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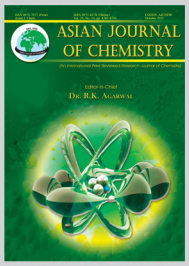

GC-MS Analysis of the Essential Oil and Petroleum Ether Extract of Different Regions of Korean Ginger (*Zingiber officinale*) and Antioxidant Activity

ILL-MIN CHUNG, NAGELLA PRAVEEN, SUN-JIN KIM and ATEEQUE AHMAD*

Department of Applied Life Science, Konkuk University, Seoul 143-701, South Korea

*Corresponding author: Fax: +82 24467856; Tel: +82 2 5503730; E-mail: ateeque97@gmail.com

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The composition of the rhizomes of *Zingiber officinale* essential oil and petroleum ether extract of two different regions of Korea namely Busan and Youngam were examined by gas chromatographic-mass spectroscopic analysis (GC-MS). The essential oil yield (mL/100 g dry weight) were 0.40 (Busan region) and 0.60 % (Youngam region), respectively. Thirty seven and thirty five compounds comprising 98.72 and 80.34 % of the total peak area were identified in the Busan and Youngam regions, respectively. The common major components of essentials oils in these two regions are camphene (18.32, 14.08 %), α-phellandrene (8.83, 5.21 %), bicyclo[3.1.0]hexan-2-ol 2-methyl-5-(1-methyl ethyl)-1α,2α,5α- (2.10, 12.68 %), zingiberene (6.68, 11.15 %), zingiberenol (1.71, 1.05 %), linalool (4.11, 2.25 %), Z-citral (1.81, 3.73 %), α-farnesene (6.72, 2.98), geraniol (7.61, 3.26 %). Forty compounds each comprising 100.00, 99.99 % of the total peak area were identified in Busan and Youngam regions varieties of ginger, respectively of petroleum ether extract. The common major constituents are sabinene (5.91, 2.30 %), borneol (3.26, 2.97 %), 3-cyclohexene-1-methanol α,α-trimethyl (2.50, 2.54 %), geraniol (6.35, 7.98 %), 2,6-octadienal 3,7-dimethyl (12.63, 13.19 %), 2,6-octadien-1-ol 3,7-dimethyl acetate (6.94, 8.68 %), bicyclo[3.1.1]hept-2-ene 2,6-dimethyl-6-(4-methyl-3-petenyl)-(23.18, 18.56 %), naphthalene 1,2,4α,5,6,8α-hexahydro-4,7-dimethyl-1-(1-methylethyl)-(8.10, 9.73 %), α-sesquiphellandrene (10.11, 12.48 %), nerolidol (1.46, 2.74 %). The essential oil and hexane extract from two varieties of ginger was investigated for scavenging of the diphenylpicrylhydrazyl (DPPH) radical activity and the results demonstrate that the hexane extract is more potential than the essential oil from the ginger as a natural antioxidant and thus inhibit undesired oxidation process.

Key Words: *Zingiber officinale*, Zingiberaceae, Essential oils, Antioxidant activity.

INTRODUCTION

Ginger, one of the most important spices in the world, is known for its medicinal and flavoring potentials. The medicinal properties are attributed to its spicy, pungent constituents, mainly gingerols, which stimulate the thermoregulatory receptors[1]. This inflammation influences stomach and bile secretion by reflex action[2]. The volatile components give peculiar aromatic smell. Wide application of the oil in the food and cosmetic industries and the existence of many varieties have led to many studies of the oil. Although the variety and age of the rhizome at harvest and distillation affect the yield and composition of the essential oil and hence its flavor[3]. More useful references are available on ginger composition[4,5]. West African gingers, known for their stronger, more pungent and coarser flavors[3,6]. Volatile aromatic components of ginger (*Zingiber officinale* Roscoe) rhizomes from Korea also reported[7].

Although the substantial data of its chemical composition is available, there are no complete previous essential oil reports that have been recorded for *Z. officinale* from Korea. In the present work, we investigated the chemical composition of the volatile oil and for the first time petroleum ether extract extracted from Korean ginger rhizomes of two different regions. The essential oil and hexane extract from two varieties of ginger was investigated for scavenging of the diphenylpicrylhydrazyl (DPPH) radical activity. The main aim of this study was therefore to determine the main constituents of the essential oil, especially petroleum ether extract growing in Korean regions and to evaluate the antioxidant activity of both oils and petroleum ether extract.

EXPERIMENTAL

Domestic ginger rhizomes were purchased from the local market in Seoul, Korea in November 2010.

Essential oil isolation: The rhizomes of both regions *i.e.*, Busan region and Youngam region, *Z. officinale* (500 g) after crushing were subjected to hydro-distillation in Clevenger-type apparatus for a minimum of 5 h. The resulting essential oils were obtained in a yield of 0.40 and 0.60 %, respectively w/w after drying over anhydrous sodium sulphate and stored at 4 ºC until use.

GC-MS analysis of essential oil: Samples of essential oil were diluted in hexane (spectroscopic grade) and analyzed in a Finnigan Focus GC/ Finnigan Focus DSQ MS system (Thermo Co., Germany) apparatus equipped with VB-WAX bonded PEG capillary column (30 m × 0.25 mm internal diameter, 0.25 μm film thickness). Helium (1 mL/min) was used as a carrier gas. Sample volume was injected in the split mode 10 μL (split less). The injector was kept at 150 ºC. The column was maintained at 50 ºC for 10 min and then programmed to 200 ºC at 2 ºC and held for 0.5 h at 200 ºC. Detector temperature was held at 250 ºC. The MS was operated in EI mode at 70 eV in the m/z range 25-350. The identification of the compounds was performed by matching their recorded mass spectra of the GC-MS data system. Quantitative data

TABLE-1
COMPOSITION OF KOREAN *Zingiber officinale* RHIZOMES ESSENTIAL OIL FROM TWO DIFFERENT REGIONS

RT	Compounds	Busan region (%)	Youngam region (%)
3.63	α-Pinene	1.47	–
4.24	Camphene	18.32	14.08
7.11	α-Phellandrene	8.83	5.21
7.29	α-Myrcene	–	1.23
7.31	Sabinene	4.28	–
7.65	α-Terpinolene	–	0.60
8.47	dl-Limonene	–	0.88
8.96	Bicyclo[3.1.0]hexan-2-ol, 2-methyl-5-(1-methyl ethyl)-(1α,2α,5α)-	2.10	12.68
12.66	Benzene 1-methyl-3-(1-methylethyl)-	–	0.58
13.38	(+)-4-Carene	–	0.65
13.50	α-Humulene	0.89	–
14.34	Octanal	0.40	0.37
17.55	6-Methyl-5-hepten-2-one	0.96	0.88
20.83	2-Nonanone	0.39	–
26.58	1*H*-3α,7-Methanoazulene-2,3,4,7,8α-hexahydro-3,6,8,8-tetramethyl-	0.54	–
30.82	Cyclohexanol 5-methyl-2-(1-methylethenyl)-	–	0.56
31.73	Linalool	4.11	2.25
32.29	Bicyclo[2.2.1]heptan-2-ol,1,7,7-trimethyl acetate	1.21	0.90
33.15	Cyclohexanemethanol 4-ethenyl α, 4α-trimethyl-3-(1-methylethenyl)-, [1R-(1α,3α,4α)]-	0.42	–
33.64	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-	0.52	–
34.25	2-Undecanone	1.37	–
38.40	2,6-Octadienal, 3,7-dimethyl-, (Z)-	1.31	0.74
38.69	z-Citral	1.81	3.73
38.85	α-Himachalene	–	0.82
39.28	δ-Elemene	–	4.23
39.62	1*H*-Cyclopropa[α]naphthalene, decahydro-1,1,3α-trimethyl-7-methylene	–	0.86
39.65	1-Naphthalenol, 1,2,3,4,4α,7,8,8α-octahydro-1,6-dimethyl-4-(1-methylethyl)-	4.72	–
41.87	Zingiberene	6.68	11.15
41.99	δ-Cadinene	–	1.45
42.29	α-Bisabolene	0.93	–
43.72	α-Farnesene	6.72	2.98
44.32	Naphthalene, 1,2,3,4,4α,5,6,8α,octahydro-7-methyl-4-methylene-1-(1-methylethyl)-	9.76	1.40
44.52	Benzene 1-(1,5-dimethyl-4-hexenyl)-4-methyl	–	1.90
44.72	α-Citronellol	–	0.39
45.59	Germacrene B	1.48	–
46.39	*cis-p*-Mentha-2,8-diene-1-ol	0.72	0.40
48.22	Geraniol	7.61	3.26
51.45	1-Hydroxy-1,7-dimethyl-4-isopropyl-2,7-cyclodecadiene	0.40	–
54.36	Khusinol	0.64	0.34
54.86	Ledol	0.63	–
57.40	Nerolidol	1.11	0.82
58.44	Cyclohexanemethanol 4-ethenyl-α, 4α-trimethyl-3-(1-methylethenyl)-	1.76	1.11
59.54	Sesquisabinene hydrate	1.05	0.49
60.11	Zingiberenol	1.71	1.05
62.40	1-Hydroxy-1,7-dimethyl-4-isopropyl-2,7-cyclodecadiene	0.53	–
63.92	α-Eudesmol	–	0.32
64.34	2-Naphthalenemethanol decahydro-α,α,4α-trimethyl-8-methylene	0.81	1.01
65.16	Isoaromadendrene epoxide	0.85	–
65.45	Neoclovene oxide	–	0.51
67.53	3α(1*H*)-azulenol 2,3,4,5,8,8α-hexahydro-6,8α-dimethyl-3-(1-methylethyl)-	1.11	0.51
68.35	Carotol	0.57	–

–: Not present.

TABLE-2
COMPOSITION OF KOREAN *Zingiber officinale* RHIZOMES PETROLEUM ETHER EXTRACT FROM TWO DIFFERENT REGIONS

RT	Compounds	Busan region (%)	Youngam region (%)
4.41	3-Carene	0.74	0.29
4.66	Camphene	2.18	0.59
4.95	α-Myrcene	0.52	0.20
5.18	l-Phellandrene	0.35	–
5.47	Sabinene	5.91	2.30
5.59	1,8-Cineole	2.57	1.03
5.99	(+)-4-Carene	0.44	–
6.11	Linalool	0.99	0.90
6.36	Bicyclo[3.1.1]hept-3-en-2-ol,4,6,6-trimethyl-[1s-(1α,2α,5α-)]	0.21	0.19
6.44	α-Terpineol	0.11	0.10
6.58	*trans*-2-Pinanol	0.17	0.13
6.66	6-Octenal 3,7-dimethyl	–	0.15
6.74	Tridecane	0.75	–
6.90	6-Dodecanol acetate	0.45	–
7.00	Borneol	3.26	2.97
7.15	3-Cyclohexene-1-methanol α,α,4-trimethyl-	2.50	2.54
7.30	Nerol	0.50	0.48
7.53	Geraniol	6.35	7.98
7.62	2,6-Octadienal 3,7-dimethyl	1.78	–
7.75	Bicyclo[2.1.1]heptan-2-ol, 1,7,7-trimethyl-acetate	1.13	–
7.89	2,6-Octadienal 3,7-dimethyl	12.63	13.19
8.09	u.i.	0.17	0.18
8.19	1,4-Methano-1*H*-indene octahydro-4-methyl-8-methylene-7-(1-methylethyl)-	0.34	–
8.23	Cedrene	–	0.42
8.49	2,6-Octadien-1-ol,3,7-dimethyl acetate	6.94	8.68
8.60	1,6,10-Dodecatriene 7,11,-dimethyl-3-methylene	0.48	0.61
8.74	(+)-α-Funebrene	0.34	0.40
9.21	Bicyclo[3.1.1]hept-2-ene 2,6-dimethyl-6-(4-methyl-3-petenyl)-	23.18	18.56
9.31	Naphthalene 1,2,4α,5,6,8α-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	8.10	9.73
9.56	α-Sesquiphellandrene	10.11	12.48
9.87	Naphthalene 1,2,3,4α,5,6,8α-hexahydro-4α,8-dimethyl-2-(1-methylethylidene)-	0.22	0.35
10.05	Nerolidol	1.46	2.74
10.32	Phenol 2-methyl-4-(1-propenyl)-	0.28	–
10.45	α-Guaiene	0.75	–
10.47	Aromadendrene oxide	–	1.22
10.66	Sesqusabinene hydrate	0.59	1.16
10.92	Zingiberenol	1.20	2.15
11.28	Cubenol	0.42	0.87
11.55	1-Hydroxy-1,7-dimethyl-4-isopropyl-2,7-cyclodecadiene	0.26	0.53
11.65	10-epi-δ-Eudesmol	0.23	0.44
11.92	Epiglobulol	–	0.44
12.17	Ledene oxide-(I)	0.61	–
12.19	Diepicedrene-1-oxide	–	1.17
12.30	3α(1*H*)-azulenol2,3,4,5,8,8α-hexahydro-6,8α-dimethyl-3-(1-methylethyl)-	0.62	1.52
12.64	Viridifloral	–	0.31
13.01	Carotol	–	0.43
13.43	2,6,10-Dodecatrienal, 3,7,11-trimethyl	0.16	0.47
13.94	6-(*p*-Tolyl)-2-methyl-2-heptanol	–	0.23
15.75	Spiro[4.5]decan-7-one dimethyl-8,9-epoxy-4-isopropyl	–	1.39
16.36	Diepicedrene-1-oxide α-D-mannofuranoside farnesyl	–	0.47

–: Not present.

were obtained from electronic integration peak areas and comparing their retention time and mass spectra library with those found in the literature and supplemented by the Wiley (Wiley 7th Mass Spectral Library) & NIST MS Search 2.0 (National Institute of Standards and Technology) GC-MS libraries.

Preparation of petroleum ether extract: The rhizomes of *Z. officinale* (250 g) each after drying in oven at 45 ºC for 4 h, after crushing immersed in petroleum ether (500 mL, 35-60 ºC) for overnight at room temperature and then the supernatant was concentrated under vacuum to yield (1.25, 1.78 g) of the extract, respectively, which was small sample dissolved in hexane (spectroscopic grade) and prepare sample after filtration for GC-MS analysis.

GC-MS analysis of petroleum ether extract: Samples of petroleum ether extract were diluted in hexane (spectroscopic grade) and analyzed in a Finnigan Focus GC/Finnigan Focus DSQ MS system (Thermo Co., Germany) apparatus

equipped with Vesteck rtx-50 capillary column (30 m × 0.25 mm internal diameter, 0.25 μm film thickness). The other conditions are same as in case of essential oil.

DPPH$^-$ radical-scavenging activity: The antioxidant activity of the both varieties of ginger essential oil and hexane extract based on the scavenging activity of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH$^-$) free radical, was determined by the method described[8]. The different concentrations (50 and 100 μg) of the tested samples (0.05 mL; extracts and tocopherol) were taken in different test tubes with 4 mL of a 0.006 % MeOH solution of DPPH$^-$. Water (0.05 mL) in place of the oil was used as control. Absorbance at 517 nm was determined after 0.5 h. Radical scavenging activity was expressed as the inhibition percentage and was calculated using the following formula, radical scavenging activity (%) = $[(A_0 - A_1)/A_0] \times 100$, where A_0 is the absorbance of the control and A_1 is the absorbance of the extract/standard.

RESULTS AND DISCUSSION

Chemical constituents of essential oil: The constituents identified by GC-MS analysis in order of elution of VB-WAX bonded capillary column are presented in Table-1. The common major components of essentials oils in these two regions are camphene (18.32, 14.08 %), α-phellandrene (8.83, 5.21 %), bicyclo[3.1.0]hexan-2-ol 2-methyl-5-(1-methyl ethyl)-1α,2α,5α- (2.10, 12.68 %), zingiberene (6.68, 11.15 %), zingiberenol (1.71, 1.05 %), linalool (4.11, 2.25 %), z-citral (1.81, 3.73 %), α-farnesene (6.72, 2.98 %), geraniol (7.61, 3.26 %), naphthalene 1,2,3,4,4α,5,6,8α,octahydro-7-methyl-4-methylene-1-(1-methylethyl)-(9.76, 1.40 %). However, the comparison of present results which shows some qualitative and quantitative differences in the composition of ginger oil. The identification of the compounds was performed by matching their recorded mass spectra of the GC-MS data system. Quantitative data were obtained from electronic integration peak areas and comparing their retention time and mass spectra library with those found in the literature and supplemented library. Other methods of identification and took help of by comparing mass data with data of library[9,10].

Chemical constituents of petroleum ether extract: The constituents identified by GC-MS analysis in order of elution of Vesteck rtf-50 capillary column are presented in Table-2. The common major constituents are sabinene (5.91, 2.30 %), borneol (3.26, 2.97 %), 3-cyclohexene-1-methanol α,α-trimethyl (2.50, 2.54 %), geraniol (6.35, 7.98 %), 2,6-octadienal 3,7-dimethyl (12.63, 13.19 %), 2,6-octadien-1-ol 3,7-dimethyl acetate (6.94, 8.68 %), bicyclo[3.1.1]hept-2-ene 2,6-dimethyl-6-(4-methyl-3-petenyl)- (23.18, 18.56 %), naphthalene 1,2,4α,5,6,8α-hexahydro-4,7-dimethyl-1-(1-methylethyl)-(8.10, 9.73 %), α-sesquiphellandrene (10.11, 12.48 %), nerolidol (1.46, 2.74 %). This is the first report of identified components in petroleum ether extract of ginger rhizomes.

DPPH$^-$ radical-scavenging activity: The free radical-scavenging activity of the ginger essential oil and hexane extract was tested through DPPH$^-$ method[8] and the results were compared with tocopherol. DPPH is usually used as a substrate to evaluate antioxidative activity of antioxidants. The method is based on the reduction of methanolic DPPH$^-$ solution in the presence of a hydrogen donating antioxidant, due to the formation of the non-radical form DPPH-H by the reaction. The hexane extract and essential oil was able to reduce the stable radical DPPH$^-$ to the yellow-coloured diphenylpicrylhydrazine. It has been found that cysteine, glutathione, ascorbic acid, tocopherol, polyhydroxy aromatic compounds (*e.g.*, hydroquinone, pyrogallol, gallic acid) and aromatic amines (*e.g.*, *p*-phenylene diamine, *p*-aminophenol), reduce and decolorize 1,1-diphenyl-2-picrylhydrazyl by their hydrogen donating ability[11]. In this study essential oil and hexane extract from ginger also showed a remarkable antioxidant activity, one of the possible mechanisms is polyphenolic-associated compounds (formation of non-extractable complex between high molecular weight phenolics and polysaccharides). Those kinds of phenolic compounds show antioxidant activity due to their redox properties, which play an important role in absorbing and neutralizing free radicals, quenching singlet and triple oxygen or decomposing peroxide. The essential oil and hexane extract exhibited a concentration-dependent antiradical activity by inhibiting DPPH$^-$ radical, the hexane extract is more potential than the essential oil from the two ginger varieties (Table-3). The essential oil and hexane extract concentration of 100 μg exhibited good free radical scavenging activities *i.e.*, above 80 %, the activity increased with increasing concentration. The DPPH activity of tocopherol showed higher degree of free radical-scavenging activity than that of the extracts at each concentration points. Similar to our results Bozin *et al.*[12] reported that lower concentration of rosemary and sage essential oils exhibited highest antioxidant activity. Yin *et al.*[13] reported that organosulfur compounds derived from the ginger extract exhibited non-enzymatic antioxidant activity. Anahi Dandlen *et al.*[14] also reported that higher concentration of essential oil from thyme species exhibited highest antioxidant activity.

TABLE-3
ANTIOXIDANT ACTIVITY OF EXTRACTS FROM TWO VARIETIES OF GINGER MEASURED AS PERCENTAGE INHIBITION OF DPPH RADICAL

Sample	Inhibition (%)	
	50 (μg)	100 (μg)
Ginger essential oil (Variety 1)	85.1	86.7
Ginger essential oil (Variety 2)	90.1	91.6
Ginger hexane extract (Variety 1)	90.3	95.4
Ginger hexane extract (Variety 2)	88.6	92.8

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