Note

Effect of Relative Humidity during Storage on the Autoxidation of Linoleic Acid Encapsulated with a Polysaccharide by Hot-Air-Drying and Freeze-Drying

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Linoleic acid was encapsulated with gum arabic, maltodextrin and pullulan at different weight ratios by hot-air-drying and freeze-drying. The autoxidation processes of the encapsulated linoleic acid were observed at 37°C and at various relative humidities. Linoleic acid encapsulated by hot-air-drying was more stable at the lower humidities regardless of the kind of wall material. Linoleic acid encapsulated with gum arabic by freeze-drying also showed a similar dependence on the humidity. Linoleic acid in the microcapsules freeze-dried with maltodextrin and pullulan was very stable against autoxidation at intermediate humidities, while it was very easily autoxidized at low or high humidity. This tendency was remarkable for microcapsules prepared with pullulan.

Keywords: autoxidation, encapsulation, linoleic acid, relative humidity

Microencapsulation of an unsaturated lipid as a core material with a wall material can retard its autoxidation. Many factors such as the kind of wall material (Imagi *et al*., 1992), the ratio of the core material to wall material (Minemoto *et al*., 1999), the drying method (Minemoto *et al*., 1997), and storage conditions (Minemoto *et al*., 1997; Yoshii *et al*., 1997) affect the autoxidative stability of the encapsulated lipid. The relative humidity or water activity during storage affects both the state of the dehydrated wall material layer (Rosenberg *et al*., 1985; 1990) and the autoxidation kinetics of the unsaturated lipid (Labuza *et al*., 1971). The structure of the dehydrated wall material layer depends on the drying method (Minemoto *et al*., 1997; Desobry *et al*., 1997). However, few systematic studies of these effects of the factors on the stability of encapsulated lipid have been done.

In this context, the autoxidation processes of linoleic acid encapsulated with three kinds of polysaccharides at different weight ratios by hot-air-drying and freeze-drying were measured at various relative humidies during storage.

Materials and Methods

Materials Linoleic acid with a purity of > 90% was purchased from Tokyo Kasei Kogyo, and was used as received. Methyl palmitate, which was used as the internal standard for the gas chromatographic analysis, was also purchased from Tokyo Kasei Kogyo, and its purity was greater than 95%. Gum arabic was purchased from San-ei Chemical Industries, Osaka. Moltodextrin with a dextrose equivalent of 2–5 was purchased from Matsutani Chemical Indutries, Osaka. Pullulan (PI-20), the molecular mass of which was about 2×10^5, was supplied by Hayashibara, Okayama.

Encapsulation of linoleic acid with polysaccharide The encapsulation of linoleic acid with a polysaccharide was carried out using the single-droplet method (Charlesworth & Marshall,

1960) in a manner similar to that in a previous study (Minemoto *et al*., 1997; Minemoto *et al*., 1999; Minemoto *et al*., 2000). The weight ratios of linoleic acid to the wall material were varied at 0.2, 0.5, 1.0 and 2.0. The details of the encapsulation are described in the above references.

Autoxidation of encapsulated linoleic acid The autoxidation process of the encapsulated linoleic acid was measured at 37°C and at different relative humidities. The relative humidities were regulated at 12, 44, 75 and 96% by placing a Petri dish filled with a saturated LiCl, K_2CO_3, NaCl and K_2SO_4 solutions, respectively, in a desiccator in which the microcapsules were stored. The desiccator was placed in a temperature-controlled chamber in the dark. At appropriate intervals, a microcapsule was removed, and the amount of unoxidized linoleic acid within the microcapsule was quantified by the gas chromatographic analysis using methyl palmitate as the internal standard. The analytical conditions were the same as in a previous study (Minemoto *et al*., 1999).

Results and Discussion

Figure 1 shows the autoxidation processes of linoleic acid encapsulated with gum arabic, maltodextrin and pullulan by hot-air-drying and freeze-drying at different relative humidities at 37°C. The weight ratio of linoleic acid to a polysaccharide was 1.0. Linoleic acid encapsulated with gum arabic either by hot-air-drying or by freeze-drying was resistant to autoxidation except when the relative humidity was 96%. When linoleic acid was encapsulated with maltodextrin or pullulan by hot-air-drying (Fig. 1 (b-1) or (c-1)), the acid was easily autoxidized at any relative humidity. For linoleic acid encapsulated with maltodextrin or pullulan by freeze-drying (Fig. 1 (b-2) or (c-2)), the relative humidity significantly affected the autoxidation of linoleic acid. Linoleic acid was hardly autoxidized at the intermediate humidities (44% and 75%), while it was easily autoxidized at low (12%) and high (96%) relative humidities.

The autoxidation processes of linoleic acid encapsulated with

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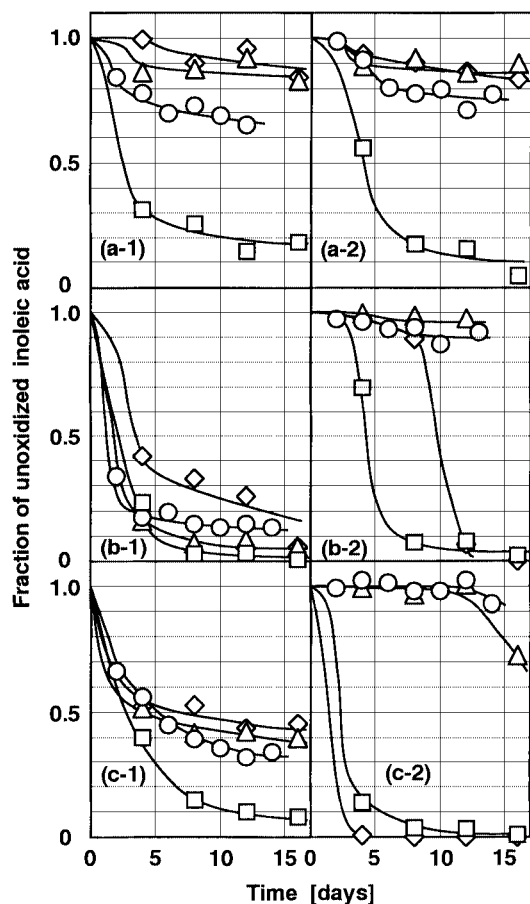E-mail: adachi@kais.kyoto-u.ac.jp

Fig. 1. Autoxidation processes of linoleic acid encapsulated with (a) gum arabic, (b) maltodextrin and (c) pullulan at a weight ratio of 1.0 by (1) hot-air-drying and (2) freeze-drying. Autoxidation was observed at 37°C and at (◇) 12%, (△) 44%, (○) 75% and (□) 96% relative humidity.
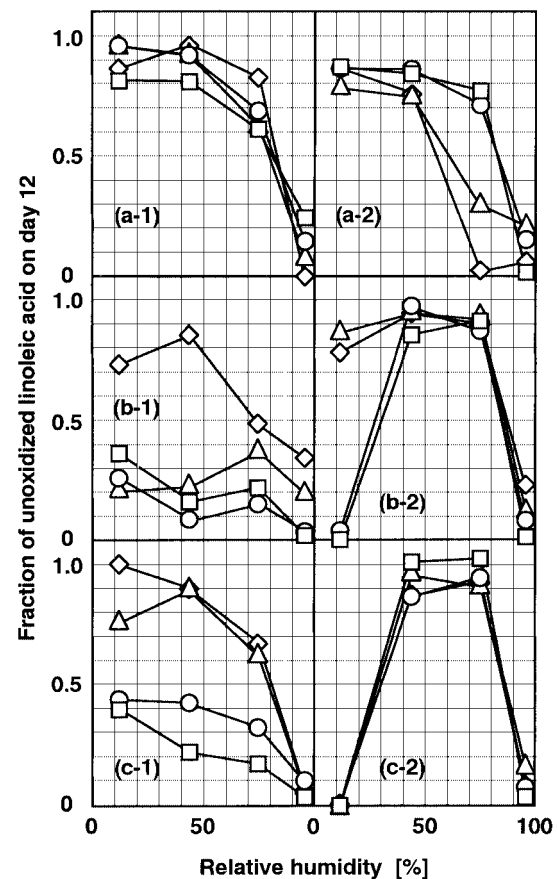

Fig. 2. Effect of the relative humidity during storage on the autoxidative stability of linoleic acid encapsulated with (a) gum arabic, (b) maltodextrin and (c) pullulan by (1) hot-air-drying and (2) freeze-drying. The fraction of unoxidized linoleic acid on day 12 was used as the stability indicator. The weight ratios of linoleic acid to a polysaccharide were (◇) 0.2, (△) 0.5, (○) 1.0 and (□) 2.0.

the polysaccharides at the different weight ratios were also measured at 37°C (data not shown). To estimate the effect of the relative humidity during storage, the fraction of unoxidized linoleic acid on day 12, which was selected as an indicator for the stability of the encapsulated linoleic acid, was plotted versus the relative humidity in Fig. 2. Linoleic acid encapsulated with gum arabic either by hot-air-drying or by freeze-drying (Fig. 2 (a-1) or (a-2)) was more unstable at the higher humidities. Linoleic acid encapsulated with maltodextrin or pullulan by hot-air-drying (Fig. 2 (b-1) or (c-1)) was also more easily autoxidized at higher humidities. There was a tendency that linoleic acid encapsulated at the lower weight ratio was hard to autoxidize. As shown in Figs. 2 (b-2) and (c-2), a peculiar dependence of the autoxidative stability of linoleic acid on the relative humidity was observed when the acid was encapsulated with maltodextrin and pullulan by freeze-drying. Linoleic acid was very stable against autoxidation at the intermediate humidities, but was easily autoxidized at the low and high humidities. This dependence was remarkable for linoleic acid encapsulated with pullulan at any weight ratio and for that encapsulated with maltodextrin at the high weight ratios.

A dense matrix layer of wall material would be formed at the surface of the microcapsule during the early stage of hot-air-drying. The layer served as a barrier for the diffusion of oxygen

from the surrounding into the microcapsule. This would be the reason for the relatively high stability against the autoxidation at low humidity. The layer adsorbed more water at the higher relative humidities, and it would then become semifluid to facilitate the migration of the inner linoleic acid particles toward the surface of the microcapsule (Minemoto *et al.*, 1997). The linoleic acid that migrated to the surface would be easily autoxidized. The microcapsule prepared by freeze-drying was very porous (Minemoto *et al.*, 2000), but we postulated (Minemoto *et al.*, 1997) that each linoleic acid particle would be covered with the matrix layer. At low humidity, oxygen could easily diffuse through the layer resulting in the autoxidation of linoleic acid. The low stability of linoleic acid at the high humidity would be due to the same reason mentioned above. At the intermediate humidity, the wall material adsorbed water molecules in two or three layers (Minemoto *et al.*, 1997). Since oxygen has a hydrophobic property, it would be difficult for it to diffuse through the water layers. This would be one reason for the high stability of the linoleic acid encapsulated by freeze-drying and storage at intermediate humidities.

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