Bull. Fac. Fish. Hokkaido Univ.
38(4), 405-413. 1987.

Bluish Discoloration of Kombu-dashi*

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Abstract

The occurrence of bluish discoloration in kombu extract (kombu-dashi) was studied using commercial kombu, *Laminaria japonica*. The authors demonstrated that this discoloration is due to a reaction between iodine in the kombu and starch remaining in the cooker. The results obtained are as follows:

1) The temperature of the kombu extraction water had no effect on the bluish discoloration.

2) When the ratio of water to kombu was below 1 : 150, the bluish discoloration did not occur.

3) Kombu-dashi containing below 0.005% starch solution showed no coloration.

4) The bluish discoloration weakened in proportion to the number of times the rice cooker was rinsed after being used to make rice gruel.

5) When the initial pH of the kombu-dashi was more acidic, the color change phenomenon was fast and deep.

6) A difference in bluish discoloration was observed according to individual kombu fronds.

7) A difference in bluish discoloration was not observed in regards to different parts of individual fronds.

8) Potassium iodide was added in place of kombu, the same discoloration was observed.

The primary factor for the occurrence of this bluish discoloration is the amount of available chlorine. If available chlorine is abundant in city water, kombu must not come into contact with starch if discoloration is to be suppressed.

Introduction

When kombu-dashi is made, although rare, at times the kombu-dashi becomes blue as if a coloring agent has been added. This bluish discoloration has been the cause of concern to some of consumers[1,2]. However, this discoloration does not always occur in city water. The reason why this bluish discoloration occurs is not known at present.

The authors consider that this phenomenon is due to the addition of sodium hypochlorite to city water for the purpose of sterilization. The sodium hypochlorite turns the iodine compound in kombu into free iodine[3~6].

This iodine then reacts with starch, remaining on imperfectly washed cookers, so-called iodine-starch reaction[7,8], and this bluish discoloration occurs.

Herein the mechanism and protection against this bluish discoloration in

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* This work was orally presented to the Annual Meeting of Japan. Soc. Sci. Fish., at Tokyo in April, 1986.

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kombu-dashi is presented.

Materials and Methods

Kombu samples: Makombu (*Laminaria japonica*) fronds harvested and sun-dried in 1985 at Toi-cho, a town near Hakodate were used. They were cut into squares of about 3 cm.

Preparation of kombu-dashi: Three g of kombu squares were immersed in 150 ml of city water for 1 hour at room temperature (17-23°C).

Preparation of 5% starch solution: With the aid of heat, 2.5 g of soluble starch was dissolved in 50 ml of city water.

Reaction of bluish discoloration: Fifty ml of starch solution and 100 ml of kombu-dashi were mixed together, and this mixture was titrated with a 1 : 100 dilution of sodium hypochlorite (0.885 g Cl/ml). During the titration, the color reaction proceeded by first being colorless, then gradually becoming deep blue and finally fading again to colorless. The color grading was organoleptically divided into the following four stages; −, Colorless; +, Pale; Brightness below 15-16 in Color Standard[9], ++, Medium; The depth was defined as when the white magnet stirrer could be seen, +++, Deep; The depth was defined as when the white magnet stirrer could not be seen.

Appearance of bluish discoloration in kombu-dashi: The items investigated were as follows: 1) Kombu extraction water temperature. 2) Amount of kombu. 3) Amount of soluble starch. 4) Number of times rice cooker was rinsed. 5) Effect of initial pH value on reaction. 6) Individual differences in kombu fronds. 7) Differences in parts of individual fronds. 8) Discoloration due to potassium iodide.

pH value of reactant: If necessary, the pH values of the reactants were measured using the Horiba F-8 AT pH meter.

Results and Discussion

The results of our studies on this bluish discoloration reaction in kombu-dashi are as follows:

1) *Kombu extraction water temperature*

In order to investigate the effect of the extraction water temperature on discoloration, three g of Kombu squares were immersed at 0°C, 20°C, 40°C, 60°C, 80°C and 90°C in 150 ml of city water for 1 hour, respectively. As shown in Table 1., the extraction water temperature had no effect.

2) *Amount of kombu*

Kombu squares was added to 150 ml of city water at the following rates; 1.5 g, 1.0 g and 0.5 g. The results are as given in Fig. 1. As can be seen when less than 1.0 g of kombu was used, this bluish discoloration did not occur.

3) *Effect of soluble starch on discoloration*

A five% soluble starch solution was diluted to 1/1, 1/10, 1/100 and 1/1000. As is shown in Fig. 2., below 1/1000 dilution no discoloration was observed. There was no notable relation between pH value and bluish discoloration.

4) *Relation between number of times rice cooker was rinsed and discoloration*

Rice gruel was made in a rice cooker, and the cooked rice was removed from the

Table 1. Effect of the kombu extraction water temperature on discoloration.

NaClO titer (ml)	0°C	20°C	40°C	60°C	80°C	90°C
0.0	−	−	−	−	−	−
0.2	−	−	−	−	−	−
0.4	−	−	−	−	−	−
0.6	−	−	−	−	−	−
0.8	−	−	−	−	−	−
1.0	+	+	−	+	−	−
1.2	++	++	−	+	−	−
1.4	++	+++	+	+	−	−
1.6	+++	+++	+	++	−	+
1.8	+++	+++	++	++	−	++
2.0	+++	+++	++	++	+	++
2.2	+++	+++	++	+++	+	++
2.4	++	+++	+++	+++	+	++
2.6	++	+++	+++	+++	++	++
2.8	+	+++	+++	+++	++	+++
3.0	+	+++	+++	+++	++	+++
4.0	+	+++	+++	+++	+++	+++
5.0	−	++	++	++	+++	++
6.0	−	+	++	++	++	++
7.0	−	−	+	+	+	+
8.0	−	−	+	+	+	+
9.0	−	−	+	−	−	−
10.0	−	−	−	−	−	−
11.0	−	−	−	−	−	−
12.0	−	−	−	−	−	−
13.0	−	−	−	−	−	−
14.0	−	−	−	−	−	−
15.0	−	−	−	−	−	−
16.0	−	−	−	−	−	−
17.0	−	−	−	−	−	−
18.0	−	−	−	−	−	−
19.0	−	−	−	−	−	−
20.0	−	−	−	−	−	−

Color grading: − ; Colorless, + ; Pale, ++ ; Medium, +++ ; Deep.

rice cooker. Then, the rice cooker was rinsed out using city water. The rinse water was used in place of the 5% solution of soluble starch. The number of rinsings was once, twice, three times, four times and five times. The results are as shown in Fig. 3. The bluish discoloration became weaker in proportion to an increase in the number of rinsings.

5) *Initial pH of reaction system*

Before titering, 1N-HCl or 1N-NaOH was added to the kombu-dashi. The

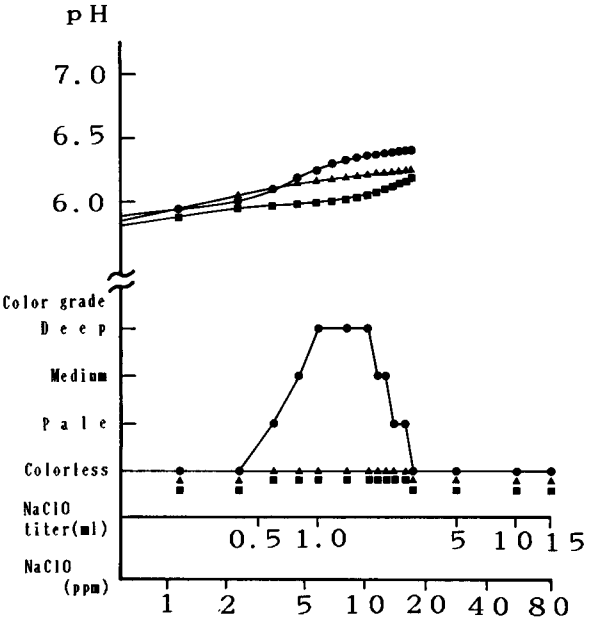

Fig. 1. Effect of the amount of kombu on discoloration. Ratio of kombu and water: ●; kombu 1.5 g/water 150 ml, ▲; kombu 1.0 ml/water 150 ml, ■; kombu 0.5 g/water 150 ml.

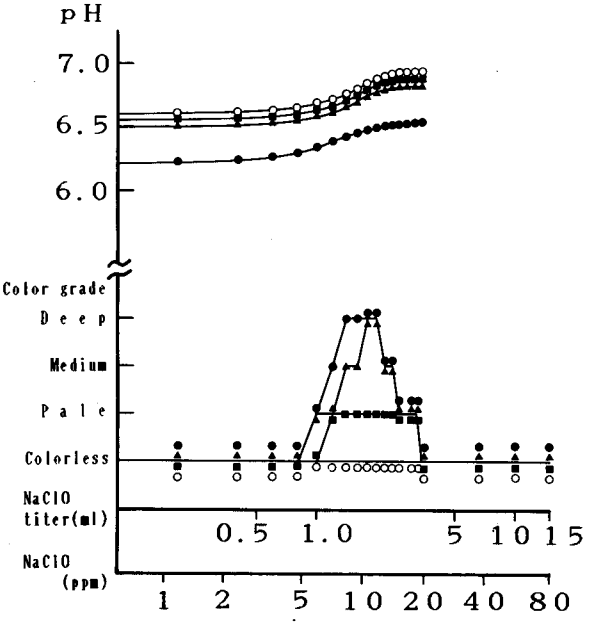

Fig. 2. Effect of the soluble starch concentration on discoloration. Dilution of 5% soluble starch solution: ●; 1/1, ▲; 1/10, ■; 1/100, ○; 1/1000.

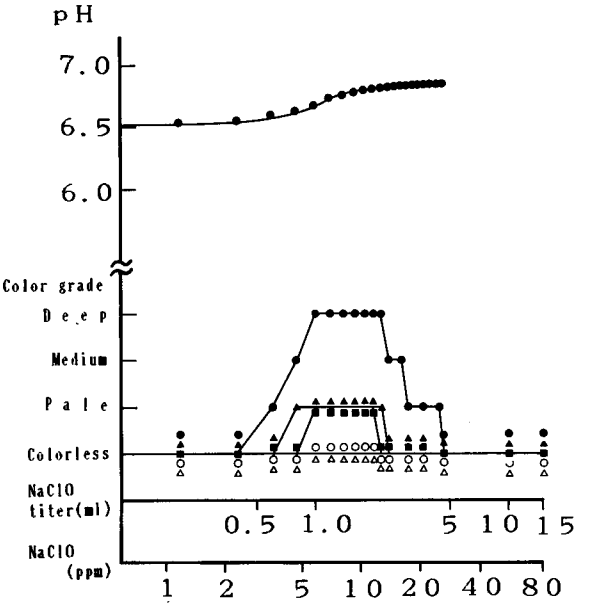

Fig. 3. Relation between number of times rice cooker was rinsed and discoloration. Number of rinsings: ●; once, ▲; twice, ■; three times, ○; four times, △; five times.

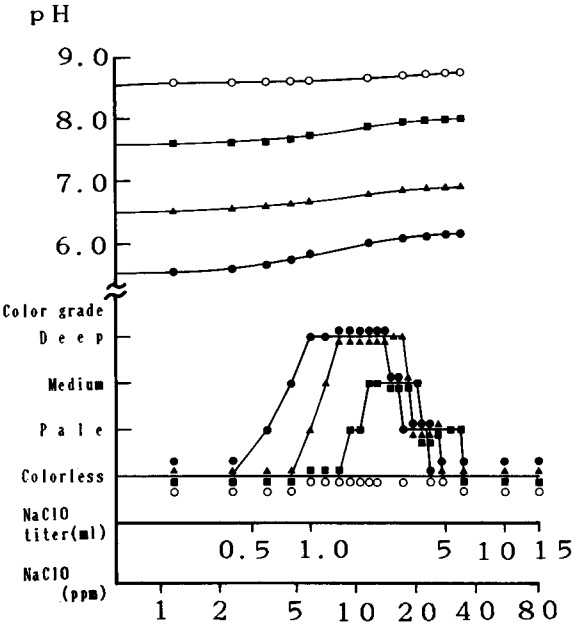

Fig. 4. Effect of initial pH of reaction system on discoloration. Initial pH: ●; 5.56, ▲; 6.55, ■; 7.59, ○; 8.57.

Table 2. Individual differences on discoloration in kombu fronds.

NaClO titer (ml)	Sample number									
	1	2	3	4	5	6	7	8	9	10
0.0	−	−	−	−	−	−	−	−	−	−
0.2	−	−	−	−	−	−	−	−	−	−
0.4	−	−	−	−	−	−	−	+	−	−
0.6	+	−	+	+	−	−	−	++	−	+
0.8	++	−	++	++	−	−	−	+++	−	++
1.0	+++	−	+++	+++	+	−	−	+++	−	+++
1.2	+++	−	+++	+++	+	−	−	+++	−	+++
1.4	+++	−	+++	+++	++	+	−	+++	−	+++
1.6	+++	−	+++	+++	+++	++	−	+++	−	+++
1.8	+++	−	+++	+++	+++	+++	+	+++	−	+++
2.0	+++	+	+++	+++	+++	+++	++	+++	−	+++
2.2	+++	++	+++	+++	+++	+++	+++	+++	−	+++
2.4	+++	+++	+++	+++	+++	+++	+++	+++	−	+++
2.6	+++	+++	+++	+++	+++	+++	+++	+++	−	+++
2.8	+++	+++	+++	+++	+++	+++	+++	+++	−	++
3.0	+++	+++	+++	+++	+++	+++	+++	+++	−	+
4.0	++	+++	+++	+++	+++	++	+++	+++	−	−
5.0	+	+++	++	+++	+++	+	+++	+++	−	−
6.0	−	+++	++	++	++	−	+++	+++	−	−
7.0	−	+++	+	++	+	−	+++	+++	−	−
8.0	−	+++	+	+	−	−	+++	+++	−	−
9.0	−	+++	−	+	−	−	+++	+++	−	−
10.0	−	++	−	−	−	−	+++	++	−	−
11.0	−	+	−	−	−	−	+++	+	−	−
12.0	−	−	−	−	−	−	++	+	−	−
13.0	−	−	−	−	−	−	+	−	−	−
14.0	−	−	−	−	−	−	+	−	−	−
15.0	−	−	−	−	−	−	−	−	−	−
16.0	−	−	−	−	−	−	−	−	−	−
17.0	−	−	−	−	−	−	−	−	−	−
18.0	−	−	−	−	−	−	−	−	−	−
19.0	−	−	−	−	−	−	−	−	−	−
20.0	−	−	−	−	−	−	−	−	−	−

Color grading: − ; Colorless, + ; Pale, ++ ; Medium, +++ ; Deep.

initial pH of each kombu-dashi was 5.56, 6.55, 7.59 and 8.57. The results are as shown in Fig. 4. The lower the pH value, the sooner and the deeper the color change occurred. The bluish discoloration did not occur in the alkaline range.

6) *Individual differences in kombu fronds*

In order to investigate individual differences in kombu fronds, ten samples were used. The sampled parts are as shown in Fig. 5. The results are as shown in Table

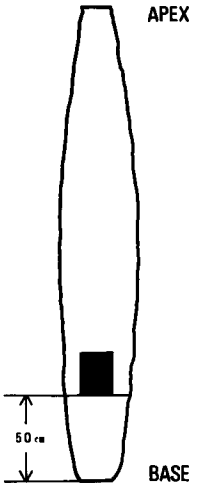

Fig. 5. The sampled parts.

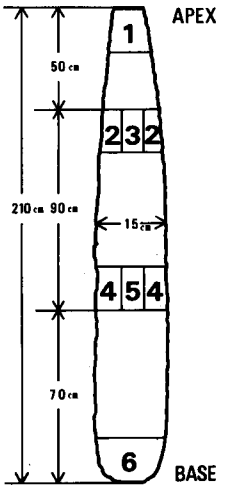

Fig. 6. The sampled parts.

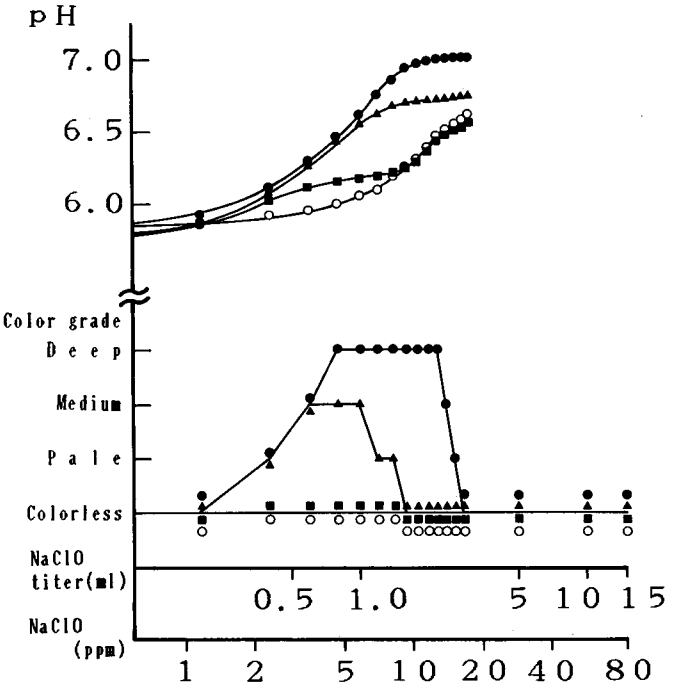

Fig. 7. Effect of the amount of potassium iodide on discoloration. Amount of potassium iodide: ●; 0.01 g, ▲; 0.003 g, ■; 0.002 g, ○; 0.001 g.

Table 3. Differences on discoloration according to each part of an individual kombu frond.

NaClO titer (ml)	Position number					
	1	2	3	4	5	6
0.0	−	−	−	−	−	−
0.2	−	−	−	−	−	−
0.4	−	−	−	−	−	−
0.6	+	−	−	−	+	+
0.8	++	−	+	−	++	++
1.0	+++	+	++	−	+++	+++
1.2	+++	++	+++	+	+++	+++
1.4	+++	+++	+++	++	+++	+++
1.6	+++	+++	+++	+++	+++	+++
1.8	+++	+++	+++	+++	+++	+++
2.0	+++	+++	+++	+++	+++	+++
2.5	+++	+++	+++	+++	+++	+++
3.0	+++	+++	+++	+++	+++	+++
3.5	+++	+++	+++	+++	+++	+++
4.0	+++	+++	+++	++	+++	+++
4.5	+++	+++	+++	+	+++	+++
5.0	+++	+++	+++	+	++	+++
5.5	++	+++	+++	−	+	+++
6.0	++	+++	++	−	+	+++
6.5	+	++	++	−	+	+++
7.0	+	++	+	−	−	+++
7.5	−	+	+	−	−	++
8.0	−	+	−	−	−	++
8.5	−	−	−	−	−	+
9.0	−	−	−	−	−	+
9.5	−	−	−	−	−	+
10.0	−	−	−	−	−	−

Color grading: − ; Colorless, + ; Pale, ++ ; Medium, +++ ; Deep.

2. Only one out of ten samples showed no discoloration. In this sample it is surmised that either the quantity of iodine salts in the kombu-dashi was below the discoloring limit or the iodine salts did not readily change into free iodine. Individual differences in kombu fronds was recognized.

7) *Differences in parts of individual kombu fronds*

In order to investigate whether there are differences according to each part of an individual kombu frond, one kombu sample was selected. The sampled parts are as shown in Fig. 6. The results are as shown in Table 3. Differences were not recognized.

8) *Discoloration due to potassium iodide*

A potassium iodide dilution was used in place of a kombu square. As shown

in Fig. 7., when potassium iodide was introduced into 150 ml of city water at a rate below 0.002 g, no discoloration was observed.

9) *Counterplans concerning bluish discoloration*

When kombu-dashi is made, although rare, at times the kombu-dashi becomes blue as if a coloring agent has been added. This bluish discoloration caused some consumers to feel uneasy[1,2]. Recently, few reports concerning bluish discoloration in kombu-dashi have been presented. Therefore, from a food hygienic point of view, the authors set out to demonstrate this kombu-dashi blue discoloration, and so as to prove that this reaction is not due to the contamination of harmful coloring agents but is due to the iodine-starch reaction.

In Japan, the city water law stipulates that the amount of available chlorine in city water must be more than 0.1 ppm. Available chlorine sterilizes city water, in order to supply hygienic city water to the users. The higher the concentration of contaminant organisms in the water, the more the amount of available chlorine is needed. At present, the concentration of available chlorine in tap water is 0.80 ppm in Tokyo, 0.40 ppm in Kyoto, and 0.82 ppm in Osaka. If these concentrations are maintained in tap water, and kombu-dashi is made with this water, it is sufficiently possible to generate this bluish discoloration only with starch.

This bluish discoloration in kombu dashi occurs naturally only whom available chlorine in city water comes into contact with starch remaining in an incompletely washed cooker. If the amount of available chlorine in city water increases, it is possible that more cases of bluish discoloration will be generated. Yet, if this bluish discoloration in kombu-dashi occurs, it should be recognized that this is not the influence of harmful coloring agents but is a natural phenomenon.

Summary

When kombu-dashi is made, it rarely becomes blue. This bluish discoloration reaction is caused by the chemical reaction between iodine in kombu, avaiable chlorine in city water, and starch remaining in cookers.

References

1) Nippon Kombu Shinbun, No. 562 (1971. 2. 28), No. 563 (1971. 3. 8), No. 673 (1974. 8. 8), No. 675 (1974. 8. 28), No. 721 (1976. 1. 8), No. 723 (1976. 1. 28), No. 727 (1976. 3. 8), No. 800 (1978. 3. 18), No. 803 (1978. 4. 18). (In Japanese).
2) The Asahi's Hakodate edition, (1985. 11. 13), (1985. 11. 29). (In Japanese).
3) Imaeda, K., Imanishi, I., Osawa, K., Okazaki, N., Katayanagi, S., Momijisawa, I., Kawauchi, Z. and Sugii, A. (1971). *Teiryo Bunseki*. 214 p. Hirokawa Shoten, Inc., Tokyo. (In Japanese).
4) Morinaga, K. (1983). *Sanka to Kangen*. 236 p. Syokabo, Inc., Tokyo. (In Japanese).
5) Sabata, T. (1984). *Suido no Bunka, Seio to Nippon*. 285 p Shinchosha, Inc., Tokyo. (In Japanese).
6) Matsumoto, H., Nakagawa, M., Tsukada, S. and Yamaguchi, H. (1985). *Shin Koshyu Eiseigaku*. 476 p. Hirokawa Shoten, Inc., Tokyo. (In Japanese).
7) Yagi, K. (1981). *Shokuhin Kagaku*. 165 p. Kodansha, Inc., Tokyo. (In Japanese).
8) Pharmaceutical Society of Japan (1980). *Eiseishikenho Chukai*. 1229 p. Kanahara Shuppan, Inc., Tokyo. (In Japanese).
9) Nippon Shikisai Kenkyusho (1954). *Iro No Hyojun*. 29 p Nippon Shikisaisha, foundation, Tokyo. (In Japanese).