Studies on the "Browning" of Canned Crab Meat (*Paralithodes camtschatica* Til.) I. The Difference in the Chemical Composition of Normal and Brownd Canned Crab Meat

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The color of normal commercial canned crab meat is generally white, but in the canned crab prepared in land factories in Hokkaido it is occasionally observed that the part of white meat has become brown in color. Because of this so-called "browning" phenomenon in canned crab meat, the merchandise value is greatly reduced. This phenomenon is a problem in the production of canned crab.

Occasionally, hydrogen sulfide which is formed during the heating of raw material causes the discoloration of canned foods. But in canned crab the browning is not considered to be due to the hydrogen sulfide because the crab meat is prevented from direct contact with the inner side of the container by a parchment paper or the coated enamel. Also the browning of the canned crab meat will certainly not be concerned with enzymatic reaction either because the canned foods are processed at comparatively high temperatures.

Since MAILLARD¹⁾ has pointed out that the phenomenon of browning is due to a condensation reaction between the aldehyde group of reducing sugar and the amino group of amino acid or protein, the browning of many foods has been explained by this reaction. Recently TARR^{2a)} observed that MAILLARD's reaction was also seen in the browning of cod meat during heating.

Here the difference in chemical components between normal canned crab and brownd canned crab, especially in components which take part in MAILLARD's reaction (NH_2 -radical and aldehyde radical), was investigated.

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Experiments

1. Sample and experimental method

As samples, two cans each of brownd and normal cans taken from the supply of

canned crab meat at the export inspection office were used. This supply of cans had been processed at Wakkanai in the autumn of 1956 and stored for 6 months. The samples were divided into two groups which contained one browned can and one normal can.

In the cans of group I, meat and juice were separately analysed, and in the cans of group II, meat and juice were homogenized and analysed together. The analysis was carried out concerning to the following items.

(i) Water-content (by drying method). (ii) pH (by glass electrode). (iii) Volatile basic nitrogen (by CONWAY's method³⁾). (iv) Total nitrogen (by micro-KJELDAHL's method). (v) Amino nitrogen (by POPE-STEVEN'S method⁴⁾). (vi) Protein-nitrogen (by STUZER's method). (vii) Color reflection ratio (by SHIMAZU A.K.A. photo electric colorimeter using a red filter, L₃). (viii) Formaldehyde (by GAILLOT's method⁵⁾). (ix) Distribution of nitrogen (by VAN SLYKE's method). (x) Kinds of free amino acids (by paper chromatography^{6,7,8)}). (xi) Reducing sugar (by SOMOGYI's method⁹⁾). (xii) Detection of free sugar in the juice (by paper chromatography^{7,10,11,12)}).

2. Experimental results

As to the contents of the cans, there are remarkable differences between browned cans and normal cans. The meat of normal cans was more elastic than that of browned cans. The former was pure white, but the latter was brown. The color reflection ratio for the normal can of group I was 26.5 whereas in group II the normal can showed a ratio of 25.0. On the other hand, the browned can in group I was 19.5 and in group II the ratio was 19.0. It was also interesting that the browned canned crab meat has a caramel smell and generated fluorescence when the meat was subjected to the ultraviolet rays.

The results determined by various chemical compositions in those samples are shown in Table 1. As seen in Table 1, the amount of water content, the volatile basic nitrogen and pH of the browned canned crab were larger than those of the normal canned crab. There was no remarkable difference in the amount of total nitrogen between the two materials. It is remarkable that the amount of protein-nitrogen in the browned can was less than that in the normal can, and the amount of free amino acid was vice versa. As to the amount of free reducing-sugar, the amount in the browned can was larger than that in the normal can in the flesh, but the juice was less in the browned can and more in the normal can. It was noticeable that the amounts of free amino-nitrogen and free reducing sugars in the browned can were larger than those of the normal can.

According to the results detected by paper chromatography, amino acids such as glycine, serine, ornithine, tyrosine, alanine, histidine and arginine were found in the normal can, but, asparatic acid was not found. However, in the browned cans, a slight touch of arginine, histidine, and alanine was found, but an unknown spot of which Rf

Table 1. Differences in the chemical components between the browned canned crab and the normal can.

Sample Items		Group I		Group II	
		Normal canned crab	Browned canned crab	Normal canned crab	Browned canned crab
		meat		contents	
Water content (%)		78.9	82.3	79.3	79.5
pH		5.8	6.3	6.0	6.2
V.B.-N (mg%)		22.0	37.4	27.2	39.6
Total-N (%)		3.04	3.19	2.92	3.07
Protein-N (%)		1.60	0.94	1.60	1.50
Amino-N (mg%)		149	208	105	128
Reducing sugar (mg%)	in meat	18.5	33.9	35.6	33.7
	in juice	43.3	14.8		
Formaldehyde (mg%)		28.9	9.9	—	—

Table 2. Difference of nitrogen distribution between the browned canned crab and the normal can.

Sample Fraction		Group I				Group II			
		Normal can (meat)		Browned can (meat)		Normal can (contents)		Browned can (contents)	
		in sample (mg%)	in total-N (%)	in sample (mg%)	in total-N (%)	in sample (mg%)	in total-N (%)	in sample (mg%)	in total-N (%)
Total-N		84.74	100	118.10	100	52.64	100	59.21	100
20% H ₂ SO ₄ insoluble-N		12.03	14.20	29.00	24.50	7.64	14.50	18.31	30.90
20% H ₂ SO ₄ soluble-N		72.71	85.80	89.10	75.50	45.00	85.50	40.90	69.10
Amide-N		0.42	0.50	1.43	1.31	0.54	1.03	1.20	2.14
Humine-N		2.13	2.51	3.51	2.97	2.10	3.99	3.65	6.17
Total-N in form of bases		8.96	10.60	8.40	7.11	5.89	11.20	4.49	7.59
Amino-N in form of bases		3.30	3.89	2.35	1.99	3.09	5.87	2.48	4.19
Arginine-N		6.14	7.31	3.90	3.30	3.28	6.24	1.95	3.39
Histidine-N		1.58	1.86	3.13	2.65	0.51	0.97	0.83	1.40
Lysine-N		0.51	0.60	0.82	0.69	0.07	0.13	0.43	0.73
Cystine-N		0.73	0.86	0.55	0.47	2.02	3.84	1.28	2.16
Total-N in form of monoamino-fraction		61.20	72.3	75.75	64.10	36.50	69.4	31.60	53.40
Amino-N in form of m.a.-fraction		27.90	32.9	23.69	20.10	25.10	47.7	11.20	18.90
Non-amino-N in form of m.a.-fraction		33.30	39.4	52.06	44.00	11.40	21.7	20.40	34.50

was near 0.85 was clearly observed.

When the nitrogen distribution in hydrolysates of each sample of both groups was estimated, the results obtained are shown in Table 2. As seen in Table 2, the amount of 20% H_2SO_4 -insoluble nitrogen in the browned can was larger than that in the normal can, therefore the total amount of basic nitrogen and mono-amino nitrogen was generally less than those of the normal can.

Further, the amounts of various kinds of reducing sugars isolated from the juice in each can of group I were estimated, and the results obtained are shown in Table 3.

Table 3. Differences of the components of free reducing sugars in the juice between the browned canned crab and the normal can.

Kind of free sugars	Sample	Group I					
		Normal canned crab		Browned canned crab			
		Detection	The amounts of free sugars		Detection	The amounts of free sugars	
			in the juice (mg%)	in total sugar (%)		in the juice (mg%)	in total sugar (%)
Galactose	++	1.25	9.26	++	2.25	14.5	
Glucose	++	2.38	17.6	+ -	2.03	13.1	
Arabinose	+	2.65	19.6	++	3.00	19.4	
Ribose	++	3.25	24.1	+ -	2.60	16.8	
Rhamnose	+	2.70	20.0	+	3.05	19.7	
Lactose	++	-	-	+	-	-	
Sum		12.23	90.6		12.93	83.5	
Total amount of free sugar		13.50	100		15.5	100	

As seen in Table 3, 83 to 91% of the total amount of the free sugars consisted of galactose, glucose, arabinose, ribose, and rhamnose. The amounts of glucose and ribose were less than those in the normal can.

Discussion

In the above experimental results, it is noticeable that (1) the amounts of free amino nitrogen and free reducing sugars in the browned canned crab meat were comparatively larger than those in the normal can, and those amounts were opposite in the juice, (2) there was a small amount of reducing substances, such as formaldehyde, in the browned canned crab meat, (3) the amount of arginine in free amino acid of the meat of the browned canned crab was less than that of the normal can, (4) the amounts of glucose and ribose in the juice of browned canned crab were less than those of the normal can, (5) browned canned crab had a caramel smell and showed fluorescence. As a cause for the browning phenomenon of the canned crab, when the

aminocarbonyl reaction between the amino- and aldehyde-radicals is considered, in the means described as follow, it may be considered that facts found in numbers 3, 4, and 5 will suggest the occurrence of MAILLARD's reaction in canned crab, but the fact noted in 1 seems apparently to conflict with the reaction.

TARR^{2b)} has found that the browned fish meat caused by heating has less amount of ribose than that of the meat before heating. It was found that in heating the amount of amino acid decreased with the proceeding of MAILLARD's reaction¹³⁾. Therefore it is considered certain that the amounts of free amino acids and reducing sugars in the browned canned crab were less than those of the normal can both of which were processed under the same conditions.

However, the author considered that from fact (1) which indicated the amount of free amino nitrogen and free reducing sugars were rich in the browned canned meat suggests a promotion in the reaction under a mild condition¹⁴⁾. Consequently in fact (1) it may show that the raw material which has become browned canned crab meat has a rich amount of the two kinds of components already before heating. Then why are the amounts of the two components abundant in the raw material which will become browned canned crab?

This may be due to the freshness of the raw material. This point will be investigated in a later part of these studies.

Fact (2) will not necessarily suggest that the loss of the amount of reducing substances results from the amino-carbonyl reaction which is considered to be a cause for the browning. In the present stage of the research concerning this reaction, it has not been ascertained yet whether aldehyde radical in free formaldehyde may combine with amino radical in free amino acids or not.

From facts (3) and (4), it may be suggested that the amino radical in arginine in free amino acids may combine with aldehyde radicals in glucose and ribose. Tarr^{2c)} has suggested that the browning of cod meat during the heating may occur due to the reaction between aldehyde radicals in the sugar components and amino radical, considering that ribose may be generated from desoxy-ribonucleic acid by ribonuclease and that glucose formation may occur from glycogen.

As a source of amino radical in the amino-carbonyl reaction, the free amino acids were taken into consideration in this experiment. Besides that component, terminal NH₂-radical in protein must be considered. This will be investigated in a later part.

References

- 1) MAILLARD, C. C.: *Compt. rend.*, 154, 66 (1912).
- 2a) TARR, H. L. A.: *J. Fish. Res. Bd. Canada*, **8**, 74 (1950).
- 2b) ———: *Nature*, **171**, 344 (1953).
- 2c) ———: *Food Tech.*, **8** (1), 15 (1954).
- 3) CONWAY, E. J.: Translated by ISHIZAKA, O. *Microdiffusion Analysis and Volumetric Error*, 75 p. (1952) (Nankodo Co., Ltd. Tokyo).

- 4) POPE, C. G. & STEVENS, M. F.: *Biochem J.* **33**, 1076 (1939).
- 5) THORPE, J. F. & WHITELEY, M. A.: *A Student's Manual of Organic Chemical Analysis*, 192 p. (1926) (Longmans, Green Co., Ltd. New York).
- 6) NEUBERG, C. & KERB, J.: *Z. Biochem.*, **40**, 498 (1912).
- 7) FUJII, K. & UKITA, M.: "*Hakko-Kogaku*" (Fermentation Engineering), **32** (10), 348 (1954).
- 8) UMETSU, M.: *ibid.*, **32** (7), 267 (1954); **33** (8), 349 (1955).
- 9) SOUDA, T. & EGAMI, F.: "*Tatorui-Kagaku*" (The Chemistry of Polysaccharides), 54 p. (1956) (Kyoritsu Shuppansha Co., Ltd. Tokyo).
- 10) HAWTHORNE, J. R.: *Nature*, **160**, 714 (1947).
- 11) DIMLER, R. G. *et al.*: *Anal. Chem.*, **24**, 1411 (1952).
- 12) SOMOGYI, M.: *J. Biol. Chem.*, **160**, 61 (1945); **195**, 19 (1952).
- 13) PATTON, A. R.: *Science*, **107**, 623 (1948); **108**, 659 (1948).
- 14) ADACHI, T.: *J. Agr. Chem. Soc. Japan.*, **30** (7), 372 (1956).