Natural Science Report, Ochanomizu University, Vol. 6, No. 1, 1955
お茶の水女子大学 自然科学報告 第6巻 第1号

Studies on change of taste of persimmon during the process of ripening.

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Persimons are astringent when they are green whether they are sweet kind or astringent kind. But with sweet persimons, astringency is gradually reduced as they ripen, while with the astringent kind they are still astringent even they are ripe.

These changes have been studied from the standpoints of sugars and tannins contained in the persimons.

Experimental

We selected Fuyuu-kaki to represent the sweet kind and Hachiya-kaki to represent astringent kind.

The fruits and leaves of these trees were picked every half month from June to November and the quantity of sugars and tannins in them were determined by usual method, while the quality was determined by paper chromatography.

I. Sugars

1) Quantitative determination of sugars amounts during the process of ripening. (fruits only)

i. Preparation of samples;

After the calyx and seeds were removed, fruits were ground into paste in the mortar. 5 gr. of this paste were extracted with 100 cc of distilled water and filtered, and the residue was washed with 50 cc of water and filtered again. Both the filtrate and the washing were put together and distilled water was added till the volume reached exactly 200 cc.

a) Reducing sugars

The foregoing solution was used directly.

b) Soluble nonreducing sugars

The foregoing solution was hydrolysed with dil. HCl by the ordinary method.

c) Total carbohydrate

5 gr. of the above-mentioned fruit-paste, 50 cc of distilled water and 50 cc of 3% HCl were mixed in a round flask and hydrolysed by refluxing for two hours. Then it was neutralized

and distilled water was added till the volume amounted exactly to 200 cc.

ii. Quantitative determination

Semimicro-Bertrand method was used.

iii. Results

The results are shown in Fig. I.

2) Detection of sugars by paper chromatography.

i. Preparation of samples;

The leaves were ground in the motar and extracted with distilled water. The extract was condensed under the reducing pressure. The concentrated solution thus obtained was used as sample.

The fruits were treated in the same way as the leaves, except extraction was made 80% EtOH and distilled water respectively.

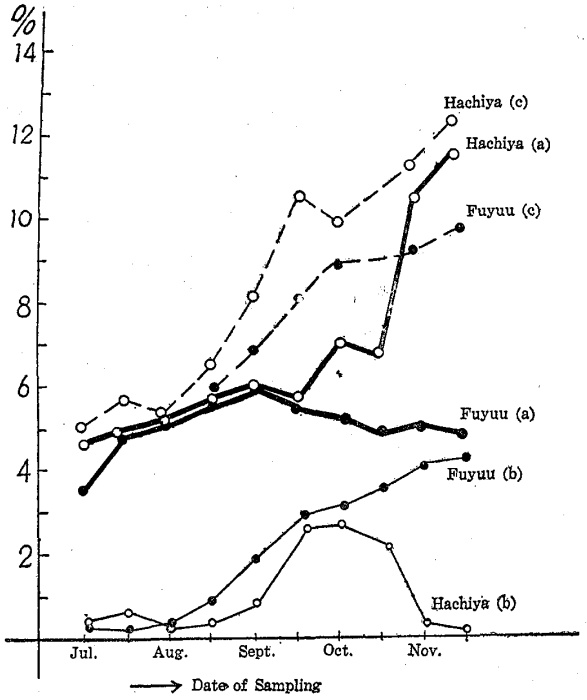

Fig I. Changes in sugars during the process of ripening.

(note) Moisture was always 84–85.5% throughout the experiment. So we calculated the sugar percentage in the fresh fruits.

(a) ▬▬ Reducing sugars
(b) —— Non-reducing sugars
(c) – – – Total carbohydrates

ii. Paper chromatography

Solvent;

n-BuOH : AcOH : H_2O (4 : 1 : 5 v/v)

(upper layer was used)

Condition of development;

One dimentional. 18–20°C 17–19 hrs.

Detection of sugars on the chromatogram;

(1) Ammoniacal $AgNO_3$

The developed chromatogram was dried to remove the solvent and was sprayed with a mixture of equal volumes of 0.1N $AgNO_3$ and 5N NH_4OH. The chromatogram was placed in the oven at 105°C for 5–10 minutes.

(2) Benzidine

500 mg. of benzidine, 200 cc of glacial acetic acid, and 80 cc. of absolute ethanol were mixed. The chromatograms were

sprayed with the reagent and heated at 100–105°C for 15 minutes.

(3) Kalium Periodate and Permanganate

2% aqueous solution of KIO_4 and 1% aqueous solution of $KMnO_4$ containing 2% Na_2CO_3 were mixed at the rate of 4 : 1 just before mixture was used.

The chromatogram, when dry, was sprayed with the reagent and heated for a few minutes at 100°C.

(4) Aniline Hydrogen Phthalate

The reagent was obtained by adding 930 mg. aniline and 1.6 gr. phthalic acid to 100 cc water-saturated n-BuOH. The dried paper was sprayed with this reagent and heated for 5 minutes at 105°C.

iii. Results

The results are shown in table I.

Table I. R_f value and color of spots detected.

Sample	R_f	Color			
		Reagent (1)	Reagent (2)	Reagent (3)	Reagent (4)
Both Ripe Hachiya-kaki and Ripe Fuyuu-kaki	0.23	purplish brown	brown	grayish yellow	light brown
	0.18	same above	same above	same above	brown grayish
	0.14	—	—	same	brown
Leaves of both Hachiya and Fuyuu	0.18	purplish brown	brown	above same above	brown
pure Fructose	0.23	same above	same above	same above	light brown
pure Glucose	0.18	same above	same above	same above	brown grayish
pure Sucrose	0.14	—	—	same above	brown

The results of the studies on sugars are as follows.

(1) The amount of reducing sugars gradually increased as the fruits of Fuyuu-kaki and Hachiya-kaki ripened.

In the fruits of Fuyuu, the amount of reducing sugar became almost constant in the middle of September while in the case of Hachiya the sugar-increase still continued and in November reached maximum. Moreover, the amount of total reducing sugars was much greater than Fuyuu.

(2) Nonreducing sugar showed a greater increase in Fuyuu than in Hachiya.

(3) Glucose, Fructose and Sucrose were detected both in the fruits of Fuyuu and Hachiya when they were ripe.

But in the leaves glucose only was detected.

II. Tannins

1) Changes in soluble tannin contents.

i. Preparation of samples.

The preparation was made in the same way as sugar-determination. Leaves were treated in the same way, too.

ii. Quantitative determination of tannins.

Tannins and other oxydative organic compounds were oxidized at the same time with standard solution of $KMnO_4$,

meahwhile tannins were removed with gelatin, and the remaining oxydative organic compounds were oxidized by the same $KMnO_4$ solution.

The difference between the volumes of $KMnO_4$ solution needed for oxidation, made it possible to calculate the amount of tannins.

(1) 2.5 cc of indigocarmin solution (1.5 gr. of indigocarmin and 12.5 cc of conc. H_2SO_4 were disolved in 12.5 cc of water) and 75 cc of water were added to 1 cc of the test solution. Then it was titrated by standard $KMnO_4$ solution. (1 cc of this $KMnO_4$ solution corresponded to 1.98 mg. of tannins)

(2) To 10 cc of test solution there were added 5 cc of gelatin solution (25 gr. of gelatin was dipped in saturated aquaous solution of NaCl for one hour, and then heated to resolve).

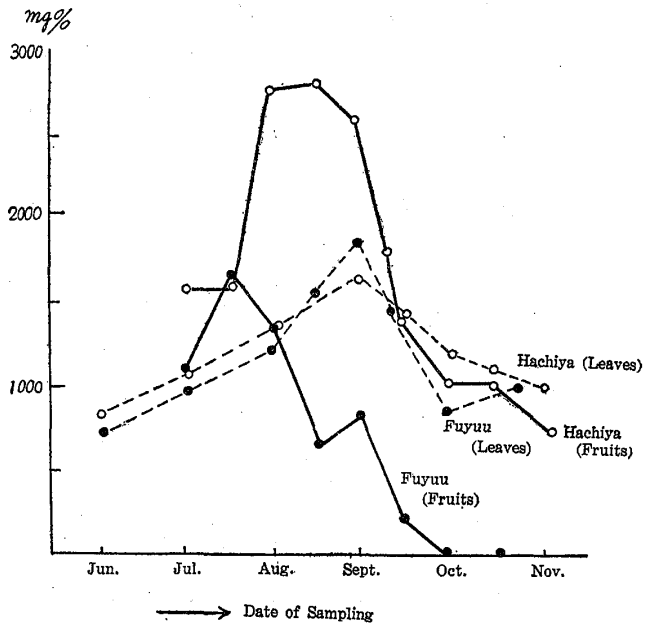

Fig II. Changes in soluble tannin contents during the process of ripening.

After it was cooled, water was added to make the volume 1 litre, 10 cc of acidified solution of NaCl (to 975 cc of satu-

rated aqueous solution of NaCl 25 cc of conc. H_2SO_4 was added) and 1 gr. of powder of kaolin. The mixture was shaken for a few minutes, and filtered, 2.5 cc of this filtrate was titrated in the same manner as (1). 1.98 mg. was multiplied by the difference of values of titration (1) and (2) to find out the amount of tannin.

iii. Results

The results are shown in Fig. II.

2) Detection of tannins by paper chromatography.

i. Preparation of samples

(a) Leaves

After being dried and mealed, leaves were extracted with ethylacetate. The extract was concentrated under reducing pressure, then disolved with water and filtered. Filtration was concentrated again for paper chromatography.

(b) Fruits

(1) Water extract

Fruits were ground in the mortar, and extracted with hot water and filtered. The filtrate was concentrated.

(2) Hydrolyzed solution

To water extract (1) equal volume of 5% HCl was added and refluxed for two hours. The hydrolyzed solution thus obtained was extracted with ether. From the ether extract, ether was removed by heating it at about 40°C.

In the case of ripe fruits, the fruit meat in paste condition was hydrolyzed directly.

ii. Paper chromatography

Solvent;

n-BuOH : AcOH : $CHCl_3$: H_2O (49 : 2 : 1 : 53 v/v)
(upper layer was used)

Condition of development;

One dimentional. 18–20°C 18–19 hrs.

Detection of tannins on the chromatogram;

1% aqueous solution of ion alum was sprayed on the dried paperchromatogram. Immediately the colour appeared.

iii. Results

The results are shown table II.

The results obtained concerning tannins are as follows;

(1) Leaves

No difference was found between Hachiya and Fuyuu. As to seasonal changes in tannin-content, it was found that the amount of tannins increases from the end of summer to the beginning of autumn. (This tendency is the same as Fam. Fagus.)

Table II. R_f value and color of spots detected

Sample			R_f value and Color		
Aqueous extract	Green fruits	Fuyuu	0.59 (purple)		
		Hachiya	0.59 (purple)		
	Ripe fruits	Fuyuu	non		
		Hachiya	0.59 (purple)		
	Leaves	Fuyuu	0.77 (greenish brown)	0.62 (brown)	0.58 (purple)
		Hachiya	0.76 (greenish brown)	0.62 (brown)	0.58 (purple)
Hydrolyzed solution	Green fruits	Fuyuu	0.65 (brown)*	0.61 (purple)	
		Hachiya	0.65 (brown)*	0.61 (purple)	
	Ripe fruits	Fuyuu	0.65 (brown)*	0.61 (purple)	
		Hachiya	0.65 (brown)*	0.61 (purple)	
pure Gallic acid			0.65 (brown)*		
pure Phloroglucine			0.61 (purple)		

(note) * shows the color brought out by ammoniacal $AgNO_3$

(2) Fruits

The amount of water-soluble tannin was always much greater in Hachiya than Fuyuu.

Soluble tannin in Fuyuu disappeared from the middle of September to the beginning of October, while the soluble tannin in Hachiya was found even in November in a fairly large quantity.

Experiments on kind of tannin by paper chromatography revealed only one kind which was identical with one of the three kinds contained in the leaves.

Summary

The difference of taste between the Hachiya-kaki (astringent kind) and Fuyuu-kaki (sweet kind) have been studied from stand-point of sugars and tannins.

In the fruits of Fuyuu, the amount of reducing sugars became almost constant in the middle of September, while in the case of Hachiya the sugar-increase still continued up to November and red. sugar-amount became twice as much as there was in Fuyuu.

As for the nonreducing sugar (sucrose), it showed the same increase in both Fuyuu and Hachiya till October. Then in Hachiya it decreased almost to nothing in November, but in Fuyuu it continued to increase up to November. The difference offers an interesting subject for further study. The amount of total carbohydrates in Hachiya was greater than in Fuyuu when reipened.

The amount of water-soluble-tannins was always greater in Hachiya than Fuyuu. Water soluble-tannin in Fuyuu disappeared from the middle of September to the beginning of October, while the tannin in Hachiya was found even in November in a fairly large quantity.

It is concluded that the difference of the taste between the ripe Fuyuu and Hachiya is based on not the difference of sugar-contents but the change of soluble-tannin into insoluble-tannin in Fuyuu when ripened.

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(*Received August* 31, 1955)