VOLATILE FLAVOR COMPONENTS OF FRESH GINSENG

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ABSTRACT

Volatile flavor components of fresh ginseng (Panax ginseng C.A. Meyer) were studied by a combination of SE-54 fused silica capillary gas chromatography and mass spectrometry.

Steam distillate of fresh ginseng roots was extracted with oxygen-free diethylether and concentrated. This aroma concentrate was separated into neutral, acidic, phenolic, and basic fractions. The neutral fraction, containing over two hundred compounds, was aromatically the closest to fresh ginseng with the key-flavor components predominantly being monoterpenes and sesquiterpenes. The sesquiterpene compounds were identified as being azulenic, menthenic, and napthalenic with a mass of 204.

INTRODUCTION

Since Garriques first isolated crude saponin from American ginseng (*Panax quinquefolium* L.), many studies have been carried out on *Panax ginseng* C.A. Meyer. These have, for the most part, concentrated on ginseng saponin as the chemically, biochemically, and pharmacologically active component. Few have focused on the volatile flavor components of ginseng.

Those flavor components that have been studied so far include panacene and terpene in *Panax ginseng* ether soluble fraction studied by Kondo and Tanaka[1]; fatty acids investigated by Yamakuchi[2]; sterols and the structure of panaxynol reported by Dakahashi[3]; steroids in Korean ginseng studied by Chung[4] and Ko[5] using gas chromatography; and the monoterpenes, a few alcohols and esters investigated by Lee[6] and Kim.[7]

The ginseng flavor components, though present in small quantities, is a very complex mixture of over 200 constituents. This investigation was undertaken to identify the volatile flavor components in fresh Korean ginseng.

MATERIALS AND METHODS

Materials

4-year old fresh ginseng root, cultivated on a farm in KUM SAN area and harvested in October, 1983, was used.

Methods

a) *Steam distillation:* 8.8 kg of fresh ginseng was washed with water and placed in a 50 L stainless steel vessel with 10 L of water (autoclave illustrated in Fig. 1).

The sample was heated to, and maintained at, about 84°C at 1 atmosphere. Distillation was continued for 5 hours from the first appearance of a condensate, and resulted in 5.7 L of distillate.

b) *Extraction of flavor components:* The dis-

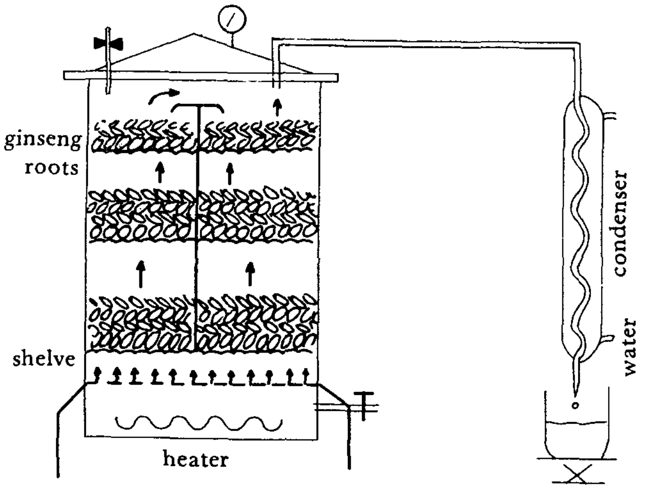

Fig. 1. Apparatus for steam distillation.

tillate was saturated with sodium chloride and immediately extracted with ethyl ether. This extract was concentrated to a volume of 500 ml. 200 ml of this aromatic concentrate was further reduced to approximately 1 ml for analysis by gas chromatography (GC) and gas chromatography-mass spectrometry.

c) *Fractionation of aromatic concentrate:* The remaining 300 ml was shaken three times with 10% sodium carbonate, then three times with 3% sodium hydroxide, and finally three times with 3% hydrochloric acid. This separated the concentrate into acidic, phenolic, and basic fractions, respectively, (Kami, 1975)[8] with the remaining neutral fraction.

d) *GC conditions:* A Varian Model 3700 gas chromatograph with a flame ionization detector and a 0.25 mm i.d. x 30 m fused silica capillary column coated with SE-54 was used. The column temperature was 34°C for 10 min and programmed to 190°C at a rate of 2°C/min, and the flow rate of nitrogen carrier gas was 0.5 ml/min.

e) *GC-MS conditions:* GC column and conditions were as described above for GC. Other operating parameters were as follows: column oven temperature and programmed rate of gas chromatograph was 40°C to 100°C at a rate of 5°C/min and to 200°C at a rate of 30°C/min; ionizing voltage, 70 eV; emission current at 1 mA; ion source temperature 250°C; ion source pressure, 1.2×10^{-5} torr.

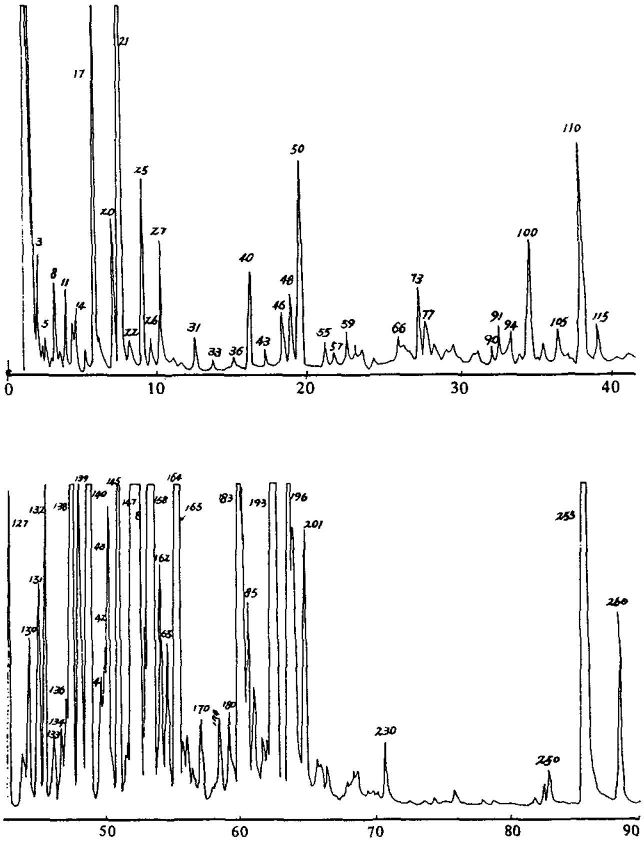

Fig. 2. Gas chromatogram of ginseng flavor components.

The peak assignment was performed by comparison of tR values with authentic samples and the NIH/EPA library searching via computer sorting.

RESULTS AND DISCUSSION

Yields of steam volatile compounds and their distilling rates are listed in Table 1.

The total flavor compounds obtained from 8.8kg of fresh ginseng was 2.4288g, which is equivalent to a 0.028% yield.

It can also be seen in Table 1 that 40% of

Table 1. Yield and steam distilling rate of ginseng flavor compounds.

Time (hr.)	1	2	3	4	5	Total
Distillate (L)	1.01	1.55	1.15	1.02	0.98	5.71
pH	4.89	5.03	5.13	5.09	5.28	–
Ether extract (g)	0.9550	0.9115	0.4837	0.0430	0.0356	2.4288
Yield (w/w) %	1.09×10^{-2}	1.03×10^{-2}	0.50×10^{-2}	0.48×10^{-3}	0.40×10^{-3}	0.028

* Distillation is carried out on autoclave at 84°C, 1 atm.

the armoatic compounds extracted with ethyl ether was distilled within the first hour, and 80% distilled by the second hour. Therefore, it can be assumed that the distillation of the volatile components of fresh ginseng largely occurs at the beginning of distillation.

As shown in Table 2, this aromatic concentrate, extracted with diethyl ether and then concentrated, consisted of 60.9% neutral fraction, 11.4% phenolic fraction, 6.9% of the acidic fraction and 9% of the basic fraction.

Among these, the neutral fraction had an earthy odor closest to the fresh ginseng smell, and a pale yellow color. The other fractions had an odor quite different from the original fresh ginseng: The acidic fraction was sharp, acidic, irritating, and butylic-like, the phenolic compounds were very sharp and cresol-like, while the basic fraction was sweet and warm.

We, therefore, next turned our attention to separating and identifying the neutral fraction constituents, as well as the total aroma concentrate by GC and GC-MS.

Table 2. Composition of flavor components in steam distillates of fresh ginseng roots.

Fraction	Yield (mg)	Composition (w/w) %
Total amount	2428.8	100
Neutral Fr.	1478.2	60.9
Phenolic Fr.	277.6	11.4
Acidic Fr.	167.9	6.9
Basic Fr.	218.8	9.0

A gas chromatogram of ginseng aroma concentrate is shown in Figure 2.

The chromatogram shows that the ginseng flavor concentrate contained over 250 constituents. Mass spectroscopy was performed on 60 of these compounds with the highest amount present.

Identification was made by comparing and matching the mass spectra with NIH/EPA library via computer sorting, and the GC retention data with those of authentic compounds.

Table 3. Volatile flavor components of fresh ginseng roots (Panax Ginseng C.A. Meyer)

No. of peak	Rt. (min)	Components	Composition area %	Identification
1	1.69	2-methyl-1-propanol	0.48	tR
8	3.12	2-pentanol	0.10	〃
14	4.56	ethyl buthanoate	0.05	〃
16	5.24	buthyl ethanoate	0.04	〃
43	17.59	1-heptanol	0.02	〃
57	22.32	P-cymene	0.02	〃

Table 4. Volatile flavor components of fresh ginseng roots (Panax Ginseng C.A. Meyer) identified by GC/MS.

No. of peak	Rt. (min)	M^+	Characteristic mass spectral ions (rel. intens, %)	Compounds	Composition area %
17	5.74	102	85(100), 56(52), 67(19), 81(9), 53(4)	Tetrahydro-2-hydroxy-2H-pyran	0.35
20	7.39	106	91(100), 106(30), 65(16), 84(10)	Ethyl benzene	0.15
21	8.01	106	91(100), 106(48), 77(21), 65(21), 86(6)	1.3-Cyclopentadiene, 5-isopropylidene	0.97
25	9.39	106	91(100), 106(50), 77(14), 56(6), 65(6)	O-dimethyl benzene	0.25
25	10.81	114	70(100), 55(92), 57(80), 81(34), 96(5)	4-methyl hexanal	0.20
31	12.92	136	93(100), 92(25), 91(17), 79(13), 121(8)	α-pinene	0.06
36	15.96	106	77(100), 106(83), 105(70), 78(46), 51(32)	benzaldehyde	0.02
40	16.37	136	93(100), 77(25), 79(21), 69(21), 121(18)	4 (10) - Thujene	0.15
55	21.52	136	68(100), 93(72), 79(42), 84(32), 121(23)	Limonene	0.04
77	27.86	154	93(100), 71(68), 55(44), 80(33), 121(20)	Linalool	0.10
90	32.39	154	59(100), 93(68), 79(64), 53(52), 67(34)	α-terpineol	0.02
91	32.99	136	93(100), 121(84), 80(82), 137(48), 55(48)	Ocimene (VAN)	0.07
110	38.74	164	149(100), 164(30), 91(121), 119(18), 105(8)	P-isopropyl benzoic acid	0.35
131	43.91	204	189(100), 204(27), 133(24), 105(22), 147(19)	triisopropyl benzene	0.51
133	45.24	204	204(100), 133(90), 161(80), 148(72), 105(66)	Cycloprop(e) azulene, Octahydro tetramethyl	0.26
138	47.41	204	161(100), 91(62), 105(60), 133(58), 204(42)	Cycloprop(a) Naphthalene ″	4.80
140	48.91	204	93(100), 81(98), 68(72), 121(54), 147(42)	Cyclohexane, 2,4-diiso propyl	6.68
141	49.54	204	189(100), 105(99), 161(94), 92(92), 204(92)	Cyclopyop(e) azulene decahydro, tetramethyl	0.43
143	50.94	204	105(100), 93(94), 69(84), 147(84), 133(78)	Guaia-1 (5), 11-diene	0.78
145	15.21	204	161(100), 105(44), 92(40), 133(22), 204(12)	isomer of #138	1.73
147	52.31	204	161(100), 189(74), 105(72), 93(56), 175(52)	β-patchoulene	15.40
148	52.31	204	94(100), 81(26), 121(26), 107(16), 67(16)	Eudesma - 4(14), 11 - diene	
158	53.42	204	69(100), 93(93), 79(38), 55(34), 107(12)	(E) - β - Farnesene	7.07
162	54.24	204	189(100), 133(66), 204(58), 92(44), 105(43)	β - Maaliene	0.67
164	55.32	204	121(100), 93(87), 107(62), 79(44), 161(33)	0-Menth-8-ene, 4-isopropyl-l vinyl	7.31
165	55.32	222	82 (100), 93(98), 68(76), 107(58), 121(45)	(E, E) - Farnesol	
170	56.91	204	161(100), 204(60), 135(58), 119(48), 105(46)	0 - Menth - 2-ene, 4 - isopropyl-1 - vinyl	0.40

Table 5. Characteristic mass data of volatile flavor components unidentified from fresh ginseng roots.

No. of peak	Rt. (min)	M^+ (proposed)	Characteristic mass spectral ions (rel intens, %)	Composition area %
48	18.61		67(100), 108(16), 98(30), 93(28), 70(40), 82(45), 79(55)	0.12
50	19.31		55(100), 152( ), 109(22), 95(15), 84(58), 69(50), 57(70)	0.31
66	26.47		93(100), 137(68), 105(40), 86(64), 69(52), 77(48), 55(90)	0.02
73	27.40		137(100), 153(27), 124(23), 81(13), 69(23), 55(18)	0.12
105	36.76		91(100), 163(12), 119(14), 105(52), 77(18), 65(10)	0.03
115	39.74		119(100), 162(48), 147(78), 91(42), 77(14), 65(12)	0.03
127	42.44	201	121(100), 205( ), 189(24), 161(28), 148(70), 133(60), 105(66), 94(78)	0.96
132	44.64	201	148(100), 204(37), 189(38), 133(55), 119(32), 105(38), 91(42)	0.08
134	45.77	201	189(100), 205( ), 147(52), 133(54), 119(44), 105(58), 91(44)	0.23
139	47.87		162(100), 147(60), 119(40), 107(70), 79(74), 79(74), 55(79)	1.29
142	50.14	204	189(100), 163(64), 149(66), 133(62), 119(52), 107(80), 91(84)	0.64
163	54.71	204	94(100), 204(35), 161(40), 133(44), 80(94), 67(93), 55(90)	0.48
180	58.97	204	161(100), 123(100), 205(62), 189(56), 107(82), 92(74), 81(71)	0.59
183	59.97	204	161(100), 204(38), 123(70), 107(64), 92(54), 81(54), 55(45)	4.01
185	60.97	204	91(100), 205(49), 159(68), 105(80), 79(72), 69(62)	0.45
193	62.57	222	207(100), 135(25), 123(30), 96(32), 81(18), 67(30)	5.50
196	63.77		92(100), 131(24), 117(36), 105(46), 77(57), 67(74), 55(87)	3.45
201	64.71	204	93(100), 205(68), 161(82), 105(78), 81(94), 69(78), 55(78)	1.14
255	85.64		103(100), 131(33), 117(63), 91(68), 77(43), 55(91), 55(94)	9.08

27 compounds, thus newly identified or reconfirmed as being present in fresh ginseng, are shown in Table 4. 6 compounds identified by GC retention data are shown in Table 3.

As shown in Figure 2, the chromatogram shows that the major ginseng flavor components, consisting about 80% of the total peak area, are eluted after the first 40 minutes.

a'-pinene, limonene, linaool, a'-terpineol, b'-farnesene, reported previously, was reconfirmed by mass spectra. However, many (low) volatile alcohols, aldehydes, ketones and esters presumed to be present in the neutral fraction could not be detected. This loss seems to be due to the loss of the volatile compounds during the steam distillation which did not use cold trapping.

As shown here in Table 4, the pattern of characteristic mass spectral ions indicates that a sesquiterpene compound with the mass of 204 is an important constituents of ginseng flavor.

The presence of the azulenic compounds in the peaks #133, 141, 143, and 147; the naphthalenic compounds in the peaks #138, 145, 148, and 162; and menthenic compounds in the peaks #164, and 170 are very interesting for chemical and pharmacological reasons.

Farnesol found in peak 165 is probably formed from b'-farnesene during steam distillation.

Besides these compounds, there could also be many derivatives with pharmacological effects, and a further study is necessary to identify these.

Table 5. shows the characteristic mass spectral ion of the unidentified flavor compounds. The fragmentation patterns strongly suggested sesquiterpenoids showing a definite molecular ion peak m/z 204.

Questioner: Have you ever comparatively analyzed the volatile portion of white and red ginseng?

Kim: Yes, we did. But the main volatile components of Red and White Ginseng were similar.

수삼의 휘발성 향기 성분

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수삼(Panax ginseng C.A.Meyer)의 휘발성 향기성분을 SE-54 fused silica capillary를 이용한 개스크로와 질량분석방법을 이용해서 연구했다.

수삼을 수증기 증류해서 얻어진 증류물을 diethyl ether로 추출해서 농축하고 이 농축물을 중성, 산성, 페놀성 및 염기성 분획으로 분리했다.

가장 방향이 풍부하고 원 수삼취와 비슷한 중성분획을 분석한 결과 인삼의 주요한 향기성분은 200종 이상 많은 성분중 monoterpene과 sesquiterpene계 성분이었다. Sesquiterpene 화합물은 질량 204를 갖는 azulene, menthene, napthalene계 화합물이었다.

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