Changes of catechins in green tea drinks during production process.

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Summary
Preliminary test on the stability of constituents in green tea drinks has shown that caffeine is highly stable but catechins are rather unstable. The dominant change of catechins seemed to be isomerization influenced by pH of the infusion at the heating. The effects of pH and temperature on reaction kinetics of degradation of green tea catechins were investigated. The reaction of catechins was accelerated at pH higher than 6.0, and inhibited at pH lower than 5.0. A great difference of apparent activation energies of degradation of catechins in green tea infusion was observed at lower and higher temperature than 82 °C.

Simulation test of the production process of canned or PET bottled green tea drinks was performed. Green tea catechins decreased in almost all of the process. The largest decrease of catechins occurred during retort sterilization. An addition of small amount of L-ascorbic acid (AsA) was effective on the stabilization of catechins in green tea drink. Avoiding excess heating through the process and adjusting pH of tea infusion slightly acidic by an addition of small amount of acid such as AsA are required to retain catechins in canned or PET bottled green tea drinks.

Keywords
Green tea drink, Heat processing, Catechins, Isomerization, pH

Introduction
Canned or PET bottled green tea drinks are supplied as packaged beverages for consumer use in Japan. The production volume of these drinks keeps remarkable increasing because of suiting consumers' favor. Most of these drinks are low acid beverages so high temperature heat processing for a fixed time is required to sterilize the spores of thermophilic anaerobes according to Japanese hygienic regulations. Therefore, it is important to minimize changes of functional constituents in green tea drinks during heat processing.

In this study, the effects of pH and temperature on reaction kinetics of degradation of green tea catechins were investigated (1). Stability of green tea catechins during processing of canned or PET bottled green tea drinks including sterilization by a retort or heat exchanger was also investigated (2).

Materials and Methods
Standard reagents of catechins were obtained from Kurita Kogyo Co., Ltd., Japan. Middle grade of dried green tea leaves ('Yabukita') were used for preparation of green tea infusion. A reaction apparatus was designed to simulate the extraction, hot filling, and sterilization. In the apparatus, the solution was heated up to 135 °C within 30 seconds and cooled to ambient temperature within 5 seconds. Catechins were determined by the HPLC method described by Terada et al. (3) with a few modifications.
Results and Discussion

Experiment 1. Reaction kinetics of catechins in green tea infusion. The log of the ratio remaining to the initial concentration of -EGC, -EGCg, -EC, and -ECg in green tea infusion for each temperature was plotted against heating time (Fig.1). The reaction fitted apparent first order kinetics for the four kinds of catechins at the temperature examined, but the reaction rate constants were different for each kind of catechins. Each Arrhenius plot showed not a straight line but a concave one consisting of two straight lines which crossed each other at a specific turning point. The turning point temperature was commonly observed on each Arrhenius plot at 2.82 x 10^-1 (1/K); at 82 °C (Fig.2). The apparent activation energies obtained were slightly different between the four kinds of catechins (Table). It was 7.3 to 11.4 times larger above the turning point temperature. This meant that the actual reaction rate measured at a temperature higher than 82 °C was faster than the reaction rate predicted by extrapolation from the one measured below 82 °C. The stability of catechins in green tea infusion was subject to the turning point temperature.

<table>
<thead>
<tr>
<th>Catechins</th>
<th>Activation energies (kcal/mol)</th>
<th>( E_a &lt; 82^\circ C )</th>
<th>( E_a &gt; 82^\circ C )</th>
<th>( E_a/E_{a1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-ECg</td>
<td></td>
<td>3.2</td>
<td>35.8</td>
<td>11.2</td>
</tr>
<tr>
<td>-EC</td>
<td></td>
<td>3.2</td>
<td>38.1</td>
<td>7.3</td>
</tr>
<tr>
<td>-EGC</td>
<td></td>
<td>3.6</td>
<td>41.1</td>
<td>11.4</td>
</tr>
<tr>
<td>-EGCg</td>
<td></td>
<td>4.7</td>
<td>37.9</td>
<td>8.1</td>
</tr>
</tbody>
</table>

\( E_{a1} \), activation energy at lower than 82°C, \( 2.83 \times 10^{-3} \) (1/K).

\( E_{a2} \), activation energy at higher than 82°C, \( 2.83 \times 10^{-3} \) (1/K).

Experiment 2. Effects of pH on reaction kinetics of green tea catechins. A similar experiment was done with or without an addition of AsA to the green tea infusion. The reaction also fitted an apparent first order kinetics (Fig.3). 'Total catechins' were shown as the sum of -EGC, -EGCg, -EC, and -ECg to simplify the comparison. The turning point temperature on the
Green Tea Infusions with or without an Addition of AsA at 25, 40, 55, O.

Symbols: •. in green tea infusion with 20 mg/100 ml of AsA; O. in green tea infusion without an addition of AsA.

Fig. 3 Apparent First Order Reaction Rate Plot of 'Total Catechins' in Green Tea Infusions with or without an Addition of AsA. 'Total catechins', the sum of - EC, - ECG, - EGC, and - EGCg.

Upper figure, with an addition of 20 mg/100 ml of AsA; lower figure, without an addition of AsA. Initial concentration of 'total catechins' in green tea infusion with an addition of AsA. 93.3 mg/100 ml; in green tea infusion without an addition of AsA, 93.9 mg/100 ml.

Experiment 3. Stability of green tea catechins during processing of canned green tea drink. The simulation test of the process of canned green tea drink was performed. Variation of catechins in the process of canned green tea drink including retort sterilization was shown in Fig. 5. Catechins decreased in almost all of process including holding in a filler bowl (95 °C) or a reservoir (55 °C). The largest decrease of catechins occurred during retort sterilization. An addition of small amount of AsA was effective on the stabilization of catechins in green tea drink. For example, in the case of retort sterilization at 121 °C for 6 min. (lethality, F0=4), the decrease of catechins in green tea drink was restrained 45% by an addition of AsA (20 mg/100 ml).

Fig. 4 Arrhenius Plot of Apparent First Order Reaction Rate Constant of 'Total Catechins' in Green Tea Infusions with or without an Addition of AsA.

Symbols: •. in green tea infusion with 20 mg/100 ml of AsA; O. in green tea infusion without an addition of AsA.

Fig. 5 Variation of catechins in the process of canned green tea drink including retort sterilization

□. without an addition of L-ascorbic acid (AsA); ■, with an addition of AsA (20 mg/100 ml); ●, standard condition for evaluating the next process.
Experiment 4. Stability of green tea catechins during processing of PET bottled green tea drink. The simulation test of the process of PET bottled green tea drink was performed. Variation of catechins in the process of PET bottled green tea drink including sterilization in heat exchanger was shown in Fig. 6. The decrease of catechins in green tea drink was restrained by an addition of small amount of AsA, however, the largest decrease occurred during sterilization in heat exchanger. The decrease of catechins was negligible by an addition of AsA (20mg/100ml) in the case of the sterilization at 135 °C for 32 sec. (F0=4) by heat exchanger.

![Diagram showing the process of PET bottled green tea drink](image)

**Fig. 6** Variation of catechins in the process of PET bottled green tea drink including sterilization in heat exchanger.

- , without an addition of L-ascorbic acid (AsA); ■, with an addition of AsA (20 mg/100 ml); □, standard condition for evaluating the next process.

References

