Deterioration Mechanism for Tea Infusion Aroma by Retort Pasteurization

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After retort pasteurization, the change in the aroma pattern of green, oolong and black tea drinks was investigated.

By pasteurization, such volatile compounds as leaf alcohol and its esters had deteriorated. Others such as linalool and geraniol were liberated from non-volatile precursors. It was revealed that such changes in the aroma compounds destroy the aroma balance of each tea drink, causing the off-flavor called retort smell.

From enzymatic experiments, it was clarified that the precursors of mono-terpene alcohols induced during pasteurization are those water-soluble glucosides dissolved in the green tea extract.

At the present time, canned tea extract infusions (green, oolong and black tea) are very popular drinks in Japan. About 500,000 kl of these types of drinks were consumed in 1988.

In the production of tea drinks, the deterioration of tea flavor is an extremely important problem, and improvements to the flavor of tea drinks has become important. Especially, the retort smell produced during retort pasteurization seriously effects the flavor of tea drinks.

In this paper, changes of the aroma compounds found in tea drinks after retort pasteurization were surveyed by using the gas-chromatography technique. Furthermore, the formation mechanism for the retort aroma in tea drinks was also studied.

Experimental

1. *Production process for a canned tea drink.* Tea (1 g/100 ml) was extracted with hot distilled water at 80°C for 2 min. The tea extract was adjusted to pH 6.0 by NaHCO₃ after adding ascorbate as an antioxidant, before the tea infusion was warmed to 93°C and canned. The canned tea infusion was pasteurized for 8 min at 120°C.

2. *Preparation of the tea aroma fraction from tea drink.* A tea infusion (1 l) was distilled by steam distillation at

30–40°C under 30 mm of Hg for 120 min. Before the distillation, 50 µg of ethyldecanoate was added to the tea infusion as an internal standard for determining the relative amount of each tea aroma compound. After distillation, the tea aroma fraction in the distillate was extracted by ether. The ether extract was dried by Na₂SO₄ and concentrated to 50 mg.

3. *Identification and determination of the tea aroma compounds.* Each tea aroma compound was identified by a GS-MS analysis using a Hitachi-M-80A GC-MS instrument (ionization voltage, 20 eV; electron current, 110 µA; ion acceleration voltage, 3 kV; column, PEG 20M, 0.35 mm × 50 m; temp., 60–200°C, 2°C/min). The spectral data was compared with the data for authentic compounds and those previously reported,^{1,2)} and the retention time on the gas-chromatogram was compared with that of authentic compounds. The relative amount of each compound is shown by the ratio of the peak area of each compound to that of the internal standard on the gas-chromatogram.

4. *Effect of pasteurization conditions on canned tea drink flavor.* Pasteurizing was done for 5, 10, 15 and 20 min at 100, 115, 120 and 125°C. The changes in the content of tea aroma compounds in each pasteurized sample were investigated.

5. *Investigation of the formation mechanism for retort smell.* The amounts of aroma compounds in a tea infusion extracted from 10 g of tea were determined before and after incubating for 16 hr at 38°C with 10 mg of pectinase (EC 3.1.1.11 from tomato, Sigma).³⁾ The inhibitory effects of

Hg²⁺ and CN⁻ on the aroma formation by pectinase were surveyed by adding these inhibitors to the reaction mixture.

Results

1. Changes in the tea aroma pattern after retort pasteurization

As shown in Table I, almost all the volatile compounds in the oolong tea and black tea infusions decreased after retort pasteurization. However, some volatile compounds such as terpene alcohols and its oxides, benzyl alcohol, β -ionone, (Z)-jasnone and indole, increased distinctly in the green tea infusion after pasteurization.

After retort pasteurization, the green tea drink had a strong off-flavor aroma which we

call the retort smell. Black tea and oolong tea drinks lost their fresh and flowery aroma, this being especially marked for black tea.⁴⁾

2. Quantitative changes in the tea aroma compounds by retort pasteurization

In Fig. 1, the quantitative changes in linalool, geraniol, 4-vinylphenol and indole found in the green tea drink aroma are shown under different conditions.

The amounts of these compounds increased only after pasteurization for a long period (20 min) at 100°C, as is shown for linalool and geraniol. However, the quantitative changes in those compounds were induced immediately at 125°C, and the induced amounts of those compounds reached maximum levels after 10 min.

Table I. CHANGES IN TEA AROMA COMPOUNDS IN GREEN, OOLONG AND BLACK TEA INFUSIONS BEFORE AND AFTER RETORT PASTEURIZATION

Tea compound	Green tea		Oolong tea		Black tea	
	Before	After	Before	After	Before	After
Hexanal	0.015	Trace	0.569	0.084	0.370	0.163
1-Penten-3-ol	0.352	0.740	0.890	Trace	0.089	0.202
(E)-2-Hexenal	0.231	Trace	0.164	Trace	1.462	0.490
(Z)-2-Penten-1-ol	—	—	0.590	0.069	0.342	0.283
6-Methyl-5-hepten-2-on	—	—	0.177	Trace	1.991	1.325
(Z)-3-Hexenol	0.129	Trace	0.118	Trace	0.494	0.414
Linalooloxide I	0.064	0.132	0.244	0.134	1.494	1.134
Linalooloxide II	0.131	0.359	0.075	Trace	0.375	1.013
(E,E)-2,3-Heptadienal	0.253	0.753	0.508	0.476	0.254	0.731
Benzaldehyde	0.225	0.128	0.562	0.092	0.300	0.248
Linalool	0.525	0.710	0.363	0.103	2.106	2.004
3,7-Dimethyl-1,5,7-octatrien-3-ol	—	—	0.463	0.116	—	—
(Z)-3-Hexenylhexanoate	0.108	Trace	0.032	Trace	0.257	Trace
(α)-Terpineol	—	—	0.172	Trace	0.365	Trace
Linalooloxide III	0.126	0.236	0.072	Trace	—	—
Methyl salicylate	—	—	0.179	0.107	1.395	0.721
Geraniol	0.171	0.354	0.159	0.081	1.957	1.222
Benzyl alcohol	0.153	0.740	0.590	0.090	0.121	0.527
2-Phenylethanol	0.320	0.119	0.072	Trace	—	—
β -Ionone + (Z)-Jasmone	0.640	2.861	0.607	1.656	2.338	3.124
Nerolidol	1.342	Trace	2.894	0.083	0.310	0.195
Jasminelactone	—	—	0.084	Trace	—	—
4-Vinylphenol	—	0.710	—	—	—	—
Indole	0.170	0.971	0.190	Trace	—	—

The samples for the assay of aroma compounds were prepared from the same tea infusion before and after retort pasteurization.

The relative amounts of aroma compounds are shown as the ratio of peak area of each compound to that of an internal standard (ethyl decanoate) on the gas-chromatogram.

Fig. 1. Quantitative Changes of Linalool, Geraniol, 4-Vinylphenol and Indole in the Aroma Compounds of Green Tea Infusions after Retort Pasteurization at Different Temperatures.

With pasteurization temperatures between 100 and 120°C, the amounts of those compounds increased with increasing pasteurization time.

3. Liberation of volatile compounds from the green tea extract by pectinase

In Fig. 2, the result of a preliminary experiment by using pectinase is shown. The liberation of linalool and geraniol in the tea infusion reached the maximum level after 14–16 hr of incubation with pectinase after adding 10 mg of pectinase to an infusion made by 10 g of green tea.

As shown in Table II, hexanal, 1-penten-3-ol, 1-pentenol, (*E*)-2-hexenal, (*Z*)-3-hexenol, (*E,E*)-2,4-heptadienal, methyl salicylate, lin-

alool, linalooloxides, geraniol, (*Z*)-jasnone, nerolidole and indole were liberated by the abovementioned enzymatic reaction in the green tea infusion.

As the pectinase used was not purified, it is considered that other enzymes may have been present in this enzyme preparation. Therefore, the inhibitory effects of Hg^{2+} , an inhibitor of the hydrolysis enzyme, and CN^- , an inhibitor of metal-containing oxidase, were tested.

In Table II, the inhibitory effects of Hg^{2+} and CN^- on the formation of those compounds by pectinase are also summarized.

The liberation of hexanal, (*E*)-2 hexenal and (*Z*)-3 hexenol was inhibited by Hg^{2+} and CN^- . The enzymatic induction of other compounds such as linalool, geraniol, nerolidol, methyl

Fig. 2. Time Course of the Pectinase Reaction on the Liberation of Linalool and Geraniol in a Green Tea Infusion.

Amount of pectinase: 10 mg in 1 l of a green tea infusion made from 10 g of green tea.

Temperature: 38°C.

The relative amounts of linalool and geraniol were assayed by GC from the aroma preparations of pectinase-reacted tea infusions.

salicylate, indole, (*Z*)-jasnone and jasminalactone was suppressed by Hg^{2+} , while jasminalactone and indole were accelerated in the enzymatic formation by adding CN^- . These results show that the liberation of volatile compounds found in a green tea infusion was induced by hydrolysis and oxidation with the added enzyme preparation from the non-volatile compounds dissolved in the green tea infusion. It was also found that the liberation of some compounds was prompted by inhibiting the oxidative reaction.

Discussions

The formation mechanisms for tea aroma during the tea manufacturing process has been partially revealed. C-6 Alcohols (as leaf alcohol) and C-6 aldehyde (leaf aldehyde) have been produced from leaf lipid by enzymatic hydrolysis, oxidation, cleavage and reduction.⁵⁻⁹⁾ Linalool and geraniol were liberated from those glucosides accumulated in tea shoots by tea leaf glucosidase.¹⁰⁻¹²⁾ In tea

shoots, linalool- β -D-glucopyranoside and geraniol- β -D-glucopyranoside have also been identified.^{3,13)}

It is known that almost all parts of the precursors of tea aroma compounds are consumed and changed to volatile compounds by enzymatic reactions during fermentation in oolong and black tea. However, green tea is produced after the inactivation of endogenous enzymes in fresh leaves by steaming and by chemical compounds, which includes the precursors of tea aroma compounds in fresh shoots that are unchanged in made tea.

Therefore, it is thought that, in oolong and black tea, the water-soluble compounds changing to volatile compounds are negligible in the hot-water infusion. On the other hand, some water-soluble precursors of volatile compounds are dissolved in a green tea infusion. It is considered that the increase of the amounts of mono-terpene alcohols originates from the hydrolysis of those glucosides dissolved in a green tea infusion at temperatures over 100°C. Regarding oolong and black

Table II. INHIBITORY EFFECTS OF Hg AND CN ON THE FORMATION OF AROMA COMPOUNDS IN A GREEN TEA INFUSION BY PECTINASE

Compound	Control relative-amount ^a	Effects of pectinase ^b		
		Enzyme ^c	With Hg ²⁺ 10 ⁻ M	With CN ⁻ 10 ⁻ M
1-Penten-3-ol	0.010 (1)	3.1	1.4	5.9
1-Pentanol	0.022 (1)	4.0	0.9	4.0
Hexanal	0.065 (1)	1.7	0.2	0.9
(E)-2-Hexanal	0.030 (1)	1.5	2.1	trace
(Z)-3-Hexenol	0.099 (1)	1.0	0.4	0.5
Methyl salicylate	0.019 (1)	1.2	0.7	1.7
(E,E)-2,4-Heptadienal	0.100 (1)	1.5	1.0	2.7
Linalool	0.367 (1)	1.4	0.8	1.6
Geraniol	0.117 (1)	1.8	0.2	1.8
Nerolidol	0.144 (1)	4.5	0.4	4.2
(Z)-Jasmone	0.054 (1)	4.2	0.8	5.4
Jasminelactone	0.049 (1)	2.5	0.8	8.2
Indole	0.071 (1)	1.8	0.6	4.8

Control, the original green tea infusion.

^a The relative amount of each aroma compound to the internal standard in the original green tea infusion.

^b The inhibitory and activation ratio for the formation of aroma compounds by pectinase without and with the inhibitor. (Peak area of each compound in the green tea infusion treated by pectinase without and with inhibitors/peak area in the original infusion.)

^c Enzyme: Tea infusion treated by pectinase without inhibitors. (10 mg of pectinase was added in 1 l of tea infusion made from 10 g of green tea and the infusion was incubated for 16 hr at 38°C.)

Hg²⁺ and CN⁻: Tea infusion treated by pectinase with each inhibitor.

teas, such phenomea are rarely found because those glucosides dissolve very little in the tea infusions.

Other compounds increased by retort pasteurization such as 4-vinylphenol, β -ionone and indole may be liberated from *p*-coumaric acid and unknown precursors dissolved in the green tea infusion by hydrolysis under a high-temperature conditions.

C-6 Alcohol and aldehydes were also induced by pectinase. The formation of the glucosides of these compounds has been assumed in injured tissues.³⁾ However, as the enzymatic formation of these compounds was inhibited by Hg²⁺ and CN⁻, these compounds may be

not produced from the glucosides. It is thought that these compounds have been induced from a small quantity of leaf lipid in the green tea infusion by the hydrolysis and oxidative reactions of coexisting enzymes in the pectinase preparation that was used.

However, no formation of hexanal, hexenal and hexenol was recognized after retort pasteurization. The leaf lipid may have not been converted into small molecular compounds under retort pasteurization conditions, or the hexanal, hexenal and hexenol produced may have been destroyed during the pasteurization process.

From these results, it is thought that the origins of the off-flavor in tea drinks due to retort pasteurization may be induced by the two factors. The first is a deterioration of unstable aroma compounds such as leaf-alcohol and its esters by retort pasteurization, as was shown in the oolong and black tea infusions. The other is the liberation of volatile compounds from non-volatile precursors such as linalool and geraniol that are found in a green tea infusion.

Those phenomena may destroy the tea aroma balance and be the cause of the off-flavor tasted in tea drinks.

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