Bull. Fac. Fish. Hokkaido Univ.
29(1), 56–64. 1978.

The Quality of Frozen Sand Lance Treated with a Water-Dispersible Tocopherol Mixture

Kōzō Takama*, Sei-ichi Andou* and Kōichi Zama*
Shigeo Nakamura** and Shin'ichiro Akatsuka**

Abstract

The studies were carried out to determine the effect of XOE-T, a water-dispersible tocopherol mixture, to prevent deterioration of sand lance, caused by oxidative rancidity during frozen storage.

The tocopherol treatment resulted in the effective inhibition of dark-color development and rancidity as determined by TBA-V, POV, COV and AV measurements. Both pepsin and trypsin digestibilities and available lysine content of lipid-free material obtained from fried fish were proportionally related to the oxidative rancidity of frozen stored fish just before frying.

The tocopherol treatment is of value in maintaining the nutritive quality and the external appearance of the fried fish and the water-dispersible tocopherol mixture, XOE-T, is effective in maintaining the quality of frozen stored fish for at least up to 4.5 months.

Fatty fish readily undergoes oxidative rancidity and quality deterioration, which creates problems during fish utilization, processing and preservation.

Synthesized antioxidants, such as BHA, PG and NDGA have been shown to be effective against oxidative rancidities of fatty foods and edible oils.

However, the use of these synthesized antioxidants is subject to regulation for food hygiene.

Considerable researches[1–3] have been carried out on the application of the natural antioxidant tocopherol, especially on its effect on the keeping qualities of edible oils.

Toyama and Shimazu[4] have reported on the applicability of a tocopherol mixture for the protection of marine products, such as salted salmon flesh, salted-and-dried saurel and boiled-and-dried anchovy, from deterioration due to oxidation. The use of tocopherol has been limited, because tocopherol is not soluble in water.

This investigation reports on the effect of XOE-T, a water-dispersible tocopherol mixture originated by the authors, on the keeping quality of frozen sand lance, a small fatty fish, prepared for frying.

Materials and Methods

Sand lance, *Ammodytes personatus* (Girard), caught in July, 1976 in Funka

* *Laboratory of Food Chemistry I, Faculty of Fisheries, Hokkaido University* (北海道大学水産学部食品化学第一講座)
** *Eisai Co., Ltd. Fine Chemicals Division.* (エーザイ株式会社化成品部)

Bay, Hokkaido, were used in this study. The average body weight and length of fish used were 27 g and 18 cm, respectively. After gutting and beheading, the average weight was 22 g/fish.

Sample fish were opend along the dorsal fin and rinsed with tap water. After draining for a few minutes, the fish were separated into three groups: (1) the untreated control group (C); (2) the sample dipped in a 1% aqueous solution of XOE-T, a water-dispersible tocopherol mixture, (0.2% concentration as mixed tocopherol), the water system group (W); and (3) the sample dipped in olive oil containing 1% of the XOE-T, the oil system group (O). All dipped samples were drained for a few minutes.

The treated samples (2) and (3) together with the control sample (1) were immediately covered with corn-starch and packed in a polyethylene bag (400 g as sample fish) and then stored at −20°C.

At 1.5 month intervals, frozen sample fish in the polyethylene bags were placed in a refrigerator and thawed overnight. They were cut along the ventral line into boneless and bony parts, and separated into two groups. One group was used for determining chemical properties just before frying. The other group was fried in fresh salad oil (Ajinomoto Co., Ltd.) at 180°C for 2 min. The fried fish were drained on filter paper for a few minutes and the frozen stored fish sample and the fried sample were used to determine the following.

The TBA-V was determined according to the method described by Vyncke[5], and expressed as absorbancy at 538 nm per 5 g-sample.

The POV, AV, IV, SV and refractive index (n_D^{20}) of the lipid were determined according to the standered methods of J.O.C.S.[6], and COV was determined by the method of Kumazawa and Ōyama[7]. Changes in the color of the lipid were measured as extinction at 370 nm through a 1 cm thick cell in 1% $CHCl_3$ solution.

The lipid-free materials from acetone and ether extractions were used to determine the digestibilities in vitro with pepsin and trypsin. The amount of available lysine in the lipid-free material was also determined. The determination for the digestibility and for the available lysine content were made by procedures previously described[8].

A sample of unfried fish meat (100 g) was ground in a meat-chopper, and its lipid extracted (Bligh and Dyer[9]). The fried sample was also ground in a meat-chopper and 10 g-portions were used to extract lipid with 150 ml of acetone and the extraction was repeated 2 more times. After filtering through a sintered glass funnel, the residue was re-extracted 3 times with 150 ml of ether.

Chromatography was done on a Mallinckrodt silicic acid column (using 50-portions of lipid) to fractionate the non-phospholipid (NPL) and the phospholipid (PL) in the extracted lipid. Three fractions were obtained from the column successive elutions with $CHCl_3$, acetone and methanol. On TLC, the lipids eluted with $CHCl_3$ and acetone were identified as NPL, and the lipid eluted with methanol was PL.

Results and Discussion

The properties and the fatty acid compositions of the olive oil and the salad oil used are shown in Tables 1 and 2, respectively. The classes of lipid contained

Table 1. *Properties of olive and salad oils*

	Olive oil*	Salad oil**
Iod. V.	82.4	121.6
Sap. V.	186.9	184.2
Acid V.	0.5	0.4
n_D^{20}	1.4712	1.4756
Color ($E_{370}^{1\%}$ $CHCl_3$)	0.010	0.015
POV	0	0
COV	0	0

* Yakuhan Seiyaku Co., Ltd.
** Ajinomoto Co., Ltd.

Table 2. *Fatty acid compositions of olive and salad oils*

C_n : F_m	Olive oil*	Salad oil**
16:0	15.6	7.0
16:1	1.9	0.3
16:2, 17:1	-	0.1
18:0	2.3	2.6
18:1	65.0	36.2
18:2	12.6	36.8
20:0	1.2	1.1
18:3	0.9	11.6
20:2	0.3	-
20:3	-	0.2
22:1, 20:4	-	3.9

* Yakuhan Seiyaku Co., Ltd.
** Ajinomoto Co., Ltd.

Table 3. *Lipid classes of sand lance*

	g/100 g lipid	mg/100 g fish
Non-phospholipid	89.4	4,917
Triglyceride	84.3	4,637
Partial glyceride	0.1	6
Free fatty acid	3.0	165
Sterol	0.9	49
Others	1.1	60
Phospholipid	10.6	583
Lecithin	7.0	385
Cephalin	2.8	154
Lysophospholipid	0.8	44

Total lipid content: 5.5%

in the sand lance were estimated with TLC-densitometric procedures (Table 3).

Fig. 1 shows the decrements of NPL and PL in the frozen stored fish sample. The changes in NPL content of the control (C) showed the largest decrement, about

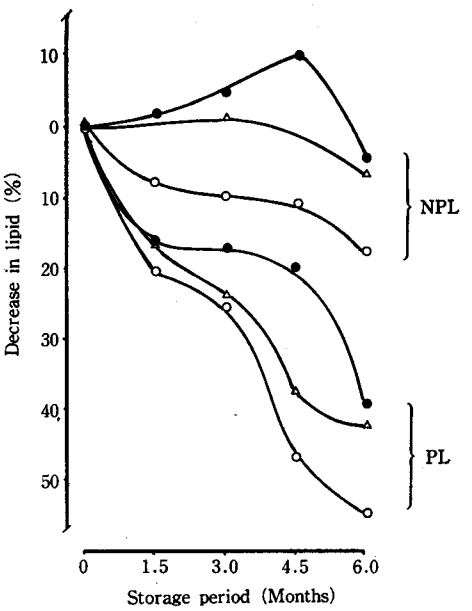

Fig. 1. Effect of "XOE-T" treatments and frozen storage on decrements of non-phospholipid (NPL) and phospholipid (PL) of sand lance
Symbols: ○ C (untreated)
△ W (treated with "XOE-T" dispersed in water)
● O (treated with "XOE-T" dispersed in oil)

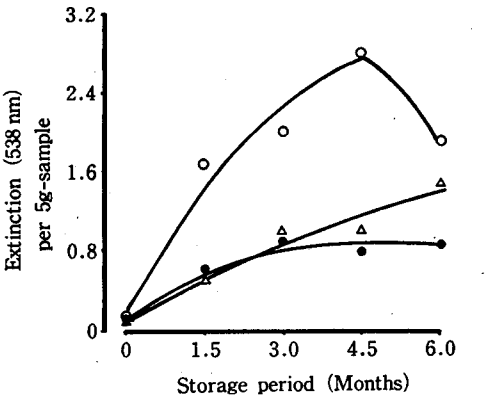

Fig. 2. Effect of "XOE-T" treatments and frozen storage on TBA values of sand lance
Symbols are the same as shown in Fig. 1.

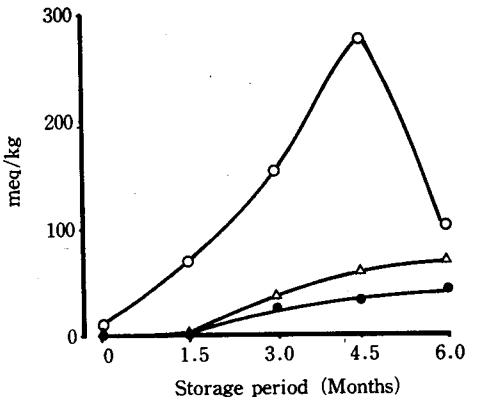

Fig. 3. Effect of "XOE-T" treatments and frozen storage on POV of sand lance
Symbols are the same as shown in Fig. 1.

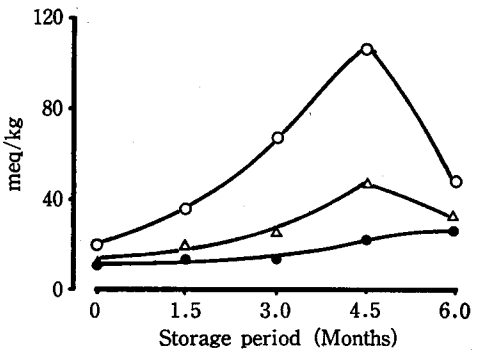

Fig. 4. Effect of "XOE-T" treatments and frozen storage on COV of sand lance
Symbols are the same as shown in Fig. 1.

17% after 6 months, whereas in the tocopherol treated water (W) and oil (O) systems the decremental value ranged from 5 to 7%.

PL in the C decreased rapidly, about 55% after storage for 6 months, whereas in the tocopherol treated samples (W and O), the decrease was about 40% after 6 months.

The formation of TBA reactive compounds were highest in the C as compared with the tocopherol treated samples, and reached its maximum at 4.5 months storage (Fig. 2). However, the tocopherol treated samples had a lower formation of TBA reactive compounds than the C. The tocopherol treatment seems to be effective in protecting frozen fish samples for at least 4.5 months of storage.

The changes in the POV and COV are similar to that of TBA-V, and it also appears that the tocopherol treatments act effectively in preventing oxidative deterioration (Figs. 3 and 4). The AV of the C and W samples closely resembles each other and had larger values than that of the O (Fig. 5). The quantitative changes in lipid and the changes in TBA-V, POV and COV seem to indicate that the tocopherol treatment suppressed the later oxidative decomposition of accumulated FFA which were formed due to lipid hydrolysis during storage. On the other hand, the formation of FFA seems to be inhibited in the O. Mezeaud and Bilinski[10] pointed out, using rainbow trout muscle homogenate, that FFA formed by phospholipid hydrolysis is considered to be used immediately for the synthesis of prostaglandin-like phospholipid during incubation at 20°, and even at 4°C. It appears in the O sample, prepared by using the olive oil, that the formed FFA was immediately used for the synthesis of phospholipid, even if phospholipid had been hydrolyzed. In either event, the results suggest a relationship between the inhibition of the structural and functional deterioration of fish protein caused by frozen storage in the O sample.

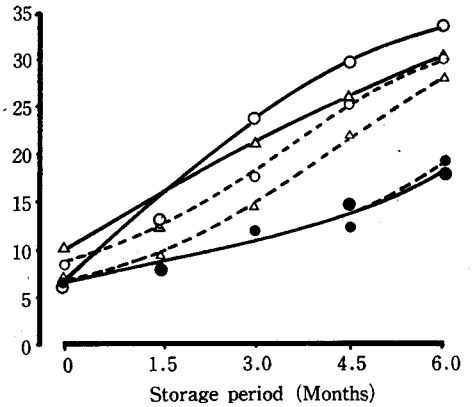

Fig. 5. Effect of "XOE-T" treatments and frozen storage on AV of sand lance
Symbols are the same as shown in Fig. 1.
Solid line: before frying, Dotted line: after frying

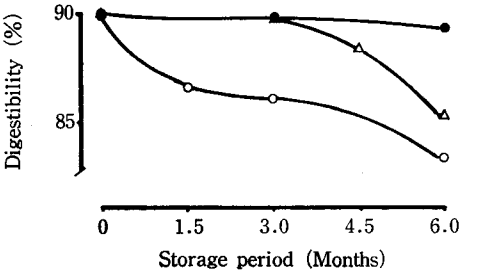

Fig. 6. Pepsin digestibilities of lipid-free materials obtained from fries of sand lance treated with "XOE-T"
Digestibility = TCA soluble-N after digestion ×100/Total-N, Symbols are the same as shown in Fig. 1.

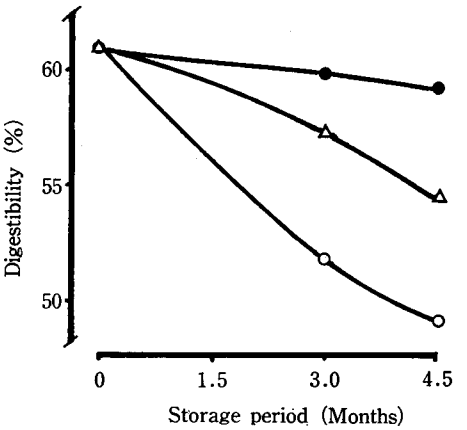

Fig. 7. Trypsin digestibilities of lipid-free materials obtained from fries of sand lance treated with "XOE-T" Digestibility = TCA soluble-N after digestion × 100/Total-N, Symbols are the same as shown in Fig. 1.

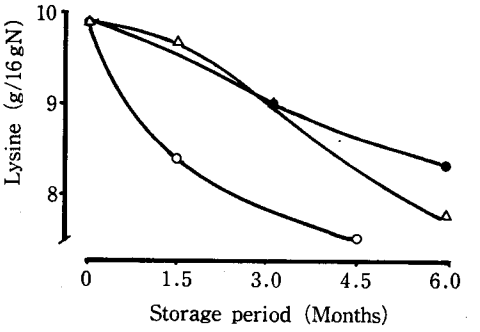

Fig. 8. Available lysine contents of lipid-free materials obtained from fries of sand lance treated with "XOE-T" Symbols are the same as shown in Fig. 1.

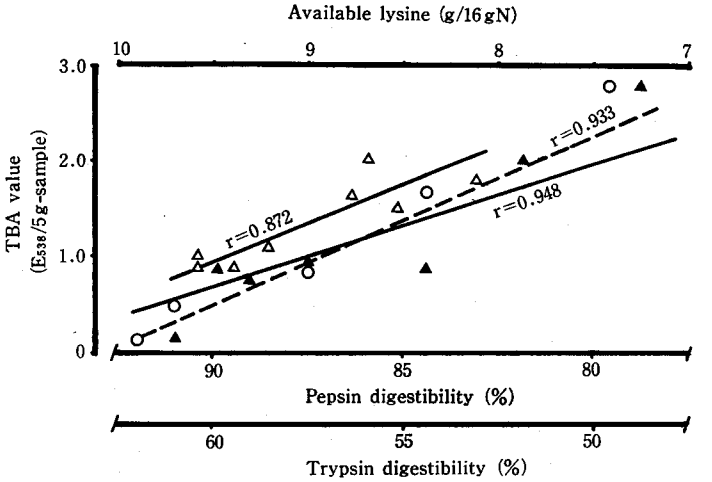

Fig. 9. Relationships of TBA values of frozen stored sand lance to available lysine contents, pepsin and trypsin digestibilities of lipid-free materials obtained from fried sand lance Symbols: ○ Available lysine content, △ Pepsin digestibility, ▲ Trypsin digestibility

The digestibility by pepsin (Fig. 6), was 89.9% prior to storage of the samples. The rate slowed following a prolonged storage period, to the level of the C about 83% after 6 months. In the tocopherol treated W and O, the rates reached about 85 and 89%, respectively after 6 months.

The digestibility by trypsin was 61.2% prior to storage of the samples and decreased with an increasing duration of storage in the order to 59, 54 and 48%

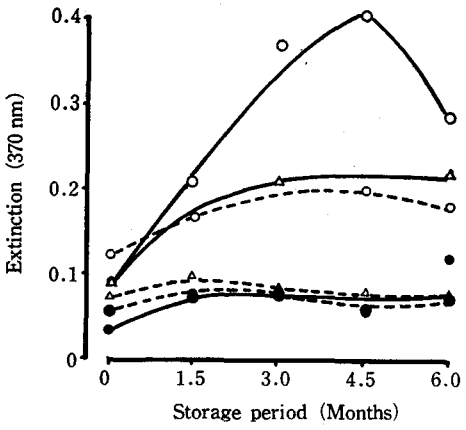

Fig. 10. Effect of "XOE-T" treatments and frozen storage on dark-color of lipid of sand lance
Symbols are the same as shown in Fig. 1.
Solid line: before frying
Dotted line: after frying

for the O, W and C, respectively after 4.5 months storage (Fig. 7).

There is a remarkable decrease in the available lysine in the C as compared with the tocopherol treated fish (Fig. 8). The decrement in the available lysine content was rapid in the C and was about 24% after 4.5 months storage, whereas the W and the O were 21% and 15%, respectively after 6 months storage.

The decrease in the available lysine content and the digestibilities in vitro by pepsin and trypsin of fried samples are correlated proportionally with the development of oxidative rancidities of frozen stored fish sample prior to frying, as indicated in TBA-V (Fig. 9). Protection from oxidative rancidity is important for the utilization of fatty fish, and the performance of the antioxidative treatment on such fish seems to be efficient in terms of food chemistry and nutrition.

The lipid of the C had a darker color when compared with those of the tocopherol treated samples (Fig. 10). However, there was a difference between the O and the W as the O gave a paler color than that of the W. The color of the extracted lipids from the O and W samples were similar to each other after frying. From this, it appears that the O was paler than the W due to dilution with olive oil used for preparation of the O. The difference in lipid color of untreated fish and tocopherol treated fish in clearly shown in Fig. 11.

We conclude that the tocopherol treatment with XOE-T, a water-dispersible tocopherol, on fish to be freeze stored can protect fatty fish against oxidative rancidity. The effectiveness of such an antioxidant treatment on fatty fish can be gauged from a nutritional point of view, and the treatment also exerts protective action on external quality of the fried fish.

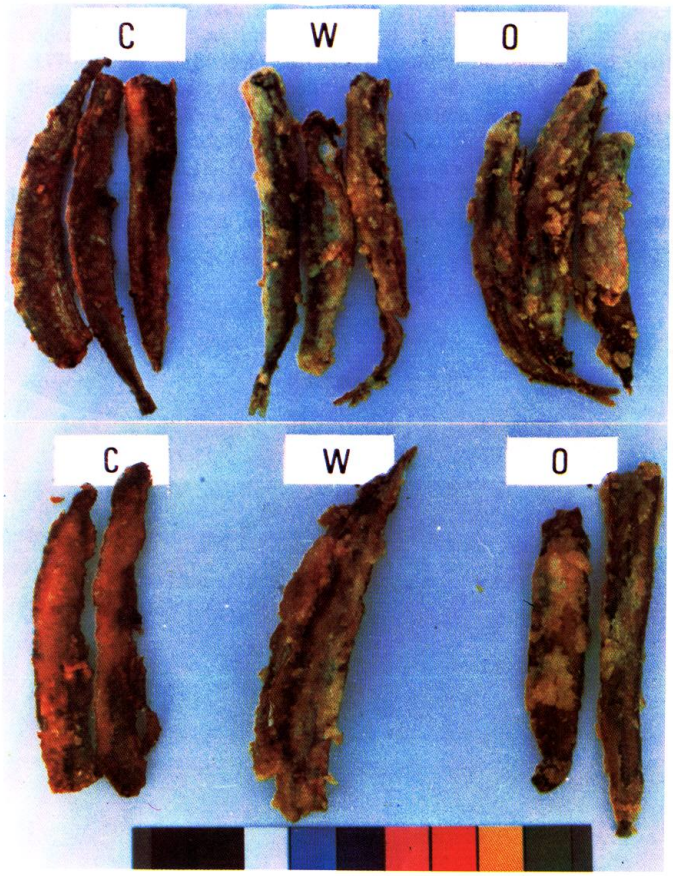

Fig. 11 Photographs of fries of frozen stored sand lance
Upper: fried after storage for 3 months at –20°C
Lower: fried after storage for 4.5 months at –20°C
C: untreated, W: treated with "XOE-T" dispersed in water,
O: treated with "XOE-T" dispersed in oil

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