CHEMICAL CHARACTERIZATION AND ANTIOXIDANT PROPERTIES OF MAILLARD REACTION PRODUCTS FORMED BY PORCINE PLASMA PROTEIN HYDROLYSATE AND REDUCING SUGAR

Qian Liu [1], Jing Li [1], Baohua Kong [1,*], Na Jia [2], Peijun Li [1], Dongmei Zheng [1], Hongwei Zhang [1]

[1] College of Food Science, Northeast Agricultural University, Harbin, Heilongjiang, China

[2] College of Chemsitry, Chemical Engineering and Food Safety, Bohai University, Jinzhou, Liaoning, China

Abstract –This study investigated the chemical characterization and antioxidant properties of Maillard reaction products (MRPs) prepared by porcine plasma protein hydrolysate (PPH) with three monosaccharides (e.g., glucose, fructose, and galactose) to 95 °C for different lengths of time (0–6 h). The results revealed that the pH value and free amino group content decreased as the reaction time increased ($P < 0.05$). There was an obviously increase in the reducing power, ABTS radical scavenging activities of the MRPs with increasing heating times ($P < 0.05$). The PPH–galactose combination rendered higher browning intensity, intermediate products and antioxidant activities than the PPH–glucose or PPH–fructose combination. The reducing power, ABTS scavenging activities were significantly correlated with UV absorbance and browning intensity in each model systems. The results indicate that the Maillard reaction could improve the antioxidant capacity of PPH.

Key Words –Porcine plasma protein hydrolysate, Maillard reaction products, Reducing sugar, Chemical characterization, Antioxidant property

I. INTRODUCTION

Maillard reaction (MR) is a very complex reaction between carbonyls and amines. It occurs spontaneously during food processing and storage with higher temperature. The reaction involves reducing sugars with amino acids, peptides or proteins that condense and progress into a complex network of reaction products which are known as Maillard reaction products (MRPs) [1]. Not only the MRPs can modify important food properties including colour, flavour and functionality, but they may also associate with the formation of compounds with strong antioxidant activity, such as radical chain-breaking activity [2], metal chelating activity [3], radical scavenging activity and the ability to improve the oxidative stability of food products.

The objective of present investigation was to determine the antioxidant activities (reducing power and radicals scavenging activities) of MRPs derived from PPH with different types of reducing sugar. Meanwhile, the formation of non-fluorescent intermediate products and browning products and the changes in the pH and free amino group content, due to non-enzymatic glycation, were characterised to gain more insight into the antioxidant activity.

II. MATERIALS AND METHODS

1. Preparation of MRPs

Preparation of PPH was performed using the method of Liu et al. [4]. The MR model system consisted of PPH (2.0 g) and glucose, fructose or galactose (2.0 g) dissolved in distilled water to 100 mL. The mixture was transferred to screw-sealed tubes, tightly capped and heated in a water bath to 95 °C. The samples were removed after heating for 0, 0.5, 1, 2, 3, 4, 5 or 6 h.

2. UV absorbance and browning

Appropriate dilutions (10-fold) of the MRPs was made, and the absorbance was measured at 294 nm (early MRPs) and 420 nm (late MRPs) using a UV-1800 spectrophotometer (Pgeneral, Beijing, China) for the UV absorbance and browning intensity, respectively.

3. pH value and free amino group content

The pH value was measured using a DELTA 320 pH metre. And the free amino group content was determined according to the method of Benjakul and Morrissey [5].

4. Reducing power and ABTS radical scavenging activities

The reducing power of the MRPs was determined using the procedure described by Oyaizu [6] with some modifications. And the method described by Ozgen et al. [7] was used to measure the ABTS radical scavenging activity.

III. RESULTS AND DISCUSSION

1. Changes in UV absorbance and browning intensity

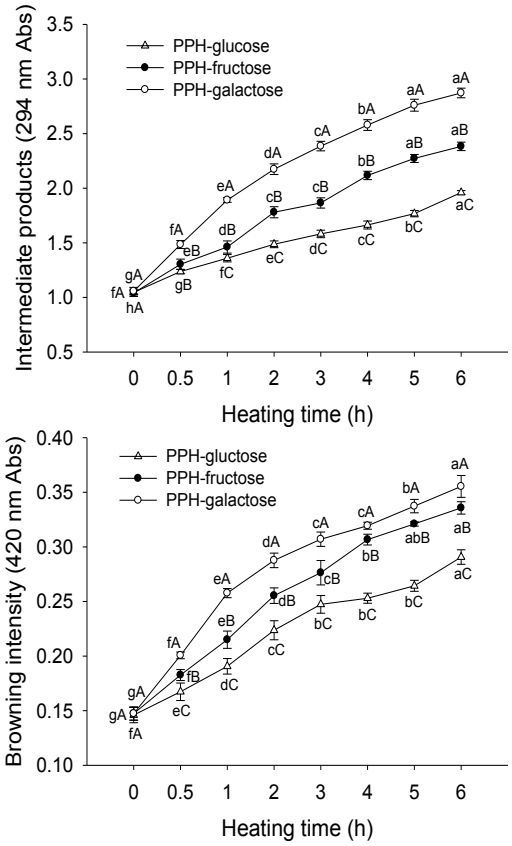

Fig. 1. Intermediate products (absorbance at 294 nm) and browning intensity (absorbance at 420 nm) of PPH–reducing sugar MRPs produced by heating to 95 °C for different lengths of time.

The UV absorbance at 294 nm and at 420 nm was usually used to determine the intermediate MRPs and the final stage of MRPs, respectively. As indicated in Fig. 1, there was a rapid increase in the UV absorbance and browning intensity of the PPH–reducing sugar solution as the heating time increased ($P < 0.05$). The PPH–galactose model system exhibited higher UV absorbance and browning intensity than the fructose and glucose systems ($P < 0.05$). The UV absorbance levels at 294 nm of the MRPs at 0 h were 1.05, 1.04 and 1.06 in the glucose, fructose and galactose model system, respectively; there were 1.9-, 2.3- and 2.7- fold increases when the heating time was increased to 6 h.

These results were in agreement with Sun et al. [8] who found that a sharp increase of the absorbance at 294 and 420 nm of MRPs which derived from the hydrolysate of mechanically deboned chicken residue and sugar system with the increase of heating temperature. In our present work, galactose model system rendered the greatest UV absorbance and the browning intensity, the similar increases have been reported in hydrolyzed β-lactoglobulin–sugar dispersion [9].

2. Changes in pH value and free amino group content

The pH values of the MRPs in the PPH–sugar model system reduced gradually as the heating time increased ($P < 0.05$) (Fig. 2). And the PPH–galactose model system rendered a lower pH than gluctose and fructose model systems. Lan et al. [10] noted that the MRPs obtained from a xylose–soybean peptide model system caused the pH to decrease as the heating time increased. These phenomena probably due to the production of formic and acetic acid from reducing sugar, and it could also be attributed to the reaction of amines to form compounds with lower basicity.

As illustrated in Fig. 2, the free amino group content of the MRPs followed a pattern similar to the pH. The free amino group contents of the MRPs at 0 h were 5.68, 5.63 and 5.66 mM in the PPH–glucose, –fructose and –galactose model systems, and they decreased by 10.0%, 9.1% and 12.5%, respectively, when heated for 6 h ($P < 0.05$). The loss was more extensive in the PPH–galactose MRPs than in other model systems. In general, galactose was more reactive in forming the glycated PPH than glucose and fructose, as demonstrated by the greater decrease in free amino groups with the concomitant increase in the UV absorbance and browning intensity.

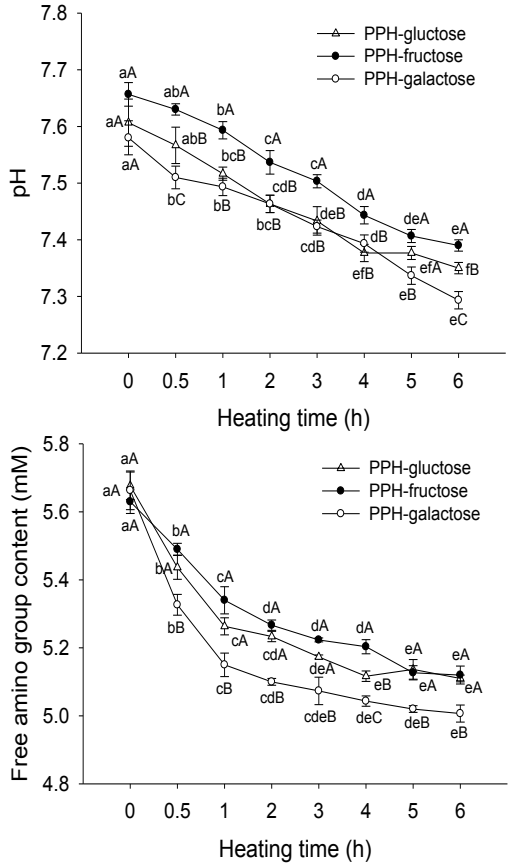

Fig. 2. Changes in the pH and free amino group content of the PPH–sugar MRPs during heating for different lengths of time.

3. Reducing power

The reducing power of the MRPs, as monitored by the absorbance at 700 nm, was enhanced with increasing heating times ($P < 0.05$), the MRPs prepared with galactose demonstrate the greatest reducing power (Fig. 3). The result also revealed that MRPs could function as electron donors. Dong et al. [9] reported that the reducing power of MRPs from hydrolyzed β-lactoglobulin–glucose model system increased as a function of heating time, and this mainly due to the formation of Amadori products in the primary phase of MR. The intermediate reductone compounds of MRPs were also suggested to break the radical chain by donation of a hydrogen atom, and the hydroxyl groups of MRPs play an important role in reducing activity. Furthermore, glycosylation may induce structural changes in PPH–sugar systems, which generated a wide range of compounds, resulting in the formation of products that contribute to the reducing power. And the reducing capacity of a compound may serve as a significant indicator of its potential antioxidant activity.

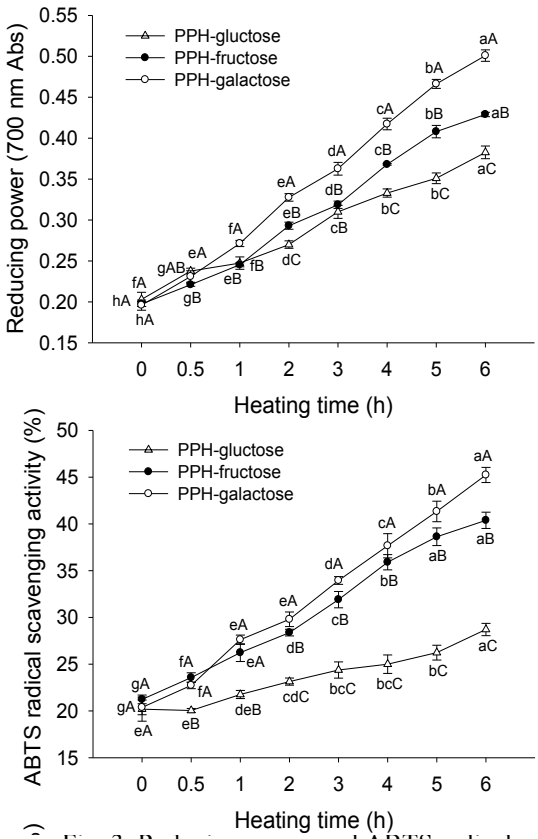

Fig. 3. Reducing power and ABTS radical scavenging activities of PPH–reducing sugar MRPs produced by heating to 95 °C for different lengths of time.

4. ABTS radical-scavenging activity

As it seen in Fig. 3, the ABTS radical-scavenging activity increased significantly ($P < 0.05$) from 20.19%, 21.24% and 20.38% (0 h) to 28.71%, 40.38% and 45.24% (6 h) in the PPH–glucose, –fructose and –galactose model systems, respectively. The PPH–galactose model system showed greater radical scavenging activities than those in the glucose and fructose model systems ($P < 0.05$). Intermediates or the final brown polymer can function as hydrogen donors, sugar caramelization can also contribute to the antiradical activity measured by ABTS radical scavenging determination.

5. Relationship between antioxidant and physicochemical properties

In order to explain the relationship between antioxidant activities (reducing power and ABTS radical scavenging activities) and physicochemical properties (UV absorbance and browning intensity), correlation analysis was performed to establish possible linkages between different parameters in PPH–galactose model system (Table 1). The results showed that reducing power were significantly correlated with UV absorbance (r = 0.973) and browning intensity (r = 0.949). And the ABTS radical scavenging activities also exhibited the same positively correlation with physicochemical properties.

Table 1 Correlation coefficients (r) between antioxiadnt and physicochemical properties of MRPs in PPH-galactose model system

Property	UV absorbance	Browning intensity
Reducing power	0.973	0.949
ABTS radical scavenging activity	0.978	0.953

IV. CONCLUSION

Based on the results of present work, MRPs derived from PPH–reducing sugar systems exhibited strong antioxidant activities via electron donating and radical scavenging, which were dependent upon the MR heating times. MRPs prepared by heating PPH with galactose yielded a greater antioxidant activity than with glucose and fructose. Moreover, the increase in antioxidant activity coincided with an increase in the colour, UV absorbance and browning intensity of the MRPs. These results suggest that MRPs from a PPH–sugar system are a potential food antioxidant.

ACKNOWLEDGEMENTS

This study was supported by the Research Fund of Young Scholars for the Doctoral Program of Higher Education of China (Grant No. 20122325120018) and Foundation for University Key Teacher by the Heilongjiang Educational Committee.

REFERENCES

1. Jing, H., & Kitts, D. D. (2002). Chemical and biochemical properties of casein–sugar Maillard reaction products. Food and Chemical Toxicology, 40: 1007–1015.
2. Morales, F. J., & Babbel, M. B. (2002). Antiradical efficiency of Maillard reaction mixtures in a hydrophilic media. Journal of Agricultural and Food Chemistry, 50: 2788–2792.
3. Bersuder, P., Hole, M., & Smith, G. (2001). Antioxidants from a heated histidine–glucose model system. Investigation of the copper (II) binding ability. Journal of American Oil Chemical Society, 78: 1079–1082.
4. Liu, Q., Kong, B. H., Jiang, L. Z., Cui, X. H., & Liu, J. (2009). Free radical scavenging activity of porcine plasma protein hydrolysates determined by electron spin resonance spectrometer. LWT–Food Science and Technology, 42: 956–962.
5. Benjakul, S., & Morrissey, M. T. (1997). Protein hydrolysates from Pacific whiting solid waste. Journal of Agricultural and Food Chemistry, 45: 3423–3430.
6. Oyaizu, M. (1986). Antioxidant activity of browning products of glucosamine fractionated by organic solvent and thin-layer chromatography. Nippon Shokuhin Kogyo Gakkaishi, 35: 771–775.
7. Ozgen, M., Reese, R. N., Tulio, A. Z., Scheerens, J. C., & Miller, A. R. (2006). Modified 2,2'-Azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) method to measure antioxidant capacity of selected small fruits and comparison to ferric reducing antioxidant power (FRAP) and 2,2'-Diphenyl-1-picrylhydrazyl (DPPH) methods. Journal of Agricultural and Food Chemistry, 54: 1151–1157.
8. Sun, W. Z., Zhao, M. M., Cui, C., Zhao, Q. Z., & Yang, B. (2010). Effect of Maillard reaction products derived from the hydrolysate of mechanically deboned chicken residue on the antioxidant, textural and sensory properties of Cantonese sausages. Meat Science, 86: 276–282.
9. Dong, S. Y., Panya, A., Zeng, M. Y., Chen, B. C., McClements, D. J., & Decker, E. A. (2012). Characteristics and antioxidant activity of hydrolyzed β-lactoglobulin–glucose Maillard reaction products. Food Research International, 46: 55–61.
10. Lan, X. H., Liu, P., Xia, S. Q., Jia, C. S., Mukunzi, D., Zhang, X. M., Xia, W. S., Tian, H. X., & Xiao, Z. B. (2010). Temperature effect on the non-volatile compounds of Maillard reaction products derived from xylose–soybean peptide system: Further insights into thermal degradation and cross-linking. Food Chemistry, 120: 967–972.