

## Influence of Isolation Method on the Composition of Apricot (*Prunus armeniaca* var. *ansu* Max.) Flavor

Young-Hoi Kim, Jai-Jin Kwag, Young-Ju Kwon and Kwang-Kyu Yang

Korea Ginseng and Tobacco Research Institute, Taejon

### Abstract

Volatile components of fresh apricot (*Prunus armeniaca* var. *ansu* Max.) were isolated by simultaneous distillation-extraction at two different pH values of 3.1 and 7.0 and by headspace trapping method. The volatiles were analyzed by GC and GC-MS. A total of 80 components were identified in the three aroma concentrates, including 9 naphthalene derivatives that were not previously reported in apricot. Of components identified in native pH (3.1) sample, the major components were aliphatic C<sub>6</sub> aldehydes and alcohols, monoterpene alcohols, benzyl alcohol,  $\beta$ -phenylethyl alcohol and naphthalene derivatives, while those in neutral pH(7.0) sample and headspace volatiles were aliphatic C<sub>6</sub> aldehydes and alcohols. Simultaneous distillation-extraction at pH 3.1 was significantly increased the concentration of n-hexanal, trans-2-hexenal, cis-3-hexen-1-ol, linalool oxide, linalool,  $\alpha$ -terpineol, nerol, geraniol, benzyl alcohol,  $\beta$ -phenylethyl alcohol and naphthalene derivatives. These results demonstrate that above the components are present in glycosidically bound forms in apricot.

Key words: apricot volatiles, influence of isolation method

### Introduction

Recently, Williams *et al.*<sup>(1-4)</sup> and Winterhalter *et al.*<sup>(5,6)</sup> reported that most of the monoterpene alcohols and C<sub>13</sub> norisoprenoids in fruits such as grape, passion fruit and quince may be originated from glycosidically bound nonvolatile precursors by acidic and enzymatic hydrolysis. Similar phenomena about the glycosides bound nature of volatile components were also observed in tobacco leaves,<sup>(7,8)</sup> tea shoots,<sup>(9,10)</sup> papaya<sup>(11)</sup> and apple<sup>(12,13)</sup>.

Furthermore, Engel and Tressl<sup>(14)</sup> reported that most of the monoterpene alcohols are not present in passion fruit in the free form but rather present in the bound, glycosidic form, and these nonvolatile glycosides can be transformed into volatile components by enzymatic hydrolysis or thermal acid-catalyzed treatment.<sup>(2,14)</sup> Other volatile components that could be originated from nonvolatile glycosides include benzyl alcohol,  $\beta$ -phenylethyl alcohol, benzaldehyde and aliphatic alcohols.<sup>(10,15)</sup>

On the other hand, it was known that aroma concentrate of apricot isolated by vacuum steam distillation includes a large amounts of monoterpene alcohols and benzaldehyde which are responsible

for the floral and fruity note of the aroma.<sup>(16)</sup> From the above mentioned reports, it is possible that glycosidically bound monoterpene alcohols in apricot can be transformed into free volatile components by the action of enzymes or by acid hydrolysis at elevated temperature.

The present study was undertaken to elucidate the influence of the isolation method on the composition of volatile component of apricot by comparing three different isolation methods. The glycosidically bound nature of some volatile components can be shown.

### Materials and Methods

#### Materials

Fresh, ripe apricot fruits (*Prunus armeniaca* var. *ansu* Max.) were obtained from the local market.

#### Isolation of volatile components

The fruit was deseeded manually, and a total of 3.0 kg of fruit was blended with 6.0l of distilled water for 1 min in a Waring blender. The blended juice, possessing a pH value of 3.1, divided into three equal portions. The pH of one portion was adjusted to 7.0 by adding 0.5N sodium hydroxide solution. The volatiles of juices, possessing pH value of 3.1 and 7.0, were isolated by means of simultaneous

Corresponding author: Young-Hoi Kim, Korea Ginseng and Tobacco Research Institute, Yuseong-Gu 305-345, Taejon

steam distillation-extraction at atmospheric pressure in a modified Likens-Nickerson apparatus using glass distilled n-pentane-diethyl ether (1:1) for 2 hrs.<sup>(17)</sup> and n-pentadecane(1.10 mg) was added as an internal standard.

The isolated volatiles were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to a volume of 0.3 ml by using a Vigreux column before injection.

The volatiles of apricot juice of another portion were collected by the dynamic headspace trapping method.<sup>(18)</sup> The sample was placed in a round glass container and the system was purged for 8 hrs with a 200 ml/min flow of purified nitrogen gas. The trap consisted of Pyrex glass tube(15cm  $\times$  0.9mm) packed with 2g of Tenax GC(Supelco, Inc., U.S.A.) and activation of Tenax GC was performed under a 30 ml/min nitrogen stream for 12 hrs at 250°C and the sample was stirred during purging at a moderate rate using a magnetic stirrer. The collected volatiles were eluted from the trap with 30 ml of diethyl ether and the ether extract was concentrated to a volume of 0.3 ml by using a Vigreux column.

#### Gas chromatography(GC) and gas chromatography-mass-spectrometry (GC-MS)

The concentrated extract were analyzed by a Hewlett-Packard(HP) 5880A GC, equipped with a flame ionization detector(FID) and a 30m  $\times$  0.32 mm(ID) fused silica capillary column coated Supelcowax 10. The oven temperature was programmed from 60°C to 230°C at 3°C/min and then held at 230°C for 30 min. The injector and detector temperatures were 250°C. The samples were injected in the split mode with a split ratio of 1:80. The carrier gas was nitrogen at a flow rate of 1.2 ml/min. Quantitative determination (FID response factors = 1.00 for all components) was carried out by using a HP 5880A integrator.

The linear Kovats retention indices( $I_k$ ) of volatile components were calculated by using n-paraffin homologues mixture( $\text{C}_6$ - $\text{C}_{26}$ , Supelco, Inc., U.S.A.) as references.<sup>(19)</sup>

GC-MS was carried out on a Varian 3700 GC that was coupled by an open-split interface to a Finnigan MAT 212 MS with SS 188 data system and a 30m  $\times$  0.25mm (ID) fused silica capillary column coated Supelcowax 10 was used. The column temperature was programmed from 60°C to 230°C at 3°C/min and then held at 230°C for 30 min. The

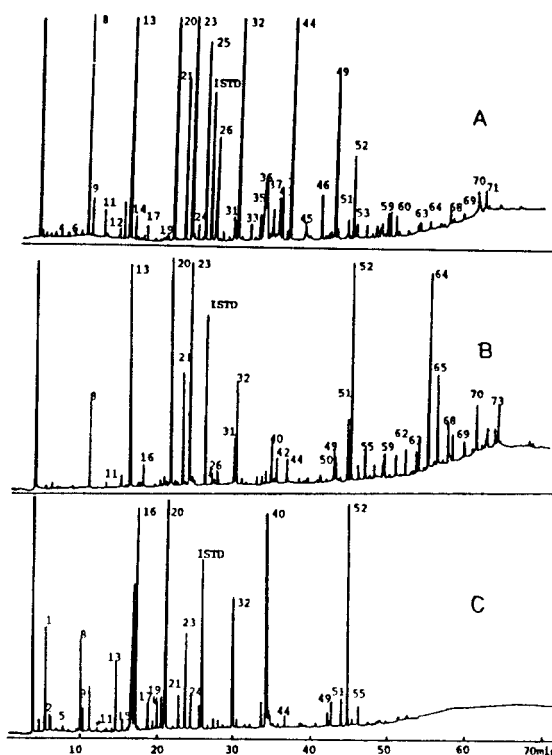


Fig. 1. Gas chromatograms of aroma concentrates isolated from apricot by simultaneous distillation-extraction at pH 3.1 (A) and pH 7.0 (B) or headspace trapping method (C)

operating conditions were as follows: a split ratio, 1:50; the rate of helium gas, 1.0 ml/min; ion source temperature, 250°C; ionization voltage, 70 eV; emission current, 1 mA.

Identification of each components was made by comparing retention indices with those of authentic standards, computer library matching and mass spectral data books.<sup>(20,21)</sup>

#### Results and Discussion

Fig. 1 shows the gas chromatograms of apricot concentrates of apricot obtained by steam distillation at pH 3.1(A), pH 7.0(B) and by headspace trapping method(C). Table 1 lists 80 components identified in the three apricot concentrates. Among them, 64 components were identified by comparing the retention indices with authentic standards and mass spectra with that of published mass spectral data, and the other 16 components were tentatively identified by comparing the published mass spectral

data only. Of components identified in native pH(3.1) sample, the major components were n-hexanal, trans-2-hexen-1-ol, trimethyltetrahydronaphthalene, linalool,  $\alpha$ -terpineol, benzyl alcohol,  $\beta$ -phenylethyl alcohol and hexadecanoic acid, while those in neutral pH(7.0) and headspace sample were n-hexanal, n-hexanol and trans-2-hexen-1-ol.

During our investigation of apricot volatiles, we observed a considerable differences in the composition of volatiles by using different isolation techniques. The aroma pattern obtained at the neutral pH

value of 7.0(B) was similar to that obtained by headspace trapping method(C). In contrast to that, steam distillation at the native pH value of pH 3.1(A) led to a much more various spectrum. Apricot fruit possesses high content of organic acids<sup>(22)</sup> and, therefore, a sample used for steam distillation, prepared diluting apricot pulp with distilled water, showed a pH value of 3.1. In this acidic condition, chemical transformation of aroma components during thermal treatment of steam distillation is possible.

In this study, glycosides isolation procedures

**Table 1.** Components identified from aroma concentrates of apricot fruits

Peak no <sup>a)</sup>	Components	I <sup>b)</sup> <sub>k</sub>	mg/kg		
			pH 3.1	pH 7.0	Headspace
1	Ethyl acetate	813	0.08	0.03	0.34
2	Ethyl propionate	941	+ <sup>c)</sup>	- <sup>d)</sup>	0.08
3	n-Propanol	996	0.06	-	0.13
4	Decane	1000	+	+	-
5	$\alpha$ -Pinene	1030	+	+	0.04
6	Ethyl butyrate	1065	0.04	+	0.04
7	Camphene	1096	0.03	0.03	0.04
8	n-Hexanal	1110	1.61	0.36	0.53
9	1-Penten-3-ol	1116	0.09	-	0.18
10	n-Butanol	1131	0.27	-	+
11	1,4-Cineol	1171	0.14	0.05	0.07
12	Limonene	1221	0.08	0.06	0.04
13	trans-2-Hexenal	1259	3.45	1.03	0.22
14	n-Pentanol	1274	0.17	-	-
15	$\alpha$ -Phellandrene	1277	0.09	0.03	0.05
16	p-Cymene	1303	0.04	0.11	1.61
17	Terpinolene	1313	0.13	0.05	0.04
18	Trimethyltetrahydronaphthalene	- <sup>e)</sup>	0.04	-	-
19	n-Hexenyl acetate	1354	0.06	0.04	0.38
20	n-Hexanol	1383	3.53	3.73	4.26
21	cis-3-Hexen-1-ol	1415	1.00	0.52	0.16
22	Rose oxide	-	0.05	+	-
23	trans-2-Hexen-1-ol	1437	3.18	3.76	0.62
24	Rose oxide	-	0.14	+	0.17
25	Trimethyltetrahydronaphthalene	-	1.39	-	0.04
26	Linalool oxide (furanoid)	1510	0.76	0.07	-
27	Trimethyltetrahydronaphthalene	-	+	+	-
28	Linalool oxide (furanoid)	1552	0.77	-	-
29	Furfural	1560	0.19	-	-
30	$\alpha$ -Ionone	1560	0.13	0.05	-
31	Benzaldehyde	1570	0.17	0.21	-
32	Linalool	1574	4.85	0.45	0.22
33	Trimethyltetrahydronaphthalene	-	0.12	-	0.07
34	5-Methylfurfural	-	-	-	0.04
35	Terpinen-4-ol	1645	0.75	0.04	-
36	Decahydronaphthol	-	0.54	-	-

Table 1. Continued.

Peak no <sup>a)</sup>	Components	I <sub>k</sub> <sup>b)</sup>	mg/kg		
			pH 3.1	pH 7.0	Headspace
37	$\gamma$ -Butyrolactone	1666	0.55	0.11	0.19
38	Trimethyltetrahydronaphthalene	-	0.08	-	0.06
39	Decahydronaphtol	-	+	-	-
40	Phenylacetaldehyde	1689	0.27	0.27	1.22
41	$\beta$ -Terpineol	-	0.11	0.04	-
42	Decahydronaphtol	-	0.53	0.13	-
43	Ocimenol	1715	0.32	0.04	+
44	$\alpha$ -Terpineol	1740	2.17	0.11	0.09
45	Trimethyltetrahydronaphthalene	-	0.31	-	-
46	Nerol	1837	0.34	0.03	0.03
47	$\gamma$ -Heptalactone	1850	0.04	0.03	0.04
48	$\beta$ -Damascenone	1873	0.07	-	0.11
49	Geraniol	1885	1.07	0.15	0.19
50	Hexanoic acid	1902	0.09	0.10	-
51	Benzyl alcohol	1929	0.19	0.30	0.18
52	$\beta$ -Phenylethyl alcohol	1945	0.73	1.23	1.35
53	cis-Jasmone	1954	0.09	0.04	-
54	$\beta$ -Ionone	1976	0.05	+	0.04
55	$\delta$ -Octalactone	1987	0.16	0.16	0.15
56	Eicosane	2000	0.04	0.05	-
57	3,4-Dimethoxyacetophenone	-	0.15	0.03	-
58	$\beta$ -Ionone epoxide	-	0.11	-	-
59	Phenol	2057	0.08	0.09	-
60	$\gamma$ -Nonalactone	2072	0.17	0.11	0.03
61	$\gamma$ -Decalactone	2104	0.05	0.10	0.03
62	$\delta$ -Decalactone	2136	0.08	0.11	0.03
63	Eugenol	2150	0.15	0.15	0.03
64	Ethyl hexadecanoate	2194	0.07	1.36	-
65	$\gamma$ -Undecalactone	2254	0.05	0.42	-
66	Decanoic acid	2270	0.04	0.03	-
67	Tricosane	2300	0.04	0.03	-
68	Dihydroactinidiolide	2377	0.04	0.12	-
69	Indole	2393	0.05	0.10	-
70	Dodecanoic acid	2535	0.19	0.31	-
71	Benzoic acid	2574	0.14	0.03	-
72	3,4-Didehydro- $\beta$ -ionol	-	0.03	0.11	-
73	Hexacosane	2600	0.07	0.12	-
74	Dibutyl phthalate	>2600	+	0.03	-
75	Tetradecanoic acid	>2600	1.41	0.34	-
76	Pentadecanoic acid	>2600	0.08	0.11	-
77	Hexadecanoic acid	>2600	1.63	1.04	-
78	Hexadecenoic acid	>2600	0.11	-	-
79	Octadecanoic acid	>2600	0.65	0.19	-
80	Octadecadienoic acid	>2600	0.64	0.08	-

a) Peak numbers correspond to the numbers in Fig. 1

b) Kovats indices on Supelcowax 10

c) Amounts less than 0.01 mg

d) Not detected

e) Tentatively identified

were not adopted but steam distillation at different pH value were adopted. According to the results of Engel and Tressl<sup>(14)</sup>, and Chen et al.<sup>(23)</sup>, the non-volatile glycosides are susceptible to the acidic hydrolysis under elevated temperature, and also in this study, steam distillation at native pH value of 3.1 formed many categories of components that were only minor components or did not exist in the pH 7.0 sample or headspace sample. As shown in Table 1, components that have been shown to be glycosidically bound in this study were monoterpene alcohols such as linalool,  $\alpha$ -terpineol, nerol and geraniol, aromatic alcohols such as benzyl alcohol and  $\beta$ -phenylethyl alcohol, and naphthalene derivatives of three groups.

It is interesting that three groups of naphthalene derivatives, the isomers of trimethyltetrahydronaphthalene (peak 18, 25, 27, 33 and 38) with the same molecular weight ( $M^+174$ ) and similar mass spectra, the isomers of decahydronaphthalene (peak 36, 39, and 42) with the same molecular weight ( $M^+152$ ) and trimethyldihydronaphthalene (peak 45,  $M^+172$ ), were identified in the pH 3.1 sample only. The isomers of trimethyltetrahydronaphthalene had been identified previously in passion fruit<sup>(24)</sup>, wine<sup>(25)</sup>, salted and pickled prunes<sup>(23)</sup>, tomato paste<sup>(26)</sup> and thermal degradation products of  $\beta$ -carotene.<sup>(27)</sup> These hydrocarbons appear to be identical with 2, 2, 6, 7-tetramethyl bicyclo [4.3.0] nona 4, 7, 9(1)-triene and three closely related components identified in quince volatiles by Winterhalter and Schreier.<sup>(5)</sup> However, since no authentic standards were available, their identification can only be considered tentative.

On the other hand,  $C_6$  aldehyde and alcohols such as n-hexanal, trans-2-hexenal, n-hexanol, cis-3-hexen-1-ol and trans-2-hexen-1-ol could be considered as lipid oxidation products and these components may be originated from unsaturated fatty acids by the action of lipid oxidation enzymes, because there was no attempt to inhibit the enzyme systems of the fruit in this study, although some authors have revealed the occurrence of some glycosidically bound aliphatic alcohols.<sup>(16)</sup> The fact that a considerable amounts were observed not only in native pH value of 3.1 but also in neutral pH value of 7.0 and headspace trapped samples suggests that these components in apricot fruits are originated enzymatically from unsaturated fatty acids by aerobic

oxidation.

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## 살구의 휘발성 성분 조성에 대한 분리방법의 영향

김영희 · 곽재진 · 권영주 · 양광규

한국인삼연초연구소

살구의 휘발성 향기성분 조성에 대한 분리 방법의 영향을 조사코저 살구 과육(pH 3.1)을 simultaneous distillation-extraction(SDE)법, headspace trapping법 또는 이를 pH 7.0으로 중화시킨 후 SDE법에 의해 얻어진 정유성분의 조성을 분석 비교하였다. GC-MS 및 GC에 의한 표준품과 머무름 시간의 비교에 의해 확인된 80종의 성분들 중 pH 3.1에서 SDE법에 의해 얻어진 정유성분 중에는 다른 두 가지 방법에 의해 얻어진 정유성분에서는

검출되지 않거나 또는 미량으로 검출된 n-hexanal, trans-2-hexenal, cis-3-hexen-1-ol, linalool oxide, linalool,  $\alpha$ -terpineol, nerol, geraniol, benzyl alcohol,  $\beta$ -phenylethyl alcohol 및 naphthalene 유도체들이 많이 검출되었으며 이러한 결과는 살구에서 비휘발성인 glycoside 형태로 존재하는 위와 같은 성분들이 산성조건하에서 수증기 증류시 glycoside 결합이 가수분해되어 휘발성 성분으로 유리되는데 기인하는 것으로 판단되었다.