Changes of Chemical Compounds during Green Tea Manufacturing

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Introduction

Green tea in Japan is manufactured with the following procedures: fresh leaves are steamed to inactivate enzymes, and then the steamed leaves are subjected to pressing and heating with a series of the treatments, i.e., primary rolling, rolling, secondary rolling, final rolling, and drying. The resulted product is called crude green tea (Aracha). To increase storability and to improve taste and flavor, the crude green tea is heated at 110°–130°C. This procedure is called firing (Hi-ire), and the product is fired green tea (Hi-ire cha), which is generally sold on the market. In addition, the crude green tea is roasted at 150°–170°C to produce roasted green tea (Hoji-cha), which has strong roasted flavor.

Changes of volatile compounds in tea leaves during the green tea manufacture were reported by Fukatsu[8] and Hara[9]. The present author and his co-workers have studied changes of non-volatile compounds during the green tea manufacture[1-3,13]. In addition, reactions occurring between several compounds during the manufacture were also investigated, and the formation of Amadori compounds (which take part in the taste of green tea) by the reaction of amino acids with sugars was reported[4,5]. Furthermore the formation of a precursor of the brown compound by the reaction between amino acid and catechin was also reported[6,7]. The results of these investigations are briefly given in the present paper.

Changes of chemical compounds during green tea manufacturing

Changes of contents of chemical compounds during the manufacture are shown in Tables 1 to 4. During the process of manufacturing crude green tea, chlorophyll changed to pheophytin, and contents of glycolipids and phospholipids decreased. However, no appreciable changes were observed with other compounds. During the firing, amino acids, vitamin C, free reducing sugars, glycolipids, phospholipids and some others decreased. During the roasting, most compounds decreased. Particularly, amino acids, vitamin C, and glucose decreased to 20–40% of their contents in the crude green tea. The extract of each sample obtained with boiling water was used to measure the absorbance at 450 nm. The result showed that the absorbance increased during the heating of the crude green tea. It indicates that the water-soluble brown compounds are produced by heating of crude green tea.

Changes of chemical compounds by heating in a model system

As described above, heating of crude green tea caused the decrease of non-volatile compounds and the formation of the brown compounds. To examine what compounds are involved in the reaction responsible for these changes, model experiments were carried out. Mixtures of theanine, (−)-epicatechin, glucose, or caffeine were prepared and freeze-dried. They were heated at 130°C for 30 min

Table 1. Changes of chemical compounds during manufacture of crude green tea

(% of dry weight)

Compound	Steamed leaves	Primary rolled leaves	Final rolled leaves	Crude green tea
Amino acids	2.06	2.13	2.10	2.08
Tannin	10.20	10.20	10.50	10.65
Caffeine	2.62	2.62	2.62	2.63
Free reducing sugars	2.40	2.52	2.40	2.72
Vitamin C	0.51	0.56	0.56	0.56
Water extract	39.65	40.10	40.65	40.90
Conversion ratio of chlorophyll to pheophytin	11.61	18.72	36.24	41.23

Table 2. Changes of chemical compounds during heating of crude green tea

(% of dry weight)

Compound	Crude green tea	Fired green tea[a)]	Roasted green tea[b)]
Amino acids	3.41	2.84	0.77
Tannin	12.45	12.04	10.73
Caffeine	2.40	2.33	2.36
Free reducing sugars	1.91	1.51	1.13
Vitamin C	0.53	0.41	0.21
Water extract	39.33	38.20	36.54
Convertion ratio of chlorophyll to pheophytin	49.20	63.40	76.30

a): Heated at 130°C for 30 min.
b): Heated at 160°C for 30 min.

Table 3. Changes of lipids during manufacture of crude green tea

(% of dry weight)

Lipid class	Fresh tea shoot	Crude green tea	Fired green tea[a)]	Roasted green tea[b)]
Total neutral lipids	0.75	0.83	0.72	0.75
Total glycolipids	2.19	1.78	1.26	1.08
Total phospholipids	1.52	1.25	1.03	0.86

a): Heated at 130°C for 30 min.
b): Heated at 170°C for 30 min.

and then dissolved in boiling water. The absorbance of the solution at 450 nm, and changes in the amount of each compound were measured. The result showed that the mixture of theanine and glucose gave the greatest increase of the absorbance and the greatest decrease of each content. It was caused by the carbonyl-amino reaction. The mixture of theanine and (−)-epicatechin followed. From these results it was considered

Table 4. Changes of free sugars during heating of crude green tea

(% of dry weight)

Compound	Crude green tea	Fired green tea[a)]	Roasted green tea[b)]
Sucrose	3.02	2.87	2.01
Glucose	0.37	0.16	0.13
Fructose	0.42	0.20	0.19

a): Heated at 130°C for 30 min.
b): Heated at 150°C for 30 min.

that amino acids react with sugars and with catechins during the green tea manufacture.

Products of reaction by heating between amino acids and sugars

It is generally known that when foodstuffs are heated, the Amadori compounds are produced by the reaction of amino acids with sugars, and these compound influence flavor, taste, color, etc. of the foodstuffs[10]. As it was inferred from the result of the model experiment that amino acids react with sugars during the green tea manufacture, the problem whether the Amadori compound is produced or not was examined. As a result, the Amadori compound A was isolated, and it was identified as 1-deoxy-1-L-theanino-D-fructopyranose (Fig. 1), which is a product of the reaction of theanine with glucose, by using NMR, GC-MS, etc. When crude green tea was heated at 130°C, this substance increased in the amount until about 30 min of heating, and then turned to decrease after that time (Fig. 2). The quality of fired green tea showed a positive correlation ($r=0.558$, significant at 10% level) with the content of this substance (Fig. 3). As this substance tastes sweet, it must play a role to improve the taste of fired green tea. In addition, as the Amadori compound is known to give caramel-like sweet flavor when heated[12], the Amadori compound A is considered to improve the flavor of fired green tea, too. Besides the Amadori compound A, other Amadori compounds produced by the reaction between aspartic acid, threonine, serine, or alanine and glucose were detected in the green tea.

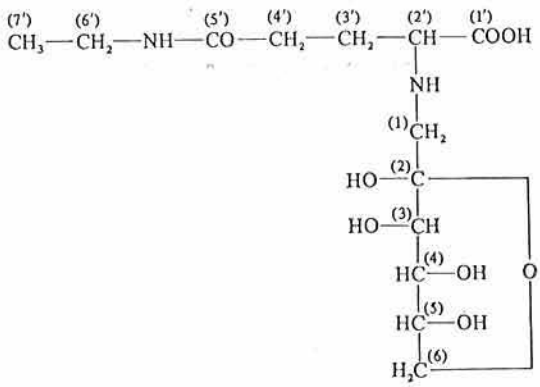

Fig. 1. Structure of 1-deoxy-1-L-theanino-D-fructopyranose (Amadori compound A)

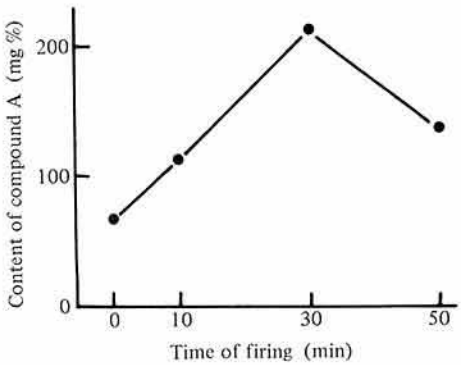

Fig. 2. Changes in the content of the Amadori compound A during heating of crude green tea
Heating temperature: 130°C.

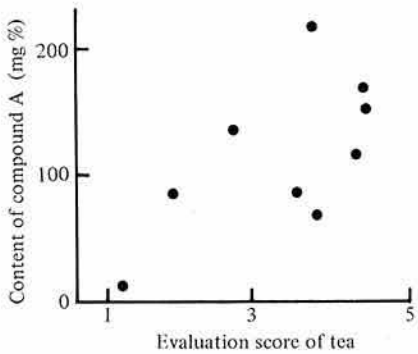

Fig. 3. The relation between the content of the Amadori compound A and the evaluation score of tea

Products of reaction by heating between amino acids and catechins

The model experiment mentioned above showed that heating of the mixture of amino acid and catechin produced the brown compounds by the reaction between both the substances. To examine further in detail, the catechin mixture extracted from green tea

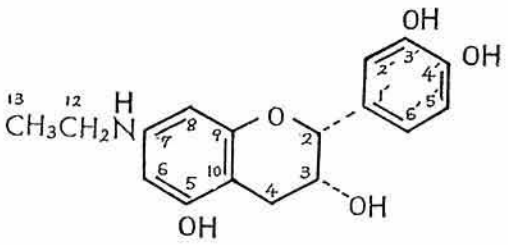

Fig. 4. Structure of 7-*C*-ethylamino-(−)-epicatechin

was mixed with amino acid mixture composed of theanine, glutamic acid, serine, and arginine. This mixture was freeze-dried, and heated at 150°C for 30 min. In addition, the catechin mixture alone and the amino acid mixture alone were similarly freeze-dried and heated. Then, these mixtures were dissolved in boiling water, and absorbance of the solution at 450 nm was measured. When the catechin mixture alone or amino acid mixture alone was used, only a few brown compounds were produced. However, when the mixture of catechin mixture and amino acid mixture was used, a substantial amount of the brown compounds were produced.

Accordingly, the mixture of (−)-epicatechin and alanine was freeze-dried, and then heated at 140°C for 40 min to examine the reaction product. The result showed that the compound B was produced as a precursor of the brown compound. The compound B was identified as 7-*C*-ethylamino-(−)-epicatechin (Fig. 4), by using, NMR, GC-MS, etc. This substance was actually detected in green tea. It suggests that during green tea manufacturing the compound B, a precursor of the brown compound, is produced by the reaction between amino acid and catechin, and from that precursor the brown compound itself is produced. When the over-firing is done in the course of green tea manufacturing, the tea quality lowers, giving brown coloration of tea infusion. Therefore, the firing at the condition not to cause the formation of precursors, like the compound B, of the brown compound seems to be better.

Conclusion

The process of manufacturing green tea is divided into two parts: (1) fresh tea leaves are heated, under pressure, at relatively low temperature (below 100°C) to prepare crude green tea, and (2) the crude green tea was heated or roasted at the temperature higher than 100°C with the purpose of increasing storability and improving the taste and flavor.

During the crude green tea manufacture, the green color of leaves becomes lighter gradually, due to the change of chlorophyll to pheophytin. During the process of crude green tea manufacture, volatile compounds in tea leaves undergo great changes[8]. But, non-volatile compounds did not show substantial changes. On the contrary, during the process of firing or roasting, most non-volatile compounds decreased in their amount, particularly amino acids, sugars, vitamin C, etc. decreased considerably.

During the second process of manufacturing green tea, it was made clear that the Amadori compounds were produced by the reaction between amino acids and sugars. These compounds are considered to contribute to the improvement of the taste and flavor, which occurs by firing the crude green tea. It was also made clear that the brown compounds were produced by the reaction between amino acids and catechins during the second process.

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