

# Oxidation of Synthetic Triacylglycerols Containing Eicosapentaenoic and Docosahexaenoic Acids: Effect of Oxidation System and Triacylglycerol Structure

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**ABSTRACT:** Thirteen synthetic triacylglycerols (TAG) containing eicosapentaenoic acid (EPA) or docosahexaenoic acid (DHA) were oxidized in the presence of 2,2'-azobis(2,4-dimethyl-valeronitrile) (AMVN) and 2,2'-azobis(2-amidinopropane)dihydrochloride (AAPH) as aqueous and nonaqueous radical initiators to investigate the influence of TAG structure and oxidation system on the oxidative stability of TAG that contain highly unsaturated fatty acids (HUFA). A 2:1 (mol/mol) mixture of trieicosapentaenoylglycerol and tripalmitoylglycerol was most susceptible to the AMVN-initiated oxidation among three types of TAG that contained EPA and palmitic acid (2:1, mol/mol). Compared with 1,2 (or 2,3)-dieicosapentaenoyl-3(or 1)-palmitoylglycerol (EEP) and 1,3-dieicosapentaenoyl-2-palmitoylglycerol (EPE), the oxidative rate of EEP was somewhat higher. A similar result was obtained for DHA-containing TAG. The oxidative rate of TAG that contained EPA and palmitic acid (1:2, mol/mol) showed a positive correlation with the amount of EPA in a single TAG molecule. Moreover, in the nonaqueous system, the oxidative rate of EPA-containing TAG was affected by unsaturation and carbon chainlength of constituent fatty acids. In the AAPH-initiated oxidation in the aqueous system, the oxidative rate of TAG with EPA and palmitic acid was higher with the increased quantity of EPA in a single TAG molecule. Also, constituent fatty acids modified the oxidative rate of EPA-containing TAG in an aqueous system. The glycerol position of EPA and DHA also affected the oxidative rate of the TAG. EPA and DHA located at the 1,2 (or 2,3)-position of glycerol were more oxidizable than those at the 1,3-position during AAPH-initiated oxidation. Thus, 1,2(or2,3)-dipalmitoyl-3(or 1)-eicosapentaenoylglycerol was oxidized faster than 1,3-dipalmitoyl-2-eicosapentaenoylglycerol. These observations suggest that the oxidative stability of TAG that contain HUFA could be modulated by the oxidation system and TAG structure. *JAOCS* 74, 1041–1045 (1997).

**KEY WORDS:** Docosahexaenoic acid, eicosapentaenoic acid, fish oil, marine oil, oxidation, triacylglycerol.

Highly unsaturated fatty acids (HUFA), such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), rich in

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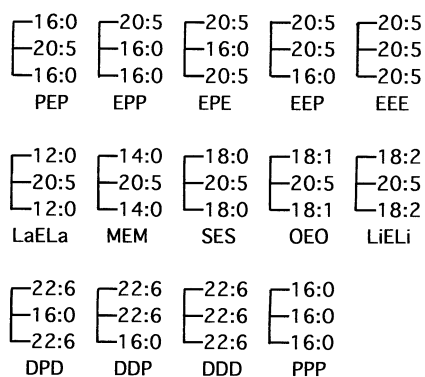
marine oils, are potentially useful in medicines and functional foods because of their specific physiological effects. However, they are susceptible to oxidation and produce undesirable flavor and toxic products, such as hydroperoxides and (hydroperoxy) alkenals, during storage (1–3). Although antioxidants, such as tocopherols, are generally available to inhibit lipid peroxidation in foods, their effect is insufficient in fish oils. Lipid structure has been proposed to affect the oxidative stability of unsaturated fatty acids. Several researchers have investigated the relationship between oxidative stability and triacylglycerol (TAG) structure of vegetable oils (4–13). We also compared the oxidative stability of randomized and native marine oils and found that fish oils that contained highly unsaturated TAG, containing two or three moles of EPA and DHA, were very unstable (14). In a previous paper (15), we investigated the autoxidative rate and autoxidation products of synthetic TAG that contained EPA, and found that the results depended on the numbers of EPA in a single TAG molecule.

In this paper, 13 chemically synthesized TAG that contained EPA or DHA were oxidized in aqueous and nonaqueous systems with oil- and water-soluble radical initiators to investigate the influence of TAG structure and oxidation system on the oxidative stability of TAG that contain HUFA.

## EXPERIMENTAL PROCEDURES

**Materials.** DHA and EPA (purity >95%) were provided by Nihon Suisan Kaisha Ltd. (Tokyo, Japan). 1-Palmitoylglycerol, 2-palmitoylglycerol, 1,2-dipalmitoylglycerol, 1,3-dipalmitoylglycerol, 1,3-dilauroylglycerol, 1,3-dimyristoylglycerol, 1,3-distearoylglycerol, 1,3-dioleoylglycerol, 1,3-dilinoleoylglycerol, glycerol, and tripalmitoylglycerol (PPP) were purchased from Sigma Chemical Co. (St. Louis, MO). 2,2'-Azobis(2-amidinopropane)dihydrochloride (AAPH) and 2,2'-azobis(2,4-dimethyl-valeronitrile) (AMVN) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

**Synthesis of TAG with DHA and EPA.** Thirteen TAG, which consisted of EPA or DHA (Scheme 1), were chemically synthesized, based on the modified method of Awl *et al.* (16). In this scheme, the following abbreviations not already



SCHEME 1

identified are used: DDD, tridocosaheptaenoylglycerol; DDP, 1,2 (or 2,3)-didocosaheptaenoyl-3 (or 1)-palmitoylglycerol; DPD, 1,3-didocosaheptaenoyl-2-palmitoylglycerol; EEE, triecosapentaenoylglycerol; EEP, 1,2 (or 2,3)-dieicosapentaenoyl-3 (or 1)-palmitoylglycerol; EPE, 1,3-dieicosapentaenoyl-2-palmitoylglycerol; EPP, 1,2 (or 2,3)-dipalmitoyl-3-(or 1)-eicosapentaenoylglycerol; LaELa, 1,3-dilauroyl-2-eicosapentaenoylglycerol; LiELi, 1,3-dilinoleoyl-2-eicosapentaenoylglycerol; MEM, 1,3-dimyristoyl-2-eicosapentaenoylglycerol; OEO, 1,3-dioleoyl-2-eicosapentaenoylglycerol; PEP, 1,3-dipalmitoyl-2-eicosapentaenoylglycerol; SES, 1,3-distearoyl-2-eicosapentaenoylglycerol.

EEE and DDD were synthesized by esterification of EPA or DHA to glycerol in the presence of 4-dimethylaminopyridine and *N,N'*-dicyclohexylcarbodiimide as catalysts. EEP and DDP were prepared from 1,2-dipalmitoylglycerol instead of glycerol. EPP and PEP were synthesized from 1,2-dipalmitoylglycerol and 1,3-dipalmitoylglycerol, respectively. EPE and DPD were prepared from 1,3-dipalmitoylglycerol. LaELa, MEM, SES, OEO, and LiELi were prepared from the corresponding 1,3-diacylglycerols. Synthetic TAG were purified through a Florisil (deactivated with 7% water) column with diethyl ether/*n*-hexane (7:93). The purity of the eight TAG was more than 95% by high-performance liquid chromatography analysis.

**AMVN-initiated oxidation.** TAG samples (ca. 50 mg = 60  $\mu$ mol), dissolved in 1.0 mL benzene, were put in 10-mL test tubes. One mL of 2.5 mM AMVN in benzene solution was added to each sample solution to start the oxidation and then sealed with a W-type silicone cap. Samples were incubated at 37°C in the dark. Headspace gas (20  $\mu$ L) was collected every hour for 6 h and then subjected to gas chromatography. A Shimadzu (Kyoto, Japan) GC-4A gas chromatograph (GC), equipped with a thermal conductivity detector and a Molecular Sieve 5A-packed column (3.0 mm  $\times$  2 m), was used to determine the amounts of oxygen consumed during oxidation of TAG (14). The GC column temperature was 70°C, and injection and detector temperatures were 90°C.

**AAPH-initiated oxidation.** TAG samples (ca. 2 mg = 2.4  $\mu$ mol) were dispersed, together with 3.0 mL of 4% sodium deoxycholate in 25 mM phosphate buffer (pH 7.0), in a 10-

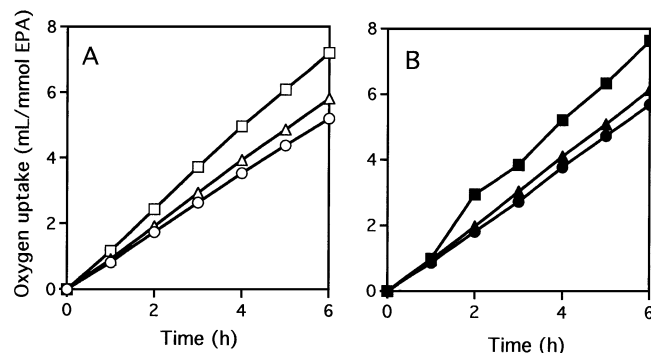
mL vial. The sample solution was mixed with 100  $\mu$ L of 4.0 mM AAPH solution and was incubated at 37°C. The uptake of oxygen in the solution was measured by the YSI model 5300 biological oxygen monitor (Yellow Springs Instrument Co., Inc., Yellow Springs, OH) (17).

All experiments were repeated more than three times. All data were presented as means  $\pm$  standard deviation and were analyzed by one-way analysis of variance, followed by analysis of differences by the *t*-test ( $P < 0.005$ ).

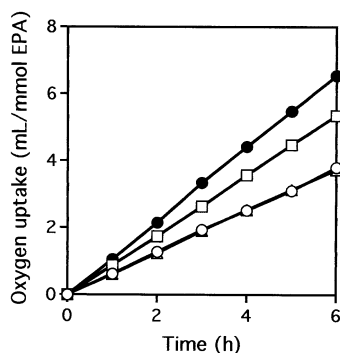
## RESULTS

**AMVN-initiated oxidation.** Three types of TAG that consisted of EPA and palmitic acid (2:1, mol/mol) were oxidized in a non-aqueous system with AMVN as the oil-soluble radical initiator (Fig. 1A). Oxidative rates, estimated from oxygen consumed, were  $1.21 \pm 0.04$ ,  $0.98 \pm 0.03$ , and  $0.87 \pm 0.04$  mL O<sub>2</sub>/mmol EPA/h for EEE/PPP (2:1), EEP, and EPE, respectively. A 2:1 (mol/mol) mixture of EEE and PPP was highly unstable and oxidized significantly faster than EEP and EPE. Similarly when TAG that consisted of DHA and palmitic acid (2:1, mol/mol) were oxidized by AMVN, oxidative rates of a 2:1 (mol/mol) mixture of DDD and PPP, DDP, and DPD were  $1.28 \pm 0.07$ ,  $1.03 \pm 0.03$ , and  $0.95 \pm 0.03$  mL O<sub>2</sub>/mmol DHA/h, respectively (Fig. 1B). Although DHA-containing TAG oxidized faster than the corresponding EPA-containing TAG, DDD/PPP (2:1) was most unstable. Moreover, the glycerol position of EPA and DHA slightly affected the oxidative stability of the TAG. HUFA located at the 1,2 (or 2,3)-position of glycerol, such as EEP and DDP, were somewhat more susceptible to AMVN-initiated oxidation than EPE and DPD at the 1,3-position.

Four types of TAG that consisted of EPA and palmitic acid (1:2, mol/mol) were subjected to AMVN-initiated oxidation. As shown in Figure 2, a 1:2 (mol/mol) mixture of EEE and PPP [EEE/PPP(1:2)] oxidized significantly faster than a 1:1 (mol/mol) mixture of EEP and PPP [EEP/PPP(1:1)], EEP and



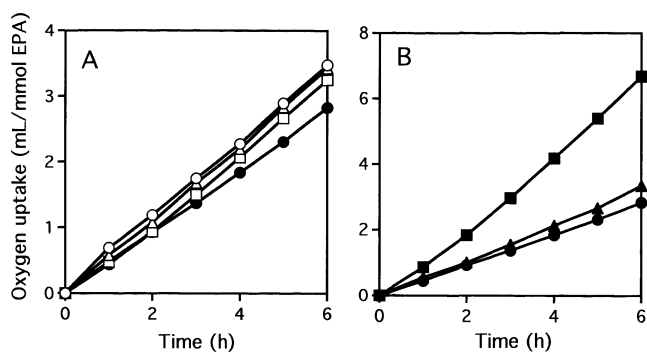
**FIG. 1.** Oxygen uptake of triacylglycerols that contain highly unsaturated fatty acid and palmitic acid (2:1, mol/mol) during 2,2'-azobis(2,4-dimethylvaleronitrile)-initiated oxidation at 37°C. (A)  $\circ$ , 1,3-dieicosapentaenoyl-2-palmitoylglycerol (EPE);  $\triangle$ , 1,2 (or 2,3)-dieicosapentaenoyl-3 (or 1)-palmitoylglycerol (EEP);  $\square$ , triecosapentaenoylglycerol (EEE)/tripalmitoylglycerol (PPP) (2:1); (B)  $\bullet$ , 1,3-didocosaheptaenoyl-2-palmitoylglycerol (DPD);  $\blacktriangle$ , 1,2 (or 2,3)-didocosaheptaenoyl-3 (or 1)-palmitoylglycerol (DDP);  $\blacksquare$ , tridocosaheptaenoylglycerol (DDD)/PPP (2:1).



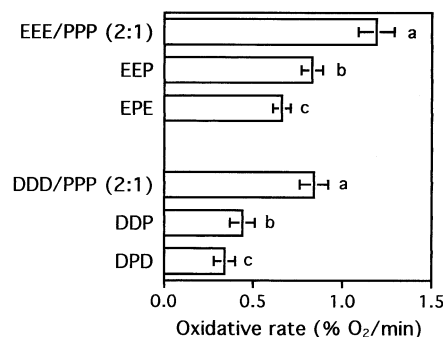
**FIG. 2.** Oxygen uptake of triacylglycerols that contain EPA and palmitic acid (1:2, mol/mol) during 2,2'-azobis(2,4-dimethyl-varelonitrile)-initiated oxidation at 37°C. ○, 1,2(or 2,3)-dipalmitoyl-3(or 1)eicosapentaenoylglycerol (PEP); △, 1,3-dipalmitoyl-2-eicosapentaenoylglycerol (EEP); □, EEP/PPP (1:1); ●, EEE/PPP (1:2). See Figure 1 for abbreviations.

PEP. The oxidative rate followed the order: EEE/PPP (1:2) ( $1.09 \pm 0.07$  mL O<sub>2</sub>/mmol EPA/h) > EEP/PPP (1:1) ( $0.89 \pm 0.05$ ) > EPP ( $0.63 \pm 0.04$ ) = PEP ( $0.62 \pm 0.03$ ). This observation indicated that the oxidative rate showed a positive correlation with the amount of EPA in a single TAG molecule. However, the glycerol position of EPA did not show a significant effect on the oxidative rate of TAG when one mole of EPA was distributed in a single TAG molecule.

To understand the effects of constituent fatty acids that coexist with EPA on the oxidative stability of TAG in a non-aqueous system, the oxidative rate was determined for TAG that consisted of saturated fatty acids with carbon chain-lengths of 12 to 18. As shown in Figure 3A, the oxidative rate was higher for LaELa ( $0.58 \pm 0.04$  mL O<sub>2</sub>/mmol EPA/h), MEM ( $0.57 \pm 0.05$ ), PEP ( $0.54 \pm 0.05$ ), and SES ( $0.47 \pm 0.04$ ), although no significant difference was observed in the oxidative rate except for SES. EPA-containing TAG were somewhat more stable with increased carbon chainlength of constituent fatty acids in a nonaqueous system.



**FIG. 3.** Oxygen uptake of triacylglycerols that contain EPA and other fatty acids (1:2, mol/mol) during 2,2'-azobis(2,4-dimethyl-varelonitrile)-initiated oxidation at 37°C. (A) ○, 1,3-dilauroyl-2-eicosapentaenoylglycerol (LaELa); △, 1,3-dimyristoyl-2-eicosapentaenoylglycerol (MEM); □, PEP; ●, 1,3-distearoyl-2-eicosapentaenoylglycerol (SES). (B) ●, SES; ▲, 1,3-dioleoyl-2-eicosapentaenoylglycerol (OEO); ■, 1,3-dilinoleoyl-2-eicosapentaenoylglycerol (LiELi). See Figure 2 for abbreviations.



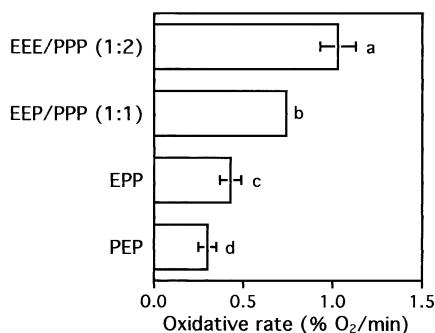
**FIG. 4.** Oxidative rate of triacylglycerols that contain highly unsaturated fatty acids and palmitic acid (2:1, mol/mol) during 2,2'-azobis(2-amidinopropane)dihydrochloride-initiated oxidation at 37°C. Each bar represents the mean  $\pm$  standard deviation of eight samples. Means not followed by a common letter are significantly different ( $P < 0.005$ ). See Figure 1 for abbreviations.

Next, TAG that consisted of one mole of EPA and two moles of stearic (18:0), oleic (18:1), or linoleic acid (18:2) were subjected to AMVN-initiated oxidation (Fig. 3B). The oxidative rates of LiELi, OEO, and SES were  $1.11 \pm 0.04$ ,  $0.56 \pm 0.05$ , and  $0.47 \pm 0.04$  mL O<sub>2</sub>/mmol EPA/h, respectively. Thus, LiELi was the most unstable TAG among the three types. The unsaturation of constituent fatty acids enhanced the oxidative rate of EPA-containing TAG in a non-aqueous system.

**AAPH-initiated oxidation.** Synthetic TAG that contained HUFA were oxidized in an aqueous system with AAPH as a water-soluble radical initiator. Figure 4 shows the oxidative rate estimated by oxygen uptake during AAPH-initiated oxidation of TAG with EPA or DHA. A 2:1 (mol/mol) mixture of EEE and PPP, EEE/PPP (2:1), consumed oxygen more rapidly than EEP and EPE. The oxidative rate followed the order: EEE/PPP (2:1) > EEP > EPE. EPA located at 1,2 (or 2,3)-position of glycerol was more susceptible to AAPH-initiated oxidation than at the 1,3-position. A similar pattern was observed in the oxidative rate of DHA-containing TAG, although at a lower rate than that of the corresponding EPA-containing TAG. The oxidative rate of a 2:1 (mol/mol) mixture of DDD and PPP, DDD/PPP (2:1), was highest and followed DDP and DPD. These observations indicated that the oxidative stability of TAG with EPA or DHA was affected by the concentration and position of HUFA in a single TAG molecule in both aqueous and nonaqueous systems.

The oxidative rate of four types of TAG that consisted of EPA and palmitic acid (1:2, mol/mol) during AAPH-initiated oxidation is shown in Figure 5. There were significant differences in oxidative rate of the four TAG. The oxidative rate followed the amounts of EPA in a single TAG molecule: EEE/PPP (1:2) > EEP/PPP > (1:1) > EPP > PEP. This observation was similar to that in AMVN-initiated oxidation. However, the oxidative rate was different between EPP and PEP in AAPH-initiated oxidation. EPA located at 1 (or 3)-position of glycerol was more oxidizable than at the 2-position.

Figure 6 shows the oxidative rate of EPA-containing TAG

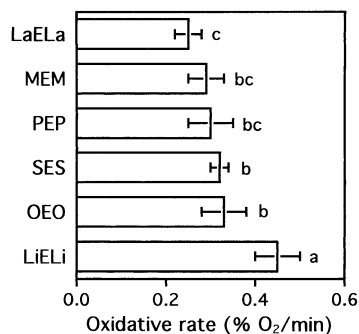


**FIG. 5.** Oxidative rate of triacylglycerols containing EPA and palmitic acid (1:2, mol/mol) during 2,2'-azobis(2-amidinopropane)dihydrochloride-initiated oxidation at 37°C. Each bar represents the mean  $\pm$  standard deviation of eight samples. Means not followed by a common letter are significantly different ( $P < 0.005$ ). See Figures 1 and 2 for abbreviations.

with different constituent fatty acids during AAPH-initiated oxidation. The oxidative rate seemed to follow the carbon chainlength of constituent fatty acids, although no significant difference was observed in the oxidative rate of TAG. SES was significantly more unstable than LaELa. This result was opposite to that in AMVN-initiated oxidation. The oxidative rate was also modulated by the unsaturation of constituent fatty acids in an aqueous system (Fig. 6). The oxidative rate of LiELi was the highest of three TAG, although the oxidative rate of OEO was almost the same as that of SES. LiELi was very unstable owing to the catalytic effect of linoleic acid. These results also indicated that the oxidative stability of TAG with HUFA depended on the type of constituent fatty acids in both aqueous and nonaqueous systems.

## DISCUSSION

To investigate the influence of TAG structure and oxidative condition on the oxidative stability of TAG with HUFA, as present in marine oils, 13 TAG containing EPA or DHA were



**FIG. 6.** Oxidative rate of triacylglycerols containing EPA and other fatty acids (1:2, mol/mol) during 2,2'-azobis(2-amidinopropane)dihydrochloride-initiated oxidation at 37°C. Each bar represents the mean  $\pm$  standard deviation of eight samples. Means not followed by a common letter are significantly different ( $P < 0.005$ ). See Figures 2 and 3 for abbreviations.

chemically synthesized, and their oxidative rates were determined during oxidation catalyzed by oil- and water-soluble radical initiators. The oxidative rate of TAG with HUFA followed the concentration and position of HUFA in a single TAG molecule, in both aqueous and nonaqueous systems. Park *et al.* (7–9) reported no effect of glycerol position of constituent fatty acids on the oxidative stability of vegetable oils. On the other hand, Raghuvver and Hammond (4) and Wada and Koizumi (6) investigated the relationship between TAG structure and oxidative stability of soybean oil. These studies reported that unsaturated fatty acids located at the 2-position were more stable than fatty acids at the 1- or 3-position. Miyashita *et al.* (18) assessed the oxidative stability of chemically synthesized TAG that consisted of linoleic acid (L) and linolenic acid (Ln) and found that LLnL was somewhat more unstable than LnLL. Frankel *et al.* (19) found that more volatile compounds formed in autoxidation of a mixture of LLL and LnLnLn than in either LLLn or LLnL. Influence of the TAG structure on the oxidative stability of vegetable oils is not always consistent. We reported that sardine oil TAG that contained two or three moles of HUFA in glycerol were unstable and that whale oil TAG in which HUFA were preferentially distributed at the 2-position were stable (14). We also determined the autoxidative rate of synthetic TAG that contained EPA and found that highly unsaturated TAG, such as EEE, were very unstable (15). The results obtained in aqueous and nonaqueous systems were basically consistent with those in autoxidation. A high concentration of EPA in a single TAG molecule enhanced the free-radical chain reaction. The present results suggest that HUFA-containing TAG, such as marine oils, could be made more stable by artificially decreasing the HUFA concentration in a single TAG molecule and by altering the glycerol position of HUFA.

Moreover, constituent fatty acids can modulate the oxidative rate of HUFA-containing TAG, although their influence is different between AMVN- and AAPH-initiated oxidation. Wada and Koizumi (6) reported that saturated fatty acid did not affect the oxidative rate of unsaturated fatty acid coexisting in TAG. On the other hand, Park *et al.* (7–9) found that the oxidative stability of unsaturated TAG was enhanced by short-chain saturated fatty acid. Yoon *et al.* (12) reported that the autoxidative rate of TAG in soybean oil was higher with decreased total carbon numbers and increased double bond numbers of the TAG molecular species. We previously measured the oxidative stability of sardine oil, interesterified with different fatty acids, and found that oleic acid could enhance the autoxidative stability of sardine oil (20). Unfortunately, the stabilizing effect of oleic acid was not observed in the present research. However, TAG that contained oleic acid were somewhat stable during AMVN-initiated oxidation. In AMVN-initiated oxidation, the higher stability of EPA-containing TAG with long-chain saturated fatty acids may be due to the concentration of EPA in a single TAG molecule being diluted by long-chain saturated fatty acids. On the contrary, the oxidative stability of EPA-containing TAG decreased with increased carbon chainlength of the saturated fatty acids in

AAPH-initiated oxidation. This may be related to the micro-molecular structure of TAG in water. Miyashita *et al.* (21,22) investigated the oxidative stability of free HUFA and HUFA-containing lipids in an aqueous system and reported that EPA and DHA, which were very oxidizable in the air, were more stable than linoleic and linolenic acids. However, our results showed that HUFA were very unstable in both nonaqueous and aqueous systems when they were highly concentrated in a single TAG molecule. Differences between these results and those obtained by Miyashita *et al.* may be due to different TAG substrates. We used simple molecular species of HUFA-containing TAG as substrates, while they used nonunified and mixed molecular species of TAG. Anyway, the oxidative stability of TAG that contain HUFA was affected by the oxidative conditions, such as in aqueous and nonaqueous systems.

These results demonstrated that TAG structure and oxidation system are important factors when determining the oxidative stability of HUFA-containing TAG.

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