Effect of Deoxygenizer on the Suppression of Lipid Deterioration of Boiled and Dried-Anchovy Engraulis japonica

II. Changes in n-3 Polyunsaturated Fatty Acids

Bo-Young JEONG, Hae-Jeom SEO*, Soo-Kyung MOON and Jae-Hyeung PYEUN*

Department of Food Science, Gyeongsang National University, Tong-Yeong, Kyeongnam 650-160, Korea *Department of Nutrition and Food Science, National Fisheries University of Pusan, Pusan 608-737, Korea

The effects of deoxygenizer (Deoxy) and sodium-erythorbate (Na-ery) on the changes in fatty acid compositions were investigated to prevent the loss of n-3 polyunsaturated fatty acids in lipid of bolied and dried-anchovy during storage.

After storage for 5 months, docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) of total lipid (TL) in Deoxy group decreased only 3.0% and 0.5%, respectively, compared to those of before storage. However, those in Control group decreased 9.5% and 2.3%, respectively. In the case of Naery group, the percentages of DHA and EPA decreased were lower than those of Control. Most of DHA and EPA in TL was lost in the early stage of storage.

Total DHA remained in phospholipid (PL), triglyceride (TG), and free fatty acid (FFA) fractions after storage for 5 months were 98%, 66% and 62% in Deoxy, Na-ery and Control group, respectively, and total EPA remained was slightly high level compared with those of DHA. The loss of DHA was more in PL than in TG.

Consequently, deoxygenizer was recognized as a good material to prevent the loss of DHA and EPA of the boiled and dried-anchovy during storage.

Key words: boiled and dried-anchovy, lipid deterioration, deoxygenizer, sodium erythorbate, docosahexaenoic acid, eicosapentaenoic acid

Introduction

Fish oil is characteristic of containing large amount of n-3 polyunsaturated fatty acids (n-3 PUFAs) such as eicosapentaenoic acid (20:5n-3, EPA) and docosahexaenoic acid (22:6n-3, DHA), unlike terrestrial organism's oil. Such the n-3 PUFAs are highly susceptible to oxidation and the resulting oxidative products decrease the nutritional value and safety of fish and fish products.

Although n-3 PUFAs play various physiological roles for human being (Dyerberg et al., 1978; Bang et al., 1980; Hirai et al., 1980; Singer et al., 1983; Kremer et al., 1985; de Brabo et al., 1991; Enslen et al., 1991),

it is hard to expect enough physiological effects unless taking the means of protection or suppression to the lipid oxidation. For these reason, many workers have proposed the use of antioxidants for the suppression of lipid oxidation in fish and fish products (Lee et al., 1965; Ke et al., 1977; Tsukuda, 1980). In recent year, deoxygenizer, an oxygen absorber, has been developed as an agent to prevent lipid oxidation. The effect of the agent has been observed for fish and fish products (Uchiyama et al., 1980; Suzuki et al., 1985; Jeong et al., 1990)

In the proceeding work (Jeong et al., 1995), authors therefore applied the deoxygenizer to the boiled and dried-anchovy and showed to suppress the increase of peroxide value and thiobarboturic acid value, and the decrease of lipid contents during storage. In the present study, changes in DHA and EPA of phospholipid, triglyceride and free fatty acid fractions in the boiled and dried-anchovy during storage were investigated in detail to make clear the effect of deoxygenizer.

Materials and Methods

Sample

The anchovy samples used for the fatty acid analysis were the same ones that reported in the previous paper (Jeong et el., 1995). Briefly, the anchovy boiled on the ship was sun-dried for about 24 hrs. The boiled and dried anchovy were divided into three groups. The first group was untreated with antioxidant (Control group) and the second group was treated with 0.02% sodium-erythorbate (Na-ery group). Samples of both groups were packed up in polyethylene film bag (PE, 60 µm in thickness) and the openings of the pack were heat-sealed. The sample of the rest group was packed up with deoxygenizer (Ageless, ZD-100, Mitsubish Gas Chemical Co., Inc.) in OPP/ Al/PE film bag $(20/7/50 \,\mu\text{m})$ in thickness, Deoxy group). All samples were stored for 5 months at 20°C. TL was extracted according to the Bligh and Dver procedure (1995) and stored at -70° C.

Lipid class fractionation

PL, TG and FFA fractions were separated from TL by thin-layer chromatography (TLC). Briefly, an aliquot of a chloroform solution of TL was submitted to preparative TLC plates coated Silica Gel G (20×20 cm, 0.25 mm in thickness) and hexane/diethyl ether/acetic acid (80:20:1, v/v/v) was used as a solvent system. Triolein, linolenic acid and phosphatidylcholine were used as authentic lipids for identification of lipid class (Sigma Chemical Co., St. Louis, MO, USA). Lipids were visualized with 0.02% 2', 7'-dichlorofluo-

rescein in ethanol. The lipid classes separated were scrapped off from the plates and extracted with chloroform/methanol (2:1, v/v), and then converted to the fatty acid methyl ester (AOCS, 1990). Methyl tricosanoate (Nu-Chek Prep, Elysian, MN, USA) was used to the quantitative analysis of DHA and EPA by gas-liquid chromatography (AOCS, 1990).

Gas-liquid chromatography

The fatty acid compositions of TL and PL, TG and FFA fractions were analyzed by GLC, using a Shimadzu GC 14A instrument (Shimadzu Seisakusho Co. Ltd., Kyoto, Japan) equipped with a Supelcowax-10 fused silica wall-coated open tubular column (30 m× 0.32 i. d., Supelco, Inc., Bellefonte, PA, USA). The injector and detector were held at 250°C and column was programmed from 180°C to 230°C at 1°C/min. The split ratio was 1:50. Helium was used as a carrier gas at the constant inlet pressure of 1.0 Kg/cm².

Results and Discussion

Fatty acid composition of TL of raw anchovy

The fatty acid compositions of TL of raw anchovy are shown in Table 1. The prominent fatty acids were DHA (22:6n-3), 16:0, EPA (20:5n-3), 18:1n-9 and 18:0, accounting for approximately 76% of total fatty acids. Particularly, DHA (32.6%) was the most abundant fatty acid. The fatty acid profile was similar to those reported by Takiguchi (1987), but different from those recorded in the Fatty Acid Composition Table (National Fisheries Research and Development Agency, 1989) and those reported by Lee et al. (1986). These differences were considered to be due to seasonal variation and difference in column used in GLC analysis.

Changes in fatty acid compositions of TL of the boiled and dried-anchovy

Changes in fatty acid compositions of TL in the

boiled and dried-anchovy during storage are shown in Tables 2, 3 and 4.

Before storage (initial), percentages of saturated and monoenoic acids were 36.6% (mainly 16:0, 22.9%) and 19.1% (mainly 18:n-9, 8.43%), respectively, and those of polyenoic acids 44.4% (mainly DHA and EPA, 29.2% and 8.04%, respectively). These fatty acid compositions of TL were different from those of the raw anchovy. Percentages of saturated acids and monoenoic acids in the boiled and dried-anchovy were higher 3% and 1%, respectively, and those of polyenoic acids lower 4% than those in the raw anchovy. DHA, 16:0 and EPA of the fatty acids were attributed greatly to their variation.

During storage, percentages of saturated and monoenoic acids of TL in all samples increased, while those of polyenoic acids decreased. After 5 months of storage, percentages of saturated and monoenoic acids of TL in Control group (Table 2) increased 8% and 5%, respectively, while those of polyenoic acids decreased 13% compared with those of initial group. The increase of the saturated and monoenoic acids was mainly due to the increase of 16:0 and 18:1n-9 during storage. On the other hand, the decrease of DHA and EPA was attributed to decrease in polyenoic acids. Similar results were observed during drying and storage of anchovy (Takiguchi, 1986, 1987, 1992), mackerel (Shimizu and Kaneda, 1969; Tashiro and Tsuvuki, 1984), flounder, whale and hairtail fish (Lee et al., 1987), menhaden oil (Fritsche and Johnston, 1988) and yellow corvenia (Ro. 1988).

In the case of Na-ery group (Table 3), changes in the fatty acid compositions of TL during storage showed similar patterns to those of Control group, but the level of these changes was low compared with those of the latter. Therefore, these results suggest that Na-erythorbate, as an antioxidant, is effective to some extent on suppression of lipid oxidation. On the other hand, the fatty acid compsitions of TL in Deoxy group (Table 4) during storage were only a little changes; after storage for 5 months, percentages of satu-

rated and monoenoic acids increased 2.8% and 0.8%, respectively, and those of polyenoic acids decreased 3.7% compared with those of initial. Thus, the level of these changes in Deoxy was the lowest of all samples tested.

Fig. 1 shows changes in the polyenoic acids to the saturated and monoenoic acids of TL in each sample during storage, in order to illustrate more clearly on the changes in fatty acid compositions.

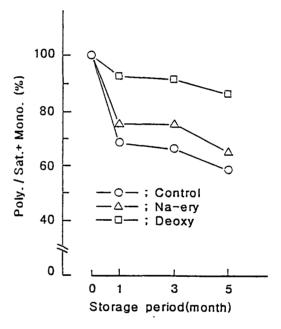


Fig. 1. Changes in polyenoic acids to saturated and monoenoic acids of TL in the boiled and dried-anchovy during storage.

During storage, the polyenoic acids decreased rapidly in the early stage of storage (up to 1 month), and then slowly. Therefore, the oxidation of DHA and EPA rapidly occurred in the early stage of storage. After 5 months of storage, the remaining rates of total polyenoic acids were 59% in Control group, 66% in Na-ery group and 86% in Deoxy group. These results suggest that lipid oxidation progressed at the fastest rate in Control group; lipid in Deoxy group was the most stable for oxidation and that in Na-ery group

was relativaly stable for oxidation compared with that of Control group. Takiguchi (1992) reported that the remaining rates of polyenoic acid of TL in the boiled and dried-anchovy, which stored at 30°C, 20°C, 0°C, - 20° and -30° for 8 months, were 58.1%, 65.7%. 63.0%, 61.0% and 89.5%, respectively, and the rates descended rapidly in the early stage of storage (up to 1 month), and then slowly. In the present study, the remaining rate of polyenoic acids of TL in Deoxy group showed a similar level to that of TL stored at =30°C for 8 months, of the results reported by Takiguchi (1992). These results indicate that the boiled and dried-anchovy enclosed deoxygenizer and stored at 20°C for 5 months showed a similar effect against lipid oxidation to that stored at -30°C for 8 months without deoxygenizer (Takiguchi, 1992). On the other hand, Suzuki et al. (1985) reported that changes in EPA and DHA of TL were not observed in sardine oil, which enclosed deoxygenizer and stored 12 months at 22° C, 2° C and -30° C.

Changes in fatty acid compositions of PL, TG and FFA fractions

In order to make clear the lipid oxidation of the boiled and dried-anchovy during storage, the fatty acid compositions of PL, TG and FFA fractions were analyzed in detail.

Table 5 shows changes in the fatty acid compositions of PL in each sample after storage for 5 months. The prominent fatty acids of PL in initial group were similar to those of TL, but the percentage of DHA was high about 5% compared to that of TL. After 5 months of storage, the percentages of saturated (mainly 16:0 and 18:0) and monoenoic (mainly 18:1n-9) acids of PL in Control group increased, while those of polyenoic acids (mainly DHA and EPA) decreased compared those corresponding to initial.

Particularly, DHA decreased 10.7% after 5 months of storage. In the case of Na-ery group, changes in fatty acid compositions of PL fractions were similar to those of Control group. However, the decreasing rates

of polyenoic acids such as DHA and EPA were lower than those of Control group. On the other hand, changes in the fatty acid compositions of PL in Deoxy group were little after 5 months of storage.

In the case of TG fractions (Table 6), the prominent fatty acid compositions in initial group were significantly different from those of PL; DHA (12.9%) was one-third of that (34.9%) of PL, and 14:0 (8.6%) and 16:1n-7 (7.82%) were more than those of PL. Therefore, TG contained much more saturated and monoenoic acids and less polyenoic acids than those of PL. After 5 months of storage, changes in these fatty acids in Control group showed similar patterns to those of PL. However, it was of interest that the percentage of EPA in TG decreased much more than that in PL.

Changes in the fatty acid compositions of FFA fractions in each sample during storage for 5 months are shown in Table 7. The prominent fatty acids of FFA in initial group were similar to those of PL. However, the percentages of these fatty acids were significantly different from those of PL; particularly, DHA (18.5%) was corresponding to one-half of that of PL and 16:0 (29.2%) much more compared with that of the latter. In contrast to the case of PL and TG fractions, the percentages of polyenoic acids such as DHA and EPA in FFA fraction increased significantly after 5 months of storage. The increasing rates of DHA and EPA in FFA fraction were the highest in Deoxy group, while those of the fatty acids the lowest in Control group. These results show that DHA and EPA derived from PL and TG mean to be lose the greatst in Control group and the least in Deoxy group.

Changes in DHA and EPA contents of PL, TG and FFA fractions

Changes in total contents of DHA and EPA of PL, TG and FFA fractions in each sample after 5 months of storage are summarized in Tables 8 and 9. The contents of DHA and EPA were calculated as mg/g lipid, using a methyl tricosanoate by GLC (AOAC, 1990),

Table 1. Fatty acid compositions of total lipid of raw anchovy

Fatty acid	Area %	Fatty acid	Area %
12:0	0.08 ± 0.00	20: 1n-7	0.15 ± 0.01
14:0	1.89 ± 0.02	22: 1n-11	0.09 ± 0.01
15:0 iso	0.07 ± 0.00	22: 1n-9	0.11 ± 0.00
15:0 anteiso	0.11 ± 0.00	22: 1n-7	0.18 ± 0.00
15:0	0.21 ± 0.26	24: 1n-9	1.73 ± 0.09
16:0 iso	0.07 ± 0.00	24: 1n-7	0.84 ± 0.25
pristanic	0.23 ± 0.00	Monoenes	18.0
16:0	20.6 ± 0.02		
17:0 iso	0.50 ± 0.02	16 ∶ 2n-4	0.95 ± 0.02
17:0 anteiso	0.10 ± 0.01	17: 2n-8	0.18 ± 0.01
17:0	0.77 ± 0.00	16∶4n-3	0.31 ± 0.00
18:0	6.34 ± 0.01	16∶4n-1	0.11 ± 0.01
19:0	0.10 ± 0.00	18: 2n-6	0.71 ± 0.01
20:0	0.21 ± 0.00	18 ∶ 2n-4	0.10 ± 0.00
22:0	0.23 ± 0.01	18 ∶ 3n-4	0.09 ± 0.01
24:0	1.83 ± 0.05	18∶3n-3	0.35 ± 0.01
Saturates	33.3	18∶4n-3	0.55 ± 0.01
		20: 2n-6	0.16 ± 0.01
14: 1n-5	0.06 ± 0.00	20:4n-6	1.74 ± 0.00
16:1n-7(+9)	2.78 ± 0.02	20:4n-3	0.27 ± 0.01
16: 1n-5	0.26 ± 0.01	20∶5n-3	8.55 ± 0.05
17: 1n-8	0.45 ± 0.01	21:5n-3	0.23 ± 0.01
18: 1n-9	8.18 ± 0.00	22∶5n-6	0.83 ± 0.36
18: 1n-7	2.64 ± 0.01	22:5n-3	0.95 ± 0.02
18: 1n-5	0.11 ± 0.01	22:6n-3	32.60 ± 0.16
20: 1n-11	0.09 ± 0.01	Polyenes	48.7
20: 1n-9	0.32 ± 0.01		

Table 2. Changes in fatty acid compositions of total lipid in Control group of boiled and dried-anchovy during storage (Area %)

during storage				(Area 70)
Fatty acid		Storage pe	riod(month)	
Tatty actu	0	1	3	5
12:0	0.11	0.11	0.12	0.14
14:0	3.01	3.62	3.99	3.94
15:0 iso	0.12	0.14	0.15	0.16
15:0 anteiso	0.12	0.13	0.15	0.16
15:0	0.53	0.65	0.69	0.72
16:0 iso	0.10	0.12	0.13	0.14
Pristanic	0.23	0.21	0.22	0.21
16:0	22.90	27.10	26.50	27.70
17:0 iso	0.27	0.33	0.38	0.38
17:0 iso 17:0 anteiso	0.12	0.13	0.29	0.21
17:0 anteiso	0.12	1.02	1.00	1.06
18:0	6,03	7.12	6.79	6.96
19:0	0.14	0.15	0.22	0.20
20:0	0.31	0.34	0.37	0.37
22:0	0.22	0.23	0.24	0.28
24:0	1.55	1.66	1.68	1.95
Saturates	36.6	43.1	42.9	44.6
14∶1n-5	0.06	0.07	0.06	0.07
16: 1n-7(+9)	3.53	4.04	4.30	4.33
16: 1n-5	0.23	0.25	0.28	0.31
17: 1n-8	0.51	0.53	0.57	0.62
18: 1n-9	8.43	9.64	9.76	10.40
18: 1n-7	2.80	3.13	3.27	3.28
18: 1n-5	0.16	0.18	0.20	0.20
20: 1n-11	0.16	0.18	0.23	0.27
20: 1n-11 20: 1n-9	0.51	0.60	0.62	0.68
20: In-7	0.23	0.19	0.31	0.28
20: In-7 22: In-11	0.13	0.17	0.19	0.21
22: 1n-11 22: 1n-9	0.13	0.15	0.28	0.17
22 : 1n-3 22 : 1n-7	0.13	0.13	0.19	0.20
24: 1n-9	1.33	1.72	1.73	1.82
		0.61		0.71
24: 1n-7	0.61		0.61	
Monoenes	19.1	21.6	22.6	23.6
16 ∶ 2n-4	0.96	1.00	1.12	1.08
17: 2n-8	0.13	0.22	0.24	0.24
16∶4n-3	0.39	0.36	0.38	0.37
16∶4n-1	0.15	0.13	0.15	0.13
18 ∶ 2n-6	0.89	0.89	0.95	0.96
18 ∶ 2n-4	0.13	0.09	0.15	0.11
18∶3n-4	0.11	0.02	0.16	0.15
18: 3n-3	0.43	0.40	0.48	0.43
18∶4n-3	0.68	0.57	0.28	0.49
20: 2n-6	0.19	0.19	0.21	0.20
20:4n-6	1.12	0.97	0.52	0.95
20: 4n-3	0.32	0.27	0.25	0.24
20: 5n-3	8.04	6.36	6.29	5.76
21:5n-3	0.20	0.10	0.15	0.08
22:5n-6	0.56	0.42	0.45	0.38
22:5n-3	0.85	0.69	0.70	0.64
22:6n-3	29.20	22.50	22.00	19.70
Polyenes	44.4	35.2	34.5	31.9
	77.7			

Table 3. Changes in fatty acid compositions of total lipid in Na-ery group of boiled and dried-anchovy during storage (Area %)

during storage				(Area %)
Fatty acid			riod(month)	
	0	<u> </u>	3	5
12:0	0.11	0.08	0.11	0.14
14:0	3.01	3.29	3.26	3.65
15:0 iso	0.12	0.13	0.13	0.15
15:0 anteiso	0.12	0.08	0.13	0.13
15:0	0.53	0.60	0.60	0.67
16:0 iso	0.10	0.12	0.11	0.13
Pristanic	0.23	0.23	0.24	0.19
16:0	22.90	25.30	25.10	26.50
17:0 iso	0.27	0.37	0.35	0.20
17:0 anteiso	0.12	0.26	0.26	0.13
17:0	0.86	1.01	0.98	1.00
18:0	6.03	7.05	6.74	6.93
19:0	0.14	0.24	0.25	0.13
20:0	0.31	0.37	0.35	0.36
22:0	0.22	0.29	0.26	0.26
24:0	1.55	1.70	1.90	1.78
Saturates	36.6	41.1	40.8	42.4
14: 1n-5	0.06	0.06	0.07 .	0.05
16: 1n-7(+9)	3.53	3.80	3.84	4.19
16: 1n-5	0.23	0.27	0.28	0.26
17: 1n-8	0.51	0.60	0.64	0.54
18∶1n-9	8.43	9.17	9.51	10.40
18: 1n-7	2.80	3.18	3.14	3.27
18: 1n-5	0.16	0.18	0.18	0.20
20: 1n-11	0.16	0.23	0.22	0.23
20: 1n-9	0.51	0.58	0.56	0.65
20: 1n-7	0.23	0.27	0.28	0.30
22: 1n-11	0.13	0.19	0.14	0.24
22: 1n-9	0.19	0.25	0.24	0.20
22: 1n-7	0.17	0.19	0.20	0.22
24: 1n-9	1.33	1.67	1.74	1.84
24: 1n-7	0.61	0.68	0.72	0.75
Monoenes	19.1	21.3	21.8	23.3
16: 2n-4	0.96	1.05	1.12	1.05
17: 2n-8	0.13	-0.24	0.21	0.23
16∶4n-3	0.39	0.37	0.43	0.31
16: 4n-1	0.15	0.14	0.14	0.11
18 ∶ 2n-6	0.89	0.93	0.90	1.01
18: 2n-4	0.13	0.14	0.14	0.07
18 : 3n-4	0.11	0.17	0.17	0.07
18: 3n-3	0.43	0.51	0.53	0.42
18: 4n-3	0.68	0.62	0.56	0.56
20 ∶ 2n-6	0.19	0.21	0.22	0.19
20: 4n-6	1.12	1.07	1.03	1.00
20: 4n-3	0.32	0.29	0.28	0.24
20: 5n-3	8.04	6.79	6.77	6.34
21:5n-3	0.20	0.17	0.20	0.29
22:5n-6	0.56	0.50	0.47	0.41
22:5n-3	0.85	0.77	0.75	0.78
22: 6n-3	29.20	23.60	23.60	21.20
Polyenes	44.4	37.6	37.5	34.3

Table 4. Changes in fatty acid compositions of total lipid in Deoxy group of boiled and dried-anchovy during storage (Area %)

during storage	Storage period(month)				
Fatty acid					
	0	11	3	5	
12:0	0.11	0.10	0.11	0.12	
14:0	3.01	2.96	3.28	3.41	
15:0 iso	0.12	0.11	0.13	0.13	
15:0 anteiso	0.12	0.12	0.12	0.13	
15:0	0.53	0.54	0.56	0.59	
16:0 iso	0.10	0.10	0.11	0.11	
Pristanic	0.23	0.25	0.20	0.21	
16:0	22.90	23.90	23.20	24.80	
17:0 iso	0.27	0.32	0.32	0.33	
17:0 anteiso	0.12	0.18	0.19	0.19	
17:0	0.86	0.92	0.90	0.93	
18:0	6.03	6.68	6.14	6.20	
19:0	0.14	0.24	0.21	0.16	
20:0	0.31	0.31	0.32	0.30	
22:0	0.22	0.23	0.24	0.21	
24:0	1.55	1.67	1.59	1.60	
Saturates	36.6	38.6	37.6	39.4	
14: 1n-5	0.06	0.06	0.07	0.07	
16:1n-7(+9)	3.53	3.43	3.67	3.73	
16∶1n-5	0.23	0.26	0.26	0.26	
17: 1n-8	0.51	0.50	0.56	0.61	
18: 1n-9	8.43	8.74	8.67	8.53	
18∶1n-7	2.80	2.97	2.89	2.84	
18: 1n-5	0.16	0.16	0.18	0.16	
20: 1n-11	0.16	0.18	0.21	0.17	
20: 1n-9	0.51	0.53	0.60	0.56	
20: 1n-7	0.23	0.23	0.26	0.23	
22: 1n-11	0.13	0.14	0.18	0.16	
22: 1n-9	0.19	0.21	0.27	0.22	
22: 1n-7	0.17	0.17	0.19	0.16	
24: 1n-9	1.33	1.43	1.55	1.49	
24: 1n-7	0.61	0.72	0.66	0.71	
Monoenes	19.1	19.7	20.2	19.9	
16: 2n-4	0.96	0.95	0.98	0.97	
17:2n-8	0.13	0.21	0.21	0.21	
16 ∶ 4n-3	0.39	0.39	0.30	0.33	
16 ∶ 4n-1	0.15	0.14	0.12	0.11	
18 ∶ 2n-6	0.89	0.89	0.98	0.97	
18 ∶ 2n-4	0.13	0.14	0.14	0.11	
18:3n-4	0.11	0.11	0.13	0.12	
18∶3n-3	0.43	0.47	0.53	0.51	
18∶4n-3	0.68	0.60	0.75	0.73	
20 ∶ 2n-6	0.19	0.20	0.21	0.19	
20:4n-6	1.12	1.13	1.11	1.02	
20 · 4n-3	0.32	0.31	0.36	0.30	
20:5n-3	8.04	7.26	7.81	7.47	
21:5n-3	0.20	0.20	0.21	0.19	
22:5n-6	0.56	0.59	0.55	0.51	
22:5n-3	0.85	0.81	0.84	0.79	
22: 6n-3	29.20	27.30	27.00	26.20	
Polyenes	44.4	41.7	42.2	40.7	

Table 5. Fatty acid compositions of phospholipid of boiled and dried anchovy after storage for 5 months (Area %)

Fatty acid			ples	
ratty actu	Initial	Control	Na-ery	Deoxy
14:0	1.96	2.70	2.75	1.76
15:0 iso	0.08	0.11	0.11	0.07
15:0 anteiso	0.11	0.15	0.13	0.10
15:0	0.45	0.63	0.60	0.44
16:0 iso	0.10	0.06	0.12	0.05
Pristanic	0.32	0.13	0.17	0.21
16:0	22.80	26.40	24.90	22.50
17:0 iso	0.23	0.34	0.25	0.24
17:0 anteiso	0.18	0.16	0.09	0.10
17:0	0.81	0.94	0.94	0.80
18:0	6.11	7.01	7.01	5.98
19:0	0.09	0.29	0.13	0.11
20:0	0.17	0.28	0.33	0.17
22:0	0.11	0.36	0.36	0.14
24:0	1.51	2.42	2.26	1.69
Saturates	35.0	42.0	40.2	34.4
14: 1n-5	0.10	0.07	0.09	0.04
16: 1n-7(+9)	2.89	3.97	3.67	2.71
16: 1n-5	0.21	0.21	0.19	0.19
17: 1n-8	0.38	0.57	0.51	0.40
18: 1n-9	8.19	11.00	10.70	8.89
18: 1n-7	2.98	3.60	3.68	3.08
18: 1n-5	0.08	0.11	0.14	0.09
20: 1n-9	0.22	0.46	0.49	0.22
20: 1n-7	tr	0.24	0.20	0.20
24: 1n-9	1.18	1.87	1.84	1.32
24: 1n-7	0.53	0.77	0.78	0.72
Monoenes	16.8	22.9	22.3	17.9
16: 2n-4	0.69	0.67	0.78	0.58
17: 2n-8	0.14	0.19	0.19	0.16
16:4n-3	0.53	0.19	0.31	0.35
16:4n-1	0.23	0.12	0.17	0.13
18 ∶ 2n-6	0.78	0.87	0.88	1.11
18: 3n-3	0.32	0.29	0.34	0.42
18: 4n-3	0.34	0.36	0.35	0.36
20: 2n-6	0.17	tr	tr	tr
20:4n-6	1.17	1.12	1.17	1.07
20:4n-3	0.16	0.23	0.15	0.24
20:5n-3	7.30	6.01	6.19	7.08
22:5n-6	0.56	0.44	0.46	0.63
22:5n-3	0.82	0.65	0.76	0.85
22:6n-3	34.90	24.20	25.80	34.80
Polyenes	48.1	35.3	37.6	47.8

Table 6. Fatty acid compositions of triglyceride of boiled and dried anchovy after storage for 5 months (Area %)

ths				(Area %
Fotty soid		Sam	ples	
Fatty acid	Initial	Control	Na-ery	Deoxy
12:0	0.66	0.71	0.91	0.50
14:0	8.60	10.70	10.60	9.00
15:0 iso	0.34	0.46	0.43	0.35
15:0 anteiso	0.31	0.42	0.36	0.31
15:0	1.00	1.31	1.29	1.04
16: 0 iso	0.23	0.30	0.12	0.24
16:0	21.00	25.40	25.00	22.40
17:0 iso	0.45	0.57	0.47	0.40
17:0 anteiso	0.22	0.29	0.23	0.21
Phytanic	1.13	1.22	1.02	1.05
17:0	1.01	1.22	1.13	1.04
18:0	5.10	6.03	5.21	5.13
19:0	0.22	0.19	0.15	0.12
20:0	0.72	0.78	0.63	0.57
22:0	0.42	0.45	0.42	0.17
Saturates	41.4	50.1	48.0	42.5
14: 1n-5	0.10	0.34	0.35	0.09
16: 1n-7(+9)	7.82	8.56	8.25	7.71
16: 1n-5	0.20	0.24	0.23	0.20
17: 1n-8	0.88	0.44	0.44	0.67
18: 1n-9	8.76	10.50	10.50	9.02
18: 1n-7	2.72	3.05	2.73	2.69
18: 1n-5	0.27	0.34	0.35	0.29
20: 1n-11	0.50	0.58	0.41	0.39
20: 1n-9	1.17	1.57	1.35	1.20
20: 1n-7	0.57	0.66	0.54	0.49
22: 1n-11	0.40	0.64	0.39	0.23
22: In-11 22: In-9	0.56	0.41	0.59	0.25
24: 1n-9	1.72	1.93	2.17	1.77
Monoenes	25.7	29.3	28.3	25.0
16:2n-4	0.63	0.57	0.56	0.64
17: 2n-8	0.29	0.37	0.33	0.31
16:4n-1	0.60	0.46	0.54	0.59
18: 2n-6	1.66	1.59	1.61	1.62
18:3n-3	1.14	0.88	0.98	1.18
18:4n-3	2.17	1.51	1.77	2.33
20: 2n-6	0.19	0.06	0.22	0.12
20: 2n-6 20: 4n-6	0.71	0.50	0.50	0.67
20: 4n-3	0.55	0.32	0.44	0.53
20:4n-3 20:5n-3	10.50	5.92	6.71	10.30
20 : 5n-5 22 : 5n-6	0.52	0.34	0.71	0.45
22:5n-3	1.01	0.65	0.33	0.45
22 : 6n-3	12.90	7.54	8.97	12.80
Polyenes	32.9	20.7	8.97 23.7	32.4
1 Olychics	54.5	40.1	4J. i	J4. 4

Table 7. Fatty acid compositions of free fatty acids of boiled and dried anchovy after storage for 5 months (Area %)

		Samples				
Fatty acid	Initial	Control	Na-ery	Deoxy		
14:0	4.45	3.00	2.65	2.27		
15:0 iso	0.56	0.19	0.14	0.09		
15:0 anteiso	0.68	0.12	0.16	0.12		
15:0	1.70	1.29	1.09	0.70		
16:0 iso	0.65	0.19	0.17	0.10		
16:0	29.20	28.80	27.70	25.90		
17:0 iso	0.33	0.34	0.27	0.23		
17:0 anteiso	0.30	0.19	0.12	0.08		
17:0	1.33	1.33	1.12	0.87		
18:0	8.43	7.98	8.48	5.65		
19:0	0.18	0.13	0.12	0.09		
20:0	0.54	0.35	0.30	0.21		
22:0	1.12	0.56	0.16	0.31		
24:0	1.11	1.25	1.46	0.95		
Saturates	50.6	45.7	44.2	37.6		
16: 1n-7(+9)	4.64	4.26	4.22	3.28		
16: 1n-5	0.30	0.23	0.24	0.20		
17: 1n-8	0.76	1.00	0.81	0.55		
18: 1n-9	8.12	9.24	9.42	8.02		
18: 1n-7	2.17	2.25	2.32	2.18		
18: 1n-5	0.14	0.08	0.26	0.09		
20: 1n-9	0.44	0.27	0.20	0.15		
24: 1n-9	1.13	1.13	1.48	0.85		
24: 1n-7	0.22	0.58	0.42	0.38		
Monoenes	17.9	19.0	19.4	15.7		
16: 2n-4	0.98	0.60	0.60	0.56		
17: 2n-8	0.22	0.18	0.18	0.16		
16:4n-1	0.31	0.04	0.19	0.07		
18: 2n-6	0.96	1.36	1.45	1.17		
18:3n-3	0.32	0.35	0.37	0.40		
18:4n-3	0.84	0.38	0.49	0.45		
20: 4n-6	1.15	1.20	1.15	1.37		
20:4n-3	0.18	0.12	0.14	0.27		
20:5n-3	7.06	7.67	7.71	9.87		
22:5n-6	0.19	0.42	0.39	0.50		
22:5n-3	0.71	0.77	0.72	0.88		
22:6n-3	18.50	22.20	23.10	30.90		
Polyenes	31.4	35.3	36.5	46.6		

Table 8. EPA contents of PL, TG and FFA fractions in each sample of boiled and dried anchovy after storage for 5 months

Class	Initial	Control	Na-ery	Deoxy
PL	262¹	197(75%)2	188(72%)	235(90%)
TG	124	35(28%)	49(40%)	122(98%)
FFA	5	16	27	28
Total	391	248(63%)	264(68%)	385(98%)

¹Milligram per 100g sample.

Table 9. DHA contents of PL, TG and FFA fractions in each sample of boiled and dried anchovy after storage for 5 months

Class	Initial	Control	Na-ery	Deoxy
PL	12291	778(63%)2	774(63%)	1131(92%)
TG	149	44(30%)	64(43%)	149(100%)
FFA	12	45	79	87
Total	1390	867(62%)	917(66%)	1367(98%)

¹, ² See the foothnotes in Table 8.

and then converted to mg/100 g sample. The EPA contents of PL. TG and FFA fractions in initial group were 262 mg, 124 mg and 5 mg/100 g, respectively, and those of DHA were 1,229 mg, 149 mg and 12 mg/ 100 g, respectively. Thus, DHA and EPA were rich in PL compared with TG. After 5 months of storage, the contents of DHA and EPA decreased the greatest in Control group; DHA decreased from 1,229 mg to 785 mg in PL and from 149 mg to 44 mg in TG, and EPA decreased from 262 mg to 199 mg in PL and from 124 mg to 35 mg in TG. In contrast to these results, the contents of DHA and EPA in FFA fraction in Control group increased during storage: DHA increased from 12 mg to 45 mg and EPA from 5 mg to 16 mg after storage for 5 months. Therefore, DHA and EPA contents during storage decreased in PL and TG, while those in FFA increased. These changes showed similar patterns in the cases of Na-ery and Deoxy group during storage, but the level of these changes was different from each other; the contents of DHA and EPA decreased were the least in Deoxy group and less in Na-ery group compared with those in Control group. Total contents of DHA and EPA remained in PL, TG and FFA fractions were 867 mg and 248 mg, respectively, in Control group, 917 mg and 264 mg, respectively, in Na-ery group and 1,367 mg and 385 mg, respectively, in Deoxy group, after storage for 5 months. Therefore, the decreasing rate of DHA in all samples was higher in PL than in TG, while that of EPA higher in TG than in PL. On the other hand, the remaining rates of DHA and EPA in each sample after 5 months of storage were 62~63% in Control group, 66~68% in Na-ery group and 98% in Deoxy group compared with those in initial group. These results show that the loss of DHA and EPA was 37~38% in Control group, 32~34% in Na-ery group and only 2% in Deoxy group after storage for 5 months.

In general, lipid oxidation rapidly occurs in the fatty acids containing the more double bonds compared with those containing the less double bonds (Miyashita and Takagi, 1986; Cho et al., 1987).

From these results, DHA and EPA in Deoxy

²Percentage remaining compared to Initial.

group were protected perfectly from lipid oxidation for 5 months of storage. Hence, the use of deoxgenizer is recommended for suppression of lipid deterioration by oxidation during long-term storage of the boiled and dried-anchovy.

Acknowledgement

The authors would like to thank Mr. Hong-Min Choi and In-Jae Hwang for their help in carrying out the lipid analyses, Gyeongsang National University, and Mr. Dae-Youl Her and Hee-Rae Jang, The Powered Anchovy Dragnet Fisheries Corporated, and Prof. Woo-Geon Jeong, Gyeongsang National University, for providing anchovy sample.

References

- A. O. C. S. 1990. "A. O. C. S. official method Ce 1 b-89, in Official Methods and Recommended Practices of the AOCS", Fourth edition, Vol. I , American Oil Chemists' Society, Champaign, Illinois, USA.
- Bang, H. O., J. Dyerberg and H. M. Sinclair. 1980. The composition of the Eskimo food in north western Greenland. Am. J. Clin. Nutr., 33, 26 57~2661.
- Bligh, E. G. and W. J. Dyer, 1959. A rapid method of lipid extraction and purification. Can. J. Biochem. Physiol., 37, 911~917.
- Cho, S. Y., K. Miyashita, T. Miyazawa, K. Fujimoto and T. Kaneda. 1987. Autoxidation of ethyl eicosapentaenoate and docosahexaenoate. JAOCS, 64, 876~879.
- de Bravo, M. G., R. J. de Antueno, J. Toledo, M. E. De Tomas, O. F. Mercuri and C. Quintans. 19 91. Effects of an eicosapentaenoic and docosahexaenoic acids concentrate on a human lung carcinoma grown in nude mice. Lipids, 26,

- 866~870.
- Dyerberg, J., H. H. Bang, E. Stoffersen, S. Moncada and J. R. Vane. 1978. Eicosapentaenoic acid and prevention of throbosis and atherosclerosis? Lancet, ii, 117~119.
- Enslen, M., M. Milton and A. Malnoe. 1991. Effect of low intake of n-3 fatty acids during development on brain phospholipid fatty acid composition and exploratory behavior in rats. Lipid, 26. 203~208.
- Fritsche, K. L. and P. V. Johnston. 1988. Rapid autoxidation of fish oil in diets without antioxidants. J. Nutr., 118, 425~426
- Hirai, A., T. Hamazaki, T. Terano, T. Nishikawa, Y. Tamura, A. Kumagai and J. Sajiki. 1980. Eicosapentaenoic acid platelet function in Japanese. Lancet, ii, 1132~1133.
- Jeong, B. Y., H. J. Seo. S. K. Moon and J. H. Pyeun. 1995. Effect of deoxygenizer on the suppression of lipid deterioration of boiled and dried anchovy *Engraulis japonica*. I. Changes in lipid class compositions. Submitted for publication in J. Korean Fish. Soc., 28(6), 770~778.
- Jeong, B. Y., T. Ohshima, C. Koizumi and Y. Kanou. 1990. Lipid deterioration and its inhibition of Japanese oyster *Crassostrea gigas* during frozen storage. Nippon Suisan Gakkaishi, 56, 2083~ 2091.
- Ke, P. J., D. M. Nash and R. G. Ackman. 1977. Mackerel skin lipids as an unsaturated fat model system for the determination of antioxidative potency of TBHQ and other antioxidant compounds. JAOCS, 54, 417~420.
- Kremer, J. M., J. Bigauoette, A. V. Michalek, M. A. Timchalk, L. Lininger, R. I. Rynes, C. Huyck, J. Zieminski and L. E. Bartholomew. 1985. Effects of manipulation of dietary fatty acids on clinical manifesttations of rhemumatoid arthritis. Lancet, ii, 184~197.
- Lee, E. H., H. U. Chang and K. U. Chin. 1965. On the effect of boiled-dried anchyy treated with

- BHA from deterioration due to the oxidation of oil. Agr. Chem. Biotech., 6, 47~50 (in Korean).
- Lee, E. H., K. S. Oh, T. H, Lee, Y, H. Chang, S. K. Kim and H. Y. Park. 1986. Fatty acid content of five kinds of boiled-dried anchovies on the Market. J. Korean Fish. Soc., 19, 183~186 (In Korean).
- Lee, K. H., J. Suh, I. H. Jeong, S. H. Song, J. J. Lee and H. S. Ryu. 1987. Lipid oxidative browing in dried fish meat-1. Oxidation of fish oil and browning. J. Korean Fish. Soc., 20, 33~40 (In Korean).
- Miyashita K. and T. Takagi. 1986. Study on the oxidative rate and prooxidant activity of free fatty acids. JAOCS, 63, 280~1384.
- National Fisheries Research and Development Agency. 1989. "Chemical Composition of Marine Products in Korea", Pusan, Korea.
- Ro, R. H. 1988. Changes in lipid components of salted-dried yellow corvenia during processing and storage. J. Korean Fish. Sco., 21, 217~224 (In Korean)
- Shimizu, E. and K. Kaneda. 1969. Changes occurring in the lipids during the processing and roasting of salted and dried fish, Science of Cookery. 2, 113~115 (In Japanese).
- Singer, P., W. Jaeger, M. Wirth, S. Voigh, E. Naumann, S. Zimontkowski, Ł. Hajdue and W. Goedicke. 1983. Lipid and blood pressure-lowering effect of mackerel diet in man. Atherosclerosis, 49, 99~108.
- Suzuki, H., S. Wada, S. Hayakawa and S. Tamura. 1985. Effects oxygen absorber and temperature on $\omega 3$ polyunsaturated fatty acids of sardine

- oil during storage. J. Food Sci., 50, 358~360.
- Takiguchi. A. 1986. Lipid oxidations in niboshi, boiled and dried-anchovy, with different lipid contents. Nippon Suisan Gakkaishi, 52, 1029~1034 (In Japanese).
- Takiguchi. A. 1987. Lipid oxidation and hydrolysis in dried anchovy products during drying and storage. Nippon Suisan Gakkaishi, 53, 1463~1469 (In Japanese).
- Takiguchi, A. 1992. Lipid Oxidation and brown discoloration in niboshi during storage at ambient and low temperatures. Nippon Suisan Gakkaishi, 58, 489~494 (In Japanese).
- Tashiro, I. and H. Tsuyuki. 1894. Rancidity of lipids in meat of salted semi-dried horse mackerel during storage. Nippon Shokuhin Kogyo Gakkaishi, 31, 511~519 (In Japanese).
- Tsubouchi, T., K. Matsui, H. Kusaka, S. Ohta and S. Kamimura. 1985. Changes in fatty acid composition during the drying and smoking of pacific saury. Yukagaku, 34, 563~567 (In Japanese).
- Tsukuda, N. 1980. Oxidative stabilities in sardine lipids and the effect of antioxidants on frozen sardine. Nippon Shokuhin Kogyo Gakkaishi, 27, 388~392 (in Japanese).
- Uchiyama, H., S. Ehira, K. Kakuda, T. Uchiyama, H. Nakamura and Y. Uchida. 1980. A new method for long period preservation of semi-dried fish and baked eel. "Shirayaki". Bull. Tokai Reg. Fish. Res. Lab, 102, 31~49 (in Japanese).

Received October 2, 1995 Accepted November 9, 1995