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Research Article

Lipid Peroxidation Inhibitation Activity of Maillard Reaction Products Derived from Sugar-amino Acid Model Systems

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Abstract: The present study aimed to evaluate the lipid peroxidation inhibitation activity of Maillard Reaction Products (MRPs) derived from sugar (glucose, fructose, lactose and maltose) and 18 amino acid model systems in soybean oil. MRPs were produced by heating at 130°C for 2 h. Of the 18 amino acids-fructose model systems studied, MRPs derived from fructose-leucine, fructose-methionine, fructose-phenylalanine and fructose-isoleucine model sytems showed high lipid peroxidation inhibitation activity and best performance was observed from fructose-phenylalanine MRPs. Interestingly, glucose-phenylalanine MRPs also exhibited high inhibitation activity and inhibitation activity of both glucose-phenylalanine and fructose-phenylalanine MRPs exceeded 87% even with concentration at 1.1 wt % after 8 days storage.

Keywords: Inhibitation, lipid peroxidation, maillard reaction products

INTRODUCTION

The Maillard Reaction (MR) is a nonenzymatic browning reaction, which represents a series of complex reactions between carbonyl groups of reducing sugars and free amino groups, mainly from amino acids, peptides and proteins (Jiang *et al*., 2013a, b). The MR is one of the major food protein modifying reactions occurring during thermal food processing and storage and the formed Maillard Reaction Products (MRPs) render food important properties, including the color, flavor and stability (Stanic-Vucinic *et al*., 2013). Moreover, the MRPs can also offer some certain biological activities, these beneficial effects including radical chain-breaking activity, reducing power and antioxidant abilities (Hwang *et al*., 2011; Morales and Jiménez Pérez, 2001; Yu *et al*., 2012; Vhangani and Wyk, 2013; Wang *et al*., 2013; Jing and Kitts, 2002). Therefore, the bioactivities of the MRPs have been studied extensively recently.

As a major constituent, lipid is essential in the food process, which renders flavor and nutrition to food products. However, unsaturated lipids are highly susceptible to rancidity development due to oxidative spoilage. Lipid oxidation is of a great concern in the food industry and among consumers, since it would lead to the development of un-desirable off-flavors and potentially toxic reaction products (Park *et al*., 2001). Particularly, lipid peroxidation of food affects nutritive value and may cause disease conditions following consumption of potentially toxic reaction products (Jung *et al*., 2014). Antioxidants such as BHA, BHT, TBHQ, were therefore required to inhibit lipid oxidation. MRPs can be recognized as endogenous antioxidants since they are generated during the thermal food process and storage.

Presently, quite some studies have been documented the beneficial effects of MRPs on lipid antioxidation. Reaction products from oxidized lipid/amino acid system have been shown to have antioxidant effect, which can protect vegetable oils against oxidation (Alaiz *et al*., 1995, 1997). MRPs formed in casein-glucose mixtures have been exhibited to retard lipid peroxidation in an emulsified linoleic acid model (McGookin and Augustin, 1991), to prevent oxidation in lecithin system (Gu *et al*., 2009), as well as to increase the shelf-life of the full-cream milk powders (McGookin and Augustin, 1997). In addition, MRPs generated in glucose-lysine mixtures (Ruiz-Roca *et al*., 2008) as well as chitooligomer solution (Jung *et al*., 2014) have been found to inhibit lipid peroxidation in a model linoleic acid emulsion system. On the other hand, chitosan-glucose MRPs have been shown to decrease the lipid peroxidation in fresh pork during refrigerated storage (Chang *et al*., 2011) and xylan-chitosan MRPs tended to retard lipid peroxidation in lecithin liposome

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systems and fresh pork during refrigerated storage (Li *et al*., 2013).

However, little work has been conducted on the lipid peroxidation inhibitation activity of MRPs derived from sugar and 18 amino acids. The present work was therefore to evaluate the lipid peroxidation inhibitation activity of MRPs derived from aqueous sugar and 18 amino acid model systems. The generated MRPs were used as antioxidant in bulk soybean oils and the Peroxide Value (PV) of oil during storage were measured to indicate the capacity of lipid peroxidation inhibitation.

MATERIALS AND METHODS

Materials: Refined, Bleached and Deodorized (RBD) soybean oil was purchased from local supermarket. D-glucose, D-lactose, D-fructose, D-maltose and 18 L-amino acid (glycine, alanine, valine, leucine, isoleucine, phenylalanine, proline, tryptophan, serine, tyrosine, cystine, methionine, threonine, aspartic acid, glutamic acid, lysine, arginine, histidine) were from Shanghai Boao Biological Technology Co., Ltd. Soluble starch was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. All other solvents and reagents were of analytical grades.

Preparation of Maillard Reaction Products (MRPs): The MRPs preparation was according to reference (Hwang *et al*., 2011) with some modifications. Typically, each amino acid (0.1 M) except for tryptophan, tyrosine, aspartic acid, glutamic acid and cystine was individually mixed (60 : 60 mL) with glucose (0.1 M), lactose (0.1 M), fructose (0.1 M) or maltose (0.1 M) solution in 250 mL cap-glass tubes. Then tightly capped and heated at 130°C for 2 h. Afterwards, each reaction mixture was freeze-dried under vacuum and then used for antioxidant activity (in soybean oil) assays.

The tryptophan, tyrosine, aspartic acid, glutamic acid and cystine were not dissolved in distilled water. Therefore, the equimolar amounts of tryptophan (2.4504 g), tyrosine (2.1744 g), aspartic acid (1.5972 g), glutamic acid (1.7655 g) and cystine (2.8836 g) were accurately weighted in cap-glass tubes and then added with 60 mL of 0.1 M glucose, lactose, fructose or maltose solution. Heat treatment and preparation of aqueous MRPs were prepared in same way as described above. All aqueous MRPs were prepared in duplicate.

Antioxidant activity evaluation: Antioxidant activity of MRPs in soybean oil evaluation was carried out using Schaal oven method with some modifications (Gámez-Meza *et al*., 1999). Typically, 0.6 g MPRs were added with 120 g soybean oil into a 150 mL beaker, placed in an electric blast drying oven at 63±1°C. The Peroxide Value (PV) in the samples was measured in duplicate according to the standard method (GB/T 5538-2005/ISO 3960, 2001), at periods of 0, 2, 4, 6 and 8 days, respectively. The percentage inhibition of activity was calculated as $(PV_0\text{-}PV_1)\ /PV_0 \times 100\%$, where PV_0 is PV of the control, PV_1 is the PV of the sample.

Statistical analysis: An Analysis of Variance (ANOVA) was performed using the SPSS 13.0 statistical analysis system. The level of confidence required for significance was defined at $p<0.05$ with Tukey's test. All aqueous MRPs were prepared in duplicate and the PV in each sample was measured in duplicate. The results were expressed as mean±Standard Deviations (S.D.).

RESULTS AND DISCUSSION

The effects of MRPs generated from fructose-amino acids model systems on the lipid peroxidation inhibitation activity were shown in Table 1. After 2 days storage with electric blast drying oven at 63±1°C, higher

Table 1: Antioxidant activity in soybean oil of MRPs from fructose-amino acids systems[a]

Fructose-amino acids systems for MRPs preparation	Inhibitation of activity of MRPs during storage (%)[b] 2 days	4 days	6 days	8 days
Fructose-glycine	4.40±0.21	-4.05±0.17	0.41±0.19	-4.58±0.26
Fructose-histidine	10.99±0.46	0.58±0.03	14.17±0.51	13.43±0.43
Fructose-phenylalanine	6.60±0.29	52.02±2.61	67.76±2.38	58.00±1.97
Fructose-leucine	29.67±1.35	49.71±2.06	58.11±2.71	47.14±1.86
Fructose-serine	21.98±1.24	5.78±0.29	13.76±0.58	2.86±0.15
Fructose-threonine	23.08±1.02	2.31±0.11	11.70±0.57	2.43±0.10
Fructose-methionine	28.57±0.98	49.71±2.53	64.54±1.92	53.29±1.79
Fructose-isoleucine	28.57±1.33	38.73±1.62	51.33±2.14	37.71±1.77
Fructose-alanine	14.29±0.46	23.70±1.25	29.77±1.34	13.43±0.56
Fructose-arginine	19.78±2.08	10.41±0.44	24.85±1.14	5.00±0.22
Fructose-valine	19.78±0.86	14.45±0.54	23.61±0.97	15.14±0.67
Fructose-cystine	14.29±0.69	-7.51±0.37	14.37±0.54	6.29±0.29
Fructose-proline	21.98±0.95	13.30±0.57	25.05±1.08	12.29±0.52
Fructose-lysine	16.48±0.67	12.14±0.62	40.45±1.88	39.14±2.45
Fructose-tryptophan	20.88±1.09	26.59±0.89	41.48±1.97	26.29±1.05
Fructose-aspartic acid	24.18±0.86	-21.39±1.07	0.82±0.03	-15.86±0.61
Fructose-tyrosine	15.39±0.65	-39.88±1.92	-5.54±0.23	-7.86±0.28
Fructose-glutamic acid	18.68±0.83	0.58±0.02	16.43±0.63	4.57±0.19

[a]: 0.6 g MRPs were added with 120 g soybean oil into a 150 mL beaker, placed in an electric blast drying oven at 63±1°C; MRPs, maillard reaction products; [b]: All values are mean±S.D. (n = 2)

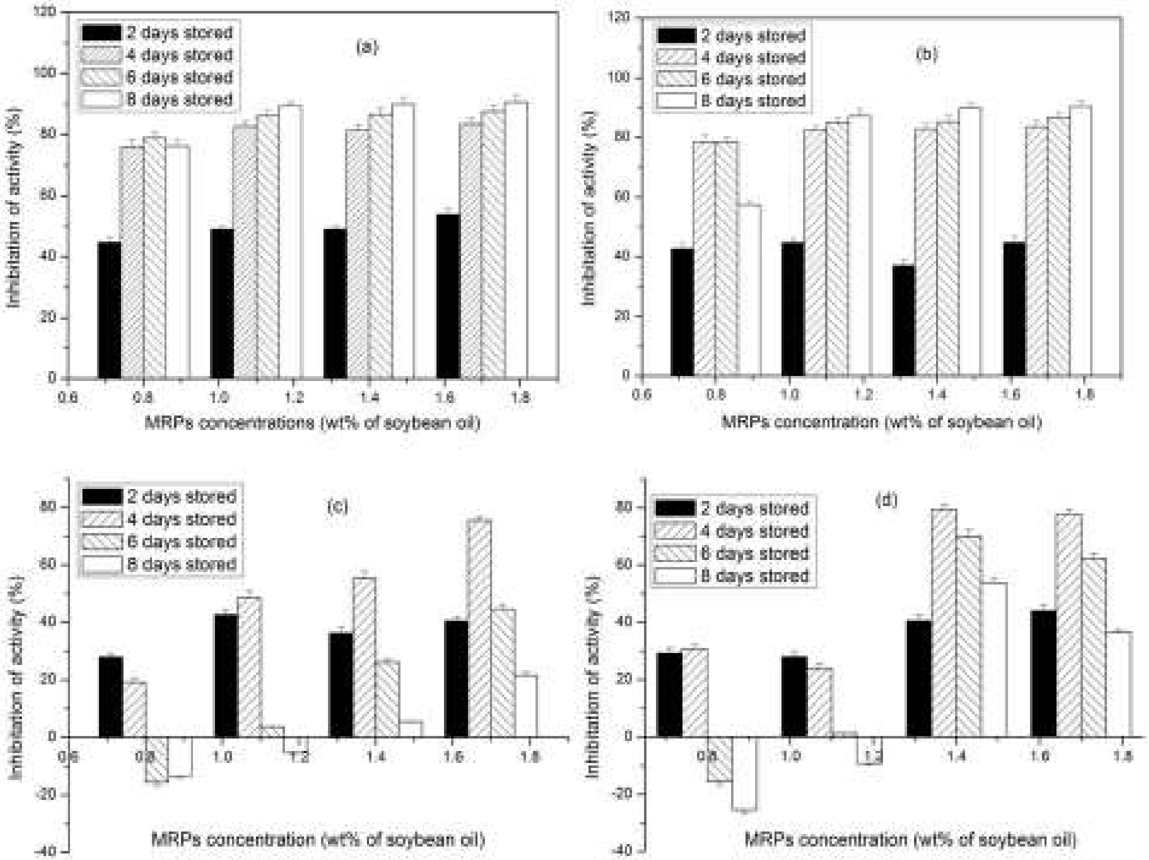

Fig. 1: Effects of MRPs concentrations on the lipid peroxidation inhibitation activity in soybean oils; (a): MRPs derived from fructose-phenylalanine model system; (b): MRPs derived from glucose-phenylalanine model system; (c): MRPs derived from maltose-phenylalanine model system; (d): MRPs derived from lactose-phenylalanine model system
MRPs were added with 120 g soybean oil into a 150 mL beaker; Placed in an electric blast drying oven at 63±1°C; MRPs: Maillard reaction products

lipid peroxidation inhibitation activity ($p<0.05$) was observed from heated fructose-leucine, fructose-methionine as well as fructose-isoleucine model systems; after 4 days storage, higher inhibitation activity ($p<0.05$) was however found from heated fructose-leucine, fructose-methionine and fructose-phenylalanine model systems; fructose-methionine and fructose-phenylalanine MRPs exhibited higher activity ($p<0.05$) after 6 days storage and fructose-phenylalanine MRPs gave best performance ($p<0.05$) after 8 days storage. Interestingly, all heated fructose-amino acids model systems, except for fructose-histidine and fructose-lysine, exhibited a decreasing inhibitation activity when storage time was increased from 6 to 8 days. Reasons for these were not clear. MRPs derived from a fructose-tryptophan system were found to prevent the oxidation of sardine lipid during storage at 37°C (Chiu *et al*., 1991). In the present study, the heated fructose-tryptophan system have exhibited lipid peroxidation inhibitation activity, with inhibitation activity at 41.48±1.97%, however, its inhibitation activity was quite lower than that exhibited by MRPs derived from fructose-phenylalanine, fructose-methionine, fructose-leucine and fructose-isoleucine systems.

Figure 1 presented the effects of sugar (fructose, glucose lactose and maltose)-phenylalanine MRPs concentrations on the lipid peroxidation inhibitation activity in soybean oil. In general, the inhibitation activity was not always increased with the MRPs concentrations increasing. Higher inhibitation activity for both maltose-phenylalanine and lactose-phenylalanine MRPs was observed after 4 days storage. The inhibitation activity was 75.5±1.09% when maltose-phenylalanine MRPs concentration at 1.7 wt %, as well as 79.5±1.59% and 77.8±1.82% when lactose-phenylalanine MRPs concentrations at 1.4 and 1.7 wt % respectively. Better performance was found at glucose-phenylalanine and fructose-phenylalanine MRPs. After 4, 6 and 8 days, respectively storage, similar inhibitation activity ($p<0.05$) was found between these two MRPs when they are at same concentrations and at same storage time, except for concentration at 0.8 wt % after 8 days storage. Both inhibitation activity exceeded 87% even with concentration at 1.1 wt % after 8 days storage. Interestingly, the DPPH and ABTS radical scavenging activity of MRPs derived from:

- Fructose-methionine, -leucine and-methionine as well as
- Glucose-methionine, -leucine and -methionine was moderate and higher antioxidant activity was observed from MRPs derived from fructose-cysteine and glucose-cysteine (Hwang *et al*., 2011)

CONCLUSION

Of the 18 amino acids-fructose model systems evaluated, MRPs derived from fructose-leucine, fructose-methionine, fructose-phenylalanine and fructose-isoleucine model systems showed high lipid peroxidation inhibitation activity in soybean oil and best performance was observed from fructose-phenylalanine MRPs. Interestingly, glucose-phenylalanine MRPs also exhibited high inhibitation activity and inhibitation activity of both glucose-phenylalanine and fructose-phenylalanine MRPs exceeded 87% even with concentration at 1.1 wt % after 8 days storage.

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