Use of Fatty Acid Metal Salts for Preventing Maillard Reaction-Driven Browning of Lecithins

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Abstract: We previously reported that fluid soybean lecithin (SL) undergoes heat deterioration by the newly reported pseudo-Maillard rearrangement reaction. To inhibit heat deterioration, SLs were treated with metal silicates, such as magnesium silicate and calcium silicate. When soybean fatty acid was added to SL before treatment with calcium silicate, the color index after heating improved significantly as the acid value increased from 10 to 35 mg KOH/g. To elucidate the role of soybean fatty acid, calcium silicate treatment was carried out by adding several fatty acids to SL. Although saturated fatty acids had no effect on the heat deterioration of SL, unsaturated fatty acids were significantly more effective at inhibiting heat deterioration. Furthermore, for unsaturated fatty acids, it was confirmed that the calcium concentration increased in SL. Based on these results, several fatty acid metal salts were added to confirm whether heat deterioration while heating SL could be inhibited. It was observed that the heat deterioration of SL could be inhibited with fatty acid metal salts, regardless of whether the fatty acids were saturated or unsaturated and whether the metal was monovalent, divalent, or trivalent. Therefore, in this study, we clarified that the heat deterioration of SL could be inhibited by adding fatty acid metal salts to SL. Among sodium stearate, calcium stearate, magnesium stearate, barium stearate, and aluminum tristearate, the divalent fatty acid metal salts had a stronger inhibitory effect on heat deterioration than the monovalent and trivalent salts.

Key words: soybean lecithin, new pseudo-Maillard rearrangement reaction, heat deterioration, metal silicate, fatty acid metal salt

1 Introduction

Lecithin is produced from plants via the extraction and hydration of crude oil, separation of wet gum, and drying. As a natural emulsifier, it is widely used all over the world not only in food products, but also in non-food applications. In addition, lecithin has an excellent mold release effect. Oils containing lecithin are often used in the food processing field as mold release oils during cooking\(^1\). Although lecithin has extensive applications, it is well known that heat during cooking causes deterioration of lecithin. When lecithin is heated to high temperatures, it gradually turns from yellow to brown, before finally turning black and emitting a foul odor\(^2\)\(^-\)\(^7\). This deterioration of lecithin has negatively impacted food quality and is a problem in the field of food processing.

It has been reported that lecithin browning is related to the formation of four pyridinium compounds, with \(\lambda_{\text{max}} = 350 \text{ nm}\), as shown in Fig. 1\(^8\)\(^,\)\(^9\). The formation mechanism for these reactants has also been elucidated to involve a new pseudo-Maillard rearrangement reaction of 1 mol of any sugar, except 2-deoxy sugars, with 2 mol of any phosphatidylethanolamine (PE)\(^10\)\(^-\)\(^13\). It has been reported that soybean lecithin (SL) contains a small amount of oligosaccharides, such as sucrose, raffinose, and stachyose\(^14\)\(^,\)\(^15\). When lecithin is heated, it turns brown because PEs and oligosaccharides contained in lecithin undergo the Maillard reaction to produce four pyridinium compounds. Since sugars and PEs are involved in the heat deterioration of lecithin and browning of oil upon heating, removal of the sugars from this reaction system is expected to prevent the occurrence of this new pseudo-Maillard rearrangement reaction\(^16\). However, even when oil is blended with desaccharified SL and used for cooking, sugars from the food are mixed into the SL, which causes heat deterioration. Thus,
2.2 Materials

Fluid SL (total phospholipid content: 57.2%, acid value: 25.54 mg KOH/g), comprising phosphatidylethanolamine (PE; 32.6%), PE (27.2%), phosphatidylinositol (PI; 15.8%), phosphatidic acid (PA; 7.6%), and soybean oil were manufactured by Tsuji Oil Mills Co., Ltd (Mie, Japan). Soybean fatty acid (acid value: 186.14 mg KOH/g) was manufactured by Tsuno Food Industrial Co., Ltd (Wakayama, Japan). Magnesium silicate was manufactured by The Dallas Group of America, Inc. (New Jersey, USA). Calcium silicate was manufactured by Tomita Pharmaceutical Co., Ltd (Tokushima, Japan). Myristic acid, palmitic acid, oleic acid, linoleic acid, α-linolenic acid, sodium stearate, and barium stearate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Calcium oleate was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Magnesium stearate and calcium stearate were manufactured by Nitto Chemical Industry Co., Ltd. (Kanagawa, Japan).

2.3 Inhibition of heat deterioration of SL by treatment with metal silicate

2.3.1 Treatment of SL followed by heat deterioration tests

2.3.1.1 Treatment with metal silicate

SL (12.05 g) and soybean oil (17.95 g) were mixed to make 25.0 wt.% of the total phospholipid content, and heated at 60°C for 30 min to easily dissolve SL in the oil. Next, metal silicate (3.00 g) was added to 20.00 g of the mixture, and because of the improved fluidity of the oil–SL mixture, it was further heated at 60°C for 30 min. Subsequently, the metal silicate was removed by pressure filtration, and the filtrate was vacuum-dried (50°C, −0.09 MPa, 18 h).

2.3.1.2 Treatment with metal silicate after addition of soybean fatty acids

SL (12.05 g), soybean oil, and soybean fatty acids were mixed to make 25.0 wt.% of the total phospholipid content. The acid value of the mixture was adjusted from 15 to 35 mg KOH/g in 5 increments, and the total weight was kept at 30.00 g. Next, metal silicate (3.00 g) was added to 20.00 g of the mixture, and because of the improved fluidity of the oil–SL mixture, it was heated at 60°C for 30 min. Subsequently, the metal silicate was removed by pressure filtration, and the filtrate was vacuum-dried (50°C, −0.09 MPa, 18 h).

2.3.1.3 Treatment with calcium silicate after addition of several fatty acids

SL (12.05 g), soybean oil, and several fatty acids (0.023 mol each) were mixed to make 25.0 wt.% of the total phospholipid content. Next, calcium silicate (3.00 g) was added to 20.00 g of these mixtures, and because of the improved fluidity of the oil–SL mixture, the mixtures were heated at 60°C for 30 min. Subsequently, calcium silicate was removed by pressure filtration, and the filtrates were vacuum-dried (50°C, −0.09 MPa, 18 h).

2.3.1.4 Heat deterioration tests

SLs prepared using the various processing methods described above were diluted with soybean oil to prepare...
mixtures with total phospholipid content of 1 wt.%, and 6 g of these mixtures were heated in a test tube at 200°C for 15 min.

2.3.1.5 Calcium concentration measurement

To measure the calcium concentration in the mixtures treated with calcium silicate, the samples (0.2 g) were heated with sulfuric acid (2 mL) and nitric acid (20 mL) at 200°C for 18 h in a perfluoroalkoxy alkane-lined reaction vessel (100 mL). After cooling, perchloric acid (2.5 mL) was added to the solution and concentrated at 200°C for 3 h. The volume was adjusted to 50 mL with 1 vol.% hydrochloric acid (aq.). Finally, the calcium content was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPS-7510).

2.4 Inhibition of heat deterioration of SL with addition of fatty acid metal salts

2.4.1 Mixing SL with several fatty acid metal salts

Soybean oil and several fatty acid metal salts (8.5 × 10⁻⁵ mol) were mixed to obtain a total weight of 9.83 g, and the mixture was heated at 130°C for 10 min to easily dissolve the fatty acid metal salts in oil. After the mixture was cooled to 60°C or below, SL (0.17 g) was added to prepare mixtures with total phospholipid content of 1 wt.%, and the mixture was heated at 60°C for 10 min to easily dissolve SL in oil. Subsequently, 6 g of these mixtures were heated in a test tube at 200°C for 15 min.

2.4.2 Mixing SL with calcium stearate

Soybean oil and calcium stearate (at different concentrations: 0.05 wt.%, 0.10 wt.%, 0.30 wt.%, 0.50 wt.%, 1.00 wt.%) were mixed to obtain a total weight of 9.83 g, and the mixture was heated at 130°C for 10 min to easily dissolve calcium stearate in oil. After cooling to 60°C or below, SL (0.17 g) was added to prepare mixtures with total phospholipid content of 1 wt.%, and the mixture was heated at 60°C for 10 min to easily dissolve SL in oil. Subsequently, 6 g of these mixtures were heated in a test tube at 200°C for 15 min.

2.4.3 Heating SL in octane

Based on the methods described in previous papers⁹, SL (5 g) was dissolved in octane and refluxed for 9 h. Mixtures of SL with stearic acid (0.71 g, 2.5 mmol) or calcium stearate (1.52 g, 2.5 mmol) were also dissolved in octane and refluxed for 9 h. After heating for 9 h, the reactants were dried in a rotary evaporator under vacuum conditions and passed through a Sep-Pak silica cartridge. Fractions with increasing concentrations of methanol were eluted in sequence, resulting in chloroform, 25% methanol in chloroform, and 50% methanol in chloroform fractions. The fraction with 50% methanol in chloroform was analyzed using HPLC (Column: Senshu Pak. AQUASIL SS-4251 250 mm × 10 mm, i.d., Senshu, Japan; flow rate: 3.0 mL/min; solvent: a mixture of chloroform, methanol, and water (80:20:1, v/v/v); detector: UV at 350 nm).

3 Results and Discussion

3.1 Inhibition of heat deterioration of SL by treatment with metal silicate

Helmy et al. (1994)¹⁰ reported that the color of refined cottonseed oil was improved when crude cottonseed oil was added to the metal silicate during the degumming process; however, the mechanism of oil color improvement remains unknown. Still, we investigated whether metal silicate treatment could inhibit the heat deterioration of SL.

Color changes caused by the heating of metal silicate-treated SL are shown in Fig. 2A. Intact SL, i.e., untreated SL, browned after heating at 200°C for 15 min in oil (e). However, when SL with acid value adjusted to 35 mg KOH/g by adding soybean fatty acid and SL treated with magnesium silicate without acid value adjustment were heated in oil under the same conditions, the treated SLs also turned brownish and exhibited almost the same color (f and g) as intact SL (e). These results showed that the addition of soybean fatty acids or treatment with magnesium silicate alone did not inhibit the heat deterioration of SL in oil. However, when soybean fatty acids were added to SL before treatment with magnesium silicate, the color improved marginally with increasing acid value (h, i, j, k, l).

On the other hand, when calcium silicate was used for the treatment of SL, the color improved significantly with increasing acid value, as shown in Fig. 2B (h', i', j', k', l'). These results clearly show that soybean fatty acids are indispensable for inhibiting the browning of SL by metal silicate treatment, and that calcium silicate is more effective than magnesium silicate.

In order to confirm which fatty acid is involved in inhibiting the heat deterioration of SL, calcium silicate treatment was carried out after the addition of several fatty acids to SL. When saturated fatty acids, such as myristic acid, palmitic acid, and stearic acid, were added to SL before treatment with calcium silicate, the color indices after heating were 118, 125, 126, and the heat deterioration of SL could not be inhibited regardless of the carbon chain length (Table 1). On the other hand, when unsaturated fatty acids, such as oleic acid, linoleic acid, and α-linolenic acid, were added, the heat deterioration of SL was significantly inhibited and the color indices after heating were 23, 22, and 20, respectively. These results show that unsaturated fatty acids are indispensable for inhibiting the heat deterioration of SL by metal silicate treatment. It is well known that the main components of soybean fatty acids are unsaturated fatty acids, such as oleic acid and linoleic acid. It is, therefore, suggested that unsaturated fatty acids in soybean fatty acids are involved in the inhibition phenomenon. Furthermore, when myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid were added to SL before treatment with calcium silicate, the calcium concentrations of the mixtures were 9.80, 8.96, 7.94, 28.14, 29.76, and 31.05 mmol/L, respectively. The
Fig. 2A  Color changing by heating of SL treated with magnesium silicate.

a. non heating of SL, b. non heating of SL which was adjusted to acid value 35 mg KOH/g, c. non heating of SL which was treated with magnesium silicate, d. non heating of SL which was adjusted to acid value 35 mg KOH/g before treated with magnesium silicate, e. after heating of SL, f. after heating of SL which was adjusted to acid value 35 mg KOH/g, g. after heating of SL which was treated with magnesium silicate, h. after heating of SL which was adjusted to acid value 15 mg KOH/g before treated with magnesium silicate, i. after heating of SL which was adjusted to acid value 20 mg KOH/g before treated with magnesium silicate, j. after heating of SL which was adjusted to acid value 25 mg KOH/g before treated with magnesium silicate, k. after heating of SL which was adjusted to acid value 30 mg KOH/g before treated with magnesium silicate, l. after heating of SL which was adjusted to acid value 35 mg KOH/g before treated with magnesium silicate.

Fig. 2B  Color changing by heating of SL treated with calcium silicate.

a’. non heating of SL, b’. non heating of SL which was adjusted to acid value 35 mg KOH/g, c’. non heating of SL which was treated with calcium silicate, d’. non heating of SL which was adjusted to acid value 35 mg KOH/g before treated with calcium silicate, e’. after heating of SL, f’. after heating of SL which was adjusted to acid value 35 mg KOH/g, g’. after heating of SL which was treated with calcium silicate, h’. after heating of SL which was adjusted to acid value 15 mg KOH/g before treated with calcium silicate, i’. after heating of SL which was adjusted to acid value 20 mg KOH/g before treated with calcium silicate, j’. after heating of SL which was adjusted to acid value 25 mg KOH/g before treated with calcium silicate, k’. after heating of SL which was adjusted to acid value 30 mg KOH/g before treated with calcium silicate, l’. after heating of SL which was adjusted to acid value 35 mg KOH/g before treated with calcium silicate.

Fig. 3  Color changing by heating of SL with calcium stearate.

a”. non heating of SL, b”. non heating of SL with 1 wt % of calcium stearate, c”. after heating of SL, d”. after heating of SL with 0.05 wt % of calcium stearate, e”. after heating of SL with 0.1 wt % of calcium stearate, f”. after heating of SL with 0.3 wt % of calcium stearate, g”. after heating of SL with 0.5 wt % of calcium stearate, h”. after heating of SL with 1.0 wt % of calcium stearate.
calcium concentration with unsaturated fatty acids was more than three times that with saturated fatty acids. Thus, saturated fatty acids are probably less capable of extracting calcium from calcium silicate and producing fatty acid calcium salts. Based on these results, it is suggested that calcium is transferred to SL during calcium silicate treatment with unsaturated fatty acids, and calcium contributes to inhibiting the heat deterioration of SL.

### 3.2 Inhibition of heat deterioration of SL with addition of fatty acid metal salts

It is suggested that the heat deterioration of SL is inhibited by calcium from calcium silicate, indicating that calcium exists as a fatty acid salt. Therefore, several fatty acid metal salts were added to confirm whether heat deterioration could be inhibited while heating SL. When SL was heated with sodium stearate, calcium stearate, calcium oleate, magnesium stearate, barium stearate, and aluminum tristearate, the color indices after heating were 93, 22, 23, 25, 22, and 63, respectively. It was observed that the heat deterioration of SL could be inhibited by fatty acid metal salts, regardless of whether the fatty acids were saturated or unsaturated and whether the metal was monovalent, divalent, or trivalent, as shown in Table 2. We newly clarified that the heat deterioration of SL could be inhibited by adding fatty acid metal salts to SL.

The heat deterioration of SL could be inhibited only when metal silicate treatment of the mixture was carried out after adding fatty acids to SL. This result shows that metal silicates and fatty acids form fatty acid metal salts, which inhibit the heat deterioration of SL. Furthermore, the addition of saturated fatty acids could not inhibit the heat deterioration of SL even after treatment with calcium silicate because the saturated fatty acids could not extract calcium to form fatty acid metal salts. In contrast, when saturated fatty acid metal salts were used directly, the heat deterioration of SL was clearly inhibited. This shows that the metal salts of fatty acids have an inhibiting effect on deterioration, and the type of fatty acid is irrelevant.

Among sodium stearate, calcium stearate, magnesium stearate, barium stearate, and aluminum tristearate, the divalent fatty acid metal salts had stronger heat deterioration inhibiting effects than the monovalent and trivalent salts. These results show that divalent fatty acid metal salts strongly inhibit the Maillard reaction of PEs and sugars. In addition, even if the oil had a phospholipid content of 1%, heat deterioration could be significantly inhibited by blending 0.3% calcium stearate, as shown in Fig. 3.

Hayashi et al.\(^{12}\) described that upon heating SL in octane, the browning of the solution was accompanied by the production of four novel pyridinium derivatives and an increase in UV absorption at 350 nm. These pyridinium derivatives were formed by the Maillard reaction of 1 mol of any sugar, except 2-deoxy sugars, with 2 mol of any PE. It is believed that fatty acid metal salts inhibit this Maillard reaction.

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### Table 1 Calcium concentration in SL after calcium silicate treatment with several fatty acid, and color index by heating.

| No. | Fatty acid | Calcium concentration (mmol/L)\(^{※}\) | Color \(\text{Lovibond Index}\)\(^{※※}\) |
|-----|------------|------------------------------------------|------------------------------------------|
| 1   | –          | 1.86                                     | 0+40+8.1                                 |
| 2   | C14 : 0    | 9.80                                     | 0.1+50+6.7                               |
| 3   | C16 : 0    | 8.96                                     | 0+60+6.5                                 |
| 4   | C18 : 0    | 7.94                                     | 0+60+6.6                                 |
| 5   | C18 : 1    | 28.14                                    | 0+10+1.3                                 |
| 6   | C18 : 2    | 29.76                                    | 0+10+1.2                                 |
| 7   | C18 : 3    | 31.05                                    | 0+10+1.0                                 |

\(※\) Per fatty acid 1 mol.

\(※※\) The color index were calculated based on the color analysis as 10\(×\)B + 1\(×\)Y + 10\(×\)R.

### Table 2 Color index by heating of SL with several fatty acid metal salts.

| No. | Additives     | Color \(\text{Lovibond Index}\)\(^{※※}\) |
|-----|---------------|------------------------------------------|
| 1   | –             | 0+40+8.1                                 |
| 2   | Sodium stearate| 40+5.3                                   |
| 3   | Calcium stearate| 8+1.4                                   |
| 4   | Calcium oleate | 8+1.5                                   |
| 5   | Magnesium stearate| 7+1.8                                  |
| 6   | Barium stearate | 7+1.5                                   |
| 7   | Aluminum tristearate| 20+4.3                                 |

\(※※\) The color index were calculated based on the color analysis as 10\(×\)B + 1\(×\)Y + 10\(×\)R.
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fatty acid metal salts strongly inhibit the heat deterioration of SL. The novel treatment described herein may be highly useful in the food processing industry for preventing the heat deterioration of lecithin.

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