

Volatile Flavor Components in Chinese Quince Fruits, *Chaenomeles sinensis koehne*

Tae-Yung Chung, Dae-Sun Cho and Jae-Chul Song*

Department of Food & Nutrition, Pusan National University, Pusan

*Department of Food & Nutrition, University of Ulsan, Ulsan

모과의 휘발성 Flavor 성분에 관한 연구

정태영 · 조대선 · 송재철*

부산대학교 식품영양학과, *울산대학교 식품영양학과

Abstract

Volatile flavor components in the chinese quince fruits were trapped by simultaneous steam distillation-extraction method, and these were fractionated into the neutral, the basic, the phenolic and the acidic fraction. In the identification of carboxylic acids, the acidic fraction was methylated with diazomethane. Volatile flavor components in these fractions were analyzed by the high-resolution GC and GC-MS equipped with a fused silica capillary column. The total of one hundred and forty-five compounds from the steam volatile concentrate of the chinese quince fruits were identified: they were 3 aliphatic hydrocarbons, 1 cyclic hydrocarbon, 4 aromatic hydrocarbons, 9 terpene hydrocarbons, 17 alcohols, 3 terpene alcohols, 6 phenols, 21 aldehydes, 7 ketones, 28 esters, 27 acids, 3 furans, 2 thiazoles, 2 acetals, 3 lactones and 9 miscellaneous ones. The greater part of the components except for carboxylic acids were identified from the neutral fraction. The neutral fraction gave a much higher yield than others and was assumed to be indispensable for the reproduction of the aroma of the chinese quince fruits in a sensory evaluation. According to the results of the GC-sniff evaluation, 1-hexanal, cis-3-hexenal, trans-2-hexenal, 2-methyl-2-hepten-6-one, 1-hexanol, cis-3-hexenol, trans, trans-2, 4-hexadienal and trans-2-hexenol were considered to be the key compounds of grassy odor. On the other hand, esters seemed to be the main constituents of a fruity aroma in the chinese quince fruits.

Key words: volatile flavor components, GC and GC-MS method, chinese quince fruits

Introduction

The tree of chinese quince, *Chaenomeles sinensis Koehne*, usually from 3-6m high, has an erect trunk with crooked branches. It bears pink or white solitary flowers and has alternate, ovate leaves tapering at one end and fruits resembling large yellow apples. Each carpel bears many seeds covered by mucilage. The plant is native

to central Asia and widely then distributed in all parts of Korea.

The fruit of chinese quince has a strong and characteristic aroma and is used for food, such as raw materials of tea, a fruit syrup, a fruit jam, gruel, rice cake, fruit wine and so forth. Several of nonvolatile flavor constituents of chinese quince, such as amino acids, organic acids, sugars and polyphenols have been studied by Kim *et al*⁽¹⁾, in Korea. However, the aroma substances of chinese quince have not received attention till recently. In the case of foreign

Corresponding author: Tae-Yung Chung, Department of Food Science and Nutrition, Pusan National University, San 30, Tongnae-gu Jangjundong, Pusan 609-735

countries, the aroma substances of marmello fruit, *Cydonia oblonga* Miller, which belong to the same pome fruits of *Roseaceae* family, became the subject of research in a viewpoint of flavor chemistry⁽²⁻⁶⁾.

We have undertaken the present study in order to elucidate the contribution of each volatile component to the characteristic flavor of chinese quince fruits through detailed qualitative analysis of volatile flavor components. This paper deals with the separation and identification of volatile flavor components in each fraction by the high-resolution GC and GC-MS equipped with a fused silica capillary column. The examination of a sensory characteristic of each volatile flavor component by GC-sniff evaluation has also been performed.

Materials and Methods

Materials

Fully-ripened chinese quince fruits purchased at Cheongdo market in Kyeongsangbuk-do on November 19th in 1986, were sliced and subjected to steam distillation.

Preparation and fractionation of the whole steam volatile concentrate

One kg of the sliced chinese quince fruit was placed in a 10 liter glass vessel and steam distillation was performed for 2 hours under atmospheric pressure. The steam-distillate was saturated with sodium chloride and extracted with diethyl ether. The ethereal extract was concentrated at 36-38°C under atmospheric pressure. The whole steam volatile concentrate was obtained in a yield of 1.3g from 17kg of the chinese quince fruit. The whole steam volatile concentrate was fractionated into the neutral, the basic, the phenolic and the acidic fraction as shown in Figure 1. Each fraction was concentrated by a similar method as described above.

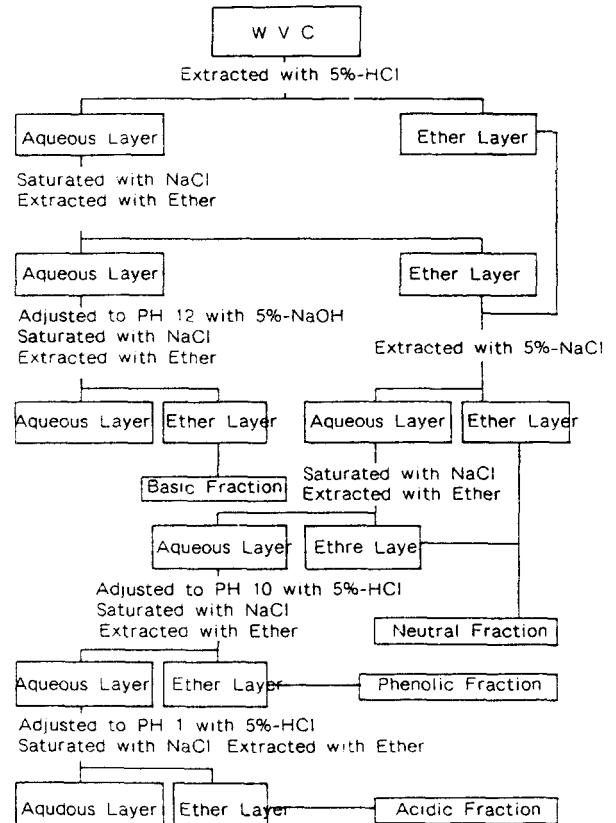


Fig. 1. Fractionation of whole steam volatile concentrate of fresh chinese quince fruits.

The acidic fraction was treated with diazomethane for methylation of the acids. These fractionated volatile flavor components were analyzed by GC and GC-MS.

Gas chromatography

Volatile flavor components in each fraction were analyzed with a Shimadzu Model 8A Gas Chromatograph equipped with a flame ionization detector (FID). A fused silica WCOT capillary column (50m×0.25mm i.d) coated with PEG 20M was used. The column oven temperature was programmed from 50°C to 190°C at a rate of 4°C/min. The injection port and detector temperatures were kept at 200°C. Nitrogen was used as the carrier gas at a flow rate of 1.5ml/min with

a split ratio of 1:25.

GC-sniff evaluation of volatile flavor components was performed with a Gasukuro Kogyo Model 350 Gas Chromatograph equipped with a FID. Carrier gas was kept at a flow rate of 3.48ml/min with a split ratio of 1:1.5.

Gas chromatography-mass spectrometry

GC-MS spectra were recorded by a Jeol Model DX-300 Mass Spectrometer equipped with the same column described above. The ionization voltage was 70eV and the ion source temperature kept at 250°C. The column oven temperature was programmed from 50°C to 170°C at a rate of 4°C/min and the injection port temperature was 200°C. Helium was used as the carrier gas at a flow rate of 1.0ml/min with a split ratio of 1:50.

Results and Discussion

Yield and odor of each fraction

Table 1 shows the yield and odor description of each fraction obtained from the whole steam

Table 1. Yield and odor of each fraction obtained from the whole steam volatile concentrate of fresh chinese quince fruits

Fraction	Yield (g)*	Odor**
NF	0.82	Oily, fresh chinese quince fruit-like
BF	0.13	Burnt, pyridine-like
PF	0.02	Medicinal, cresol-like
AF	0.19	Rancid, vinegar-like
UR	0.14	

NF, neutral fraction ; BF, basic fraction ;

PF, phenolic fraction ; AF, acidic fraction ;

UR, unrecovery.

* Yield from 17kg of fresh chinese quince fruits

** The ethereal solution of each fraction was absorbed on a filter paper and the filter paper was air-dried to remove the solvent and then subjected to the organoleptic test

volatile concentrate of the chinese quince fruits. Most of the volatile flavor components were present in the neutral fraction and the odor of the neutral fraction was exactly similar to that of the whole steam volatile concentrate. The neutral fraction of chinese quince fruits had a fresh chinese quince fruit-like aroma with an oily odor. The others except for the neutral fraction showed very low yields. The basic, the phenolic and the acidic fraction had a burnt or pyridine-like, medicinal or cresol-like and rancid or vinegar-like odor, respectively.

As a result of organoleptic contribution of each fraction shown in Table 2, there would be a close relationship between the neutral fraction and the whole steam volatile concentrate. The neutral fraction would be considered to be indispensable for the reproduction of chinese quince fruit odor.

Table 2. Organoleptic contribution of each fraction on the whole steam volatile concentrate by five-stage scoring method

Fraction	Score*					Total	Mean	Significance
	+2	+1	0	-1	-2			
NF	8 ^{a)}	2	0	0	0	20	2	**
BF	0	0	1	5	4	-12	-1.2	
PF	0	0	2	6	2	-8	-0.8	
AF	0	0	1	3	6	-14	-1.4	

* +2, closely resemble; +1, slightly resemble; 0, indistinguishable;

-1, slightly different; -2, completely different

** Level of significance in each fraction was found within 5%

a) A fraction was individually subjected to ten members whose the panelists were composed of forty women

Identified volatile flavor components

Volatile flavor components identified in the chinese quince fruits are given in Table 3. The total of one hundred and forty-five compounds, such as 3 aliphatic hydrocarbons, 1 cyclic hydro-

carbon, 4 aromatic hydrocarbons, 9 terpene hydrocarbons, 17 alcohols, 6 phenols, 21 aldehydes, 7 ketones, 28 esters, 27 acids, 3 furans, 2 thiazoles, 2 acetals, 3 lactones and 9 miscellaneous were identified. A synthetic antioxidant for

food such as BHT (Peak 180) would be considered to be a contaminant originated from diethyl ether used as solvent. Volatile flavor components identified in each fraction are described individually below.

Table 3. Volatile flavor components in fresh chinese quince fruits

Peak no.	Compounds	Peak no.	Compounds
Aliphatic hydrocarbons (3)		Phenols (6)	
112	n-Pentadecane	171	Guaiacol
131	n-Hexadecane	193	Phenol
165	n-Octadecane	193'	o-Cresol
Cyclic hydrocarbon (1)		218	Eugenol
128	Cyclodecene	222	4-Vinylguaiacol
Aromatic hydrocarbons (4)		235	Isoeugenol
21	Toluene	Thiazoles (2)	
37	Ethylbenzene	60	Thiazole
40	p-Xylene	185	Benzothiazole
234	1,2-Dimethoxybenzene	Acetals (2)	
Terpene hydrocarbons (9)		10'	1,1-Diethoxyethane
107	α -Copaene	24'	1,1-Diethoxyethane
115	α -Gurjunene	Lactones (3)	
125	trans-Caryophyllene	144	γ -Hexalactone
135	α -Elemene	214	γ -Decalactone
138	Alloaromadendrene	239	Dihydroactinidiolide
146	α -trans- β -Bergamotene	Ketones (7)	
148	α -Farnesene	13	2-Butanone
150	δ -Cadinene	46	2-Heptanone
166	α -Murrrolene	48'	Cyclopentanone
Furans (3)		71	3-Hydroxy-2-butanone
91	2-Isopropylfuran	76	2-Methyl-2-hepten-6-one
108	2-Acetylfuran	183	β -Ionone
179	4,7-Dimethylbenzofuran	232	3-Hydroxy- β -ionone
Alcohols (17)		4	1-Propanal
12	Ethanol	6	2-Methylbutanal
22	2-Butanol	8	2-Butenal
23	1-Propanol	10	1-Butanal
30'	2-Methyl-1-propanol	11	3-Methyl-1-butanal
33	3-Methyl-3-pentanol	27	Tiglaldehyde
35	2-Pentanol	30	1-Hexanal
38	1-Butanol	43	cis-3-Hexenal
51	3-Methyl-1-butanol	48	1-Heptanal
58	1-Pentanol	56	trans-2-Hexenal
72	2-Heptanol	75	trans-2-Heptenal
79	1-Hexanol	84	trans, trans-2,4-Hexadienal

Peak no.	Compounds	Peak no.	Compounds
81	cis-3-Hexenol	99	2-Furfural
89	trans-2-Hexenol	113	Benzaldehyde
119	1-Octanol	122	5-Methylfurfural
173	Benzyl alcohol	139 ¹	Neral
175	2-Phenylethanol	153	Geranial
188	trans-2-Decenol	155	m-Hydroxybenzaldehyde
Terpene alcohols (3)		162	p-Hydroxybenzaldehyde
116	Linalool	216	2,4-Dihydroxy-5,6-dimethyl-benzaldehyde
127	Terpine-4-ol	221	2,4-Dihydroxy-3,6-dimethyl-benzaldehyde
141	α -Terpineol	233	Ethyl palmitate
Aldehydes (21)		250	Ethyl palmitoleate
Esters (28)		255	Ethyl palmitolate
5	Ethyl formate	263	Methyl linoleate
9	Ethyl acetate	Acids (27)	
14	Ethyl propionate	A-1	Ethanoic acid
15	Ethyl isobutyrate	117	Propanoic acid
24	Ethyl butanoate	A-2	Isobutanoic acid
25	Ethyl 2-methylbutanoate	A-3	Butanoic acid
28	Ethyl 3-methylbutanoate	A-4	2-Methylbutanoic acid
34	Isobutyl isobutyrate	A-5	3-Methylbutanoic acid
45	Ethyl crotonate	A-6	Pentanoic acid
47	Methyl hexanoate	A-7	trans-Crotonic acid
55	Ethyl 3-methylpentanoate	A-8	Hexanoic acid
65	Ethyl 3-hexenoate	A-9	5-Hexenoic acid
93	Ethyl octanoate	A-10	Heptanoic acid
103	Ethyl 2-octenoate	A-11	2-Hydroxybutanoic acid
105	Ethyl 3-octenoate	A-12	Octanoic acid
132	Ethyl decanoate	A-13	Octenoic acid [*]
136	Ethyl decenoate [*]	A-14	Nonanoic acid
139	Ethyl decenoate [*]	A-15	4-Oxo-pentanoic acid
145	Benzyl acetate	236	Decanoic acid
164	Ethyl laurate	253	Decenoic acid
168	Ethyl 2-dodecenoate	A-16	Furan-2-carboxylic acid
175	Ethyl dodecenoate [*]	A-17	Succinic acid
207	Ethyl tetradecenoate [*]	2	Propyl methyl ether
212	Ethyl tetradecadienoate [*]	22 ¹	Chloroform ^{a)}
A-18	Benzoic acid	31	Piperidine
A-19	Glutaric acid	54	2-Ethoxyethanol
A-20	Phenylacetic acid	96	cis-Linalooloxide (Furanoid)
A-21	3-Hydroxy-5-methylthiophen-2-carboxylic acid	101	trans-Linalooloxide (Furanoid)
A-22	Myristic acid	170	Dimethyl sulfone
A-23	Palmitic acid	180	BHT ^{b)}
A-24	Stearic acid	184	Phenylacetoneitrile
Miscellaneous (9)			

a) Compound considered to be a contaminant, b) Compound considered to be a contaminant from ether used as solvent

* The positions of double bond are unknown

¹ Overlapped peaks in Figure 2, 3 and 4

Neutral fraction

As shown in Figure 2, about two hundred and sixty components including small peaks as well as large ones on the gas chromatogram of the neutral fraction were separated. Most of the large peaks observed on the gas chromatogram were identified as ethanol (Peak 12), ethyl isobutyrate (peak 15), 2-butanol (peak 22), 1-propanol (peak 23), 1-hexanal plus 2-methyl-1-propanol (peak 30 and 30'), 1-butanol (peak 38), cis-3-hexenal (peak 44), 3-methyl-1-butanol (peak 52), ethyl 3-methylpentanoate (peak 56), 2-methyl-2-hepten-6-one (peak 78), 1-hexanol (peak 81), ethyl octanoate (peak 93), 2-furfural (peak 99), ethyl decenoate (peak 136), α -farnesene (peak 148), ethyl 2-dodecenoate (peak 168), trans-2-decenol (peak 188) and 2, 4-dihy-

droxy-3, 6-dimethylbenzaldehyde (peak 221). These were mainly composed of alcohols, aldehydes and esters. However, these would be desirable volatile flavor components in the chinese quince fruits. C₆ compounds such as 1-hexanal, cis-3-hexenal and 1-hexanol among these would be formed through hydrolysis and breakdown of unsaturated fatty acid precursors by enzymatic reaction⁽⁷⁻¹⁴⁾ On the other hand, a carbon skeleton of 3-methyl-1-butanol is similar to that of L-leucine. Probably, it would be biosynthesized by the presence of a specific enzyme catalyzing the conversion of leucine to that⁽¹⁵⁻¹⁹⁾.

Basic fraction

A gas chromatogram of the basic fraction was given in Figure 3. Ethyl formate (peak 5), ethyl

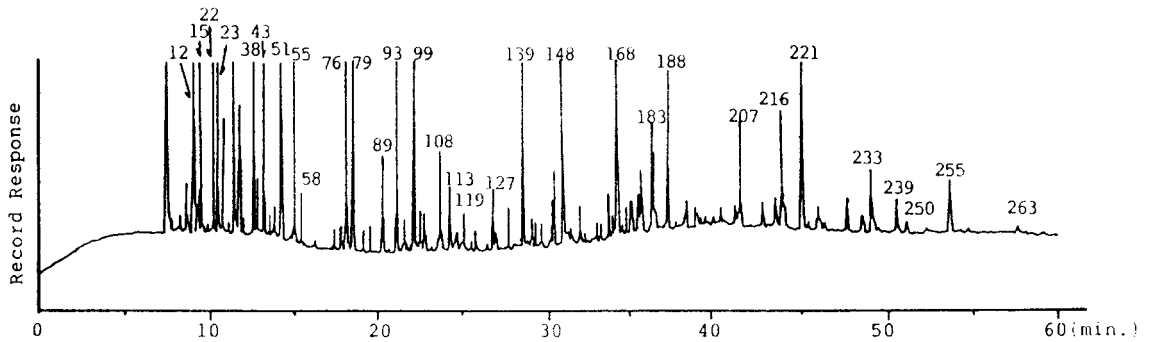


Fig. 2. Gas chromatogram of the neutral fraction obtained from the whole steam volatile concentrate of fresh chinese quince fruits.

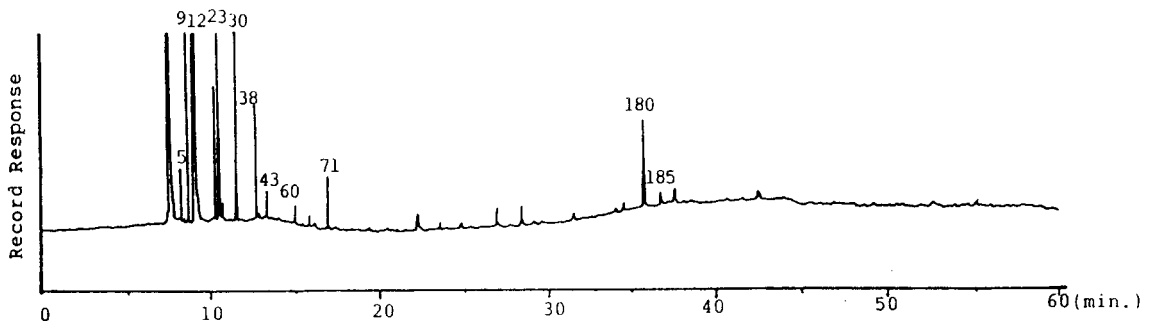


Fig. 3. Gas chromatogram of the basic fraction obtained from the whole steam volatile concentrate of fresh chinese quince fruits.

acetate (peak 9), ethanol (peak 12), 2-butanol (peak 22), 1-propanol (peak 23), 2-methyl-1-propanol (peak 30'), 1-butanol (peak 38), 3-hydroxy-2-butanone (peak 71) and BHT (peak 180) predominantly showed the large peaks, while other peaks generally indicated the small ones.

In this fraction, two thiazoles such as thiazole (peak 60) and benzothiazole (peak 185) were characteristically identified. Mass spectrum of thiazole showed a specific ionized fragments at m/e (%) 85(100, M^+), 58(67, C_2H_2S or $M^+ - HCN$), 57(15, $M^+ - HCN - H$) and so forth. As described above, the molecular ion peak occurred by the removal of a single electron from the molecule is observed as the base peak. Relative intensity of m/e 58 to the base peak indicated 67 % and it would be formed by the removal of HCN from the molecular ion peak. m/e 57 would be occurred by the removal of HCN and a hydrogen atom from the molecular ion peak.

Mass spectral data of benzothiazole was as follows: m/e (%) 135(100, M^+), 108(24, $M^+ - HCN$), 69(7, $M^+ - C_3H_3 - HCN$), 63(7, $M^+ - CS - HCN - H$), 82(7, $M^+ - C_4H_4 - H$) and 91(6, $M^+ - CS$). It is well known that vitamin B₁ has a thiazole ring nucleus, and that thiazoles are formed by the thermal interaction of sulfur-containing amino acids and reactive compound, such as carbohydrates or carbonyls⁽²⁴⁾. However, two thiazoles identified above would be occurred by the thermal decomposition of vitamin B₁ of Maillard-type reactions during simultaneous steam distillation.

A carbon skeleton of 2-furfural is fundamentally similar to those of five-membered ring such as fructose and/or ascorbic acid. Probably, it would be considered to be formed through thermal degradation of carbohydrates or the oxidation of ascorbic acid during simultaneous steam distillation⁽¹⁶⁾.

α -Farnesene occurs rarely in nature and has been isolated from the essential oil of marmello fruits⁽⁴⁾, while β -farnesene is reported frequently

as a component of various essential oils⁽²⁰⁾. It is noteworthy from the chemotaxonomical point of view that the chinese quince and marmello fruits, which belong to the same pome fruits of *Roseaceae* contain a large amount of α -farnesene in the essential oil.

A structure of 2-methyl-2-hepten-6-one is partially similar to those of carotenoids which have yellow inclining to red. It would be formed through the thermal decomposition or the oxidation of carotenoids⁽²¹⁾.

Four ethyl esters such as ethyl 3-methylpentanoate, ethyl octanoate, ethyl decenoate and ethyl 2-dodecenoate have been predominant over other esters in chinese quince fruit oil. These esters of saturated and unsaturated acids would play an important role as the main aroma constituents of chinese quince fruit oil. It is also significant that chinese quince fruit oil contained predominantly the ethyl esters, while other fruits such as apple, pear and banana contained the esters of methyl, ethyl, propyl, butyl, amyl and hexyl alcohols as the flavoring constituents^(22,23).

Phenolic fraction

A gas chromatogram of the phenolic fraction was shown in Figure 4. Total six phenols, such as guaiacol (peak 171), phenol (peak 193), o-cresol (peak 193'), eugenol (peak 218), 4-vinylguaiacol (peak 222) and isoeugenol (peak 235) were identified as small peaks by means of GC and GC-MS. All the other peaks except for these would be contaminated from both the neutral and the acidic fractions during fractionation of the whole steam volatile concentrate.

Guaiacol showed the predominant characteristics of the cleavage patterns at m/e (%) 124(86, M^+), 109(100, $M^+ - CH_3$), 81(49, $M^+ - CH_3CO$), 27(20, $CH_2 = CH$), 39(16, C_3H_3), 52(14, $M^+ - CH_3O - CO$) and 29(8, $M^+ - CH_3O - C_5H_4$). These cleavage patterns due to hetero atom suggest that this compound would be a benzene derivative with a methoxy and a hydroxyl radical in the molecular structure.

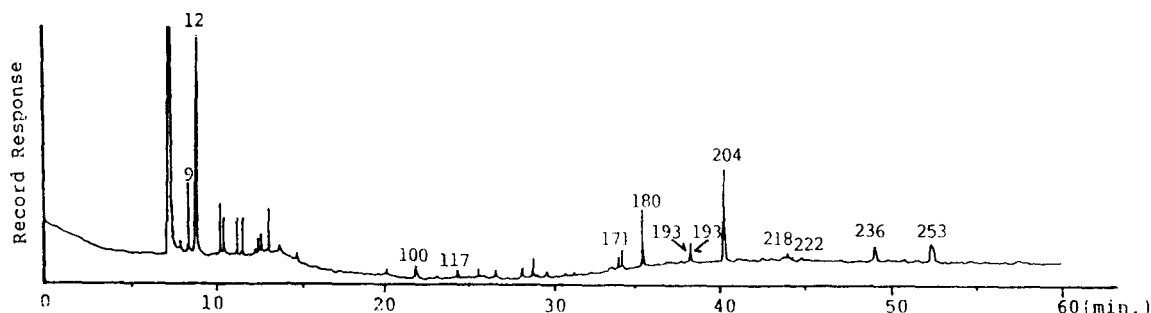


Fig. 4. Gas chromatogram of the phenolic fraction obtained from the whole steam volatile concentrate of fresh chinese quince fruits.

Eugenol characteristically showed the ionized fragments at $m/e(\%)$ 164(100, M^+), 149(49, $M^+ - CH_3$), 77(38, C_6H_5), 103(27, $M^+ - C_3H_6 - H - H_2O$), 91(26, $M^+ - C_3H_5 - CH_3OH$), 55(25, $CH_2 = C = CH_2 + CH_3$), 51(24, $H_2O + CH_3OH + H$), 131(23, $M^+ - CH_3 - H_2O$), 137(22, $M^+ - C_3H_3$), 133(20, $M^+ - CH_3O$), 121(19, $M^+ - C_3H_6 - H$) and 39(16, C_3H_3). According to mass spectral data, this compound would have a hydroxyl, a methoxy, a propenyl and a phenyl group in the molecular structure. Hence, it would be regarded as eugenol.

4-Vinylguaicol has been frequently identified in the cooked and/or roasted foods⁽²⁵⁻²⁷⁾. According to the author's study on the volatile flavor concentrate of the fresh tomato fruits⁽²⁸⁾, this compound was identified in the volatile flavor concentrate obtained from simultaneous steam

distillation, while it was not detected in the volatiles of headspace gas. It is well known that this is formed by the thermal decarboxylation of ferulic acid⁽²⁹⁾. Probably, there would be a possibility that this compound was produced by the thermal degradation during GC analysis. Hence, ferulic acid would be considered to be a precursors of this compound.

Acidic fraction

A gas chromatogram of the acidic fraction methylated with diazomethane was given in Figure 5. The total of 24 acids were identified as their methyl esters by the techniques using GC and GC-MS. In GC-MS analysis, the molecular ion peak of a methyl ester of a straight-chain aliphatic acid was clearly observed. The molecular ion peak was generally weak in the range of

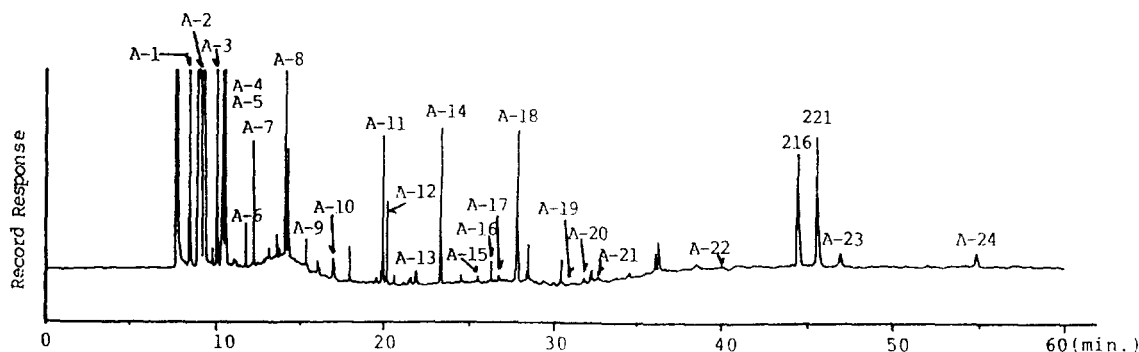


Fig. 5. Gas chromatogram of the acidic fraction obtained from the whole steam volatile concentrate of fresh chinese quince fruits.

m/e 130 to about 200, but became somewhat more intense beyond this range. In the case of a methyl ester of aliphatic acid unbranched at the α -carbon, the most characteristic peak due to the familiar McLafferty rearrangement and cleavage one bond removed from the carbonyl group gave a strong peak at m/e 74. In addition to such a tendency, the ion peaks due to elimination of CH_3O from the molecular ion peak and cleavage at each C-C bond gave an important information for the structure elucidation of a methyl ester.

On the other hand, the methyl esters of dibasic carboxylic acids, such as succinic and glutaric acid, never gave their molecular ion peak. Mass spectral data of dimethyl succinate gave the characteristic cleavage patterns at m/e(%) 146(0, M^+), 115(100, $\text{M}^+ \cdot \text{CH}_3\text{O}$), 15(80, CH_3), 55(73, $\text{M}^+ \cdot \text{CH}_3\text{COOH} \cdot \text{CH}_3\text{O}$), 28(31, C_2H_4), 27(29, C_2H_3), 114(28, $\text{M}^+ \cdot \text{CH}_3\text{OH}$), 59(20, COOCH_3 or $\text{M}^+ \cdot \text{CH}_2\text{CH}_2\text{COOCH}_3$), 29(19, $\text{C}_2\text{H}_4 + \text{H}$), 87(15, $\text{CH}_2\text{CH}_2\text{COOCH}_3$ or $\text{M}^+ \cdot \text{CH}_3\text{COO}$) and 45(10, COOH). In this mass spectral data, $\text{M}^+ \cdot 87(\text{CH}_2\text{CH}_2\text{COOCH}_3)$ and $\text{M}^+ \cdot 59(\text{COOCH}_3)$ would suggest to be a dimethyl ester of dibasic carboxylic acid such as dimethyl succinate.

Dimethyl glutarate showed the predominant characteristics of the cleavage patterns at m/e(%) 160(0, M^+), 129(38, $\text{M}^+ \cdot \text{CH}_3\text{O}$), 100(37, $\text{M}^+ \cdot \text{CH}_3\text{COOH}$), 99(54, $\text{M}^+ \cdot \text{COOCH}_3 \cdot 2\text{H}$), 87(16, $\text{CH}_2\text{CH}_2\text{COOCH}_3$ or $\text{M}^+ \cdot \text{CH}_2\text{COOCH}_3$), 59(100, COOCH_3 or $\text{M}^+ \cdot \text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3$), 55(44, $\text{M}^+ \cdot \text{CH}_3\text{OH} \cdot \text{CH}_2\text{COOCH}_3$), 43(19, $\text{C}_3\text{H}_6 + \text{H}$), 42(30, C_3H_6 or $\text{M}^+ \cdot 2\text{X} \cdot \text{COOCH}_3$), 41(24, C_3H_5 or $\text{M}^+ \cdot \text{CH}_3\text{C}(\text{H}) \cdot \text{COOCH}_3$) and 15(53, CH_3). The information from these cleavage patterns suggests that $\text{M}^+ \cdot 101(\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3)$, $\text{M}^+ \cdot 118(2\text{X} \cdot \text{COOCH}_3)$ and $\text{M}^+ \cdot 73(\text{CH}_2\text{COOCH}_3)$ would be a dimethyl ester of glutaric acid.

Mass spectral data of methyl benzoate was as follows: m/e(%) 136(32, M^+), 106(8, $\text{M}^+ \cdot \text{CH}_3\text{OH}$), 105(100, $\text{M}^+ \cdot \text{CH}_3\text{O}$), 78(5, $\text{C}_6\text{H}_5 + \text{H}$), 77(C_6H_5 of $\text{M}^+ \cdot \text{COOCH}_3$), 76(4, C_6H_4 or $\text{M}^+ \cdot \text{CH}_3\text{COOH}$),

74(4, $\text{M}^+ \cdot \text{CH}_3\text{OH} \cdot \text{HCHO}$), 51(36, $\text{M}^+ \cdot \text{COOCH}_3 \cdot \text{C}_2\text{H}_2$) and 39(4, C_3H_3). It is considered that the peaks at m/e 77 and 105 would be a methyl ester of benzoic acid.

GC-sniff evaluation

The results of GC-sniff evaluation are given in Table 4. According to the Table 4, no one single aroma and component would be responsible for the reproduction of the aroma of the chinese quince fruits. The main components of grassy aroma would be considered to be C_6 compounds such as 1-hexanal, cis-3-hexenal, trans-2-hexenal, 1-hexanol, cis-3-hexenol, trans-2-hexenol and trans,trans-, 4-hexadienal. On the other hand, all the other esters except for ethyl formate and ethyl acetate identified in fresh chinese quince fruits were expressed as fruity or floral odor. However, these esters would have reasonably potent aromas and contribute to some extent to the total aroma of fresh chinese quince fruits. They may then be responsible for the main characteristic aroma of that fruit.

1-Octanol, terpinen-4-ol, benzyl alcohol and 2-phenylethanol among alcohols identified from the essential oil of chinese quince fruits also gave off a desirable fruity or floral smell. They would be considered to play an important role as the aroma constituents of chinese quince fruit oil.

Although all aldehydes identified from chinese quince fruit oil were not necessarily the desirable aromas, a few of them had fruity or floral odor. Furfural and 5-methylfurfural, long known to be present in roasted food aroma through the caramelization of carbohydrates and the decomposition of pentosans, are nearly useless for the reconstruction of chinese quince fruit aroma.

Free carboxylic acids such as acetic propionic, isobutyric, butyric, isovaleric, valeric, caproic, enanthic, caprylic, pelargonic, capric and decenoic acid individually gave unpleasant odor, but it would be an important factor for the

Table 4. Organoleptic characteristics of each volatile flavor component by GC-sniff evaluation

Peak no.	Aroma characteristic	Peak no.	Aroma characteristic
2	Ether-like	58	Fusel-like
4	Aldehyde-like	76	Grassy
5	Pungent	79	Grassy
6	Fruity	81	Grassy
9	Ether-like	84	Grassy
11	Acrid	89	Grassy
12	Alcohol-like	96	Camphor-like
14	Pineapple-like	99	Burnt
15	Apple-like	100*	Vinegar-like
21	Solvent-like	101	Sweet
23	Alcohol-like	108	Sweet
24	Fruity	113	Burnt
25	Fruity	117	Acidic
28	Fruity	119	Orange-like
30	Grassy	121*	Acidic
34	Fruity	122	Burnt
37	Solvent-like	127	Fruity & floral
38	Burnt	129*	Rancid
40	Petroleum-like	132	Fruity
43	Grassy	136	Floral
51	Pungent	139	Fruity & floral
55	Fruity	145	Floral
56	Grassy	148	Terpene-like
149*	Acidic	204*	Acidic
153	Lemon-like	207	Floral
164	Floral & fruity	212	Fruity & floral
168	Fruity	214	Peach-like
169*	Acidic	216	Almond-like
173	Fruity	221	Fruity
175	Floral	222	Burnt
179	Aromatic	232	Violet-like
180	Phenol-like	233	Aromatic
187*	Acidic	236	Acidic
188	Grassy & waxy	253	Acidic
193	Cresol-like	255	Aromatic
		263	Oily

* The asterisks indicate free carboxylic acids A-1, A-2, A-3, A-6, A-8, A-10 and A-12 in methyl esters identified from the acidic fraction

reconstruction of that fruit aroma.

According to the results obtained by GC-sniff evaluation, all aroma components except for some degradation products formed during simul-

taneous steam distillation, would be certainly useful for the reconstruction of chinese quince fruit aroma. Some unidentified aroma components may then be useful for the reconstruction

of that fruit aroma. Hence, we should make a more detailed study on the unidentified aroma components in chinese quince fruit oil.

Acknowledgement

This research was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Korea, 1987.

요 약

모과의 휘발성 flavor 성분은 상압 수증기 증류법에 의해서 추출되었으며, 추출된 휘발성 flavor 성분은 중성, 염기성, 약산성 및 산성구분으로 분류되었다. 분류된 4 구분중 산성 구분은 carboxylic acid를 동정하기 위하여 diazomethane법에 의해서 methyl ester화 시켰다. 각 구분중에 함유되어 있는 휘발성 flavor 성분은 fused silica capillary column을 장치한 고분해능 GC 및 GC-MS에 의해서 분리 동정하였다. 모과의 수증기 증류유출액으로부터 얻어진 휘발성 flavor 농축액 중에서 총 145성분이 동정되었으며, 이들은 지방족 탄화수소 3성분, 환상 탄화수소 1성분, 방향족 탄화수소 4성분, terpene 탄화수소 9성분, alcohol 17성분, terpene alcohol 3성분, phenol 6성분, aldehyde 21성분, ketone 7성분, ester 28성분, 산 27성분, furan 3성분, thiazole 2성분, acetal 2성분, lactone 3성분 및 기타 9성분이었다.

Carboxylic acid를 제외한 나머지 휘발성 flavor 성분의 대부분은 중성구분으로부터 동정되었다. 중성구분은 다른 구분보다 상당히 높은 수득량을 나타내었으며, 관능 검사의 결과에서도 중성 구분은 모과의 방향성을 재현시키기 위해서 필요불가결한 것으로 나타났다. 관능검사용 GC에 의해서 얻어진 결과에 의하면 1-hexanal, cis-3-hexenal, trans-2-hexenal, 2-methyl-2-hepten-6-one, 1-hexanol, cis-3-hexenol, trans, trans-2, 4-hexadienal 및 trans-2-hexenol은 꽃 냄새의 주성분으로 생각된다.

한편으로, ester 화합물은 모과의 과일 냄새의 주성분인 것으로 생각된다.

References

1. Kim, Y.S., Lee, S.W., Lee, K. R., Kim, K.S., Cho, S.Y. and Lee, J.H. : Studies on tasty constituents in various food stuffs part I. Tasty constituents of chinese quince. *Korean J. Food Sci. Technol.*, **3**(3), 163(1971)
2. Spanyer, P., Kevei, E. and Blazovich, M. : Gas chromatographic analysis of flavors from fruits and fruits products. *Ind. Aliment Agr.*, **82**(3), 213(1965)
3. Schreyen, L., Dirink, P., Sandra, P. and Scham, N. : Flavor analysis of quince. *J. Agric. Food Chem.*, **27**, 872(1979)
4. Shimizu, S. and Yoshihara, S. : The constituents of the essential oil from Japanese quince fruit, *Cydonia oblonga miller*. *Agric. Bio. Chem.*, **41**, 1525(1977)
5. Tsuneya, T., Ishihara, M., Shiota, H. and Shiga, M. : Isolation and identification of novel terpene lactones from quince fruit (*Cydonia oblonga mill.*, marmelo). *Agric. Biol. Chem.*, **44**, 957(1980)
6. Ishihara, M., Tsuneya, T., Shiota, H., Shiga, M. and Yokoyama, Y. : The absolute configurations of marmelo lactones. *Agric. Biol. Chem.*, **47**, 2121(1983)
7. Nye, W. and Spoehr, A. : The isolation of hexanal from leaves. *Arch. Biochem. Biophys.*, **2**, 23(1943)
8. Major, R.T. and Thomas, M. : Formation of 2-hexenal from linolenic acid by macerated *Ginkgo* leaves. *Phytochemistry*, **11**, 611(1972)
9. Major, R.T., Marchini, P. and Boulton, T. : Observations of the production of α -hexenal by leaves from certain plants. *J. Biol. Chem.*, **238**, 1813(1963)
10. Major, R.T., Marchini, P. and Sproston, T. : Isolation from *Ginkgo biloba* L. of an inhibitor of fungus growth. *J. Biol. Chem.*, **243**, 3298(1968)
11. Galliard, T. and Matthew, J. A. : Lipoxxygenase-mediated cleavage of fatty acids to carbonyl fragments in tomato fruits. *Phytochemistry*, **16**, 339(1977)
12. Jadhav, S., Singh, B. and Salunkhe, D.K. : Metabolism of unsaturated fatty acids in tomato fruit; Linoleic acid, linolenic acid as precursors of hexenal. *Plant Cell Physiol.*, **13**, 449(1972)
13. Kazeniak, S.T. and Hall, R.M. : Flavor chemistry of tomato volatiles. *J. Food Sci.*, **35**, 519(1970)
14. Stone, E.J., Hall, R.M. and Kazeniak, S.J. : Formation of aldehydes and alcohols in tomato fruit from

- U-¹⁴C-labelled linolenic and linoleic acids. *J. Food Sci.*, **40**, 1138(1975)
15. Pyne, A.H. and Wick, E.L. : Volatile components of tomatoes. *J. Food Sci.*, **30**, 192(1965)
16. Schormuller, J. and Grosch, W. : Untersuchungen über aromastoffe von lebensmitteln I. mitteilung Ein beitrag zur analytik neutraler, in tomaten vorkommender carbonylverbindungen, *Z. Lebensm. -Unters. -Forsch.*, **118**, 385(1964)
17. Dalal, K. B., Olson, L. E., Yu, M.H. and Salunkhe, D. K. : Gas chromatography of the field, glass-greenhouse-grown, and artificially ripened tomatoes (*Lycopersicon esculentum* Mill.). *Phytochemistry*, **6**, 155(1967)
18. Yu, M. H., Salunkhe, D.K. and Olson, L.E. : Production of 3-methylbutanol from L-leucine by tomato extract. *Plant Cell Physiol.*, **9**, 633(1968)
19. Yu, M. H., Olson, L.E. and Salunkhe, D.K. : Precursors of volatile components in tomato fruit. II. Enzymatic production of carbonyl compounds, *Phytochemistry*, **7**, 555(1968)
20. Watanabe, I., Yanai, T., Awano, K., Kogami, K., and Hayashi, K. : Volatile components of Zinchoge flower (*Daphne odora* Thunb.). *Agric. Biol. Chem.*, **47**(3), 483(1983)
21. Stevens, M.A. : Inheritance and flavor contribution of 2-isobutyl thiazole, methyl salicylate and eugenol in tomatoes. *J. Am. Sco. Hortic. Sci.*, **95**(4), 461(1970)
22. Creveling, R.K. and Jennings, W.G. : Volatile components of Bartlett pear, Higher boiling esters. *J. Agr. Food Chem.*, **18**, 19(1970)
23. Heinz, D.E. and Jennings, W.G. : Volatile esters of Bartlett pear. V. *J. Food Sci.*, **31**, 69(1966)
24. Kato, S., Kurata, T. and Fujimaki, M. : Volatile compounds produced by the reaction of L-cysteine L-cystine with carbonyl compounds. *Agric. Biol. Chem.*, **37**, 539(1973)
25. Steinke, R.D. and Paulson, M.C. : The production of steam-volatile phenols during the cooking and alcoholic fermentation of grain. *J. Agric. Food Chem.*, **12**, 3(1963)
26. Yajima, I., Yanai, T., Nakamura, Sakakibara, H. and Habu, T. : Volatile flavor components of cooked rice. *Agric. Biol. Chem.*, **42**(6), 1229(1978)
27. Walradt, J. P., Pittet, A.O., Kinlin, T.E., Muralidhara, R. and Sanderson, A. : Volatile compounds of roasted peanuts. *J. Agric. Food Chem.*, **19**, 972(1971)
28. Chung, T.Y., Hayase, F. and Kato, H. : Volatile components of ripe tomatoes and their juices, purees and pastes. *Agric. Biol. Chem.*, **47**(2), 343(1983)
29. Fiddler, W., Parker, W. E., Wasserman, A.E. and Doerr, R.C. : Thermal decomposition of ferulic acid. *J. Agric. Food Chem.*, **15**, 757(1967)

(1987년 10월 19일 접수)