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Short communication

The functional properties of chitosan-glucose-asparagine Maillard reaction products and mitigation of acrylamide formation by chitosans

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ABSTRACT

This research aims to clarify the interactions that occur in a food model system consisting of glucose, asparagine and chitosans. Low molecular weight chitosan exerted a potent inhibitory effect (46.8%) on acrylamide and Maillard reaction products (MRPs) (> 52.6%), respectively. Compared to a previous study conducted using the fructose system, the novel findings of this research demonstrate that the formation of acrylamide and Maillard reaction products was lower with glucose than with fructose when they were used as reducing sugars in food model systems.

1. Introduction

Acrylamide is an undesirable compound in food, and known to be carcinogenic in humans. It is commonly present in heated nitrogen-containing or carbohydrate-rich compounds and oils in food systems above 100 °C (Lineback, Coughlin, & Stadler, 2012; Tareke, Rydberg, Karlsson, Eriksson, & Tornqvist, 2000). Although the mechanism of acrylamide formation is not well understood, methods of reducing the formation of acrylamide in heated foods have been proposed in recent years (Pedreschi, Kaack, & Granby, 2008). Our previous research reported that different molecular weights of chitosan had different effects on the formation of acrylamide and on the functional properties of resultant Maillard reaction products (MRPs) generated from asparagine and fructose (Chang, Sung, & Chen, 2016). The results indicated that low molecular weight chitosan showed an inhibitory effect on acrylamide formation in heated chitosan-fructose-asparagine solution. Given the fact that foods are naturally high in glucose, the present study was designed to address this overlooked area by investigating the interactions that occur in a food model system consisting of glucose, asparagine and chitosans.

2. Materials and methods

In the food model system, solutions were prepared that contained 1% chitosan, 1% glucose and 1% asparagine (w/w) according to a method described by Chang et al. (2016). The extraction and analysis of acrylamide from MRP solutions were carried out according to Chang et al. (2016). 1,1-diphenyl-2-picrylhydrazyl hydrate (DPPH) radical scavenging effects of the MRP solutions were determined spectrophotometrically based on the method reported by Kanatt, Chander, and Shimojoh (2008). The ferrous ion chelating activity was quantified spectrophotometrically according to Maillard, Billaud, Chow, Ordonaud, & Nicolas, 2007. Reducing power was measured by the ferricyanide method with modifications (Li, Lin, & Chen, 2014). Capillary viscometers (Cannon-Fenske, No 100 & 200, Pennsylvania, USA) were used to determine the passage time of the MRP solutions flowing through the capillary. Degree of deacetylation of chitosans was evaluated by the conductometric method for colloidal titration described by Toei and Kohara (1976). Data was examined with an analysis of variance using the SPSS statistic program (SPSS, version 12, 1998). Duncan's multiple range test was used to identify the difference between treatments at a 5% significance level ($p < 0.05$).

3. Results and discussion

3.1. Formation of Maillard reaction products (MRPs) and acrylamide

Figs. 1 and 2 show three different molecular weight chitosans and their effects in reducing MRP and acrylamide formation. The OD_{294} of intermediate compounds of MRPs from glucose and chitosan solutions were significant higher than those of chitosan alone (Fig. 1(A)) ($p < 0.05$). Moreover, none or very low Maillard brown pigment was observed in asparagine and chitosan sole solutions after heating (Fig. 1(B)). It indicates chitosans can interact with glucose to form intermediate compounds of MRPs. Low absorbance value of asparagine at 294 nm may be due to asparagine exhibited an ultraviolet absorption

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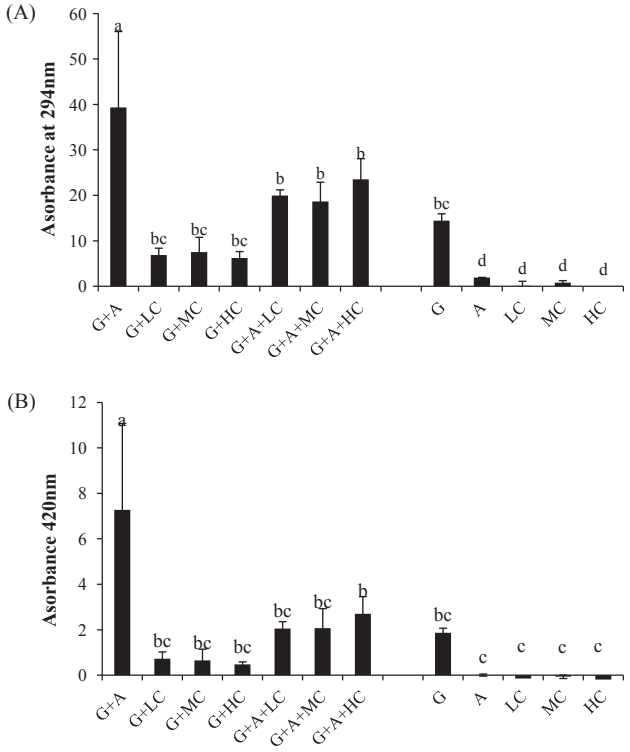

Fig. 1. UV calculated absorbance at OD_{294} (A) and browning at OD_{420} (B) of glucose-asparagine-different molecular weight chitosan MRP solutions. [a–d] Indicate significant difference between different mixtures of glucose, asparagine, and different molecular weight chitosan. (n = 3; $p < 0.05$) G, Glucose; A, Asparagine; LC, Low molecular weight chitosan; MC, Medium molecular weight chitosan; HC, High molecular weight chitosan.

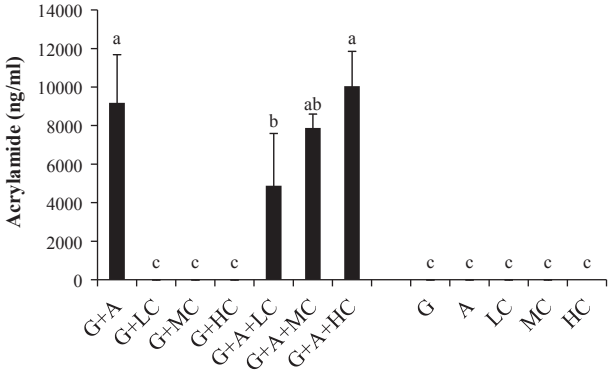

Fig. 2. Amounts of acrylamide (ng/ml) in the glucose-asparagine-different molecular weight chitosan MRP solutions. [a–c] Indicate significant difference between different mixtures of glucose, asparagine, and different molecular weight chitosan. (n = 3; $p < 0.05$) G, Glucose; A, Asparagine; LC, Low molecular weight chitosan; MC, Medium molecular weight chitosan; HC, High molecular weight chitosan.

spectrum with the maximum absorption at 340–350 nm (Shen, Kraft, & Schuster, 1993). This can also be observed from significant increasing value of lightness (L∗) and yellow (b∗) of heated glucose-asparagine solution (Data not shown).

Furthermore, the addition of low, medium and high molecular weight chitosans could significantly decreased the intermediate compounds of MRPs (49.3%, 52.6% and 40.2%, respectively) in the glucose-asparagine solution ($p < 0.05$). Compared to other literatures, the browning intensity (calculated absorbance) decreased to 2.05, 2.07 and 2.70, respectively, from the browning intensity of the 1% glucose and 1% asparagine solution (G + A) (OD_{420} = 7.28) which was lower than that of fructose and asparagine solution (10.47) reported by Chang et al. (2016). Therefore, the absorbance of MRPs was affected by different reducing sugars. In other words, fructose (ketose) generates more MRPs and acrylamide with asparagine than glucose (aldose). In our pilot research, no absorbance of MRPs was measured when 1% sucrose and 1% asparagine solution was heated at 180 °C for 30 min (unpublished data). The results suddested that the absorbance of MRPs was not related to the molecular weight of chitosan in glucose or glucose-asparagine heated solutions.

The coloured compounds of MRPs could be divided into two classes, low molecular weight coloured compounds, generated from carbohydrates and/or amino acids in aqueous solution, and high molecular weight melanoidins (Hofmann, Bors, & Stettmaier, 1999). Rao, Chawla, Chander, and Sharma (2011) reported that chitosan-glucose MRPs have reducing power, DPPH radical scavenging activity and antibacterial activity against *Escherichia coli* and *Bacillus cereus*. Scavenging of free radicals of MRPs of β-lactoglobulin glycated with sugars was influenced by the type of reducing sugar (Chevalier, Chobert, Popineau, Nicolas, & Haertle, 2001).

3.2. Effect of the addition of chitosan on the formation of acrylamide

The acrylamide concentration in heated combined mixtures of 1% glucose, 1% asparagine and 1% chitosan was examined and identified by HPLC/MS. The G + A solution was found to contain the highest acrylamide content (9180 ng/ml) compared to all the other mixtures (Fig. 2). Glucose heated with low, medium and high molecular weight chitosan (G + LC, G + MC, G + HC) did not generate acrylamide, indicating that the addition of chitosan could induce MRP formation but no acrylamide formation. However, Chang et al. (2016) reported fructose heated with low, medium and high molecular weight chitosan would generate 37.8, 36.9, and 31.5 ng/ml acrylamide, respectively. It implies 1% fructose (ketose) can react with chitosan to generate acrylamide, nevertheless, glucose (aldose) would not react with chitosan at the heating condition. Moreover, the acrylamide concentration in the G + A + LC solution was significantly lower than that of the G + A and G + A + HC solutions ($p < 0.05$). This data also evidenced the addition of 1% low molecular weight chitosan can reduce acrylamide formation by 46.8% in our food model system. As a result, the amino groups of low molecular weight chitosan can compete with asparagine for glucose. Yaylayan, Wnorowski, and Locas (2003) proposed asparagines alone may be converted thermally into acrylamide through deamination and decarboxylation reactions, it required elevated temperature (250 °C) to cleave the nitrogen-carbon covalent bond and form acrylamide. Thus it may reduce the key intermediate leading to acrylamide. The proposed interactions between these molecules could be that the solution contained more free amines of chitosan to compete with free asparagine. Overall, this undertaken research demonstrated that low molecular chitosan is a promising inhibitor of acrylamide formation.

3.3. pH of chitosan-glucose-asparagine Maillard reaction solutions

The pH value of all unheated solutions was adjusted to 6.00 ± 0.05, and the pH slightly decreased in the mixtures and 1% glucose solution after 30 min heating at 180 °C ($p > 0.05$) (data not shown). The pH values of the G + LC, G + MC and G + HC solutions were not significantly different after heating, even with the addition of asparagines. The combination of glucose and asparagine with chitosan was shown to generate less MRPs and it caused less pH decrease compared to the addition of fructose which generated more MRPs (Chang et al., 2016). DeMan (1999) suggested the reduction in pH may be due to the basicity of the cationic amino groups (NH_3^+) reacting with a carbonyl source in the reducing sugar, aldehyde, or ketone. The pH of asparagines and different molecular weight chitosan or asparagine solutions (LC, MC, HC, A) significantly increased after heating. Martins and Van Boekel (2005) proposed the intermediates and end products generated from Maillard reaction including acetic acid, formic acid,