Discrimination of Ginseng Habitat by Using Instrumental Analysis Techniques

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Abstract

In order to screen out indicators for the discrimination of ginseng habitat, some physical and chemical characteristics of Korean red ginsengs (94 kinds) and Chinese red ginsengs (50 kinds) were analyzed by using a rheometer, an electronic nose system, a combined technique of solid phase micro-extraction (SPME) and gas chromatograph equipped with an electron capture detector (GC/ECD), an X-ray fluorescence spectrometer (XRF), an inductively coupled plasma mass spectrometer (ICP/MS), a near infrared spectrometer (NIRs) and high performance liquid chromatography equipped with evaporative light scattering detector (HPLC/ELSD). The results are summarized as follows: (i) The rhizome strengths of Korean red ginsengs were significantly higher than those of Chinese red ginsengs. (ii) The electronic nose patterns of Korean red ginsengs were significantly different from those of Chinese red ginsengs. (iii) Some unidentified peaks were detected not in the headspace of Korean red ginsengs but in the headspace of Chinese red ginsengs when the headspace volatiles prepared by the SPME technique were analyzed by GC/ECD. (iv) Either the content ratios of K to Ca or Mn to Fe were significantly different between Korean red ginsengs and Chinese red ginsengs. (v) The reflectance ratios of NIRs wavenumbers such as 904 cm^{-1} to 1088 cm^{-1} for Korean red ginsengs were significantly different from those for Chinese red ginsengs. (vi) The content ratios of ginsenoside-Rg to ginsenoside-Re of Korean red ginsengs were significantly higher than those of Chinese red ginsengs. These results indicate that the rhizome strength, the electronic nose pattern, the occurrence of ECD-sensitive headspace volatile components, the content ratios of K to Ca and Mn to Fe, the NIRs pattern and the content ratio of ginsenoside-Rg_1 to -Re may be indicators for the discrimination of ginseng habitat.

Key words : Ginseng habitat, discrimination, rhizome strength, electronic nose pattern, SPME,

GC/ECD, inorganic elements, NIRs, HPLC/ELSD

Introduction

Ginseng is cultivated in Northeast of Asia. Korea and China are two chief countries in which much ginseng is cultivated and is also consumed. In Korea, more than 10,000 M/T of fresh ginseng has been produced every year since 1990 and the yearly production of fresh ginseng in China is thought to be almost the same as that in Korea [1]. Fresh ginseng is primarily processed to white ginseng and red ginseng, which are further processed to various kinds of ginseng products such as powder, extract, tea and drink. A large quantity of Korean ginseng and ginseng products has been exported to Hong Kong, Taiwan and Japan for the past few decades and they just began to be distributed in China since 2001 [2]. Chinese ginseng and ginseng products has also been being distributed in Hong Kong, Taiwan and Japan as well as in China, and recently, they also began to be distributed in Korea since the beginning of 1990's. Both of Korean ginseng and Chinese ginseng are originated from the plant-taxonomically same species, *Panax ginseng* C. A. Meyer. However, Korean ginseng has been sold in much higher price than Chinese ginseng, so counterfeited and/or imitated Korean ginseng may come illegally into the markets in Korea, China and Hong Kong.

Some scientists in Japan and Korea have tried to establish the discrimination method of ginseng habitat. Mino [3] reported that Chinese ginseng could be discriminated from Korean ginseng by using an X-ray fluorescence spectrometry (XRF). According their report, the amount ratios of Sr/Ca to Rb/K analyzed by the XRF technique would be different between Korean ginseng and Chinese ginseng. Nho et al. [4] reported that Chinese white ginseng could be discriminated from Korean white ginseng by using an electronic nose system equipped with conducting polymer sensors and Lee [5] also suggested that Chinese red ginseng could be discriminated from Korean red ginseng by using an electronic nose system equipped with metal oxide sensors. A near infrared spectrometry is reported to be useful for discriminating Korean white ginseng and Chinese white ginseng [6], and recently, an isotope ratio mass spectrometry has been also tried for the discrimination of ginseng habitat.

The climatic factors such as temperature, rain-fall, daylight-hours and no-frost period of ginseng-producing areas in Korea are much different from those in China [7-10]. Korean ginsengs are cultivated at Ganghwa, Geumsan, Poonggi and Jinan which are located at 36~38 degrees N.

L., while most of Chinese ginsengs are cultivated at Tonghua, Jian, Fusong, Jingyu and Antu which are located at 41~43 degrees N. L. The mean temperature levels of ginseng-producing areas in Korea are 10~16°C which are 6~12°C higher than those in China. The yearly rain-fall levels of ginseng-producing areas in Korea are 1,200~1,300 mm which are 200~500 mm more than those in China. In addition, both of the yearly daylight-hours and the yearly no-frost period of ginseng-producing areas in Korea are about 20% longer than those in China. Sohn et al. [11-12] reported that the flavor notes and their strengths of Korean red ginseng were significantly different from those of Chinese red ginseng and the gas chromatographic patterns for the headspace volatiles of Korean red ginseng were rather different from those of Chinese red ginseng, which seem to be closely related to the climatic factors of ginseng-producing areas in Korea and China.

The cultivation conditions such as cultivated region and transplantation method of ginseng-producing areas in Korea are also different from those in China [13-14]. Ginseng is sowed and transplanted generally on the fields in Korea, while ginseng is sowed and transplanted on the mountain tops or mountainsides in China. Ginseng seedling roots are transplanted once in Korea, while young roots of two- or three-year-old are transplanted once or twice in China. Moreover, the angle of inserting seedling roots when transplanted is about 45° in Korea, but 0~30° in China. Sohn et al. [15] reported that the strengths for breaking rhizomes of Korean ginseng were significantly higher than those of Chinese ginseng, which seem to be closely related to the cultivation conditions of Korea and China.

In this study, some physical and chemical characteristics of Korean red ginsengs were analyzed with those of Chinese red ginsengs by using a rheometer, an electronic nose system, a combined technique of solid phase micro-extraction (SPME) and gas chromatograph equipped with an electron capture detector (GC/ECD) or a nitrogen-phosphorus detector (GC/NPD), an XRF, an inductively coupled plasma mass spectrometer (ICP/MS), a near infrared spectrometer (NIRs) and high performance liquid chromatography equipped with evaporative light scattering detector (HPLC/ELSD) in order to propose a better technique for the discrimination of ginseng habitat.

Materials and Methods

Ginseng samples

Ninety-four kinds of Korean red ginsengs and fifty kinds of Chinese red ginsengs were used as ginseng samples as shown in Table 1 and Table 2. Rhizome of each ginseng sample was

Table 1. The Korean red ginseng samples used in this study

Sample[1)]	Root-year	Root-size[2)] (roots/600g)	Number of sample[3)] (First-Second-Third[4)])	Produced time
A	Six	28	18 (5-6-7)	1998~2000
		38	20 (4-11-5)	1990~2000
		58	12 (4-4-4)	2000
B	Four	28	4 (1-1-2)	1998~2000
		38	5 (2-2-1)	1997~2000
		48	1 (0-1-0)	1997
		58	2 (1-0-1)	1997
	Five	28	3 (1-1-1)	1999~2000
		38	3 (1-1-1)	1999~2000
		58	3 (1-1-1)	2000
	Six	28	2 (1-1-0)	2001
		38	2 (1-1-0)	2001
		48	2 (1-1-0)	2001
C	Five	28	3 (1-1-1)	2001
		38	3 (1-1-1)	2001
		48	2 (0-1-1)	2001
D	Five	28	3 (1-1-1)	2001
		38	3 (1-1-1)	2001
		58	3 (1-1-1)	2001
Total			94 (38-37-29)	

[1)]The Korean red ginseng samples used in this study were divided into four groups (A, B, C & D) according to their manufacturers or brand names. [2)]All the Korean red ginsengs are packaged with a tin-can and root number in a tin-can is represented by using a traditional unit of "Ji". For example, "20 Ji, 30 Ji and 50 Ji" indicates "28 roots, 38 roots and 58 roots in a package of 600 g", respectively. [3)]Korean red ginseng samples with different quality grade and/or lot number. [4)]Quality grade : First, Heaven grade; Second, Earth grade; Third, Good grade.

removed, and then its main body and lateral roots (=big tails) were ground to 20 mesh-size just before the analysis.

Reagents

All reagents used in this study were GR or HPLC grades.

Instruments

A rheometer (FUDOH RHEO METER, RT2010D.D, Rheotech Co.; Japan), an electronic nose system (FOX 3000, Alpha M.O.S. SA; France) equipped with twelve metal oxide sensors, a gas chromatograph (HP6890, Agilent Co.; U.S.A.) equipped with an autosampler (8200A/S, Varian Co.; U.S.A.) and an electron capture detector or a nitrogen-phosphorus detector, an X-ray fluo-

Table 2. The Chinese red ginseng samples used in this study

Sample[1)]	Collection place	Root-size[2)] (roots/600g)	Number of sample[3)]	Collected time
GZ	Guangzhou	28	6	2001
		38	11	2001
		58	4	2001
		70~100	1	2001
HK	Hong Kong	19	2	2001
		28	2	2001
		38	5	2001
BJ	Beijing	14	2	2001
		19	1	2001
		28	8	2001
		38	6	2001
		70~100	2	2001
Total			50	

[1)]The Chinese red ginseng samples used in this study were divided into three groups (GZ, HK & BJ) according to their collection places. [2)]All the Chinese red ginsengs are packaged with a tin-can. The root-size of Chinese red ginseng was re-classified according to Ginseng Industry Regulations of MAF, Korea. (refer to Table 1) [3)]Chinese red ginseng samples with different manufacturers and/or lot number.

rescence spectrometer (EX-3500, Jordan Valley Co.; U.S.A.), an inductively coupled plasma mass spectrometer (ICP/MS, Micromass Co.; U.K.), a near infrared spectrometer (NIRs model 6500, FOSS-NIRSystems; U.S.A.) and a high performance liquid chromatograph (Waters Associates model 510, Waters Co.; U.S.A.) equipped with an evaporative light scattering detector were used.

Measurement of rhizome strength

The rhizome strength of each ginseng sample was measured using a rheometer according to Sohn et al.'s method [15].

Analysis of electronic nose pattern

One gram of each sample powder was put in a 20 ml-vial one by one before its headspace volatiles were generated by heating at 60°C for 30 minutes and analyzed by using an electronic nose system equipped with twelve metal oxide sensors such as SY/LG, SY/G, SY/AA, SY/Gh, SY/gCTl, SY/gCT, T30/1, P10/1, P10/2, p40/1, T70/2 and PA2 [5].

Solid phase microextraction and gas chromatography (SPME/GC)

One gram of each sample powder was put in a 20 ml-vial and its headspace volatiles were

adsorbed on a 85 μm polyacrylate SPME fiber while being generated by heating at room temperature for 30 minutes before the SPME fiber was directly inserted into the GC injection port [5]. The GC column used was a DB-1 fused silica capillary (30 m×0.25 μm, 0.25 μm thick; Alltech Co.; U.S.A.); the GC detectors used was an electron capture detector; the temperatures used were 230°C for the GC injection port, 100°C to 290°C for the GC column oven, 310°C for the GC detector; and the carrier gas used was nitrogen gas of 1.5 ml per minute.

Inductively coupled plasma mass spectrometry (ICP/MS)

One gram of ginseng sample powder was put in a 1 ml-vessel, and then let decomposed by acid after nitric acid 5 ml was added. The decomposed material was dissolved and diluted to 100 ml with distilled water, and then analyzed by ICP/MS according to the method of National Agricultural Product Quality Management Service [16].

X-ray fluorescence spectrometry (XRF)

Ginseng sample powder of 20 mesh-size was put in a 100 ml-vessel and directly analyzed by an XRF according to the method of National Agricultural Product Quality Management Service [16].

Near-infrared spectrometry (NIRs)

Ginseng sample powder of 20 mesh-size was put in a 100 ml-vessel and directly analyzed by a NIRs according to Kim et al.'s method [6].

Extraction, fractionation and analysis of ginsenosides

One gram of each sample powder was extracted with 80% aqueous methanol at 80°C for 1 hour twice. The aqueous methanol extract was filtered and concentrated at 40°C under vacuum. The concentrate was suspended in small quantity of water and loaded on a short column of SepPak C_{18} cartridge (Sep-Pak Plus, Waters Co.; U.S.A.). The cartridge was washed with 25% methanol, and then polar substances in the cartridge were eluted with 90% methanol. The eluate was concentrated to 1 ml at 40°C under vacuum and ginsenosides in the concentrate were determined by HPLC/ELSD [17-18].

Results and Discussion

Rhizome strength

The rhizome strengths of Korean red ginsengs were measured by rheometry and compared with those of Chinese red ginsengs. The rhizome strengths of Korean red ginseng samples were 9.78±1.62 kg (n=158) for 20 Ji, 8.54±2.49 kg (n=136) for 30 Ji and 7.20±2.78 kg (n=158) for 50 Ji while the rhizome strengths of Chinese red ginseng samples were 7.42±2.14 kg (n=38) for 20 Ji, 6.81±2.85 kg (n=75) for 30 Ji and 4.40±2.09 kg (n=12) for 50 Ji as shown in Table 3, which suggests that the rhizome of red ginseng with bigger root-size may be stronger. There were sig-

Table 3. The rhizome strengths of Korean red ginseng (KRG) and Chinese red ginseng (CRG)

Ginseng sample	Brand[1] or Collection place[2]	Average root weight (g)		
		21.4 (20 Ji)	15.8 (30 Ji)	10.3 (50 Ji)
KRG	A	9.60 ± 1.72 (88)	7.80 ± 2.68 (57)	6.85 ± 2.83 (89)
	B	10.61 ± 0.80 (40)	9.10 ± 2.22 (46)	8.45 ± 2.59 (43)
	C	9.86 ± 1.27 (15)	10.01 ± 1.38 (16)	NA[3]
	D	8.53 ± 2.05 (15)	7.41 ± 2.89 (17)	6.37 ± 2.28 (26)
	Total	9.78 ± 1.63 (158)	8.54 ± 2.49 (136)	7.20 ± 2.78 (158)
CRG	GZ	7.41 ± 1.88 (15)	6.96 ± 2.77 (38)	4.40 ± 2.09 (12)
	HK	7.54 ± 2.42 (8)	6.42 ± 3.15 (21)	NA[3]
	BJ	7.37 ± 2.36 (15)	6.95 ± 2.73 (16)	NA[3]
	Total	7.42 ± 2.14 (38)	6.81 ± 2.85 (75)	4.40 ± 2.09 (12)

The rhizome strength of each red ginseng sample was measured by using a Rheometer (FUDOH RHEO METER, RT-2010D.D, Rheotech Co.; Japan) according to Sohn et al.'s method [17]. All data were represented as mean±standard error and each figure in the parenthesis indicates number of individual roots used for the measurement. [1]Refer to Table 1. [2]GZ, Guangzhou; HK, Hong Kong; BJ, Beijing (refer to Table 2). [3]NA, not analyzed.

Table 4. The statistical data for the differences of rhizome strengths of Korean red ginseng and Chinese red ginseng

Average root-weight (g)	D[1]	S_D[2]	DF	t-Value[3]
21.4	2.36	0.37	194	6.37**
15.8	1.73	0.39	209	4.41**
10.3	2.80	0.64	168	4.36**

[1]D indicates the difference between mean values of rhizome strengths measured from Korean red ginseng and Chinese red ginseng. (refer to Table 3). [2]Standard deviation for the mean values. [3]**, $p<0.01$; where $t_{0.01,\ 168\sim209}=2.60\sim2.61$.

nificance at 1% level between differences of the rhizome strengths of Korean red ginsengs and Chinese red ginsengs not only with 20 Ji (28 roots per 600 g) but with 30 Ji (38 roots per 600 g) or 50 Ji (58 roots per 600 g) as shown in Table 4, which suggests that the rhizome of Korean red ginseng would be stronger than that of Chinese red ginseng if the two red ginsengs with the same root-size were compared. Sohn et al. [15] also reported that rhizome strength of Korean white ginseng might be also significantly higher than that of Chinese white ginseng.

Electronic nose patterns of headspace volatiles

The headspace volatiles of red ginseng were responded to metal oxide sensors of an electronic nose system and the response changes of each sensor induced by the headspace volatiles were investigated. Figure 1 shows that the response changes of twelve metal oxide sensors induced by the headspace volatiles of Korean red ginseng and Chinese red ginseng. The response changes of SY/G, SY/Gh, SY/CTl and SY/gCT sensors induced by headspace volatiles of Korean red ginsengs were significantly lower at 1% level than those of Chinese red ginsengs, which suggests that an electronic nose system equipped with the appropriate metal oxide sensors can be useful

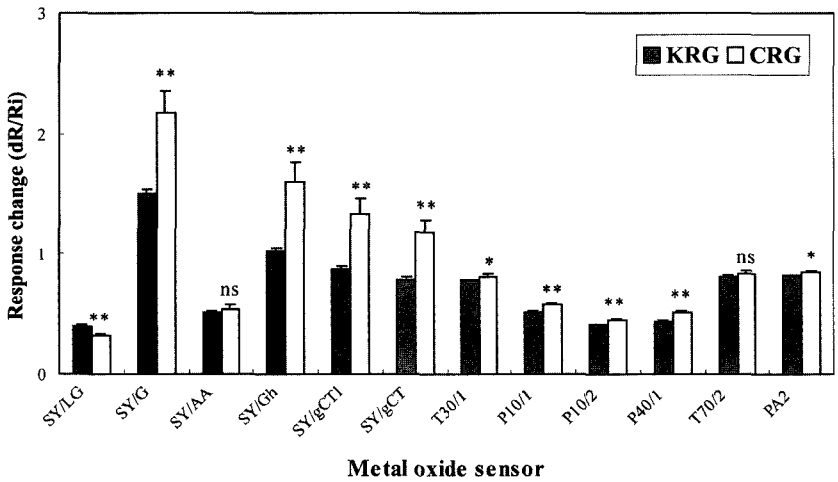

Fig. 1. The response changes of metal oxide sensors of an electronic nose system by headspace volatiles of Korean red ginseng (KRG) and Chinese red ginseng (CRG). All data were represented as mean±standard error, where ninety-four roots of KRG (sample A~D; refer to Table 1) and fifty roots of CRG (collected at Guangzhou, Hong Kong and Beijing; refer to Table 2) were used as samples. One gram of each ginseng sample powder was heated at 60°C for 30 minutes to generate headspace volatiles, and then 2.0 ml aliquots of the headspace volatiles were injected to metal oxide sensor array chamber of an electronic nose system (FOX 3000, Alpha M.O.S. SA; France) equipped with an autosampler and a data-processing system. **, $p<0.01$; *, $p<0.05$; ns, not significant.

for the discrimination of ginseng habitat. Noh et al. [4] reported that an electronic nose system equipped with conducting polymer sensors could be used for the discrimination of white ginseng habitat and Lee [5] also suggested that Korean red ginseng might be discriminated from Chinese red ginseng by using an electronic nose system equipped with metal oxide sensors.

ECD-sensitive headspace volatiles

The headspace volatiles were extracted from each red ginseng powder by using a polyacrylate SPME fiber and analyzed by using a gas chromatograph (GC) equipped with an electron capture

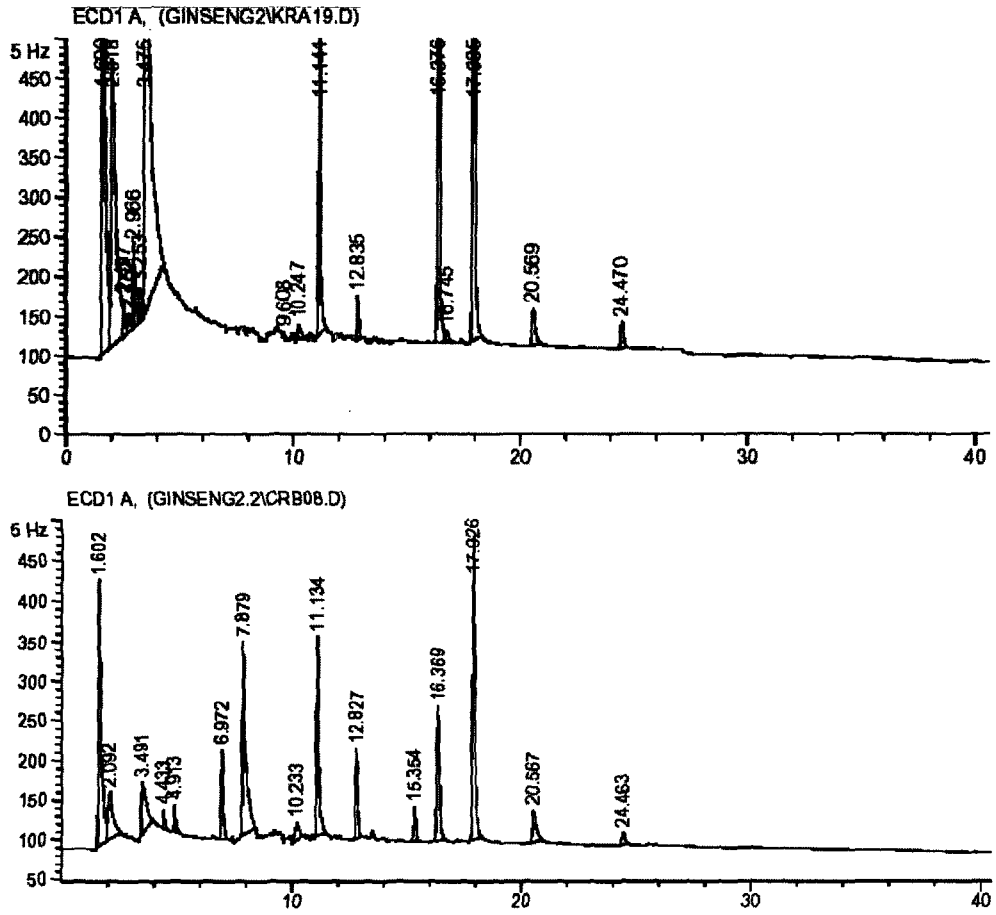

Fig. 2. The GC patterns of ECD-sensitive headspace volatile components of Korean red ginseng (KRG) and Chinese red ginseng (CRG). The headspace volatiles were generated from 1 gram of each ginseng sample powder at 35°C for 30 minutes and directly injected to GC injector by using an automatic solid phase microextraction gas chromatograph equipped with an electron capture detector (ECD). Top, KRG; bottom, CRG.

Table 5. The occurrence of ECD-sensitive headspace volatile components in Korean red ginseng (KRG) and Chinese red ginseng (CRG)

Retention time of GC peak[1)] (min)	Occurrence (%)		Remarks
	KRG	CRG	
1.6	93/93 (100)	50/50 (100)	
2.0	93/93 (100)	50/50 (100)	
3.4	93/93 (100)	50/50 (100)	
3.8	18/93 (19)	0/50 (0)	
4.4	0/93 (0)	26/50 (52)	CRG-specific
4.9	0/93 (0)	26/50 (52)	CRG-specific
5.0	14/93 (15)	5/50 (10)	
6.9	0/93 (0)	34/50 (68)	CRG-specific
7.4	3/93 (3)	18/50 (36)	
7.8	1/93 (1)	27/50 (54)	
9.2	10/93 (11)	8/50 (16)	
9.9	2/93 (2)	3/50 (6)	
10.2	93/93 (100)	50/50 (100)	
11.1	93/93 (100)	50/50 (100)	
13.5	0/93 (0)	5/50 (10)	
13.9	4/93 (4)	0/50 (0)	
15.3	0/93 (0)	19/50 (38)	

The headspace volatiles of each ginseng sample powder were analyzed by using an automatic SPME/GC/ECD system. [1)]Refer to Fig. 2.

detector (ECD) or a nitrogen-phosphorus detector (NPD). Figure 2 shows GC patterns of ECD-sensitive headspace volatiles extracted from Korean red ginseng and Chinese red ginseng. Ten or more components were detected in both the two red ginsengs and the overall patterns seem to be similar from each other. However, some components with retention time of 4.4, 4.9 or 6.9 minutes were detected in 50% or more of Chinese red ginsengs while any of them was not detected in Korean red ginsengs as shown in Table 5, which suggests that such components could be good indicators for the discrimination of ginseng habitat.

Content ratios of inorganic elements

Some minor inorganic elements of red ginsengs were determined non-destructively by ICP/MS. Figure 3 shows the contents of inorganic elements such as aluminum, manganese, iron, copper, zinc and barium analyzed by using an ICP/MS. The manganese and barium contents of Korean red ginsengs were significantly higher at 1% or 5% level than those of Chinese red ginsengs, but the Fe contents of Korean red ginsengs were significantly lower at 1% level than those of Chinese red ginsengs.

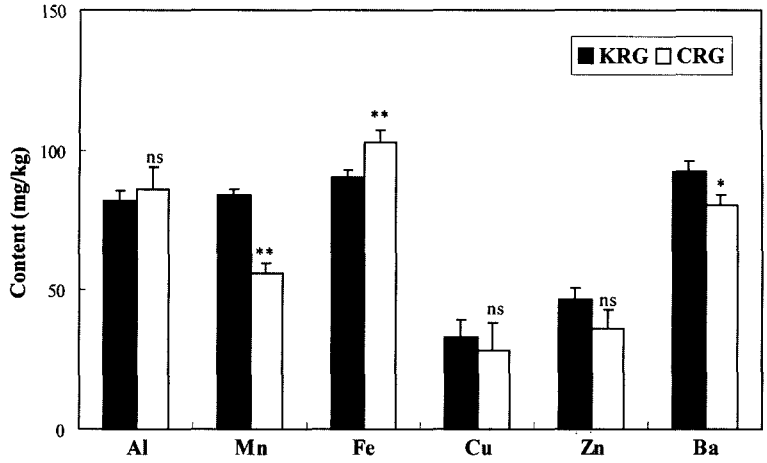

Fig. 3. The contents of inorganic elements of Korean red ginseng (KRG) and Chinese red ginseng (CRG). The inorganic element contents of ginseng sample powder was determined non-destructively by using an ICP/MS. All data were represented as mean ± standard error, where ninety-four roots of KRG (sample A~D; refer to Table 1) and fifty roots of CRG (collected at Guangzhou, Hong Kong and Beijing; refer to Table 2) were used as ginseng samples. **, $p<0.01$; *, $p<0.05$; ns, not significant.

2248, 2296, 2312, 2328 and 2432 cm^{-1}, which pattern was very similar to that of Chinese red ginsengs. However, the reflectances at wavenumber 904, 968, 1088, 1256, 1552, 1680, 1808, 1888 and 2312 cm^{-1} were much different between Korean red ginsengs and Chinese red ginsengs. In

Table 6. The content ratios of inorganic elements in Korean red ginseng (KRG) and Chinese red ginseng (CRG)

Ginseng Sample	Brand[1] or Collection place[2]	Content ratio		
		K/Ca	Mn/Fe	(K/Ca)/(Mn/Fe)
KRG	A	2.25 ± 0.29	0.97 ± 0.32	2.61 ± 0.92 (50)
	B	2.45 ± 0.31	0.95 ± 0.28	2.57 ± 1.26 (27)
	C	2.27 ± 0.19	1.19 ± 0.23	1.17 ± 0.33 (8)
	D	2.74 ± 0.22	0.86 ± 0.25	1.62 ± 0.31 (9)
	Mean	2.36 ± 0.31	0.97 ± 0.30	2.38 ± 1.06 (94)
CRG	GZ	1.94 ± 0.35	0.66 ± 0.35	3.26 ± 1.98 (20)
	HK	1.72 ± 0.26	0.57 ± 0.24	2.53 ± 1.24 (9)
	BJ	1.91 ± 0.30	0.53 ± 0.31	3.47 ± 1.99 (21)
	Mean	1.89 ± 0.32	0.59 ± 0.32	3.20 ± 1.86 (50)

The contents of inorganic elements of ginseng sample powder were determined by using both of an Inductively Coupled Plasma Mass Spectrometer (ICP/MS, Micromass Co.; U.K.) and an X-ray Fluorescence Spectrometer (EX-3500, Jordan Valley Co.; U.S.A.). All data were represented as mean ± standard error and each figure in the parenthesis indicates number of individuals used for the analysis. 1) Refer to Table 1. 2) GZ, Guangzhou; HK, Hong Kong; BJ, Beijing; refer to Table 2.

Table 7. The statistical data for the content ratios of inorganic elements in Korean red ginseng and Chinese red ginseng

Inorganic element	D[1)]	S_D[2)]	DF	t-Value[3)]
K/Ca	0.47	0.06	142	8.48**
Mn/Fe	0.38	0.05	142	6.93**
(K/Ca)/(Mn/Fe)	0.82	0.28	142	2.88**

[1)]D indicates the difference between mean values of the content ratios analyzed from Korean red ginseng and Chinese red ginseng. (refer to Table 5). [2)]Standard deviation for the mean values. [3)]**, $p<0.01$; where $t_{0.01, 142}$= 2.62.

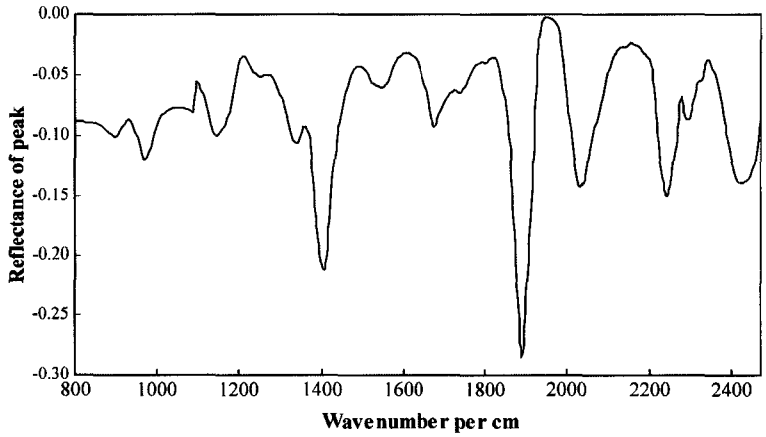

Fig. 4. The near-infrared spectral (NIRs) pattern of Korean red ginseng. The reflectance at NIRs wavenumber from 800 to 2500 cm^{-1} were scanned once per 8 cm^{-1}. The above NIRs pattern is plotted on the basis of mean value of reflectance at each NIRs peak wavenumber, where ninety-four kinds of KRG (sample A~D; refer to Table 1) were used as samples.

addition, the reflectance ratios of wavenumber 904 to 1088 cm^{-1} and wavenumber 904 to 1888 cm^{-1} of Korean red ginsengs were significantly different at 1% level with those of Chinese red ginsengs as shown in Table 8. This result suggests that the NIRs may be useful for the discrimination of ginseng habitat. Recently, the NIRs technique is being tried for the discrimination of ginseng habitat in National Agricultural Product Quality Management Service of Korea [6].

Content ratios of ginsenosides

Ginsenosides were analyzed by using a HPLC/ELSD and their contents in Korean red ginsengs were compared with those in Chinese red ginsengs. In both the two red ginsengs nine ginsenosides were identified. The contents of ginsenoside-Rg_1, -Rf, -Re and -Rd were significantly differ-

Table 8. The reflectances of near-infrared (NIR) peaks obtained from Korean red ginseng (KRG) and Chinese red ginseng (CRG)

Waven umber[1] (cm^{-1})	Reflectance of peak		Statistical data[2]		
	KRG	CRG	D	S_D	t-Value
904	-0.1052±0.0022	-0.1032±0.0020	-0.0019	0.0004	5.22**
968	-0.1244±0.0053	-0.1219±0.0047	-0.0025	0.0009	2.84**
1088	-0.0854±0.0026	-0.0877±0.0043	0.0023	0.0007	3.43**
1144	-0.1053±0.0034	-0.1051±0.0027	-0.0002	0.0005	0.43 ns
1256	-0.0566±0.0009	-0.0562±0.0007	-0.0004	0.0001	2.65**
1344	-0.1103±0.0021	-0.1100±0.0019	-0.0003	0.0004	0.84 ns
1408	-0.2169±0.0043	-0.2182±0.0045	0.0013	0.0008	1.62 ns
1552	-0.0646±0.0012	-0.0638±0.0013	-0.0008	0.0002	3.36**
1680	-0.0968±0.0008	-0.0958±0.0012	-0.0010	0.0002	5.05**
1744	-0.0683±0.0008	-0.0680±0.0009	-0.0003	0.0002	2.16*
1808	-0.0444±0.0006	-0.0439±0.0006	-0.0005	0.0001	4.62**
1888	-0.2890±0.0102	-0.2966±0.0116	0.0076	0.0020	3.78**
2032	-0.1481±0.0045	-0.1454±0.0063	-0.0027	0.0010	2.55*
2248	-0.1528±0.0032	-0.1512±0.0040	-0.0016	0.0007	2.32*
2296	-0.0914±0.0022	-0.0914±0.0025	-0.0000	0.0004	0.04 ns
2312	-0.0722±0.0013	-0.0729±0.0011	0.0007	0.0002	3.44**
2328	-0.0582±0.0014	-0.0583±0.0015	0.0001	0.0003	0.51 ns
2432	-0.1426±0.0036	-0.1421±0.0049	-0.0004	0.0008	0.52 ns
904/1088	1.233±0.059	1.180±0.073	0.053	0.0124	4.33**
904/1888	0.364±0.011	0.348±0.016	0.016	0.0026	6.07**

All the NIRs peak reflectances were represented as mean±standard deviation, where ninety-four kinds of KRG (sample A~D; refer to Table 1) and fifty kinds of CRG (collected at Guangzhou, Hong Kong and Beijing; refer to Table 2) were used as samples. [1]Refer to Fig. 6. [2]D, the difference between mean values of KRG and CRG; S_D, standard deviation for D; t-value=D/S_D; **, $p<0.01$; *, $p<0.05$; ns, not significant.

ent at 1% level between Korean red ginsengs and Chinese red ginsengs while the contents of ginsenoside-Rg_2, -Rg_3, -Rc, -Rb_2 and -Rb_1 were similar from each other as shown in Table 9. In addition, the content ratios of ginsenoside-Rg1 to -Re of Korean red ginsengs were 2.94±0.93 (n=94) which were significantly higher at 1% level than those of Chinese red ginsengs as shown in Table 10.

Conclusion

The rhizome strength, the response change ratios of metal oxide sensors such as SY/G, SY/Gh, SY/gCTl and SY/gCT induced by headspace volatiles, the occurrence of some ECD-sensitive headspace volatile components with GC retention time of 4.4, 4.9 and 6.9 minutes, the content

Table 9. The content ratios of ginsenosides in Korean red ginseng (KRG) and Chinese red ginseng (CRG)

Ginsenoside	Content (mg/g)		Statistical data[1)]		
	KRG	CRG	D	S_D	t-value
-Rg_2	0.54 ± 0.27	0.46 ± 0.22	0.08	0.04	1.93^{ns}
-Rg_1	2.53 ± 0.76	2.24 ± 0.66	0.29	0.12	2.37*
-Rg_3	0.08 ± 0.04	0.08 ± 0.09	0.00	0.01	0.24^{ns}
-Rf	0.47 ± 0.17	0.34 ± 0.18	0.13	0.03	4.13**
-Re	0.91 ± 0.31	0.52 ± 0.18	0.39	0.04	9.48**
-Rd	0.56 ± 0.61	0.34 ± 0.26	0.22	0.07	3.07**
-Rc	1.09 ± 0.34	1.10 ± 0.34	-0.01	0.06	0.19^{ns}
-Rb_2	0.90 ± 0.31	0.87 ± 0.34	0.03	0.06	0.63^{ns}
-Rb_1	3.58 ± 1.04	3.27 ± 1.29	0.31	0.21	1.44^{ns}
Sum	10.67 ± 2.73	9.23 ± 2.72	1.44	0.48	3.02**

All of ginsenoside contents were represented as mean±standard deviation, where ninety-four roots of KRG (Brand A~D; refer to Table 1) and fifty roots of CRG (collected at Guangzhou, Hong Kong and Beijing; refer to Table 2) were used as samples. [1)]D, the difference between mean values of KRG and CRG; S_D, standard deviation for D; t-value=D/S_D; **, $p<0.01$; *, $p<0.05$; ns, not significant.

Table 10. The statistical data for the difference of ginsenoside content ratios of Korean red ginseng (KRG) and Chinese red ginseng (CRG)

Ginsenoside	Content ratio[1)]		Statistical data[2)]		
	KRG	CRG	D	S_D	t-value
Triols/diols[3)]	0.65±0.13	0.59±0.17	0.06	0.03	2.31*
-Rg_1/-Re	2.94±0.93	4.59±1.69	-1.65	0.26	6.41**

[1)]Refer to Table 9. [2)]D, the difference between mean values of KRG and CRG; S_D, standard deviation for D; t-value=D/S_D; **, $p<0.01$; *, $p<0.05$. [3)]Triols, sum of ginsenoside-Rg_1, -Rf and -Re contents; diols, sum of ginsenoside-Rd, -Rc, -Rb_2 and -Rb_1 contents.

ratios of K/Ca or Mn/Fe, the reflectance ratios at NIRs wavenumbers such as 964, 1088 and 1888 cm^{-1} and the content ratios of ginsenoside-Rg_1 to -Re are thought to be useful as indicators for the discrimination of ginseng habitat.

References

1. Jeon, J. H. : *The Korean Food Yearbook* (in Korean languages), The Agriculture, Fisheries and Livestock News Co., Seoul, pp. 668-690 (1999).
2. Nam, T. H. : *Korea Agricultural Trade Information*, Agricultural and Fishery Marketing Corporation (2002).

3. Mino, Y. : *Shoyakugaku Zas*shi **44**, 276-287 (1990).
4. Noh, B. S. and Ko, J. W. : *Food Engineering Progress* **1**, 103-106 (1997).
5. Lee, S. K. : *Sensory and Chemical Analysis of Characteristic Aromas of Ginseng and Development of an Electronic Nose Method for the Discrimination of Red Ginseng Origin*, Ph. D. Thesis of Seoul National University (2001).
6. Kim, S. J., Lee, N. Y., Choi, D. S. and Jeong, M. S. : *Discrimination Method of Agricultural Product Habitat by NIRs*, National Agricultural Product Quality Management Service (2002).
7. KGTRI (ed.) : *Recent Korean Ginseng - Cultivation* (in Korean languages), Korea Ginseng and Tobacco Research Institute, Daejon, pp. 1-8 & 126-129 (1996).
8. Li, X. G. : *Processing of Chinese Medicinal Herbs*, Agriculture Publishing Co., Beijing, pp. 41-70 (1992).
9. Yang, J. X. : *Cultivation of Chinese Medicinal Herbs*, Agriculture Publishing Co., Beijing, pp. 119-177 (1993).
10. The Society for Korean Ginseng (ed.) : *Understanding of Korean Ginseng*, The Society for Korean Ginseng, Seoul, pp. 77-92 (1995).
11. Sohn, H. J., Lee, S. K. and Wee, J. J. : *J. Ginseng Res.* **24**, 148-152 (2000).
12. Sohn, H. J., Heo, J. N., Nho, K. B. and Kim, M. W. : *Korean J. Ginseng Sci.* **21**, 196-200 (1997).
13. KGTRI (ed.) : *Korean Ginseng*, Korea Ginseng and Tobacco Research Institute, Daejon, 18-26 & 44-49 (1994).
14. Sohn, H. J. and Nho, K. B. : *A Report of Business Trip to China*, Korea Ginseng and Tobacco Research Institute (1997).
15. Sohn, H. J., Nho, K. B., Lee, S. K., Choi, K. J. and Kim, M. W. : *Korean J. Ginseng Sci.* **21**, 201-208 (1997).
16. NAPQMS (ed.) : *Instrumental Analysis Techniques of Agricultural Product Habitat*, National Agricultural Product Quality Management Service (2002).
17. Lee, M. K., Park, H. and Lim, S. U. : *Korean J. Ginseng Sci.* **12**, 164-172 (1988).
18. Park, M. K., Park, J. H., Han, S. B., Shin, Y. G. and Park, I. H. : *J. Chromatography* A, **88**, 736 (1996).