

## Comparative Analysis of Volatile Flavor Compounds from *Zanthoxylum piperitum* A.P. DC.

– Research Note –

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### Abstract

The volatile flavor components of *Zanthoxylum piperitum* A.P. DC. produced in Korea and China were isolated using a Clevenger-type apparatus by steam distillation extraction, and analyzed by gas chromatography-mass spectrometry (GC/MS). The yields of oils from Korean and Chinese *Z. piperitum* A.P. DC. were 2.0 and 1.2% (w/w), respectively. From the two *Z. piperitum* A.P. DC. oils, sixty and fifty-four volatile flavor compounds were tentatively identified, and they constituted 94.78 and 87.34% of the total peak area, respectively. Piperitone (*p*-menth-1-en-3-one) (13.48%) was the most abundant compound in the Chinese *Zanthoxylum piperitum* A.P. DC. oil, followed by  $\beta$ -phellandrene, sabinene, terpinen-4-ol and linalool (each >5%). Whereas, the most abundant compound in the Korean *Zanthoxylum piperitum* A.P. DC. oil was limonene (18.04%), followed by geranyl acetate, cryptone, citronellal, cuminal and phellandral (each >5%).

**Key words:** *Zanthoxylum piperitum* A.P. DC., aroma component, steam distillation, producing region, GC/MS

### INTRODUCTION

*Zanthoxylum* is a member of the division *Angiospermae*, the sub class *Archichalmydeae*, order *Rutales* and family *Rutaceae*. It is represented by two species in Korea, *Zanthoxylum schinifolium* and *Zanthoxylum piperitum* A.P. DC. (1,2). *Z. piperitum* A.P. DC. has a greenish yellow-colored flower that blooms from April to May, and bears red brown-colored fruits with black-colored seeds that ripen from September until October. It is known to an aromatic, perennial and medicinal herbaceous plant, with the vast majority of the species occurring exclusively in Korea, Japan and China (2,3). *Z. piperitum* A.P. DC. has been used as a *miso* additive and for seasoning fried eel in Japan, in mixed spices and culinary oils in China, and the young leaves are used as *namul*. The fruit and seeds have been used as a spice and flavor masking agent for the meaty and fishy odors in Korea from ancient times (3,4). In addition, *Z. piperitum* A.P. DC. has been used as a folk medicine in north-eastern Asia, including Taiwan, China, Japan, and Korea, for the treatment of certain dermatological diseases, acute and chronic abdominal colic pain, stomach ache, inflammation, hypotension and diarrhea (2-5). Furthermore, it was recently reported that the essential oil of *Z. piperitum* A.P. DC. has anti-oxidative, DPPH radical-scavenging activities (6,7). The plant essential

oil is quite enriched with terpenoids which exert inhibitory action against microorganisms by disrupting their membranes (8). The essential oils of *Zanthoxylum* species in Korea have been studied by several researchers (9-12). However, there have been no comparative analyses of the differences in bioactive compounds of plants from different countries. Recently, many vegetables and even some medicinal plants have imported from foreign countries, especially from China. There are various extraction method of plants essential oils; simultaneous steam distillation extraction (SDE), steam distillation extraction, hydro distillation extraction and head space method etc. SDE is a useful method for extracting volatile flavor components, however it has several limitations such as using an organic solvent, boiling off-flavor and a long time. Recently, the head space solid phase micro-extraction (HS-SPME) method has largely replaced SDE for the analysis of plant aroma compounds, however it has limitations for the cell experiment and it difficult to use for testing bio-activity. In this study, the steam distillation extraction method was used; it did not use organic solvents which can contaminate plant aroma compounds. The aim of this study was to evaluate and compare the chemical variability of the volatile flavor compounds from *Z. piperitum* A.P. DC. oils.

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## MATERIALS AND METHODS

### Plant materials

*Z. piperitum* A.P. DC. harvested in the fall of 2006 in Youngju (Gyungsangbukdo) province, in the eastern part of Korea, was purchased at Gyungdong Herbal Market (Seoul, Korea) in the spring of 2007. *Z. piperitum* A.P. DC. produced in China was packaged in the fall of 2006, and imported by Jinhyung Inc. (Seoul, Korea), was also purchased at Gyungdong Herbal Market (Seoul, Korea) in the spring of 2007. These samples were kept at  $-70^{\circ}\text{C}$  in air-tight bag until the analysis was carried out.

### Isolation of the volatile flavor compounds

Dried *Z. piperitum* A.P. DC. was crushed for 10 sec in a blender (HMC-400T, Hanil Electronics, Seoul, Korea) and 1 kg samples were extracted by steam distillation extraction method for 3 hr from setting using a Clevenger-type apparatus (Hanil Lab Tech Ltd., Incheon, Korea). The essential oils obtained were dried over anhydrous sodium sulfate during over night, measured and stored in hermetically sealed dark-glass containers in a freezer at  $-70^{\circ}\text{C}$  until they were tested and analyzed by GC/MS.

### Gas chromatography-mass spectroscopy (GC/MS) analysis

An Agilent 6890 gas chromatography/5973 mass selective detector (Agilent Co., Palo Alto, CA, USA) was employed. Analysis was carried out on a HP-5MS capillary column (30 m length  $\times$  0.25 mm I.d.  $\times$  0.25  $\mu\text{m}$  film thickness; Agilent Co., Palo Alto, CA, USA) using a micro syringe. The GC/MS conditions for analysis of essential oil from *Z. piperitum* A.P. DC. are outlined in Table 1.

### Identification of the essential oil compounds

The volatile flavor compounds were identified by comparison of the mass spectra with those in an on-line computer library (Wiley 275) (Agilent Co., Palo Alto, CA, USA). Alkanes were used as reference points in the calculation of relative retention indices (RI). The RI were experimentally determined using the standard method involving retention time of *n*-alkane series [Alkane Standard Solution (04070, 04071), (C<sub>8</sub>-C<sub>20</sub>, C<sub>21-40</sub>), Standard for GC, Fluka, USA] injected after the essential oil under the same chromatographic conditions. The RIs of compounds, determined using C<sub>8</sub>-C<sub>22</sub> as external references (13) were compared with the published data (14,15). Several compounds were identified by comparison with published data (16-18), and some by identification based on co-injection with authentic com-

**Table 1.** GC/MS operating conditions for volatile aroma components analysis

GC Agilent 6890/MS Agilent 5973 (Agilent Co., Palo Alto, CA, USA)
Column HP-5MS (30 m $\times$ 0.25 mm $\times$ 0.25 $\mu\text{m}$ ; Agilent Co., Palo Alto, CA, USA)
Injector temperature: $250^{\circ}\text{C}$
Interface temperature: $250^{\circ}\text{C}$
Detector temperature: $280^{\circ}\text{C}$
Injection volume: $10^{-1}$ $\mu\text{L}$ ; previously dissolved in methylene chloride
Split ratio 10:1
Carrier gas: He (Flow rate: 1.0 mL/min)
Ionization voltage: 70 eV
Scanning interval: 0.5 sec
Detector voltage: 1.2 kV
Scanning range: m/z 33 ~ 330
Oven temperature program
Initial temperature, time: $40^{\circ}\text{C}$ , 5 min
Rate 1: $3^{\circ}\text{C}/\text{min}$
Final temperature, time: $150^{\circ}\text{C}$ , 5 min
Rate 2: $7^{\circ}\text{C}/\text{min}$
Final temperature, time: $220^{\circ}\text{C}$ , 5 min

pounds (Acoros or Sigma-Aldrich, USA). The relative amount of individual components from the oils are expressed as peak area % relative to the total peak area based on the ratio of the peaks obtained from the mass total ion chromatogram, and also marked quality percentage of identified volatile flavor compounds from the MS data. This experimental test was carried out in triplicate, with the data presented as the mean value for the individual oils.

## RESULTS AND DISCUSSION

The list of detected compounds in the steam distilled oils from two different *Z. piperitum* A.P. DC. plants from different regions, along with their retention times, retention indices, relative peak area percentages, quality percentages and percentage amounts of compound classes are given in Table 2 and 3. Mass chromatograms obtained from GC/MS are showed in Fig. 1 and 2. There were some differences observed in composition of the essential oils from *Z. piperitum* A.P. DC.

### Volatile flavor components of *Z. piperitum* A.P. DC. in Korea

The yield of the essential oil from Korean *Z. piperitum* A.P. DC. was 2.0% (w/w) (20 g of the oil/1 kg of the materials, dry basis unit) and the color of the oil was light yellow. As shown in Tables 2 and 3, sixty volatile flavor compounds were identified in *Z. piperitum* A.P. DC. from Korea; including: 43 terpenes, 1

**Table 2.** Volatile flavor compounds of *Z. piperitum* A.P. DC.

Compounds	RI <sup>1)</sup>	RI <sup>2)</sup>	QA% <sup>3)</sup>	QA% <sup>4)</sup>	PA% <sup>5)</sup>	PA% <sup>6)</sup>	Method of ID <sup>7)</sup>
Hexanal	0805	0800	83	83	0.03	0.06	A,B,C
3-Methylcyclopentanol	—	0836	—	91	—	0.01	A,B
Isomyl acetate	0838	—	86	—	0.04	—	A,B
2-Heptanone	—	0870	—	87	—	0.01	A,B,C
Heptanal	—	0901	—	87	—	0.04	A,B
( <i>E,E</i> )-2,4-Hexadienal	0910	—	97	—	0.04	—	A,B,C
$\alpha$ -Thujene	0925	0925	94	94	0.62	0.09	A,B,C
$\alpha$ -Pinene	0933	0935	96	96	3.23	0.15	A,B,C
Camphene	0944	—	98	—	0.09	—	A,B,C
Benzaldehyde	—	0959	—	94	—	0.04	A,B,C <sup>b)</sup>
Sabinene	0976	—	97	—	9.51	—	A,B,C
$\beta$ -Pinene	0978	0978	97	95	0.26	0.26	A,B,C
$\beta$ -Myrcene	0988	0988	96	96	3.55	2.87	A,B,C
$\alpha$ -Phellandrene	1003	1001	95	91	1.37	0.47	A,B,C
Octanal	—	1005	—	90	—	0.06	A,B,C
$\alpha$ -Terpinene	1017	1017	98	98	2.88	0.08	A,B,C
Limonene	—	1030	—	99	—	18.04	A,B,C*
$\beta$ -Phellandrene	1036	—	90	—	10.90	—	A,B,C
$\beta$ -terpinene	1038	—	83	—	4.59	—	A,B,C
( <i>E</i> )- $\beta$ -Ocimene	1044	1049	98	96	2.38	0.08	A,B,C
2,6-Dimethyl-5-heptenal	—	1054	—	97	—	0.20	A,B
$\gamma$ -Terpinene	1057	1058	97	97	3.29	0.16	A,B,C*
3,8-Menthadiene	—	1062	—	97	—	0.02	A,B
<i>cis</i> -Linalool oxide	—	1070	—	91	—	0.39	A,B
Perillene	—	1097	—	59	—	0.32	A,B
( <i>E</i> )-Sabinene hydrate	1075	—	97	—	0.34	—	A,B,C
Terpinolene	1092	—	98	—	1.87	—	A,B,C
Linalool	1100	1101	97	94	5.54	1.44	A,B,C
Rose oxide	—	1110	—	93	—	1.50	A,B,C
<i>cis</i> -Rose oxide	—	1118	—	76	—	0.37	A,B
( <i>E</i> )-Limonene oxide	—	1124	—	69	—	0.25	A,B,C
dehydro <i>p</i> -Cymene	1120	1128	95	64	0.29	0.53	A,B
Camphor	1140	—	90	—	0.04	—	A,B,C
Terpinen-1-ol	1146	—	95	—	0.05	—	A,B,C
Isopulegol	1150	1140	79	97	0.05	1.58	A,B,C <sup>b)</sup>
Pinocarvone	1160	—	69	—	0.08	—	A,B,C <sup>b)</sup>
Citronellal	—	1150	—	98	—	7.08	A,B,C <sup>a)</sup> *
Terpinen-4-ol	1178	1180	97	83	8.68	0.52	A,B,C*
Cryptone	1190	1190	94	69	1.71	8.51	A,B,C
( <i>E</i> )-Dihydrocarvone	—	1207	—	99	—	0.83	A,B,C <sup>c)</sup>
Neral	—	1215	—	59	—	0.08	A,B,C
$\alpha$ -Terpineol	1198	—	91	—	2.19	—	A,B,C
Octanoic acid	1221	—	91	—	0.66	—	A,B
Cuminal	1235	1230	97	95	0.97	6.21	A,B,C
Citronellol	—	1235	—	83	—	1.17	A,B,C
Piperitone	1257	1250	96	96	13.48	4.43	A,B,C <sup>c)</sup>
Geraniol	—	1258	—	94	—	2.36	A,B,C
Phellandral	1268	1270	94	94	0.47	5.21	A,B,C
Chrysanthenone	—	1274	—	78	—	1.81	A,B,C
2-Hydroxy piperitone	—	1280	—	86	—	0.46	A,B
Geranial	—	1285	—	86	—	0.83	A,B,C
( <i>E</i> )-Anethole	1281	—	95	—	0.64	—	A,B,C
Cuminol	—	1292	—	97	—	3.18	A,B
Safrole	1283	—	96	—	0.65	—	A,B,C
Thymol	1285	—	93	—	0.08	—	A,B
Nonanoic acid	1298	1298	96	93	0.07	0.42	A,B,C

Table 2. Continued

Compounds	RI <sup>1)</sup>	RI <sup>2)</sup>	QA% <sup>3)</sup>	QA% <sup>4)</sup>	PA% <sup>5)</sup>	PA% <sup>6)</sup>	Method of ID <sup>7)</sup>
$\alpha$ -Terpinyl acetate	1320	1336	91	91	1.82	0.81	A,B
Eugenol	1346	—	98	—	0.04	—	A,B,C
Neryl acetate	1350	—	91	—	0.13	—	A,B
Citronellyl acetate	—	1354	—	95	—	3.18	A,B,C <sup>a)</sup>
$\alpha$ -Copaene	1377	—	98	—	0.57	—	A,B,C
Geranyl acetate	1386	1386	91	91	0.60	15.33	A,B,C <sup>c)</sup>
$\beta$ -Elemene	1390	—	99	—	0.16	—	A,B,C
Tetradecane	1400	—	96	—	0.02	—	A,B
<i>cis</i> -Geranyl acetate	—	1426	—	59	—	0.08	A,B
$\beta$ -Caryophyllene	1428	1430	90	90	0.25	0.03	A,B,C
Cuminyl acetate	1436	—	86	—	0.01	—	A,B,C
Cinnamyl acetate	—	1439	—	95	—	0.05	A,B
$\alpha$ -Humulene	1450	1450	97	69	0.08	0.04	A,B,C
Geranyl acetone	1452	—	93	—	0.02	—	A,B,C
Aromadendrene	1456	—	99	—	0.05	—	A,B,C
$\alpha$ -Amorphene	1478	—	97	—	0.15	—	A,B,C
$\beta$ -Selinene	1483	—	99	—	0.18	—	A,B,C
$\alpha$ -Curcumene	—	1492	—	81	—	0.04	A,B,C
$\alpha$ -Selinene	1495	—	99	—	0.16	—	A,B,C
$\alpha$ -Campholene aldehyde	—	1498	—	64	—	0.08	A,B
$\alpha$ -Muurolene	1501	—	97	—	0.19	—	A,B,C
$\delta$ -Cadinene	1530	1530	98	98	0.08	0.08	A,B,C
Calacorene	—	1547	—	64	—	0.04	A,B,C
Nerolidol	1560	1560	91	69	0.04	0.02	A,B,C
Spathulenol	1578	1578	96	91	0.17	0.03	A,B,C
Caryophyllene oxide	—	1590	—	95	—	0.09	A,B,C
Calarene	—	1635	—	83	—	0.04	A,B
T-Muurolol	1650	1650	92	90	0.11	0.03	A,B,C
Methyl palmitate	—	1881	—	98	—	0.50	A,B
Hexadecanoic acid	—	1898	—	85	—	0.54	A,B,C
2-Nonadecene	—	1900	—	69	—	1.10	A,B,C
Olate methyl ester	—	1995	—	94	—	0.34	A,B

<sup>1)</sup>Retention indices (RI) were determined by using n-alkanes (C<sub>8</sub>-C<sub>22</sub>) as external references. RI of *Z. piperitum* A.P. DC. produced in China. <sup>2)</sup>RI of *Z. piperitum* A.P. DC. produced in Korea. <sup>3)</sup>QA means quality% of the MS data (n=3) of *Z. piperitum* A.P. DC. produced in China. <sup>4)</sup>Quality% of the MS data (n=3) of *Z. piperitum* A.P. DC. produced in Korea. <sup>5)</sup>PA means peak area %; average of the relative percentage of the peak area in the MS total ion chromatogram (n=3) of *Z. piperitum* A.P. DC. in China. <sup>6)</sup>Average of the relative percentage of the peak area in the MS total ion chromatogram (n=3) of *Z. piperitum* A.P. DC. from Korea. <sup>7)</sup>Method of identification based on reference no. 14, 15. A, retention time; B, tentative identification index was performed as follows: Mass spectrum (MS) was identical with that of Wiley mass spectral database (2001, Hewlett Packard Co., Palo Alto, USA); C, retention index was consistent with that of the literature (14-18). <sup>a)</sup>Identification based on reference no. 16. <sup>b)</sup>Identification based on reference no. 17. <sup>c)</sup>Identification based on reference no. 18. <sup>\*</sup>Identification based on co-injection with authentic compounds (Acros, Sigma-Aldrich, USA).

hydrocarbon, 6 aldehydes, 2 esters, 5 ketones, 1 alcohol and 2 carboxylic acids which tentatively characterized from its oil. Identified compounds constituted 94.78% and unidentified compounds constituted 5.22% of the total peak area. There were terpene compounds in the essential oil of *Z. piperitum* A.P. DC., including 33 monoterpene compounds [ $\alpha$ -thujene,  $\alpha$ -pinene,  $\beta$ -pinene,  $\beta$ -phellandrene,  $\beta$ -myrcene,  $\alpha$ -terpinene, limonene, (*E*)- $\beta$ -ocimene,  $\gamma$ -terpinene, 3,8-menthadiene, *cis*-linlool oxide, perillene, linalool, rose oxide, *cis*-rose oxide, (*E*)-limonene oxide, dehydro-*p*-cymene, isopulegol, citronellal, terpine-4-ol,

chrysanthenone, cuminal, citronellol, geraniol, phellandral, geranial, neral, *p*-cymen-7-ol,  $\alpha$ -terpinyl acetate, citronellyl acetate, cinnamyl acetate, geranyl acetate and *cis*-geranyl acetate (76.71%)], and 10 sesquiterpenes [ $\beta$ -caryophyllene, humulene, caryophyllene oxide,  $\delta$ -cadinene, calacorene, nerolidol, spathulenol,  $\alpha$ -curcumene, calarene and T-muurolol (0.44%)]. Terpenoids (monoterpene and sesquiterpene, mainly) are the most important components of the plant aroma (8). Among them, limonene (18.04%), belonging to the monoterpenes, was the most abundant compound of the essential oil from *Z. piper-*

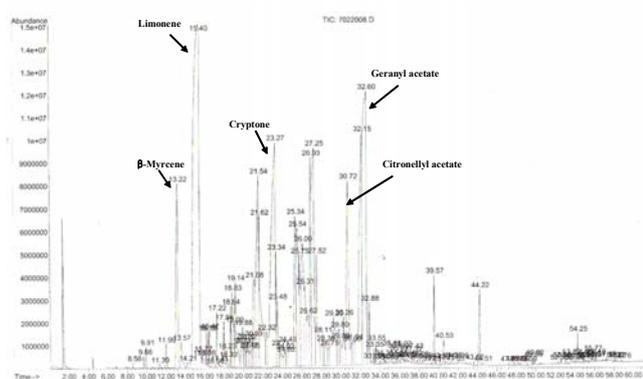
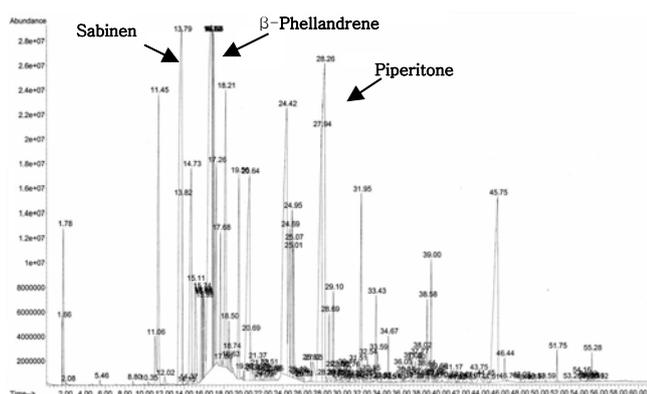
**Table 3.** Relative composition by functional group of *Z. piperitum* A.P. DC.

Functional group	No. of peak		% of peak area <sup>1)</sup>	
	I <sup>2)</sup>	II <sup>3)</sup>	I <sup>2)</sup>	II <sup>3)</sup>
Terpene	43	44	77.15	71.17
Hydrocarbon	1	1	1.10	0.02
Aldehyde	6	2	0.48	0.07
Ester	2	1	0.84	0.04
Alcohol	1	—	0.01	—
Ketone	5	4	14.24	15.31
Acid	2	2	0.96	0.73
Total	60	54	94.78	87.34

<sup>1)</sup>Average (n=3) of the relative percentage of the peak area in the MS total ion chromatogram.

<sup>2)</sup>Essential oil of *Z. piperitum* A.P. DC. produced in Korea.

<sup>3)</sup>Essential oil of *Z. piperitum* A.P. DC. produced in China.

**Fig. 1.** GC/MS chromatogram of *Z. piperitum* A.P. DC. oil from Korea.**Fig. 2.** GC/MS chromatogram of *Z. piperitum* A.P. DC. oil from China.

*itum* A.P. DC., and described as having a warm and woody flavor (19). This compound was found in the essential oil from *Citrus limon* Burmann belonging to the *Rutaceae* plants, as the predominant volatile flavor compound accounting for 68.50% (20). And also detected in *Aedes aegypt* (37.99%), and reported to have insect repellent activity (21). Limonene has also studied for an-

timicrobial activities and physico-chemical properties as a component of the essential oil from *Amomum subulatum*. In addition, limonene has reported to have hypoglycemic, antimicrobial, and antioxidant activities (22). As the most abundant component in *Z. piperitum* A.P. DC., limonene's several bioactivities and physico-functional properties would make the essential oil a beneficial, highly valuable, and worthwhile compound for industrial and medicinal purposes. One of the monoterpenoid, chrysanthenone was not found in *Z. piperitum* A.P. DC. produced in China, and this compound was among the three major constituents [chrysanthenone,  $\alpha$ -pinene and 1,8- cineol (>9%)] of volatile flavor compounds from *Chrysanthemum indicum* L. produced in Korea (23). In addition, this volatile aroma compound was also detected *Anthemis wiedemanniana* essential oil produced in Turkey, and it has also been reported to possess antimicrobial effects (24). It is noteworthy that this volatile flavor compound in *Z. piperitum* A.P. DC. would be a useful and beneficial material for their physico-chemical and bio-medicinal activity. There was 1 alcohol compound (0.01%) in *Z. piperitum* A.P. DC. distilled oil, 3-methylcyclopentanol. Ester compounds (0.84%) with methyl palmitate and oleic acid methyl ester, and 6 aldehydes (0.48%) including hexanal, heptanal, benzaldehyde, 2,6-dimethyl-5-haptanal, octanal and  $\alpha$ -campholene aldehyde were detected by GC/MS, and also found 5 ketone compounds (14.24%) with cryptone, (*E*)-dihydrocarvone, piperitone, 2-heptanone and 2-hydroxy piperiton. Among them, cryptone was described as having citrus, cucumber, and fatty flavors in the report (19).

#### Volatile flavor components of *Z. piperitum* A.P. DC. in China

The yield of essential oil from *Z. piperitum* A.P. DC. was 1.2% (w/w) (12 g of the oil/1 kg of the materials, dry basis unit) and the color of the oil was strong yellow. As shown in Tables 2 and 3, of the 54 compounds representing 87.34% of the total from Chinese *Z. piperitum* A.P. DC., there were 44 terpenes, 1 hydrocarbon, 2 aldehydes, 1 ester, 4 ketones and 2 carboxylic acids were tentatively identified. Among them, piperitone (*p*-menth-1-en-3-one) (13.48%) was the most abundant compound, and  $\beta$ -phellandrene (10.90%), sabinene (9.51%), terpinen-4-ol (8.68%) and linalool (5.54%) were the next most abundant (>5%). Piperitone, a member of the ketones, has a powerful fresh-minty-camphoraceous odor and is commonly used in flavor compositions, especially in spice blends with caraway and estragon (19). There were terpene compounds *Z. piperitum* A.P. DC. oil from China, with 31 monoterpene [ $\alpha$ -thujene,  $\alpha$ -pinene,

camphen, sabinene,  $\beta$ -pinene,  $\alpha$ -phellandrene,  $\beta$ -myrcene,  $\alpha$ -terpinene,  $\beta$ -phellandrene,  $\beta$ -terpinene, (*E*)- $\beta$ -ocimene,  $\gamma$ -terpinene, (*E*)-sabinene hydrate, dehydro-*p*-cymene, linalool, terpine-1-ol, terpinolene, isopulegol, terpine-4-ol,  $\alpha$ -terpineol, (*E*)-anethole, phellandral, cuminal, safrole, thymol,  $\alpha$ -terpinyl acetate, eugenol, cuminyl acetate, geranyl acetone, neryl acetate and geranyl acetate (68.98%), and 13 sesquiterpenes [ $\alpha$ -copaene,  $\beta$ -caryophyllene,  $\beta$ -elemene,  $\alpha$ -humulene,  $\delta$ -cadinene,  $\alpha$ -amorphene,  $\beta$ -selinene,  $\alpha$ -selinene, nerolidol,  $\alpha$ -muurolene, aromadendrene, spathulenol and T-muurolol (2.19%)]. There was 1 ester compound (isomyl acetate, 0.04%), and aldehydes compounds including hexanal and (*E,E*)-2,4-hexadienal taking up 0.07% were detected. There were also 4 ketone compounds (15.31%), pino-carvone, camphor, cryptone and piperitone; and 2 carboxylic acids, octanoic acid and nonanoic acid (0.73%). Some differences were observed in the composition of the essential oils of *Z. piperitum* A.P. DC the country of origin. In the volatile compounds of those from Korea and China, terpenes were predominant class of compounds with a ratio of 77.15% and 71.17%, respectively. Hexanal,  $\alpha$ -thujene,  $\alpha$ -pinene,  $\beta$ -pinene,  $\beta$ -myrcene,  $\alpha$ -phellandrene,  $\alpha$ -terpinene, (*E*)- $\beta$ -ocimene,  $\gamma$ -terpinene, linalool, dehydro *p*-cymene, isopulegol, terpinen-4-ol, cryptone, cuminal, phellandral, nonanoic acid,  $\alpha$ -terpinyl acetate, nerolidol, geranyl acetate,  $\beta$ -caryophyllen,  $\alpha$ -humulene,  $\delta$ -cadinene, spathulenol and T-muurolol were found to be common volatile flavor compounds *Z. piperitum* A.P. DC. from both Korea and China. Citronellal (7.08% in Korean oil but not detected in Chinese) and isopulegol (1.58% in Korean, 0.05% in Chinese, respectively) were also characterized. A monoterpene alcohol, isopulegol is widely used in the flavor industry for the production of fragrances with blossom notes (19), and is an important ingredient in various pharmaceuticals. It has been reported that isopulegol could be obtained from citronellal through cyclization (25).  $\beta$ -Phellandrene (10.90%) was the second abundant volatile flavor compound of *Z. piperitum* A.P. DC. from China. Nevertheless it was not found in *Z. piperitum* A.P. DC. produced from Korea. Limonene (18.04%) was the most volatile flavor compound of *Z. piperitum* A.P. DC. produced in Korea, however it was not detected from Chinese. A monoterpene acetate, geranyl acetate (3,7-dimethyl-2,6-octadiene-1-ol acetate) (15.33% in Korea, 0.60% in China), is a natural constituent of more than 60 essential oils including Ceylon citronella, palmarosa, lemon grass, geranium, coriander, carrot and saffras. Geraniol (2.36% in Korean, not detected in Chinese), generated from geranyl acetate by

geranyl acetate esterase, has been reported to possess *in vitro* and *in vivo* anti tumor activity (26). Geranyl acetate was described as having a sweet rose aroma (19), and present in *Z. piperitum* A.P. DC. from both Korea and China. In particular, it was abundant in *Z. piperitum* A.P. DC. produced in Korea. Our experimental results show that the quality and functional groups of oils from Korean *Z. piperitum* A.P. DC. seemed to be superior to that of Chinese, and suggests a plausible reason for preferential utilization of the essential oil from *Z. piperitum* A.P. DC. produced in Korea for specific purposes. In summary, *Z. piperitum* A.P. DC. produced in Korea contains more volatile flavor compounds and larger peak area % of total peak area than that produced in China. We tentatively identified sixty and fifty-four volatile flavor compounds, which accounted for 94.78% and 87.34% of the total peak area, respectively. The yields of the essential oils produced in Korea and China were 2.0% (w/w) and 1.2% (w/w), respectively. The main compounds of *Z. piperitum* A.P. DC. oils from Korea and China were limonene (18.04%), geranyl acetate (15.33%), piperiton (13.48%) and  $\beta$ -pellandrene (10.90%).

#### ACKNOWLEDGEMENT

The author thanks Professors Mi-Soon Lee and Young-Keun Chung for their valuable encouragement and excellent advice. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-005-J13001).

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(Received January 10, 2008; Accepted March 6, 2008)