Interdependent Oxidation of Eicosapentaenoic Acid and Docosahexaenoic Acid in Isada Krill Oil Encapsulated with Maltodextrin by Spray-drying

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Abstract: The major polyunsaturated fatty acids in krill oil extracted from Euphausia pacifica, known as Isada on the Sanriku coast, are eicosapentaenoic acid (EPA) and docosahexaenoic (DHA) acid. A kinetic model was proposed to explain the relationship between the fractions of unoxidized EPA (Ye) and unoxidized DHA (YD) in the oil spray-dried with maltodextrin and stored at 25, 50, and 70°C. The relationship between Ye and YD during storage was independent of the temperature and could be expressed using the proposed model. This indicated that the oxidation of EPA and DHA in krill oil was interdependent.

Key words: krill oil, oxidation, Isada krill, kinetic model

1 Introduction

Euphausia pacifica, an euphausiid inhabiting in the northern Pacific Ocean, is known as Isada on the Sanriku coast, which is a fishing area. Krill oil extracted from Isada is rich in n-3 polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). It also contains 8-hydroxyeicosapentaenoic acid (8-HEPE), which helps in burning fat, and astaxanthin, an antioxidant.

PUFAs help in regulating the triacylglycerol and cholesterol levels in blood and are prophylactic against brain and vascular diseases. EPA prevents blood clotting by suppressing blood coagulation and prevents arteriosclerosis and hyperlipidemia by reducing the low-density lipoprotein cholesterol and triglyceride contents. DHA prevents hyperlipidemia and hypertension and helps the brain to function normally. 8-HEPE, which is a component specific to euphausiid and is not present in fish, promotes fat burning, and this fat burning activity is 10 times higher than that of EPA. However, since these functional lipids have many unsaturated bonds, they are easily oxidized, thereby hindering their use in foods.

Encapsulating lipids with a wall material is one of the methods to suppress their oxidation. We have previously reported that the oxidation of Isada krill oil could be suppressed by encapsulating it at a solid content of 50% or 60% with maltodextrin as a wall material.

The oxidation rate of a PUFA in a bulk system can be expressed by an equation representing an autocatalytic process, in which the rate is proportional to the product of the concentrations of the unoxidized and oxidized PUFA. In addition, the oxidation rate of a PUFA in a binary system was proportional to the product of the concentration of the unoxidized and oxidized PUFAs. In this paper, we shall discuss the oxidation kinetics of EPA and DHA in Isada krill oil encapsulated with maltodextrin.

2 Model Description

As mentioned above, the oxidation rate of a PUFA in a binary system can be expressed by a kinetic model in which the rate is proportional to the product of the concentration of the unoxidized PUFAs and the sum of the concentrations of the two oxidized PUFAs. The same model is adopted to investigate the oxidation rates of EPA and DHA in microencapsulated Isada krill oil. The kinetic rate
The fractions of unoxidized EPA (Y_E) and DHA (Y_D) are defined as follows:

\[ Y_E = C_{E,0}/C_{E,T} \]  
\[ Y_D = C_{D,0}/C_{D,T} \]

Furthermore, the ratio of the rate constants is defined as follows:

\[ \kappa = k_E/k_D \]  

Using Eqs. (4), (5), and (6), Eq. (3) can be expressed as follows:

\[ \frac{dY_E}{dY_D} = \kappa \frac{Y_E}{Y_D} \]

Equation (7) can be integrated using the variable separation approach under the initial conditions of \( Y_E = Y_{E,0} \) and \( Y_D = Y_{D,0} \) to obtain Eq. (8).

\[ Y_E = Y_{E,0} \left( \frac{Y_{E,0}}{Y_{D,0}} \right)^{\kappa} = Y_{D,0} \frac{Y_{D,0}}{Y_{D,0}} Y_D^{\kappa} \]

3 Results and Discussion

The fractions of unoxidized EPA and unoxidized DHA, \( Y_E \) and \( Y_D \), respectively, in Isada krill oil encapsulated by spray drying using maltodextrin with a dextrose equivalent of 19 as a wall material are cited from our previous work. The Isada krill oil contained 30% (w/w) phospholipids and 28.9% PUFAs including 14.2% EPA and 10.8% DHA. It also contained 8-HEPE, astaxanthin, and PUFAs other than EPA and DHA. However, since EPA and DHA comprise 87% of the total PUFAs, the above-mentioned model that considered the interdependent oxidation of the two components was applied approximately. Antioxidants rosemary and sodium ascorbate were added at a weight ratio of 5% and 10%, respectively, to the oil during microencapsulation. Isada krill oil powders were stored in duplicates in small and large aluminum pouches and kept at 25, 50, and 70°C for six months. The \( Y_E \) and \( Y_D \) values were measured over time.

Figure 1 shows the relationship between \( Y_E \) and \( Y_D \) in the microencapsulated Isada krill oil stored for over six months at 25, 50, and 70°C (10). All the values lay on the same curve, regardless of the storage temperature and solid content. \( Y_E \) and \( Y_D \) were related by the following equation:

\[ Y_E = 0.986 Y_D^{0.703} \]  

The fact that the relationship between \( Y_E \) and \( Y_D \) could be represented by the same equation at all the storage temperatures validates the proposed model, which assumes that the oxidation of EPA and DHA in the microencapsulated Isada krill oil is interdependent. The antioxidants added to the Isada krill oil contributed equally to the oxidation of EPA and DHA. Since DHA is more easily oxidized than EPA (9), a value of \( \kappa \) less than 1 was justified. Since \( \kappa \) is the ratio of the rate constants for the oxidation of EPA and DHA, it should be temperature-dependent. However, the \( \kappa \) value could be considered almost constant in the temperature range tested. This was probably because the activation energies of EPA and DHA for autoxidation were almost equal: 53.7 ± 9.2 and 59.7 ± 12.0 kJ/mol, respectively (7).

In the autocatalytic model for oxidation, \( Y_{E,0} \) and \( Y_{D,0} \) rep-
resent the initial fractions of unoxidized EPA and unoxidized DHA, respectively. Since these values were not exactly equal to 1 but were very close to 1, it was reasonable that $Y_{E0}/Y_{D0}$ was close to 1.

The above results indicate that EPA and DHA oxidized interdependently in the microencapsulated Isada krill oil. In the presence of antioxidants, the oxidation behaviors of both EPA and DHA were same and independent of the storage temperature. The mechanism of oil oxidation in the microcapsules is same as that in the bulk system, despite the presence of a diffusional barrier for oxygen. The findings obtained in this study will be useful for understanding the oxidation of oils that are mainly a mixture of two PUFAs, in both bulk and microencapsulated systems.

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