Changes in the Composition and Content of Volatile Constituents in Peach Fruits in Relation to Maturity at Harvest and Artificial Ripening

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Summary

Changes in the composition and amounts of volatile constituents in white peach cv. Hakuho before and after artificial ripening, were investigated in fruits picked at three different maturity stages, in order to determine the optimum time for harvest in relation to some quality attributes.

1. Based on the color-chart value, firmness, Brix degree and titratable acidity, it was found that the eating quality of the fruits picked at the stages referred to as “hard mature” and “firm mature” was acceptable after fruit had been ripened for 4 days at ambient temperature. After the same time, fruits of the “soft mature” stage were considered to be overripe.

2. Typically, for peaches of all three maturities the volatile concentrates were separated into 89 or more peaks by capillary gas chromatography, of which 33 were identified by gas chromatography-mass spectrometry. The most abundant constituents were C₆ aldehydes, C₆ alcohols and C₆–C₁₂ lactones.

3. The total amounts of the 33 volatile constituents, which were identified at harvest and at all stages of fruit maturity, decreased rapidly after ripening for 4 days at ambient temperature. This decrease in the total amount of these volatile constituents was mainly a result of the reduction in the amount of aldehydes and alcohols which generated the “green aroma”.

4. Eleven kinds of C₆–C₁₂ lactonic compounds were detected at all the stages of maturity, and γ -decalactone was a major constituent accounting for about 40% of the total lactonic compounds. The content of almost all the lactones increased with advancing fruit maturity and during ripening.

5. Based on the evaluation of the odor threshold, it was calculated that the increase in odor units of γ -lactones made an important contribution to the “fruity aroma” with advancing maturity, in contrast to the decrease of the C₆ compounds which were responsible for the “green aroma”.

6. The most suitable picking time based on the changes in the composition and amount of volatile constituents corresponded to the firm mature stages followed by artificial ripening for 4 days including postharvest handling.

Introduction

Among the physiological changes related to the fruit quality of peaches, aroma is one of the most important characteristics. Fruit aroma is associated with small amounts of various volatile constituents such as aldehydes, alcohols, terpenoids, esters, and lactones. The appearance of these volatile constituents after ripening varies with maturity at harvest and ripening conditions (3, 5).

Many of the physiological properties related to

maturity in peaches have been studied, in order to identify a suitable indicator of maturity at harvest, and thereby maintain fruit quality after harvest (10, 11, 14). When peach fruits are immature at the time of picking, their quality is not suitable for dessert eating, and there has been a tendency in recent years to pick the peaches at almost the soft mature stage in order to improve the eating quality including the aroma. On the other hand, when fruits are left on the tree for a long period of time, they become soft, do not withstand excessive handling and transportation and have a reduced shelf life (1, 3).

The major volatile constituents of peaches have

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been identified (3, 6, 8, 11, 12, 13, 14, 15, 17). Do *et al.* (3) isolated 86 peaks and identified 17 of the volatile constituents obtained from four different stages of maturity in white peaches. They also reported that the concentration of the volatile constituents increased with advancing fruit maturity. Lactonic compounds, particularly γ -lactones have been identified as a major constituent in peach aroma (6, 8, 11, 13).

Horvat *et al.* (6) identified 33 volatile constituents from 13 peach cultivars. However, little information is available about the composition and contents of the volatile constituents in relation to fruit maturity at harvest and ripening after picking.

The objective of this study was to determine the maturity stage at which peaches should be harvested for the optimum development of volatiles and aromas during postharvest handling and artificial ripening. This was investigated by analysing the changes in the composition and contents of the volatile constituents as well as other fruit attributes associated with quality.

Materials and Methods

1. Materials

White peaches, cv. Hakuho were collected from the orchard of the Fruit Tree Research Station during August 1988. The fruits had been picked at three different stages of maturity. The maturity terms suggested by Do *et al.* (3) were adopted and the selected stages were classified as "hard mature", "firm mature" and "soft mature", which are equivalent to the terms "immature", "shipping mature" and "full ripe" defined on the basis of the maturity scale for white peaches developed by Aoyagi *et al.* (1).

2. Artificial ripening

All of the fruits picked at different stages of maturity were placed into plastic containers, and then left to ripen for 4 days at ambient temperatures of 25 ° to 30 °C. Thirty fruits of each maturity stages were used for artificial ripening.

3. Physical and chemical determinations

At harvest and after ripening, the color of the fruit surface was measured using standard color-chart. Fruit firmness was determined on opposite pared cheeks of 10 peaches using the Magness-

Taylor pressure tester with an 5/16 inch plunger.

Fifteen grams of the fruit flesh was sliced from both sides of 10 fruits of each maturity stages. The slices, amounting to 300 g, were then homogenized with 120 ml distilled water in a Waring blender. Brix degree and titratable acidity were determined on the homogenized puree. All analyses were duplicated and the Brix and acidity data were corrected on a fresh weight basis.

4. Isolation of volatile constituents by vacuum steam distillation

Samples were prepared from 10 fruits at each maturity stage. Each fruit was sliced, the pit was removed, and a total of 900 g of fruit flesh was homogenized with 360 ml of water, 0.6 g of ascorbic acid and 1.5 g of sodium chloride in order to inhibit oxidation and enzymatic activity under cooling conditions. The resultant homogenate was transferred into lacquered cans such that the net weight was 190 g.

The cans were then held at a temperature below -23 °C for one month, when analysis of the volatile constituents was carried out.

The volatile constituents were isolated by a modification of the vacuum steam distillation method developed previously by Katayama *et al.* (9). The contents from 6 cans (equivalent to 810 g fruit flesh) was thawed under tap water, and transferred to a 3 liter separable flask and 50 ml (250 μ g) of stock solution of the internal standard (s)-(+)-2-octanol (stock solution: 5 mg in 1 liter of water) was added (4). The flask was connected to a set of three cold traps, the end of which was connected to a vacuum pump. The volatile constituents containing the internal standard were distilled under a reduced pressure of 20~30 mm Hg by bubbling purified nitrogen gas through the slurry at the temperature of 35 °C for 6 hr. About 600 ml of distillate was obtained after the evaporated constituents, that had been collected in a series of traps, were pooled. The apparatus was then rinsed with 200 ml of ethyl ether. The aqueous and ether solutions were combined, and 120 g of NaCl was added to the combined solution. The water phase was separated and rewashed with 50 ml of ethyl ether. The second ethyl ether wash was added to the original ether solution to obtain 250 ml of extraction solution, which contained the volatile compounds.

The ethyl ether solution was dehydrated with 20 g of anhydrous magnesium sulfate. After filtration and separation of the magnesium sulfate, the ethyl ether fraction was concentrated to about 30 μ l by using a gentle stream of purified nitrogen gas.

5. Capillary gas chromatography (GC) and mass spectrometry

Capillary GC analysis was carried out with a 50 m $\times$ 0.25 mm fused silica capillary column coated with PEG 20M bonded (0.30 μ film thickness: Gaskuro Kogyo INC.). The column was placed in a Hitachi M-663-30 gas chromatograph fitted with a flame ionization detector (FID). The oven temperature was programmed to increase from 80 ° to 230 °C at a rate of 3 °C/min. The injector temperature was 250 °C, and Helium at a flow rate of 30 ml/min, was used as a carrier gas. Sample size was 0.4 μ l. A Hitachi M-80 B (CPU M-0101) double focus mass spectrometer (GC-MS) was used for the mass spectrometric analyses. The spectra were recorded at an ionization voltage of 70 eV and an ion source temperature of 180 °C.

Results and Discussion

The effects of maturity at harvest and ripening on the physical and chemical characteristics of white peaches cv. Hakuho are shown in Fig. 1. In general, the color-chart value and Brix degree increased with each advance in the stage of maturity at harvest. Firmness and titratable acidity decreased with the advance in maturity, and during ripening at the ambient temperature. The degree of firmness of the peaches has been shown to be highly correlated with maturity at harvest (1, 14).

From the above results and fruit appearance, it was considered that hard mature and firm mature fruits were fully ripe after being held at the ambient temperature for 4 days, whereas the soft mature fruits were considered to be over ripe. Fruit quality and aroma of firm mature fruits after ripening was optimum compared to the other stages of maturity. These results indicate that firm mature fruits are most suitable for eating 4 days after harvest (1).

Gas chromatograms of the peach volatile constituents were obtained for 6 samples at harvest and after ripening. A total of 89 or more peaks were separated from the volatile concentrates obtained

Fig. 1. Changes in fruit characteristics at harvest and after ripening at ambient temperature for 4 days in white peaches picked at different maturity stages.

from peaches at the firm mature stage (Fig. 2). Corresponding chromatograms of the peach volatile constituents of fruit of the hard mature, firm mature, soft mature, and those from fruit after ripening were numbered in the same manner.

Concentrations of the 33 volatile constituents identified in peaches at different stages of maturity and after ripening are shown in Table 1.

The constituents could be classified by functional groups into 11 kinds of lactones, 2 of aldehydes, 7 of alcohols, 4 of terpenoids, 6 of esters and 3 miscellaneous. Compared with the results previously reported (6, 13, 14, 15, 17), the present data were

Fig. 2. Gas chromatogram profile of peach volatile constituents in firm mature fruit after ripening at ambient temperature for 4 days.

in agreement with the finding on lactones, C_6 aldehydes and alcohols.

Total amounts of volatile constituents at harvest, for all stages of fruit maturity, decreased rapidly as fruit ripened during the 4 days at the ambient temperature. This decrease in the amount of the total volatile constituents was a result mainly of the decrease in the content of aldehydes and alcohols, and this decrease has most noticeable in firm mature fruit, where a four fold decrease occurred as fruit ripened.

Eleven kinds of lactonic compounds (peak no. 19, 21, 23, 25, 26, 27, 28, 29, 30, 31, 32) were detected at all the maturity stages, and their contents, except for that of γ -heptalactone, increased with advancing maturity and during ripening of the fruits picked at different maturity stages. The most abundant lactonic component reported by Horvat *et al.* (6) was γ -decalactone. On the other hand, γ -heptalactone, γ -octalactone, δ -octalactone, γ -nonalactone and marmelolactone are present in trace amounts and 6-pentyl- α -pyrone (16) was generally present at comparatively higher levels, while jasminlactone [(z)-dec-7-en-5-olide] has also been detected (4).

With increasing maturity of the fruit, the concentrations of the so-called "green aroma" components (peak no. 5, 10, 11, 12, 13) decreased drastically as shown in Fig. 3. Since enzymatic activity was in-

hibited by sodium chloride during the isolation of the volatile constituents, the concentrations of the C_6 components shown in Table 1 and Fig. 3, were considered to correspond to those in the in-

Fig. 3. Changes in the contents of the main volatile constituents responsible for the green aroma at harvest and after ripening at ambient temperature for 4 days in white peaches picked at different maturity stages.

Table 1. Changes in the concentration of volatile constituents of white peaches after ripening of fruits picked at different maturity stages.

Peak No.	Constituents	Hard mature		Firm mature		Soft mature	
		At harvest	After ripening	At harvest	After ripening	At harvest	After ripening
		(µg/kg FW)					
1	Ethyl formate	5	3	57	5	89	12
2	Ethyl acetate	177	11	315	15	113	42
3	Ethyl alcohol	29	3	62	4	40	10
4	<i>D</i> -Limonene	34	1	47	2	10	4
5	<i>t</i> -2-Hexenal	114	3	130	2	76	6
6	α -Terpinene	tr	tr	27	1	6	1
7	<i>n</i> -Hexyl acetate	70	3	116	3	37	5
8	<i>cis</i> -3-Hexenyl acetate	25	6	117	7	35	14
9	<i>t</i> -2-Hexenyl acetate	109	3	167	3	65	5
10	<i>n</i> -Hexanol	532	180	742	139	617	222
11	<i>t</i> -3-Hexenol	97	3	150	3	54	32
12	<i>cis</i> -3-Hexenol	178	16	221	16	156	4
13	<i>t</i> -2-Hexenol	895	258	921	222	1086	448
14	Acetic acid	204	2	563	4	146	2
15	2-Ethyl hexanol	500	3	548	5	97	10
16	Benzaldehyde	238	201	620	148	1402	392
17	Linalool	39	1	38	4	31	4
18	α -Terpineol	4	1	2	4	3	3
19	γ -Hexalactone	16	21	21	34	50	66
20	Benzyl acetate	2	1	2	2	1	3
21	γ -Heptalactone	7	1	4	2	10	4
22	Dihydro α -ionone	5	6	16	14	10	16
23	γ -Octalactone	2	5	3	11	8	15
24	β -Ionone	2	6	3	12	6	14
25	δ -Octalactone	tr	2	1	4	1	4
26	γ -Nonalactone	tr	3	tr	3	5	3
27	γ -Decalactone	47	114	51	250	166	227
28	Marmelolactone	2	5	6	6	4	10
29	6-Pentyl- α -pyrone	23	46	30	101	97	63
30	δ -Decalactone	17	37	15	88	73	74
31	Jasminlactone	8	15	8	22	9	34
32	γ -Dodecalactone	9	29	10	48	18	45
33	<i>n</i> -Hexadecanol	15	49	15	32	11	38
Total		3405	1038	5028	1216	4532	1832

tr = trace

tact fruit, and it is unlikely that the compound formed after disruption of the fruit tissues are included.

Along with the decrease in the concentration of the C₆ compounds, the lactonic compounds became the dominant volatile constituents in peaches as is the case in nectarines (4, 5). The content of almost all the lactonic compounds increase with advancing maturity and after ripening as shown in Table 1 and Fig. 4. However, the content of γ -heptalactone in all the cases, and 6-pentyl- α -pyrone at the soft mature stage, decreased with advancing maturity and ripening. These analytical data

corresponded to a sensory observation showing that the fruits did not display a lactonic "fruity aroma" before they reached the ripened stage. Fruits with the best aroma were those picked at the firm mature stage with subsequent artificial ripening as indicated in Table 2.

The total amounts of lactones ranged from 3% at harvest to 27% after ripening among all the isolated volatile constituents in the fruits picked at the hard mature stage. Ranges from 3 to 47% of the firm mature stage, and 10 to 30% of the soft mature stage were recorded at harvest and after ripening, respectively.

Fig. 4. Changes in the contents and the main volatile constituents responsible for the fruity aroma at harvest and after ripening at ambient temperature in white peaches picked at different maturity stages.

In order to determine the contribution of the individual lactones to the peach aroma, odor units were calculated with odor thresholds in the same manner as previously reported for tomato (2), nectarine (4, 5), peach (6) and apricot (18). These values reflect the role of the volatile constituents in the peach aroma. Table 2 lists the odor units of some of the peach constituents based on their concentration (Table 1) and odor thresholds. The data indicates that the major volatile constituents contributing to the odor at harvest in fruit at all three maturity stages include *t*-2-hexenol (odor unit: min. 12.8~max. 15.5), *t*-2-hexenal (4.5~7.6), *cis*-3-hexenol (2.2~3.2) in case of the green aroma, and γ -decalactone (4.3~15.1) and γ -dodecalactone (1.3~2.6) in case of the fruity aroma. Previous reports had indicated that the odor units of the lactones at harvest were not as high as these of after ripening (6), but the fruity aroma can be suppressed by the green aroma associated with the C_6 aldehyde and alcohol compounds (7). However in the present study, the odor units of the C_6 aldehydes and alcohols at harvest tended to decrease with advancing maturity and during ripening, and this reflected the disappearance of the green aroma with maturation or ripening.

In contrast, the odor units of most of the lactonic compounds rapidly increased during ripening along with the development of fruity aroma. Especially, γ -decalactone the odor unit of which was very

Table 2. Changes in odor units of main volatile constituents in peaches at harvest and after ripening of fruits picked at different maturity stages.

Functional group	Constituents	Odor threshold ^z	Hard mature		Firm mature		Soft mature	
			At harvest	After ripening	At harvest	After ripening	At harvest	After ripening
Aldehyde Alcohols	<i>t</i> -2-Hexenal	ppb 17 ^x	6.7	0.2	7.6	0.1	4.5	0.4
	<i>n</i> -Hexanol	500 ^x	1.1	0.4	1.5	0.3	1.2	0.4
	<i>t</i> -2-Hexenol	70 ^u	12.8	3.7	13.2	3.2	15.5	6.4
	<i>t</i> -3-Hexenol	70 ^x	1.4	0.04	2.1	0.04	0.8	0.5
	<i>cis</i> -3-Hexenol	70 ^u	2.5	0.2	3.2	0.2	2.2	0.1
Lactones	γ -Hexalactone	1600 ^{x, w}	0.01	0.01	0.01	0.02	0.03	0.04
	γ -Octalactone	7 ^{x, w}	0.3	0.7	0.4	1.6	1.1	2.1
	γ -Decalactone	11 ^{v, w}	4.3	10.4	4.6	22.7	15.1	20.6
	γ -Dodecalactone	7 ^{v, w}	1.3	4.1	1.4	6.9	2.6	6.4
	δ -Decalactone	100 ^w	0.2	0.4	0.1	0.9	0.7	0.7
	6-Pentyl- α -pyrone	150 ^{v, w}	0.2	0.3	0.2	0.7	0.6	0.4

^z Odor threshold in water.

^y Odor units are the ratios of concentration of an individual constituent (ppb) to the odor threshold (ppb).

^x Buttery, *et al.*, 1971, ^w Engel, *et al.*, 1988, ^v Horvat, *et al.*, 1990.

^u Hypothetical values considered to be equivalent within hexenol isomer.

high, seemed to contribute significantly to the peach aroma after ripening. Table 2 shows that other compounds related to the odor included γ -dodecalactone and γ -octalactone. The values of the other lactones were below the threshold of 1, and consequently, did not contribute appreciably to the peach aroma (4).

The results of this study account for the differences in aroma among the maturity stages and fruits subjected to artificial ripening. The most suitable picking time corresponded to the firm mature stage of fruit which was followed by ripening for 4 days included postharvest handling.

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採取熟度別モモ果実の追熟に伴う揮発性成分の変化

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摘 要

モモ果実の追熟に伴う揮発性成分の挙動とそれに基づく採取適期を明らかにするため、熟度の異なる3段階の果実を採取し、追熟前後における揮発性成分組成の変動について、その他の品質要因との関連において調査した。

1. 未熟果(Hard mature), 硬熟果(Firm mature), および軟熟果(Soft mature)を採取し、室温で4日間追熟したところ、色調、硬度、糖度、酸度および風味は軟熟果のそれ以外は可食適期であった。しかし、軟熟果はやや過熟状態となった。

2. モモの香気成分として、キャピラリーガスクロマトグラフィーにより89成分が検出され、そのうち33成分を同定した。主要成分は、 C_6 アルデヒドとアルコールならびにラクトン類であった。

3. 同定した33成分の全揮発性成分は、いずれの採取熟度においても採取直後に多く、追熟するにつれて減少した。この追熟による全揮発性成分の減少の主な

原因は、量的に多い青臭みを示す C_6 アルデヒドとアルコール類の減少によることがわかった。

4. モモ果実の芳香の主体をなすラクトン類として、 $C_6 \sim C_{12}$ に及ぶ11成分が認められた。完熟果における γ -デカラクトンは全ラクトンの約40%を占め、主要なラクトンであった。これらのラクトン類は熟度の進行に伴い急激に増大し、芳香の発現に寄与していると考えられた。

5. 匂い閾値の評価から熟度の進行に伴う芳香の発現は、青臭み成分としての C_6 アルデヒドとアルコール類の減少に伴って、芳香を示すラクトン類、特に γ -デカラクトンなどの急激な増加により引き起こされることが示された。

6. 果実採取後、4日程度の流通を含む追熟期間を考慮したときの揮発性成分の挙動からみた採取適期の果実は、硬熟果であると判定した。