.*

*Table 9. Comparison of volatile components identified from **Angelica gigas** Nakai and **A. acutiloba** Kitagawa*

NO.	RI[1)]	Compound Name	MF[2)]	MW[3)]	mg/kg	
					A. gigas	*A. acutiloba*
1	802	Ethyl formate	$C_3H_6O_2$	74	-	7.822
2	836	2-Methyl octane	C_9H_{20}	128	102.487	-
3	851	Butanal	C_4H_8O	72	-	12.038
4	865	Ethyl acetate	$C_4H_8O_2$	88	0.973	5.226
5	878	2-Butanone	C_4H_8O	72	-	1.595
6	888	2,4,6-Trimethyl heptane	$C_{10}H_{22}$	142	419.415	-
7	892	2-Methyl butanal	$C_5H_{10}O$	86	-	0.471
8	899	3-Methyl butanal	$C_5H_{10}O$	86	0.634	1.602
9	924	Ethanol	C_2H_6O	46	1.608	3.449
10	951	2-Methyl nonane	$C_{10}H_{22}$	142	0.926	-
11	963	3-Methyl nonane	$C_{10}H_{22}$	142	0.766	-
12	968	2,3-Butanedione	$C_4H_6O_2$	86	-	24.266
13	971	2-Pentanone	$C_5H_{10}O$	86	-	3.119
14	972	*(Z)*-2-Nonen-4-yne	C_9H_{14}	122	30.985	-
15	991	*(E)*-2-Nonen-4-yne	C_9H_{14}	122	6.245	-
16	1006	Tricyclene	$C_{10}H_{16}$	136	5.994	-
17	1029	*α*-Pinene	$C_{10}H_{16}$	136	967.750	6.477
18	1025	*α*-Thujene	$C_{10}H_{16}$	136	-	1.626
19	1037	2-Butenal	C_4H_6O	70	-	3.307
20	1037	4-Methyl-1-penten-3-one	$C_6H_{15}O$	98	7.991	-
21	1043	2-Methyl-3-buten-2-ol	$C_5H_{10}O$	86	3.963	6.626
22	1057	2,3-Pentanedione	$C_5H_8O_2$	100	-	0.567
23	1061	2-Methyl decane	$C_{11}H_{24}$	156	3.581	-
24	1067	Camphene	$C_{10}H_{16}$	136	128.498	7.488
25	1081	Hexanal	$C_6H_{12}O$	100	10.339	9.822
26	1091	2-Methyl-2-butenal	C_5H_9O	84	1.772	-
27	1092	2-Methyl-propanol	$C_4H_{10}O$	74	1.411	0.441
28	1101	Undecane	$C_{11}H_{24}$	156	8.138	0.550
29	1105	*β*-Pinene	$C_{10}H_{16}$	136	31.148	1.585
30	1109	3-Pentanol	$C_5H_{12}O$	88	-	0.513
31	1113	Alloocimene	$C_{10}H_{16}$	136	15.238	-
32	1115	*α*-Myrcene	$C_{10}H_{16}$	136	5.216	-
33	1119	Sabinene	$C_{10}H_{16}$	136	6.180	5.112
34	1123	2-Pentanol	$C_5H_{12}O$	88	-	2.863
35	1130	2-Carene	$C_{10}H_{16}$	136	1.298	-

[1)]Retention Index, [2)]Molecular formula, [3)]Molecular weight

Table 9. Continued

NO.	RI[1)]	Compound Name	MF[2)]	MW[3)]	mg/kg	
					A. gigas	*A. acutiloba*
36	1147	Butanol	$C_4H_{10}O$	74	-	2.638
37	1148	*δ*-3-Carene	$C_{10}H_{16}$	136	8.384	-
38	1160	2-Methylpropyl isobutyrate	$C_8H_{16}O_2$	144	0.899	-
39	1164	*β*-Myrcene	$C_{10}H_{16}$	136	18.055	23.840
40	1168	*α*-Fenchene	$C_{10}H_{16}$	136	0.931	-
41	1174	*α*-Phellandrene	$C_{10}H_{16}$	136	0.902	-
42	1178	*α*-Terpinene	$C_{10}H_{16}$	136	2.345	1.767
43	1181	2-Heptanone	$C_7H_{14}O$	114	0.925	-
44	1184	Heptanal	$C_7H_{14}O$	114	1.433	4.472
45	1186	Methyl hexanoate	$C_7H_{14}O_2$	130	0.679	-
46	1191	2,3-dehydro-1,8-cineole	$C_{10}H_{16}O$	152	1.372	-
47	1198	*α*-Limonene	$C_{10}H_{16}$	136	134.339	11.620
48	1205	*β*-Phellandrene	$C_{10}H_{16}$	136	8.874	4.695
49	1213	1,3,8-Menthatriene	$C_{10}H_{12}$	134	2.020	-
50	1222	Isopulegone	$C_{10}H_{16}O$	152	2.040	-
51	1231	2-Pentyl furan	$C_9H_{14}O$	138	5.825	4.481
52	1235	*(Z)*-*β*-Ocimene	$C_{10}H_{16}$	136	1.951	44.976
53	1245	*γ*-Terpinene	$C_{10}H_{16}$	136	2.639	245.559
54	1251	*(E)*-*β*-Ocimene	$C_{10}H_{16}$	136	0.923	1.443
55	1254	Pentanol	$C_5H_{12}O$	88	1.318	0.645
56	1265	Hexyl acetate	$C_8H_{16}O_2$	144	2.299	-
57	1269	*ρ*-Cymene	$C_{10}H_{14}$	134	33.553	109.650
58	1281	3-Hydroxy-2-butanone	$C_4H_8O_2$	88	-	2.666
59	1281	*α*-Terpinolene	$C_{10}H_{16}$	136	3.713	0.647
60	1288	Octanal	$C_8H_{16}O$	128	1.718	6.533
61	1300	Tridecane	$C_{13}H_{28}$	184	4.322	-
I.S.	1311	*Butylbenzene*	*$C_{10}H_{14}$*	*134*	-	-
62	1318	4-Methyl pentanol	$C_6H_{14}O$	102	0.567	-
63	1324	3-Methyl-2-butenol	$C_5H_{10}O$	86	3.852	3.236
64	1332	*(E)*-5-Undecen-3-yne	$C_{11}H_{18}$	150	-	14.156
65	1337	6-Methyl-5-hepten-2-one	$C_8H_{14}O$	126	1.485	-
66	1353	Propyl tiglate	$C_8H_{14}O_2$	142	1.832	-
67	1356	Isopropyl hexanoate	$C_9H_{18}O_2$	158	23.875	-
68	1357	Hexanol	$C_6H_{14}O$	102	-	2.046
69	1370	Butyl hexanoate	$C_9H_{18}O_2$	158	1.496	-
70	1386	2-Ethyl-5-methyl pyrazine	$C_7H_{10}N_2$	122	-	0.538

[1)]Retention Index, [2)]Molecular formula, [3)]Molecular weight

Table 9. Continued

NO.	RI[1)]	Compound Name	MF[2)]	MW[3)]	mg/kg	
					A. gigas	*A. acutiloba*
71	1389	2-Nonanone	$C_9H_{18}O$	142	1.719	1.904
72	1404	Myrtanol	$C_{10}H_{18}O$	154	24.782	-
73	1405	Trimethyl pyrazine	$C_7H_{10}N_2$	122	-	1.721
74	1411	Pentylbenzene	$C_{11}H_{16}$	148	-	2.442
75	1415	Pentyl isohexanoate	$C_{11}H_{22}O_2$	186	11.044	-
76	1419	Butyl heptanoate	$C_{11}H_{22}O_2$	186	3.027	-
77	1429	*(E)*-2-Octenal	$C_8C_{14}O$	126	1.007	0.816
78	1436	3,5-Dimethyl styrene	$C_{10}H_{12}$	132	3.035	-
79	1449	Acetic acid	$C_2H_4O_2$	60	-	3.225
80	1453	1-Octen-3-ol	$C_8H_{16}O$	128	-	1.507
81	1460	Furfural	$C_5H_4O_2$	96	-	3.555
82	1460	Limonene oxide	$C_{10}H_{16}O$	152	6.268	-
83	1462	2-Methylbutyl hexanoate	$C_{11}H_{22}O_2$	186	7.996	-
84	1466	2,6-Diethyl pyrazine	$C_8H_{12}N_2$	136	-	1.825
85	1480	Tetramethyl pyrazine	$C_8H_{12}N_2$	136	-	9.735
86	1484	Cyclosativene	$C_{15}H_{24}$	204	11.232	-
87	1490	*α*-Campholene aldehyde	$C_{10}H_{16}O$	152	13.112	-
88	1493	2-Ethyl hexanol	$C_8H_{18}O$	130	-	0.715
89	1493	*α*-Copaene	$C_{15}H_{24}$	204	5.763	-
90	1520	Benzaldehyde	C_7H_6O	106	-	1.336
91	1523	*(E)*-*ρ*-Mentha-2,8-dien-1ol	$C_{10}H_{16}O$	152	4.029	-
92	1537	*(E)*-2-Nonenal	$C_9H_{16}O$	140	3.161	2.731
93	1551	Linalool	$C_{10}H_{18}O$	154	5.452	2.082
94	1556	Butyl octanoate	$C_{12}H_{24}O_2$	200	4.707	-
95	1569	*(E)*-*ρ*-2-Menthen-1-ol	$C_{10}H_{18}O$	154	36.665	-
96	1583	Bornyl acetate	$C_{12}H_{20}O_2$	196	12.212	1.703
97	1589	*β*-Elemene	$C_{15}H_{24}$	204	-	1.275
98	1590	Aromadendrene	$C_{15}H_{24}$	204	5.512	-
99	1596	*(E)*-*β*-Caryophyllene	$C_{15}H_{24}$	204	-	8.606
100	1605	4-Terpineol	$C_{10}H_{18}O$	154	6.465	2.336
101	1624	Thujopsene	$C_{15}H_{24}$	204	5.616	-
102	1631	Myrtenal	$C_{10}H_{14}O$	150	13.803	-
103	1644	*(E)*-2-Decenal	$C_{10}H_{18}O$	154	-	2.361
104	1661	Pinocarveol	$C_{10}H_{16}O$	152	38.156	-
105	1665	*(Z)*-β-Farnesene	$C_{15}H_{24}$	204	-	7.811

[1)]Retention Index, [2)]Molecular formula, [3)]Molecular weight

Table 9. Continued

NO.	RI[1)]	Compound Name	MF[2)]	MW[3)]	mg/kg	
					A. gigas	*A. acutiloba*
106	1667	*α*-Phellandren-8-ol	$C_{10}H_{16}O$	152	13.537	-
107	1686	Vervenol	$C_{10}H_{16}O$	152	67.265	-
108	1691	*(E)*-*β*-Caryophyllene	$C_{15}H_{24}$	204	7.009	-
109	1700	*α*-Terpineol	$C_{10}H_{18}O$	154	7.049	-
110	1710	Germacrene D	$C_{15}H_{24}$	204	-	2.038
111	1714	Verbenone	$C_{10}H_{14}O$	150	45.118	-
112	1725	*(E,E)*-α-Farnesene	$C_{15}H_{24}$	204	-	3.410
113	1729	*α*-Murrolene	$C_{15}H_{24}$	204	47.597	-
114	1732	*β*-Phellandren-8-ol	$C_{10}H_{16}O$	152	29.785	-
115	1739	*r*-Elemene	$C_{15}H_{24}$	204	21.348	-
116	1753	*cis*-Piperitol	$C_{10}H_{18}O$	154	13.545	-
117	1756	Myrtanyl acetate	$C_{12}H_{20}O_2$	196	14.400	-
118	1762	*δ*-Cadinene	$C_{15}H_{24}$	204	10.759	-
119	1768	*(E,Z)*-2,4-Decadienal	$C_{10}H_{16}O$	152	2.052	-
120	1772	*β*-Citronellol	$C_{10}H_{20}O$	156	6.997	-
121	1783	3-Isopropyl benzaldehyde	$C_{10}H_{12}O$	148	3.037	-
122	1798	Myrtenol	$C_{10}H_{16}O$	152	12.291	-
123	1813	*(E,E)*-2,4-Decadienal	$C_{10}H_{16}O$	152	7.979	2.324
124	1828	Cuparene	$C_{15}H_{22}$	202	11.606	-
125	1842	*cis*-Carveol	$C_{10}H_{16}O$	152	29.343	-
126	1848	*ρ*-Cymen-8-ol	$C_{10}H_{14}O$	150	16.878	-
127	1854	Cuminol	$C_{10}H_{14}O$	150	33.660	1.652
128	1871	*trans*-Carveol	$C_{10}H_{16}O$	152	4.851	-
129	1880	Pinene oxide	$C_{10}H_{16}O$	152	16.723	-
130	1888	Dodecyl acetate	$C_{14}H_{28}O_2$	228	-	14.953
131	1903	Pentanophenone	$C_{11}H_{14}O$	162	-	0.895
132	1911	*ρ*-Meth-1-en-9-ol	$C_{10}H_{16}O$	152	5.003	-
133	1915	Phenethyl alcohol	$C_8H_{10}O$	122	-	0.714
134	1972	Dodecanol	$C_{12}H_{26}O$	186	-	13.684
135	1997	Patchulane	$C_{15}H_{26}$	206	-	2.620
136	1998	*β*-Caryophyllene oxide	$C_{15}H_{24}O$	220	2.901	-
137	2029	Globulol	$C_{15}H_{26}O$	222	7.744	-
138	2039	*(E)*-Nerolidol	$C_{15}H_{26}O$	222	-	2.452
139	2043	4-Tetradecanol	$C_{14}H_{30}O$	214	12.166	-
140	2058	Octanoic acid	$C_8H_{16}O_2$	144	2.071	-

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

Table 9. Continued

NO.	RI[1)]	Compound Name	MF[2)]	MW[3)]	mg/kg	
					A. gigas	*A. acutiloba*
141	2086	Elemol	$C_{15}H_{26}O$	222	20.669	-
142	2090	Hexadecyl acetate	$C_{18}H_{36}O_2$	284	-	12.173
143	2096	Guaiol	$C_{15}H_{26}O$	222	10.897	-
144	2124	Cyclopentadecanone	$C_{15}H_{28}O$	224	6.027	-
145	2136	Sphatulenol	$C_{15}H_{24}O$	220	58.080	-
146	2154	ɣ-Decalactone	$C_{10}H_{18}O_2$	170	-	1.129
147	2176	Tetradecanol	$C_{14}H_{30}O$	214	7.193	56.380
148	2189	2-Hydroxycyclopentadecanone	$C_{15}H_{28}O_2$	240	48.968	-
149	2217	Guaiyl acetate	$C_{17}H_{28}O_2$	264	16.180	-
150	2220	Methyl hexadecanoate	$C_{17}H_{34}O_2$	270	3.991	-
151	2226	Bulnesol	$C_{15}H_{26}O$	222	6.703	-
152	2256	Ethyl hexadecanoate	$C_{18}H_{36}O_2$	284	-	3.375
153	2230	Agarospirol	$C_{15}H_{26}O$	222	19.382	-
154	2238	*α*-Eudesmol	$C_{15}H_{26}O$	222	59.476	-
155	2250	*β*-Eudesmol	$C_{15}H_{26}O$	222	156.832	-
156	2377	Hexadecanol	$C_{16}H_{34}O$	242	3.930	31.086
157	2529	Butylidenephtalide	$C_{12}H_{12}O_2$	188	-	71.061
158	2534	3-Ethoxyphtalide	$C_{10}H_{10}O_3$	178	-	40.276
		Total			3132.926	910.081

[1)]Retention tiime, [2)]Retention time, [3)]Molecular formula, [4)]Molecular weight

CONCLUSION

The essential oils of *Angelica gigas* Nakai and *Angelica acutiloba* Kitagawa were found as a high quality oil by their composition. Volatile oils of *A. gigas* were constituted *α*-pinene, *β*-eudesmol, *α*-limonene, camphene, verbenol, sphatulenol, and 2-hydroxycyclopentadecanone, and volatile oils of *A. acutiloba* were constituted ɣ-terpinene, *ρ*-cymene, butylidenephthalide, tetradecanol, *(Z)*-*β*-ocimene, and 3-ethoxyphthaliede. These results suggest that the essential oil of *A. gigas* Nakai and *A. acutlioba* Kitagawa could usefully be used in fragrance, flavor and pharmaceutical industries and aromatherapy. Furthermore, *A. acutliba* Kitagawa could be used for insecticide industry. Also, cyclopentadecanone and 2-hydroxycyclopentadecanone were present in *A. gigas* Nakai but not *A. acutiloba* Kitagawa. Likewise, butylidenephthalide and 3-ethoxyphthalide were present in A. acutiloba Kitagawa but no A. gigas Nakai. Therefore, these four compounds can be used as indicator compounds to determine the type and origin of these plants.

요 약

토당귀(*Angeilica gigas* Nakai)와 일당귀(*Angelica acutiloba* Kitagawa)의 휘발성 유효성분을 SDE 방법으로 추출하였고 GC/MS로 분석하였다. 총 116종, 77종의 화합물이 토당귀와 일당귀에서 각각 동정되었으며, hydrocarbon류 40종과 23종, alcohol류 36종과 19종, ester류 15종과 6종, aldehyde류 12종과 13종, ketone류 8종과 10종 및 기타 5종과 6종이 각각 확인되었다. 토당귀에서 확인된 주요 휘발성 유효성분은 *α*-pinene, 2,4,6-trimethyl heptane, camphene, *α*-limonene, *β*-eudesmol, vervenol, *α*-murrolene 및 sphatulenol이었으며, *α*-pinene(30.89%)과 2,4,6-trimethyl heptane(13.39%)이 주를 이루고 있었다. *γ*-Terpinene(26.98%)과 *ρ*-cymene(12.05%)이 일당귀의 주요 휘발성 유효성분으로 확인되었으며 butylidenephthalide, 3-ethoxyphthalide, *(Z)*-*β*-ocimene, tetradecanol 및 hexadecanol도 상당량 확인되었다. 이상의 결과로 두 종에서 휘발성 유효성분의 profile이 차이가 있는 것으로 나타났다. 토당귀와 일당귀에서 회수된 휘발성 유효성분의 양은 각각 0.313%, 0.091%로 토당귀에 약 3배 정도의 유효성분을 회수하였으며, 정유성분 또한 토당귀(90.71%)에서 높은 수준을 나타내었다.

토당귀와 일당귀의 휘발성 유효성분은 향료, 향기 산업 및 제약 산업, aromatheraphy에 유용하게 사용될 수 있을 것으로 생각되며, 휘발성 유효성분의 조성으로 볼 때, 토당귀가 일당귀보다 더 유용할 것으로 사료된다.

REFERENCES

1. Kusmenoglu, G., Baser ,1. Kusmenoglu, S. and Baser, K.H.C., T. "Constituents of the essential of from the hulls of *Pistacia rera* L." *J. Essent. Oil Res.*, 7: 441-442, 1995.
2. Satil, F., Azcan, N. and Baser, K.H.C. "Fatty acid composition of pistachio nuts in Turkey." *Chem. Nat. Comut*, 39:322-324, 2003.
3. Janssen, A.M., Scheffer, I.J. and Baerheim, S.A. "Antimicrobial activities of essential oils. A 1976-1986 Lature review on possible applications." *Pharm. Weekbl. Sci.*, 9:193-197, 1978.
4. Dang, M.N., Takacsova, M., Nguyen, D.V. and Kristianova, K. "Anti-oxidant activity of essential oils from various spices." *Nahrung.*, 45:64-66, 2001.
5. Ahn, K.S., Shim, W.S. and Kim, K.H. "Detection of anticancer activity from the root of *Angelica gigas* in vitro." *J. Microbiol. Biotechnol.*, 5:105-109, 1995.
6. Ahn, K.S., Shim, W.S., Kim, H.M, Han, S.B. and Kim, I.H. "Immunosti-mulatiing components from the root of *Angelica gigas* Nakai." *Korean J. Pharmacogn.*, 27:254-261, 1996.
7. Jo, S.K., Park, H.R., Yu, Y.B., Song, B.C. and Yee, S.T. "Stability in immunomodulation activity of irradiated *Angelica gigas* Nakai." *J. Korean Soc. Food Sci. Nutr.* 29:254-261, 2000.
8. Chen, J.K. and Chen, T.T.: "Chines Medical Herbology and Pharmacology", Chapter 17, Section 3:918-924, 2004.
9. Han, D.S.: Pharmacology, Dongmyungsa Press, Seoul, 1992, pp.201-202.

10. Yun, S.Y.: Coloured resources plants of Korea, Academy Publishing Company, Seoul, 2001, p. 36.
11. Ryu, K.S. and Yook, C.S. "Studies on the coumarins of the root *Angelica gigas* Nakai (I)", *J. Pharmaceut. Soc. Kor. Aa*, 11:22-26, 1967.
12. Chi, H.J. and Kim, H.S. "Studies on essential oils of plant of Angelica genus in Korea (I). Essential oils of *Angelica gigantis* Radix", *Kor. J. Pharmacogn.* 19:239-247, 1988.
13. Lee, S.H., Jung, S.H., Lee, Y.S. and Shin, K.H. "Coumarins from *Angelica gigas* roots having rat lens aldose reductase activity." *J. Appl. Pharm.,* 10:85-88, 2002.
14. Lee, S.H., Kang, S.S. and Shin, K.H. "Coumarins and a pyrimidine from *Angelica gigas* roots." *Nat. Prod. Sci.*, 8:58-61, 2002.
15. Lee, S.H., Lee, Y.S., Jung, S.H., Shin, K.H., Kim, B.K. and Kang, S.S. "Antioxidant activities of decusinol agelate and decursin from *Angelica gigas* roots." *Nat. Prod. Sci.*, 9:170-173, 2003.
16. Kang, S.Y., Lee, K.Y., Park, M.J., Kim, Y.C., Markelonis, G.J., Oh, T.H. and Kim, Y.C. "Decursin from *Angelica gigas* mitigate amnesia induced by scopolamine in mice." *Nerobiol. Leam. Mem.*, 79:11-18, 2003.
17. Kang, S.A., Han, J.A., Jang, K.H. and Choue, R.W. "DPPH radical scavenger activity and antioxidant effects of Cham-Dang-Gui (*Angelica gigas*)." *J. Korean Soc. Food Sci. Nutr.*, 33:1112-1118, 2004.
18. Yamada, H., Kiyohara, H., Cyong, J.C., Kojima, Y., Kumazawa, Y. and Otsuka, Y. "Studies on polysaccharides from *Angelica auctiloba*." *Planta Med.* 50:163-167, 1984.
19. Tanaka, S., Hoshino, C., Ikeshiro, Y., Tabata, M. and Konoshima, M. "Studies on antiociceptive activities of aqueus extracts from different

varieties of Toki." *Yakugaku Zasshi*, 97:14-17, 1977.

20. Kobayashi, M. "Chemical evaluation of Angelica Radix." J. *Traditional Sino-Japanese Medicine*, 13:95-100, 1992.
21. Yamada, H., Kiyohara, H., Cyong, J.C., Kojjima, Y, Kumazawa, Y. and Ostuka, Y. "Studies on polysaccharides from Angelica radix (III). Chemical properties and biological activities of polysaccharides from Angelica Radix produced in the different area." *Shoyakagaku Zasshi*, 38:111-117, 1984.
22. Kiyohara, C., Cyong, J.C. and Yamada, H. "Relationship between structure and activity of and anti-complementary arabinogalactan from the roots of *Angelica acutiloba* Kitagawa." *Carbohydr. Res.*, 193:193-200, 1989.
23. Lee, C.K., Kim, H.K., Moon, K.H. and Shin, K.H. "Screening and isolated of antibiotic resistance inhibitors from herb materials-resistance inhibition of volatile components of Korea aromatic herbs." *Arch. Pharm. Res.*, 21:62-66, 1998.
24. Cho, M.G., Bang, J.K. and Chae, Y.A. "Comparison of volatile compounds in plant parts of *Angelica gigas* Nakai and *A. acutiloba* Kitagawa." *Korean J. Medicinal Crop Sci.*, 11:352-357, 2003.
25. Nikerson, G.B. and Likens, S.T. "Gas chromatography evidence for the occurrence of hop oil components in beer." *J. Chromatogr. A.*, 21:1-5, 1966.
26. Schultz, T.H., Flath, R.A., Mon, T.R., Enggling, S.B. and Teranishi, R. "Isolation of volatile components from a model system." *J. Agric. Food Chem.*, 25:446-449, 1977.
27. Kovats, E. S. 1958. *Helv. Chim. Acta.* 41:1915.
28. Lee, M. D. Instrument analysis chemical, Seoul : Freedom Academe, 1918, pp. 25~26.
29. Sadtler Research Laboratories. The Sadtler standard gas chromatography

retention index library, USA, Sadtler, 1986.

30. Davies, M.W. "Gas chromatographic retention indices of monoterpenes and sesquiterpenes on methyl silicon and Carbowax 20M phase." *J. Chromatogr. A*, 503:1-24, 1990.
31. Stehagen, E.S., Abbrahansom, F. and Mclafferty, W. The Wiley/NBS Registry of Mass Spectral Data, John Wiley and Sons, N.Y., 1974.
32. Robert. P.A. Identification of Essential oil components by gas chromatography/mass sepctrometry, Allured Publishing Corporation, IL, USA, 1995.
33. Anet, E.F.L.J. "Superficial scald, a functional disorder of stored apple. VIII. Volatile products from the autoxidation of α-farnesene." *J. Sci. Food Agric.*, 23:605-610, 1972.
34. Heath, H.B. Flavor Technology, The AVI publishing Co. Inc., Connecticut, USA, 1978.
35. Flavornet. Available online at: http://www.flavornet.org/flavornet.html (accessed 15 November 2005)
36. Paula, C.S.G. and Manuel, F.F. "Organo- and season-dependent variation in the essential oil composition of Salvia officinalis L. cultivated at two diiferent sites." *J. Agric. Food Chem.,* 49:2908-2916, 2001.
37. Ohloff, G. Scent and Fragrances, The fascination of odors and their chemical perspectives, Springer-Verlag, Berliin, Germany, 1994, pp.199~203.
38. Miyazawa, M. and Yamafuji, C. "Inhibition of Acetylcholinesterase by bicyclic monoterpenoids." *J. Agric. Food Chem.*, 52:176-178, 2005.
39. Choi, H.S., Kim, M.S. and Sawamura, M. "Constituents of the essential oil of *Angelica tenuissima*, an aromatic medicinal plant." *Food Sci. Biotechnol.*, 10:557-561, 2001.
40. Forsen, K. "Aroma constituents of *Angelica archangelica* variation in the

composition of the essential oil of strains of var. novegica and var. sativa." *Kevo Subarctic Res. Stn*, 15:1, 1979.

41. Kerrola, K., Galambosi, B. and Kallio, H. "Characterization of volatile composition and odor angelica (*Angelica archangelica* subsp. *archangelica* L.) root extracts." *J. Agric. Food Chem.*, 42:1979-1988, 1994.
42. Baruah, N.C., Sarma, J.C., Barua, N.C., Sarma, S. and Sharma, R.P. "Germination and growth inhibitory sesquiterpene lactones and a flavone from Tithonia diversifolia." *Phytochemistry*, 36:2936, 1994.
43. Goren, N., Woerdenbag, H.J. and Bozok-Johansson, C. "Cytotoxic and antibacterial activities of sesquiterpene lactones isolated from Tanacetum praeteritum subsp. praeteritum." *Planta Medica.*, 62:419-422, 1996.
44. Mansilla, H. and Palenzuela, J.A. "Minor eudesmanolides from Artemisia canariensis." *Phytochemistry*, 51:995-997, 1999.
45. Doneanu, C. and Antiescu, G. "Supercritical carbon dioxide extraction of *Angelica archangelica* L. root oil." *J. Supercrit. Fluids*, 12:59-67, 1998.
46. Ka, M.H., Choi, E.H., Chun, H.S. and Lee, K.G. "Antioxidative activity of volatile extracts isolated from Angelica tenuissimae roots, peppermint leaves, pine needles, and sweet flag leaves." *J. Agric. Food Chem.*, 53: 4124-4129, 2005.
47. Kaouadji, M., Pachtere, F.D., Pouget, C., Chulia, A.J. and Lavaitte, S. *J. Nat. Prod*. 48:872, 1986.
48. Naito, T., Ikeya, Y., Okada, M., Mistuhashi, H. and Maruno, M. "Flavonoids from *Pyrola Elliptica*." *Phytochemistry* 41:233-236, 1996.
49. Gijbels, M.J.M, Scheffer, J.J.C. and Svendsen, A.B. *Plant Med.*, 44:207, 1982.
50. Lu, G.H., Chan, K., Chan, C.L, Leung, K., Jiang, Z.H and Zhao, Z.Z. "Quantification of ligustilides in the roots of *Angelica sinensis* and related

umbelliferous medicinal plants by high-performance liquid chromatography and liquid chromatography-mass spectrometry." *J. Chromatogr. A*, 1046:101- 107, 2004.

51. Whittaker, D. The monoterpenes, In: Chemistry of Terpenes and Terpenoids. Newman, A.A. (ed.), Academic Press, London, UK, 1972, pp. 11~87.
52. Roberts, J.S., The sesquiterpenes. In: Chemistry of Terpenes and Terpenoids. Newman, A.A. (ed.), Academic Press, London, UK, 1972, pp. 88~154.
53. Ko, W.C.; Chang, L.D.; Wang, G.Y.; Lin, L,C. "Pharmacological effects of butylidenephthalide". *Phytother. Res.* 24:47-51, 1994.
54. Kanita, T.; Tsutsui, F.; Matsuda, M.; Yamashita, A.; Kozaka, N.; Sekida, S.; Satake, M. "Smooth muscle relaxants, their extraction from Angelica sinensis and compositions containing the smooth muscle relaxants." Jpn. Kokai Tokkyo Koho, 1997, JP 09077666. 15. Mitsuhashi, H.; Nagai, U.; Muramatsu, T.; Tashiro, H. Studies on the constituents of Umbelliferae plants. II. Isolation of the active principles of Ligusticum roots. Chem. Pharm. Bull. 1960, 8, 243-245.
55. Kwon, J.H.; Ahn, Y.J. Acaricidal activity of butylidenephthalide identified in Cnidiumofficinale Rhizome against Dermatophagoidesfarinae and Dermatophagoidespteronyssius (Acari: Pyloglyphidae). *J. Agric. Food Chem.* 50:4479-4483, 2002.
56. Kim, M.H., Kim, Y.G., Lee, J.H., Hong, K.P., Hong, J.K., Kong, U.J. and Lee, H.Y. "Screening of biologically active essential oils from *Ligusticum tenuissimum*." *Kor. J. Appl. Microbiol. biotechno.*, 28:97-104, 2000.
57. Miyazawa, M., Tsukamoto, T. Anzai, J. and Ishikawa Y. "Insecticidal Effect of Phthalides and Furanocoumarins from *Angelica acutiloba* against *Drosophila melanogaster*." *J. Agric. Food Chem.,* 52:4401-4405, 2004.