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Studies on the Odour of Canned Fish (Part 7)

Volatile Sulphur Compounds in Fresh and Canned Edible Portion of Short-neck Clam, *Tapes japonica*

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The volatile sulphur compounds in fresh and canned short-neck clam meats were estimated by a colorimetric method. Canned products of the clam meats were stored over a period of 50 days.

The contents of hydrogen sulphide and methyl mercaptan in fresh short-neck clam meats were 7.4 μg/100 g flesh and 10.0 μg/100 g flesh, respectively. The contents of the two compounds in canned clam meats just after canning were much higher than those in the fresh meats. They were 167 μg/100 g flesh and 42 μg/100 g flesh, respectively. But, the amounts of the two in the canned meats decreased gradually with the period of storage.

Dimethyl sulphide could not be detected in either fresh or canned short-neck clam meats.

I Introduction

Volatile acidic and basic components in fresh and steam-doiled meats of several kinds of fish[1] as well as the flavour of canned mackerel[2] were reported previously. Besides, the pattern of increase of volatile acidic and basic components in canned mackerel, cuttlefish and short-neck clam meats in the course of storage was investigated,[3] and it was shown that the increase of *n*-propylamine in canned mackerel, cuttlefish and short-neck clam meats was remarkable.[3] Taking into account of these experimental results, it has been pointed out that the examination on neutral fraction is very important in order to study the odour of canned fish.

The present paper deals with the amounts of volatile sulphur compounds in fresh short-neck clam meats as well as canned meats. Canned products of the clam meats were stored for periods up to 50 days. From a view-point of odour, it is a matter of course that sulphur compounds are generally very important and they have very close relation to odour.

Ronald et al.[4] showed that the compound responsible for the characteristic odour of fresh Pacific oyster is dimethyl sulphide. Brooke et al.[5] also showed that fresh soft-shell clam (*Mya arenaria*) meats collected during the clam's spawning season contain dimethyl sulphide, and they suggested that dimethyl sulphide donates the odour of the fresh clam. Mendelsohn et al.[6] identified hydrogen sulphide, methyl mercaptan, dimethyl sulphide, ethyl-*n*-butyl sulphide and several kinds of neutral compounds in fresh clam (*Mya arenaria*) meats, and tried to follow the changes occurring in the volatile compounds after irradiation, cooking and storage. Nishibori et al.[7] detected hydrogen sulphide only as the responsible compound for the odour which was produced cooking of asari (*Tapes philippinarum*) and shijimi (*Corbicula japonica*), but they could not show the presence of methyl mercaptan and dimethyl sulphide. In the case of oyster,[8] they detected hydrogen sulphide and a very small amount of other sulphides as odorous compounds, but they could not detect methyl mercaptan.

II Experimental

1. Sample

   Short-neck clam was purchased at Kagoshima Central Wholesale Market.

2. Collection of fresh short-neck clam meats

   Shell of the clam was cracked, and the edible portion was collected.

3. Canning process for the edible portion of short-neck clam

   1) Cooking of short-neck clam. Stand for three minutes in boiling water.
   2) Shucking.
   3) Filling. Pack 150 g of the shucked short-neck clam in a can (Sake-hira No. 2, lacquered).
   4) Addition of brine solution. Add a ladleful brine (2.5% table salt, 0.15% citric acid solution, pH 3-4. About 50 ml).
   5) Sealing. Seal under reduced pressure with "Toyo-seikan" model 5 sanitary vacuum seamer.
   6) Retorting. Heat at 8 lbs (112.7℃) for 60-70 minutes.
   7) Cooling. Cool in running water.

   Canned products were then stored room temperature until these were needed for the following experiment.

4. Estimation of volatile sulphur compounds

Hydrogen sulphide, methyl mercaptan and dimethyl sulphide were estimated according to the method of McLay.[9]

1) Reagents

(a) Amine solution. 2.5 g *N,N*-dimethy-*p*-phenylenediamine hydrochloride were dissolved in 500 ml conc. hydrochloric acid.

(b) Reissner solution. 33.8 g Ferric chloride hexahydrate were dissolved in 300 ml distilled water, and mixed with 250 ml nitric acid.

(c) Trapping agents. 3% Bismuth nitrate solution, 3% mercuric cyanide solution and 3% mercuric chloride solution were used.

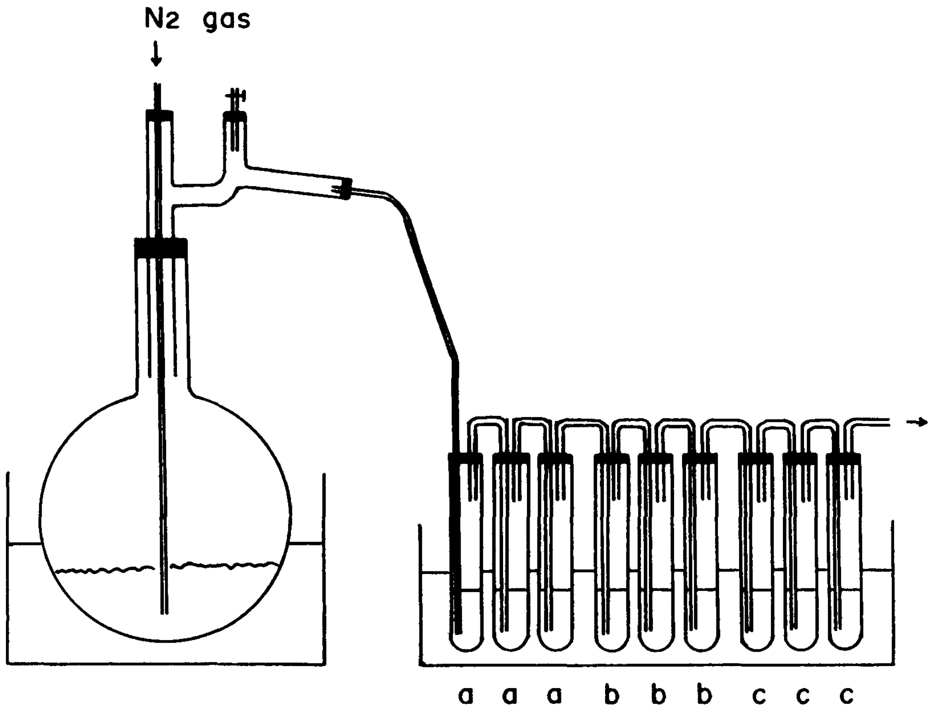

Fig. 1. Apparatus used for determination of volatile sulphur compounds. A 3-litre flask was connected to a nitrogen supply and placed in a water bath at 40℃. Trapping tubes a, b, and c were immersed in ice water. Each tube a contained 6 ml 3% bismuth nitrate solution, tube b 6 ml 3% mercuric cyanide solution and tube c 6 ml 3% mercuric chloride solution.

2) Procedure

Fig. 1 illustrates the apparatus used for determination of volatile sulphur compounds. A three-litre round-bottom flask was charged 450g minced short-neck clam meats, 350ml distilled water and 1g thymol. The flask was connected to a nitrogen gas supply, and immersed in a water bath at 40℃. Each of the first three trapping tubes contained 6ml 3% bismuth nitrate solution, the second three trapping tubes 6ml 3% mercuric cyanide solution and the third three trapping tubes 6ml 3% mercuric chloride solution. These trapping tubes were connected in a series in the order as mentioned above, and they were immersed in ice water. Nitrogen gas was bubbled through the clam slurry, and then led into the trapping agents. An aspirator was used to suck out the gas. After 5 hours the trapping tubes were disconnected, and to each tube were added 1.5ml of amine solution and 0.5ml of the Reissner solution. The solution was diluted to 10ml with distilled water and allowed to stand at room temperature for 30 minutes. The absorbance was then read with a Hitachi spectrophotometer at 670nm for the bismuth nitrate trap, at 490nm for the mercuric cyanide trap, at 500nm for the mercuric chloride trap. The amounts of hydrogen sulphide, methyl mercaptan and dimethyl sulphide were read from standard curves prepared by using solutions containing known amounts of the each compound.

III Results and Discussion

It is known that raw marine fish meats generally produce sulphur compounds during cooking[10] or storage at room temperature[11] or low temperature.[6,12,13] These sulphur compounds can be formed from amino acids[10,13] or some precursor[14] in the meats. Accordingly, the temperature of water bath immersed the flask was set at 40℃ in order to avoid the effect of heating. In addition to this, bacterial action was suppressed as far as possible through addition of thymol to the meats slurry.

Sulphur compounds in the fresh clam meats were analysed in the manner described before. Meats from the same sample of short-neck clam that was used for determination on fresh meats were canned. The canned products were stored for periods up to 50 days, and they were analysed, too. Table 1 shows the amounts of hydrogen sulphide, methyl mercaptan and dimethyl sulphide in the fresh or canned clam meats.

Table 1. Contents of volatile sulphur compounds in fresh and canned edible portion of short-neck clam. (μg/100 g sample)

Volatile sulphur compound	Fresh	Canned					
		Days of storage					
		0	8	20	30	40	50
Hydrogen sulphide	7.4	166.8	126.4	124.1	122.7	109.8	99.1
Methyl mercaptan	10.0	41.9	36.8	34.2	32.2	23.5	20.8
Dimethyl sulphide	ND	ND	ND	ND	ND	ND	ND

ND ; could not be detected.

1. Volatile sulphur compounds in fresh short-neck clam meats

In fresh clam meats, 7.4 μg/ 100 g of hydrogen sulphide and 10.μg/ 100 g of methyl mercaptan were observed. On the other hand, dimethyl sulphide was not observed. Ronald et al.[4] reported that dimethyl sulphide is responsible for the characteristic odour of fresh Pacific oysters, *Crassostrea gigas*. When the oysters were held at 20-20℃, only dimethyl sulphide was detected for the first 2 or 3 hours, then thiols began to make their appearance. Brooke et al.[5] showed that in fresh soft-shell clam, *Mya arenaria*, meats which were collected over their spawing period, the average concentration of dimethyl sulphide was 3 ppm. Pure dimethyl sulphide being recognized as a clam like odour by panelists, Brooke et al.[5] suggested that dimethyl sulphide donates the odour of fresh soft-shell clams. But, dimethyl sulphide was not observed in the fresh meats of short-neck clam as shown in Table 1.

2. Volatile sulphur compounds in canned short-neck clam meats

Just after canning, the amounts of hydrogen sulphide and methyl mercaptan in the canned meats showed remarkable increase. The level of hydrogen sulphide and methyl mercaptan was as high as 167 and 42 μg/100 g flesh, respectively. In other words, they multiplied into about 20 times and 4 fimes those of the fresh meats, respectively. The increase was definitely caused by retolting. They were probably produced from meats protein.

Mendelsohn et al.[6] showed that cooking of meats of soft-shell clam caused an increase in the concentration of hydrogen sulphide, methyl mercaptan and aldehydes. Hughes[10] found that the cooking of herring in all-glass appratus produces volatile sulphur compounds. He[10] also reported that cysteine and cystine yielded hydrogen sulphide, and methionine yielded methyl mercaptan and dimethyl sulphide on heating with glucose or other suitadle reactants. Herbert et al.[13] demonstrated that the disappearance of methionine and cyst(e)ine could be correlated with the production of volatile sulphides in the flesh of North Sea cod. These observations coincide with the rapid increase of hydrogen sulphide and methyl mercaptan in the canned short-neck clam meats just after retolting.

But, the level of hydrogen sulphide and methyl mercaptan decreased gradually with the days of storage. After 50 days storage, the amounts of the two compounds decreased to 99 μg and 21 μg/100g flesh, these were 60% and 50% of the level in the meats just after canning, respectively. The gradual decrease of hydrogen sulphide and methyl mercaptan in the meats my be caused by combination either with tin or iron of can material, or by eacape into air as components of head space gas when a can is opened. McLay[9] estimated the volatile sulphur compounds in fresh and canned herring, and he found that there was an overall decrease in volatile sulphur compounds after canning. But, in his paper[9], there is no discription on the days of storage after canning.

Dimethyl sulphide could not be detected in either fresh or canned short-neck clam meats as indicated in Table 1.

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