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Flavour components of some processed fish and fishery products of Japan

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Abstract

A study was conducted to examine the flavour components of some processed fish and fishery products of Japan by gas chromatography-mass spectrometry (GC-MS). In brief the method was to absorb the headspace volatiles at 70^{0}C into the fused silica fibre of the needle of the solid phase micro extraction fibre. The absorbed components were injected to the GC-MS. The components were identified by computer matching with library database as well as by authentic standard components. In general the number of flavour components were higher in the processed fish and fishery products (except frozen prawn) than that of the raw fish and prawn. The concentration (quantity) of the flavour components in processed fish and fishery products was much higher than that of the raw fish and prawn. Smoked salmon and baked salmon possessed double number of flavour components than that of the raw salmon. Smoking resulted the highest number of flavour components followed by baking (grilling) and canning, surimi products (kamaboko and chikuwa), drying and lastly salting. However, freezing and frozen storage resulted loss of flavour components in prawn.

Key words: Flavour components, Backing, Canning, Kamaboko, Salting, Smoking

Introduction

Processed fish and fishery products are characterized by their specific taste, flavour and sometimes by texture, which in general are referred to as 'sensory attributes'. Sensory attributes of the processed fish and fishery products are important criteria for consumers preference. It is more important if such processed fish and fishery products are eaten without any treatment or cooking. In such cases flavour is the most important attribute of the product. Fishery science and technology need to retain the original flavour of fish as well as to make the processing and product development perfectly so that the consumers can find these types of products with their desired flavour. Thus flavour of processed fish and fishery products are important for the consumers for their

good dietary satisfaction as well as for the fishery industries to get a good market share and consumers acceptance.

The flavour of processed fish and fishery products differ with the processing technology. Even such difference exist although prepared from the same species of fish. The same result may take place with the difference of size, area of fish catch, season of catch, storage condition etc. Therefore the experiment and research on processed fish and fishery products are necessary to specify and identify the flavour components of such processed fish and fishery products.

The early studies on the flavour chemistry of fish were on the identification of flavour components of a particular species of fish (Jones 1961, Ikeda 1980). Some investigations had been done on the quantification of flavour components (McGill *et al*, 1974). Some studies have been done on the relationship between the fat oxidation and the flavour of fish (Lea 1953, Yu *et al.* 1961, Aitken and Connell 1979, Forss 1960, Badings 1973, Meijboom and Stroink 1972). A few studies have been done on the identification of flavour components of pickled fish (Josephson *et al.* 1983). Some studies are done on the origin of fish flavour (Pokorny *et al.* 1987, Lindsay 1990). Despite such studies there is a remarkable lack of literature on the flavour components of processed fish and fishery products although such processed fish and fishery products have a long traditional history in every country, community and nation. The purpose of this study was to identify the flavour components of the processed fish and fishery products of Japan. Such data are not available in the literature (Lindsay 1990). The results of this study are expected to contribute to fill up the gap of literature / data in Fisheries Science.

Material and methods

Source of experimental materials

Smoked salmon, dried horse mackerel, salted pacific mackerel, canned sardine, canned tuna meat, kamaboko and chikuwa were bought from a departmental store at Nara city of Japan. Baked salmon was bought from a fish shop. Tiger prawn was bought form a fish shop at Nara city in chilled condition which after bringing to the laboratory was frozen at -20^{0}C in the deep freeze chamber of a laboratory refrigerator. The experimental materials were bought with few days interval (as fresh materials) immediately before the experiments were conducted instead of buying all items together and storage in the laboratory except frozen tiger prawn.

Sample preparation

For smoked salmon, dried horse mackerel, salted pacific mackerel, canned sardine, the muscle was separated by scissor, forcep, knife and cut into small pieces from at least three samples. Canned tuna meat, kamaboko, and chikuwa were cut into small pieces directly as they do not contain skin or shell. Frozen tiger prawn was thawed at room temperature in the laboratory inside a polyethylene packet. After thawing shell was

removed and the muscle was cut into as small pieces as the grains are. For all of the experimental materials at least three specimen were used for sample preparation.

Extraction of headspace volatiles

Immediately after sample preparation 5 g of experimental material was weighed in 20 ml vial (Perkin Elmer) and it was sealed with teflon lined rubber septum to make the vial air tight. This vial containing the sample was heated in an automated headspace sampler at 70^{0}C for 30 minutes to allow the volatile flavour components evaporate from the sample but remain in the vial. The needle of the SPME (Solid Phase Micro Extraction) fibre holder (Spelco) was pierced through the septum and the flavour components were extracted to SPME fused silica fibre (Carboxen-PDMS) for 5 minutes. The fused silica fibre of the needle of SPME was then retracted and the needle was taken out of the vial. Before the extraction of each sample's flavour components the SPME fused silica fibre was conditioned by thermal desorption in GC column through the injection port of the GC-MS. Such blank analysis was done to make sure that the fibre does not contain any other volatile component before the extraction of sample's flavour components. In some cases it was necessary to do blank analysis twice or thrice to make the SPME fused silica fibre free from any component.

Gas Chromatography-Mass Spectrometry (GC-MS)

The flavour components extracted into the fused silica fibre of SPME needle were injected and thermally desorbed for 5 minutes to the capillary column DB 624 (60 m×0.322 mm ID, 1.80 μm film thickness) through the injection port of GC-MS (Shimadzu QP 5050A). The desorbed components were subjected to GC-MS analysis under standard conditions. The mass spectrum of each peak of GC was analysed by the Mass Spectrometer and the components were identified by computer matching of mass spectra of the components with those of the data stored in the mass spectral data base (NIST). In each case the component of highest possibility is reported. Result of each experiments were checked in a subsequent set of experiments.

Analytical conditions

Capillary column DB 624 (60 m×0.322 mm ID, 1.80 μm film thickness) was used. Helium was used as carrier gas. The analytical conditions were as follows;

Oven temperature 40^{0}C, Oven equilibration time 3 minutes, Injection temperature 280^{0}C, Interface temperature 230^{0}C, Column pressure 35.0 (KPa), Column flow 1.5 (ml /min) and linear velocity 30.7, split ratio 25, total flow 40.0 (ml /min), carrier flow 40.0 (ml/min). Mass range (40-350 m/z). Scan interval (0.50 sec), threshold (5000), scan speed 1000 amu/ sec.

Confirmation of results

To confirm the results of these experiments another set of experiments was conducted by the standard authentic components (Nacalai Tesque). The experimental methods and analytical conditions were same as for the processed fish and fishery products of this research study except heating at 70°C for 30 minutes. The results obtained from GC-MS analysis by using authentic components were compared with those of the previous results to confirm the findings of this research as well as to sort out the unusual components and peaks resulted from unknown source etc.

Results

The flavour components identified in processed fish and fishery products in this investigation are listed in Table 1. Corresponding chromatograms are shown in Figs 1& 2. The number and concentration of the flavour components of processed fish and fishery products were obtained to be higher except in frozen prawn than those of the raw fish and prawn identified in our previous investigations. Among the 26 components identified in the present research study majority were aliphatic hydrocarbons (alkane, alkene, cyclic hydrocarbons); some were carbonyl compounds (aldehydes, ketone); some were alcohols, an organic acid and two were aromatic compounds according to their molecular structure. The flavour components may also be grouped according to their molecular weight. Most of them were of molecular weight less than 100, some are of molecular weight between 100 and 150; and a few above this figure. Some of the flavour components were originally present in the raw fish while the rest of the components were formed during processing. In general processed fish and fishery products possessed higher number of flavour components and the concentration of each flavour components in processed fish and fishery products are much higher than those of the raw fish expect frozen prawn. The concentration of each flavour component of the processed fish and fishery products are shown in Table 1 as peak area (total number of ions).

Smoking of salmon resulted the highest number of flavour components followed by baking of salmon (grilled salmon) and canning of sardine, surimi products (kamaboko and chikuwa), drying of horse mackerel, salting of pacific mackerel. However, freezing and frozen storage of prawn caused the loss of flavour components.

Discussion

Among the identified flavour components of processed fish and fishery products majority were originally present in raw fish and prawn which was identified in our previous investigation. Some more flavour components were identified in processed fish and fishery products which may be the result of processing except in freezing and frozen storage (Lindsay 1990). The concentration of the flavour components of processed fish and fishery products was comparatively much higher. Two reasons may lay behind

Table 1. List of the flavour components (with their quantity in terms of peak area as $\times 10^5$) identified in the processed fish and fishery products of Japan (Corresponding chromatograms are shown in Figs. 1 and 2)

No.	Component name	Retention time	Smoked salmon	Baked salmon	Dried horse mackerel	Salted Pacific mackerel	Canned sardine	Canned tuna meat	Frozen tiger prawn	Surimi products	
										Kamaboko	Chikuwa
1	Ethanol	3.15	80			17		4490		10640	11792
2	Trimethylene oxide	4.27	210								6
3	Propanal	4.29		270	294	570					
4	Acetic acid, anhydride	4.62	326	789	319						
5	2-methyl-Pentanal	4.64									3
6	Acetone	4.67					898	801	1736		
7	Dimethyl sulfide	4.86					496	954			
8	2-methyl-Propanal	8.7	250	319			161	327			
9	2-Butanone	13.23	228	624	57		314	907			
10	Ethyl acetate	13.95								497	533
11	3-methyl-Butanal	20.06	449	256			226				154
12	2-methyl-Butanal	21.4					239				
13	2-ethyl-Furan	24.2					681				
14	1-Butanol	24.29						324			
15	1-Penten-3-ol	26.45	641			1321					
16	Cyclopentanol	26.61		241	783		184			265	
17	Cyclobutanemethanol	26.62						122			
18	Toluene	31.58	311							1701	
19	Octane	32.37		24							
20	Hexanal	34.45	388	579	759	949	68	122		1821	494
21	Cyclopentanone	34.7	85								
22	Ethylbenzene	36.63	28.7								
23	Nonanal	37.75									32
24	1-Hexanol	37.86			15	28				82	
25	2-Heptanone	28.42								75	
26	Heptanal	28.65	213	524	363	108				146	53

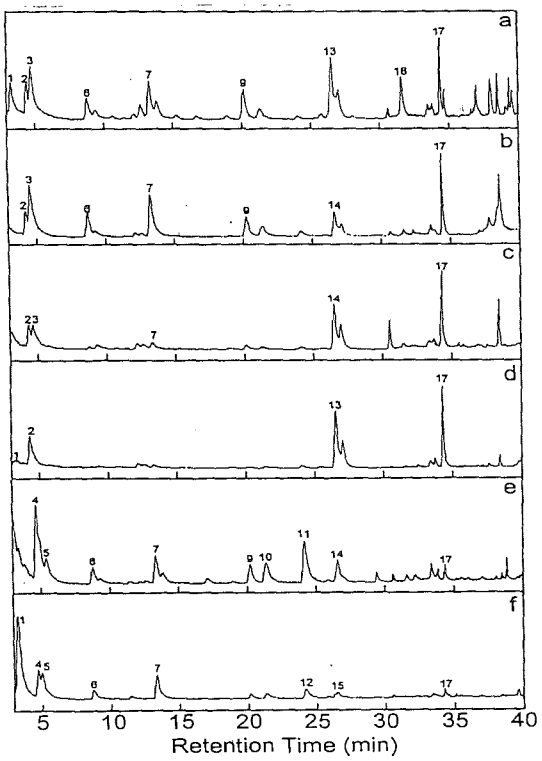

Fig. 1. GC-MS Chromatograms of the flavour components of (a) smoked salmon, (b) baked salmon, (c) dried horse mackerel, (d) salted pacific mackerel, (e) canned sardine, (f) canned tuna meat.

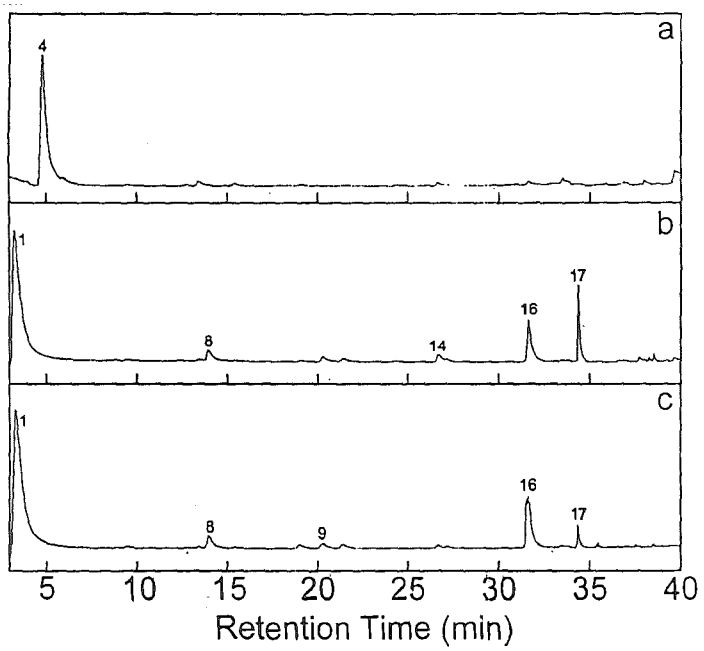

Fig. 2. GC-MS Chromatograms of the flavour components of (a) frozen tiger prawn, (b) kamaboko, (c) chikuwa.

this fact. One is that such components are further increased as a result of biochemical pathways of protein and fat of fish (Pokorny 1980). Another reason may be the concentration (quantity per unit mass) of such flavour components was found to be much higher in GC-MS analysis because the moisture content is normally reduced during processing which resulted a higher concentration of flavour components in the final product. Any one or both of the reasons are responsible for such phenomenon except during freezing and frozen storage.

During the process of smoking and baking of salmon the predominant cause of higher number of flavour components in the final product is the deposition or settling of smoke components to the fish. Biochemical changes due to slightly higher temperature may also partially contribute to the production or formation of such flavour components (Josephson and Lindsay 1987). Three undesirable components were detected in smoked salmon and baked salmon. The undesirable components are octane, ehtylbenzene and toluene. These are graded as undesirable because their role in human body or their biofactors are not known. Neither the muscle nor the skin of raw salmon contain octane, ehtylbenzene and toluene. During our previous investigation on raw fish and prawn it was found that the muscle and skin of raw salmon do not contain octane, ehtylbenzene and toluene. It appears that the smouldering by the use of special type of wood, wood shave, saw dust, straw and acceleration of smouldering by the use of octane produced a considerable fraction of smoke components of toluene, ethylbenzene and octane which continuously settled on fish during 'fish smoking' and 'fish baking' process. Ehtylbenzene and toluene may be resulted from the thermal degradation of materials (wood, straw, saw dust) used for smouldering.

During the process of canning some flavour components formed as a result of nonenzymic browning reactions during heat processing step of canning. Such enzymic activities may resulted the changes in protein and fat which finally formed some flavour components. It is also possible that some flavour components were formed during heat processing step of canning due to the effect of heat on the ingredients used in canning e.g. oil, tomato sauce, (Pokorny 1980). However the possibility of such contribution of ingredients to flavour of canned fish used in the present investigation is soybean oil because the experimental material was canned sardine with soybean oil.

In the dried horse mackerel the flavour components were formed probably as a result of oxidation of fat as well as enzymic hydrolysis of the original components of fish e.g. protein, fat. The drying process of horse mackerel is sun drying for only 3-5 days. Sometimes antioxidants are used during drying to prevent high degree of oxidation. Short period of drying results soft texture compared to the complete drying of fish by 7-10 days. In the completely dried fish the number of flavour components are usually higher than that of the dried horse mackerel, used in the present study, which is partially dried.

Similar type of result obtained in surimi based products e.g. kamaboko and chikuwa. During mincing of fish after bone separation and during texture formation steps of surimi products the enzymic hydrolysis of the original components of fish e.g. protein, fat resulted the formation or biogeneration of flavour components in surimi products. A

certain degree of oxidation may also be responsible for the phenomenon. Thermal condition may accelerated retro-aldol degradation of unsaturated aldehydes which lead to altered flavour in these products (Joseophson and Lindsay 1987).

In case of salted pacific mackerel (Shio saba) the number of flavour components was comparatively less than the expectation. Because the pacific mackerel is fatty fish and salting process should give rise to the production or formation of large number of flavour components. But the salted pacific mackerel used in the present investigation was salted in slightly different but modern way. It was realized that the sample bought from departmental store was salted at chilling temperature and ratio of salt : fish was about 1: 20 (1 part of salt for 20 parts of fish), and the process continued only for 2-3 days at chilling temperature (0-4^{0}C). This is why the number of flavour components was comparatively less than the expectation. The reason behind the formation of flavour components in salted pacific mackerel may be the oxidation of fat. Prokorny (1980) has reported such browning reactions of oxidized fat.

In almost all of the processing and storage technique the process resulted an increase in the number and concentration of flavour components. However the opposite type of result was obtained in freezing and frozen storage of prawn. Freezing and frozen storage resulted loss of two flavour components (Dimethyl sulfide and hexane). However, another component (acetone) was identified in frozen stored prawn after thawing at room temperature during the present investigation. The concentration of acetone was also much higher in thawed prawn than that of the fresh raw prawn. Loss of flavour components during freezing and frozen storage of prawn may be the condensation of volatile flavour components due to low temperature (-20^{0}C) and leaching out during thawing. The high concentration of acetone in frozen stored and subsequently thawed prawn indicates that this component may be further formed either during storage or during thawing.

From the results obtained in this research study it can be concluded that some flavour components are formed during processing and storage of fish except freezing. Such phenomenon may be influenced by the differences in processing technique, storage technique etc.

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