A comparison of volatile compounds in a fish sauce prepared by the use of soy sauce koji with those in commercial fish sauces in Japan

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SUMMARY: Volatile compounds in a fish sauce prepared from gutted frigate mackerel (FMS) were compared with those of commercial fish sauces and soy sauce. These fish sauces included three Japanese fish sauces (Ishiru from sardine (IS), Ishiru from Japanese common squid (IJCS) and Shottsuru) and four foreign fish sauces (Nampla, Nuoc mam, Patis and Yuiru). A few volatile acids (VA) were detected in FMS while many kinds of VA including butanoic and pentanoic acids were found in Shottsuru, IS, and the foreign fish sauces. In IJCS, only acetic acid was detected as VA, but many kinds of aldehydes were found. No butanoic and pentanoic acids were detected in FMS, IJCS or soy sauce. A principal components analysis indicated that the heaviness of flavor of FMS was less than that of soy sauce and that the flavor preference of FMS was greater than that of the other fish sauces.

KEYWORDS: frigate mackerel, fish sauce, soy sauce koji, volatile compounds, principal component analysis

INTRODUCTION

Fish sauce is one of the most popular condiments in Asia. Recently, the popularity of fish sauces has been rising with the growing popularity of ethnic foods such as Vietnamese and Thai dishes in Japan. However, commercial fish sauces in Japan do not always have agreeable flavors. There have been some attempts1,2) to improve the taste and flavor of fish sauces by use of soy sauce koji in fermentation. Abe et al.1) reported that the taste and flavor of fish sauce prepared from Antarctic krill with soy sauce koji was better than those of the fish sauce prepared without soy sauce koji. Nakamura et al.2) also reported that the fish sauce prepared from frozen Antarctic krill with soy sauce koji had many tasty components and no unpleasant odor.

Frigate mackerel are caught in large quantities in Toyama Bay. However, the catch is rarely utilized for human food because of its inherent disadvantages as raw material. Most of the catch is used for fertilizer as before.3)

From a more efficient utilization of frigate mackerel, the authors have tried to produce fish sauce from the fish on a test plant scale, using soy sauce koji in fermentation, and have examined the characteristics of the product from many angles.4)

This paper deals with the volatile compounds in fish sauce from frigate mackerel and a comparison of its flavor with the flavors of commercial fish sauces and soy sauce in Japan.

MATERIALS AND METHODS

Fresh frigate mackerel Auxis rochei caught in the Toyama Bay and frozen-stored at −25°C for about 60 days were used as raw materials.

Preparation of fish sauce from frigate mackerel

After thawing, about 600 kg of the fish were gutted, washed, and minced with a mincer (50H-7, Mosco Industry Co., Ltd.). Moromi (fish sauce mush) was prepared by fermentation of the mixture of the minced meat (about 500 kg), 10% soy sauce koji on a wet basis, 30% water and 16% salt with a purity of 95% at room temperature for one year. The koji used for fermentation was prepared by incubating a 1:1 mixture of steamed defatted-soy bean and roasted wheat with Aspergillus oryzae (Ichimurasaki, Bio’c Co., Ltd.). The moromi was put in a moromi bag and pressed with a compressor (KS-1, Komagata Machine Co., Ltd.). After compression, the lipid was removed and the liquid was heated to 90°C and subsequently cooled to room temperature. After cooling, the heat-treated liquid was centrifuged at 16,000 × g for several hours at room temperature with a continuous centrifuge (ADS-250L, Saito Centrifuge Industry Co., Ltd.). The supernatant thus obtained was bottled. About a 510kg final product was recovered from about 850kg of moromi.
Commercial fish sauces and soy sauce in Japan

Nampla (Thai fish sauce) and Patis (Philippine fish sauce) are fish sauces prepared from anchovy Engraulis japonica and pacific mackerel Scomber japonicus, respectively. The materials of Nuoc mam (Vietnamese fish sauce) and Yuiru (Chinese fish sauce) were unknown. Ishiru from sardine (IS) and Shottsuru are fish sauces prepared from sardine Sardinops melenostictus and sand fish Arctoscopus japonicas, respectively. Ishiru from Japanese common squid (IJCS) is a kind of fish sauce prepared from the intestine of Japanese common squid Todarodes pacificus and to which caramel and condiment were added after fermentation. Soy sauce is prepared from a mixture of defatted soybean, soybean, wheat as raw materials, and to which ethanol is added.

Analysis of chemical components

pH was measured with a glass electrode. Salt content was determined by the Volhart method and Brix was determined according to the soy sauce analysis method. Soluble solids excluding salt was calculated by subtracting salt content from Brix. Total-nitrogen (Total-N) content was determined by the Kjeldahl method. Volatile base nitrogen (VBN) was determined by the Conway's micro diffusion method.

Collection of volatile compounds of fish sauces and soy sauce by SPME method and GC/MS analysis

One ml of each specimen was put into Teflon vials (ϕ 3.0cm×h 6.7cm) and the vials were sealed. A Solid Phase Micro Extraction (SPME) fiber (75 μ m carboxen/PDMS) was inserted into the vial so that volatile compounds were absorbed on the fiber at 90 °C for 60 min. After absorption, the SPME fiber was injected into a gas chromatograph. GC/MS analysis was carried out under the following conditions: gas chromatograph: Hewlett Packard Co. Ltd. 6890 type; mass spectrometry detector: Hewlett Packard Co. Ltd. 5973 type; column: PTA-5 (length, 30m; I.D., 0.32 mm; film thickness, 1.5 μ m); column temperature: 40°C (2 min)-250°C (23 min); carrier gas: He; injection port temperature: 250°C; injection method: split less (flow rate, 1.5 ml/min); heating rate: 10°C/min; ion-trap manifold temperature: 230°C; electron impact ionization voltage: 70eV.

Determination of volatile compounds in fish sauces and soy sauce

In the GC/MS analysis, the peaks that appeared were identified by use of the standard NIST mass spectrum data base and/or by comparing their retention times with those of the authentic compounds.

Sensory evaluation of fish sauces and soy sauce

A flavor panel test was carried out by a panel consisting of a total of 40 people from Toyama Prefectural Food Research Institute and Toyama Prefectural Fisheries Experimental Station, and some specialists from the fish processing industry in Toyama Prefecture. The male-female ratio was 24 to 16. The age distribution was as follows: people in their 20's: 10; people in their 30's: 8; people in their 40's: 12; people in their 50's: 8; people in their 60's: 2. The sensory evaluation of the fish sauces and soy sauce were performed by the SD method, that is, data were statistically analyzed with a multi-variate analysis software package for the Windows operating system. The principal components analysis was made using a correlation coefficient matrix.

RESULTS AND DISCUSSION

Table 1 Chemical components of fish sauces and soy sauce.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Salt</th>
<th>SSES</th>
<th>Total-N</th>
<th>VBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>FMS</td>
<td>4.7</td>
<td>17.0</td>
<td>18</td>
<td>1.89</td>
<td>206.1</td>
</tr>
<tr>
<td>Soy sauce</td>
<td>4.6</td>
<td>16.7</td>
<td>18</td>
<td>1.55</td>
<td>174.0</td>
</tr>
<tr>
<td>Shottsuru</td>
<td>5.2</td>
<td>24.5</td>
<td>19</td>
<td>2.17</td>
<td>260.3</td>
</tr>
<tr>
<td>IJCS</td>
<td>5.2</td>
<td>20.8</td>
<td>8</td>
<td>1.48</td>
<td>124.3</td>
</tr>
<tr>
<td>IS</td>
<td>5.8</td>
<td>28.8</td>
<td>9</td>
<td>1.52</td>
<td>180.7</td>
</tr>
<tr>
<td>Nampla</td>
<td>5.5</td>
<td>24.7</td>
<td>19</td>
<td>2.08</td>
<td>282.2</td>
</tr>
<tr>
<td>Nuoc mam</td>
<td>5.5</td>
<td>24.5</td>
<td>19</td>
<td>2.08</td>
<td>251.1</td>
</tr>
<tr>
<td>Patis</td>
<td>5.4</td>
<td>29.2</td>
<td>7</td>
<td>1.35</td>
<td>204.5</td>
</tr>
<tr>
<td>Yuiru</td>
<td>6.4</td>
<td>28.2</td>
<td>8</td>
<td>1.25</td>
<td>405.8</td>
</tr>
</tbody>
</table>

Chemical components of fish sauces and soy sauce

The chemical components of fish sauces and soy sauce are shown in Table 1. The pH values and the salt contents of FMS and soy sauce were almost the same, and lower than those of the Japanese and foreign fish sauces. The soluble solids excluding salt contents of FMS, soy sauce, Shottsuru, Nampla and Nuoc mam were in the range 18-19%, while those of IJCS, IS, Patis and Yuiru were lower. The total-N content of FMS was lower than that of Shottsuru, Nampla, Nuoc mam, but it was high compared with soy sauce, IJCS, IS, Patis and Yuiru.
The VBN contents of FMS and Patis were almost the same, and were higher than those of soy sauce, IJCS and IS, but lower than those of Shottsuru, Nampla and Yuiru.

Volatile compounds in fish sauces and soy sauce

The volatile compounds detected in fish sauces and soy sauce are shown in Table 2. As a whole, 70 different volatile compounds were identified by the SPME method and the GC/MS analysis. In FMS and soy sauce, a few kinds of volatile acids (VA) and many kinds of alcohols were found. Many kinds of esters and phenols in soy sauce while none of these compounds were found in FMS. Particularly in FMS and soy sauce, maltol, which has a caramel flavor, was detected. However, soy sauce had 4-ethyl-2-methoxy-phenol (4EG), which has a smoke flavor, was identified. Many kinds of VA in including butanoic and pentanoic acids were found in Shottsuru, IS, Nampla, Nuoc mam, Patis and Yuiru. However, no butanoic or pentanoic acids were detected in FMS, soy sauce or IJCS. On the other hand, in IJCS, only acetic acid was detected as VA, but many kinds of aldehydes were found. These findings suggested that the VA content might be restrained and a flavor similar to that of soy sauce might be formed in FMS as in the case of soy sauce koji.

Principal component analysis

The results of principal component analysis of fish sauces and soy sauce are shown in Fig.1. The first principal component is a factor that is related to, so to speak, the flavor preference, which is expressed by words such as agreeability, harmoniousness, smoothness, strength and fineness of flavor. On the other hand, the second principal component is a factor related to the heaviness of the flavor. The contribution ratios of the first and second principal components were 90.7% and 8.3%, respectively.

Judging from the first principal component, the panel considered the flavor of FMS to be better than that of other fish sauces and liked it almost as much as they liked the flavor of soy sauce. On the other hand, judging from the second principal component, the flavor of FMS was lighter than that of soy sauce. The good flavor balance of FMS may be the main reason why Japanese panelists preferred FMS to other fish sauces. It may be considered that FMS was better than other fish sauces, that is, neither butanoic acid nor pentanoic acid, whose smells are disliked by Japanese, were detected in FMS, and furthermore, no aldehyde peculiar to IJCS was found in FMS. However, it is unclear why the panelists felt...
the flavor of soy sauce was heavier than that of FMS. Yokozuka et al.\textsuperscript{21} and Nakadai\textsuperscript{22} reported that some volatile compounds such as 4-hydroxy-2(or5)-ethyl-5(or2)-3(2H)-furanone, 4-hydroxy-2,5-dimethyl-3(2H)-furanone and 4-hydroxy-5-methyl-3(2H)-furanone, which have a strong caramel flavor, were uniquely found in soy sauce. Although these volatile compounds were considered to be related to the difference in the flavor between FMS and soy sauce, none of them were detected in soy sauce in this study.

Fig.1 The principal analysis of the flavor of fish sauces and soy sauce
1: FMS; 2: Soy sauce; 3: Shottsuru; 4: IJCS; 5: IS; 6: Nampla; 7: Nuoc mam; 8: Paris; 9: Yuiru. As to FMS, IJCS and IS, see Table 1. First principal component: agreeable(+), harmonious(+), smooth(+), strong(-), fine (+). Second principal components: heavy(+).

ACKNOWLEDGEMENTS

The authors wishes to express their sincere gratitude to Mr. T. Imai, Director, Food Resource Division, National Food Research Institute, for his helpful advice. The authors are also grateful to Mr. R. Sunago, President, Sunago Shoten Inc., for his cooperation in the fish sauce preparation.

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