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FORMALDEHYDE LEVELS IN FISH FROM THE KANDY MARKET

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Abstract: Of 260 samples of market fish tested for formaldehyde 34 samples tested positive with a maximum of 20 μg/g of formaldehyde with a mean for all species of 1.85 $\pm$ 3.97 μg/g. Pieces of fish dipped in formaldehyde solutions of concentrations 50 and 100 μg/g retained up to 3 μg/g (75%) formaldehyde after cooking and up to 3.2 μg/g (80%) after deep frying. The low concentrations of formaldehyde detected in fish in the market may be naturally occurring.

Introduction

Fish is a highly perishable commodity that needs early preservation. Fresh fish is normally preserved by cold storage or in ice. Attempts are also made to use organic acids to prolong the storage life of fish.[1] Illegal use of chemical preservatives such as formalin (38% solution of formaldehyde) at various dilutions to prolong the storage life of fish has been voiced as a problem faced by the consumers in Sri Lanka.

Formalin is toxic when humans are exposed even to trace amounts for a long period.[2] It affects the central nervous system and causes high acidity in blood resulting from its immediate metabolite formic acid. Cellular toxicity of formaldehyde is well established.[3] The need to eliminate addition of formaldehyde to foods as a preservative was highlighted as far back as 1900 in U.S.A. in their attempt to develop the Foods and Drugs Act.[4] Certain fish also may contain formaldehyde produced naturally. Studies on illegal use of chemical preservatives in fish, in the Tokyo Market in Japan, resulted in the discovery of biological formation of formaldehyde in gadoid fish,[5] in shell fish[6] and in cod family fish.[7] These studies showed a distinct correlation between the amount of formaldehyde and the amount of dimethylamine in the cod fish.

The objective of the present study was to monitor the concentrations of formaldehyde in fish sold in Kandy market and understand the origin and the loss of formaldehyde from fish during washing and cooking.

Materials and Methods

Fish

Fish samples (100 - 125 g) were collected twice weekly from Kandy Central Market in June to December 1990. About 10 samples of fish, belonging to the following species, were collected at a time depending on their availability: Anchovy *(Anchoviella commersonii)* (S -Halmessa), Barracuda *(Sphyraena jello)*(S - Geelawa), Devil ray *(Mobla diabolus)* (S - Maduwa), Flying fish *(Exocoetus volitans)* (S - Piyamessa), Herring *(Amblygaster sirm)* (S - Hurulla), Indian mackerel *(Rastrelliger kanagurth)* (S -Kumbalawa), Long rayed silver biddy *(Gerres filamentosus)* (S - Therally), Marlin *(Makdira indica)* (S - Koppara), Prawn *(Penaeus monodon)* (S - Issa), Red snapper *(Lutianus argentimaculatus)* (S -Rathu gal maluwa), Sail fish *(Histiophorus gladius)* (S - Talapath), Sardine *(Sardinella longiceps)* (S - Salaya), Shark *(Carcharhinus sp.)* (S - Mora), Silver biddy *(Leiognathus splendens)* (S - Karalla), Silverline half beak *(Hyporhampus jussimieri)* (S -Moralla), Skip jack *(Katsuwonus pelamis)* (S - Balaya), Spanish mackerel *(Scomberomorus commersoni)* (S - Thora), Trevally *(Caranx stellatus)* (S - Para), Yellow fin tuna *(Thunnus albacares)* (S - Kelawalla) and Woly herring *(Chirocentrus dorab)* (S - Katuwalla).

Estimation of formaldehyde

Fish samples (50 g) were cut into small pieces and minced with 100 ml of distilled water using pestle and mortar. The minced paste was acidified with 1 ml of concentrated orthophosphoric acid. The mixture was steam distilled and the distillate collected using a vertical condenser into a 25 ml volumetric flask. The volume was adjusted to mark with distilled water before analyses.

Estimation of formaldehyde was done by a colorimetric method using chromotropic acid, described earlier for estimation of formic acid by conversion to formaldehyde[8]. The distillate (2 ml) was cooled in an ice bath and 4 ml of concentrated sulphuric acid added to it while cooling. The solution was mixed well with 0.5% chromotropic acid (0.2 ml). The mixture was heated for 20 min. in a boiling water bath and allowed to cool to room temperature (25 ± 2)°C for estimation by colorimetry[9,10]

A stock solution of formaldehyde(10 mg/ml) was prepared as a working standard and stored in the refrigerator in a tightly sealed bottle. The standard solution was diluted to obtain 0.5 μg, 1.0 μg, 1.5 μg, 2.0 μg and 3.0 μg per 2 ml solutions and treated as above. Distilled water was used as blank. Absorbance of the resulting solutions were measured at 490 nm using CORNING Colorimeter 255 to prepare a standard curve.

Absorption of formaldehyde by fish

Formaldehyde free shark pieces of size 16 cm^3 were dipped in 100 ml portions of 50, 100 and 50000 $\mu g/g$ solutions of formaldehyde for 30 min. The pieces of fish were rinsed three times with 50 ml portions of distilled water. The fish and the washings were tested for formaldehyde concentrations separately.

Effect of boiling

Formaldehyde free fish samples (50 g) dipped and rinsed as above were boiled for 30 min. at 98°C with "goraka" (*Garcinia cambodia*) fruits in 50 ml of distilled water. The fish and the cooking liquid were tested separately for the formaldehyde concentrations.

Effect of frying

Formaldehyde free fish samples (50 g) dipped in formaldehyde solution and rinsed with water as above were added to 100 ml coconut oil at 180°C and deep fried at 168 - 170°C for 30 min. The fried fish and the oil were tested for formaldehyde.

Results and Discussion

Recovery on distillation

Recovery of formaldehyde by the steam distillation method was 30%. Low recovery due to decomposition of formaldehyde in food and polymerization during heating has been reported in this method[10] though the method is used widely in estimation of formaldehyde in foods.

Formaldehyde in market fish

Of 260 samples of market fish tested 13% contained formaldehyde (Table 1). Among the different types of fish tested, shark contained formaldehyde much more frequently. The concentrations of formaldehyde estimated in fish varied between 0.001 to 17.6 $\mu g/g$ with a mean of 1.85 and a high standard deviation of 3.97 $\mu g/g$. Of the other species of fish examined only 5 samples belonging to three species contained formaldehyde at concentrations less than 10 $\mu g/g$ (Table 1). It is reported that formaldehyde concentrations up to 150 $\mu g/g$ can be formed naturally in fish.[5] In herring, formaldehyde has been detected as a natural product.[11] As the concentrations of formaldehyde detected in our study in the market samples were less than 20 $\mu g/g$ it is difficult to infer whether the formaldehyde was produced naturally in the fish examined or added for preservation. As there is no information on natural

production of formaldehyde in species of fish caught in Sri Lankan shores, it is difficult to confirm the origin of formaldehyde either.

Table 1 : Formaldehyde in market fish

Fish type	Number tested	Number positive	Distribution of formaldehyde μg/g					
			.001-.01	.01-.1	.1-1	1-10	10-15	15-20
1	83	29	7	6	10	3	2	1
2	30	0	-	-	-	-	-	-
3	11	0	-	-	-	-	-	-
4	19	1	-	-	1	-	-	-
5	9	2	-	-	-	2	-	-
6	19	0	-	-	-	-	-	-
7	15	1	-	-	-	1	-	-
8	7	1	1	-	-	-	-	-
9	12	0	-	-	-	-	-	-
10	12	0	-	-	-	-	-	-
11	43	0	-	-	-	-	-	-
Total	260	34	8	6	11	6	2	1

1 = Shark; 2 = Yellow fin tuna; 3 = Spanish mackerel; 4 = Sail fish; 5 = Long rayed silver biddy; 6 = Trevally; 7 = Skip jack; 8 = Flying fish; 9 = Herring; 10 = Sardine; 11 = Others (Anchovy, Barracuda Devil ray, Indian mackerel, Marlin, Prawns, Red snapper, Silver biddy, Silverline half beak and Wolf herring)

- = not detected.

The interpretation of the presence of formaldehyde at concentrations below 150 μg/g as an additive in market fish should be done with much caution as such low concentrations could represent naturally present formaldehyde.

A study on the concentrations of formaldehyde that may get into fish on dipping in formaldehyde solutions at different concentrations is therefore important in understanding possible presence of it as an additive.

Absorption of formaldehyde by fish

The formaldehyde concentrations observed in fish after dipping in 50, 100 and 50000 μg/g formaldehyde solutions followed by rinsing with water were 1.2 , 2.3 and 284 μg/g respectively (Table 2). The concentrations of formaldehyde used should be at least of the order of a few percent for effective preservative action. At percent concentrations of formaldehyde in dipping water, the fish may retain formaldehyde concentrations of the order of a few hundred μg/g. It may be incorrect to interpret the low values of formaldehyde observed in fish in Kandy market (Table 1) as due to added formalin in view of the above observations.

Table 2 : Distribution of formaldehyde in fish and washings when fish was dipped in 50, 100 and 50000 μg/g formaldehyde solutions.

Formaldehyde content μg/g in			% distribution	
dipping solution	fish	washings	fish	washings
50	1.2 ± 0.2	0.8 ± 0.1	61 ± 5	38 ± 5
100	2.3 ± 0.2	0.6 ± 0.2	79 ± 6	20 ± 5
50000	284 ± 36	214 ± 37	57 ± 2	43 ± 2

Each value represents mean ± standard error of 5 experiments carried out in duplicate.

The concentration of formaldehyde present in formalin treated fish would depend on many parameters including the size of the fish, strength of formalin solution, the absorption coefficient, duration of dipping, and presence or absence of the skin in the fish. Thus utmost care is needed in interpreting the concentrations of formaldehyde that may be detected in fish before concluding whether the formaldehyde is added or of natural origin in fish.

Removal of formaldehyde in fish during cooking

Washing of fish prior to cooking removed up to 43% of formaldehyde (Table 2). After cooking 16 to 26% of added formaldehyde were retained in the fish while the cooking liquid contained 54 - 64% (Table 3). Hence a total of 75% appeared to remain in a fish-curry after cooking. After frying, the fish up to about 80% of added formaldehyde remained in fish. (Table 4). Thus washing and cooking operations do not appear to bring about any appreciable removal of formaldehyde already added to fish.

Table 3 : Distribution of formaldehyde in fish, washings and boiling water on cooking of fish contaminated artificially by dipping in 50 and 100 μg/g solutions of formaldehyde.

Formaldehyde content μg/g in				% distribution		
dipping solution	fish	washings	liquid	fish	washings	liquid
50	0.5 ± 0.1	0.8 ± 0.1	1.1 ± 0.1	24 ± 4	21 ± 3	54 ± 4
100	0.5 ± 0.2	0.6 ± 0.1	2.0 ± 0.2	16 ± 7	18 ± 4	64 ± 5

Each value represents mean ± standard error of 5 experiments carried out in duplicate.

Table 4 : Distribution of formaldehyde in fish and oil on frying of fish artificially contaminated by dipping in 50 and 100 μg/g solutions of formaldehyde.

Formaldehyde content μg/g in			% distribution	
dipping solution	fish	oil	fish	oil
50	1.8 ± 0.1	0.5 ± 0.1	77 ± 3	22 ± 3
100	3.0 ± 0.1	0.6 ± 0.1	82 ± 3	17 ± 3

Each value represents mean ± standard error of 5 experiments carried out in duplicate.

The low levels of formaldehyde found in fish sold in Kandy market could be added or natural formaldehyde. The formaldehyde was more commonly found in Shark. Cooking operations do not appear to reduce formaldehyde appreciably.

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