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Effect of lauric acid on the V-amylose complex distribution and properties of swelled normal cornstarch granules

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ABSTRACT

Starch–fatty acid complexes were prepared using swelled normal cornstarch (NC) and lauric acid (LA). Two different modes of adding LA to the starch slurry were employed; i.e. either adding the LA to the heated starch suspension (method I) or adding the LA to the starch suspension and then heating (method II). Effects of the modes of adding LA on the V-amylose complex distribution and digestibility were studied. Lipid content determination indicated that method I is favorable to the formation of V-amylose complex. Light and confocal laser scanning microscopic examination indicated that NC–LA complex prepared by method I seemed to be more swollen, and the V-amylose complex distributed throughout the granules, while NC–LA complex prepared by method II was mainly distributed on the surface of starch granules. The results of X-ray diffraction and thermal property demonstrated that method I was more beneficial to the formation of more crystalline structure than that of method II. The *in vitro* digestibility investigation showed that the addition of LA through method I had the ability of slowing the hydrolysis of starch.

1. Introduction

The addition of fatty acids would reduce the hydrolysis rate of starches (Crowe et al., 2000). These changes were attributed to the formation of V-amylose complexes. It is commonly known that the complexation was mainly performed between amylose and lipids. Only a small amount of amylopectin formed V-amylose complex because of steric hindrance and short branch chain length (Conde-Petit et al., 2006).

In recent years, V-amylose complexes were used to improve the functionality of starchy food, to prepare novel starches (slowly digestible or resistant) (Hasjim et al., 2010; Zhang et al., 2012) and even to create a new delivery system to protect volatile and sensitive ligands, such as genistein and poly-unsaturated fatty acids (Cohen et al., 2011; Zabar et al., 2010).

In general, two modes of adding fatty acids, heating prior to the addition of fatty acids to the starch system (method I) and heating after the addition of fatty acids to starch systems (method II), were adopted in preparing the starch–fatty acid complex. Exarhopoulos and Raphaelides (2012) employed two different modes of adding fatty acid (method I and method II) and found that the mode of adding fatty acid would influence the morphological and structural properties of the gelatinized starch–fatty acid system. Kawai et al. (2012) investigated the degree of complex formation, thermal properties, and in-vitro digestibility of gelatinized starch–fatty acid complex which was prepared by method I. Zhang et al. (2012) and Hasjim et al. (2010) pretreated gelatinized starches by different debranching enzymes (pullulanase or isoamylase) and then complexed with fatty acids to enhance their ability of complexing with lipids and then improved their digestibility. Tang and Copeland (2007) studied the properties of gelatinized wheat starch–lipid complex prepared by method II. However, the product made by gelatinized starch or pretreated by enzyme will dramatically decrease its productivity and is not practical in the food industry.

The formation of the V-amylose complex performed at a temperature below pasting temperature also attracted much attention in recent years. Nakazawa and Wang (2004) prepared starch–palmitic acid complex using native and annealing starch mixed with palmitic acid at 30 °C (namely method II) and reported that annealing pretreatment could increase the degree of complexation. D'Silva et al. (2011) investigated the pasting properties of complexes prepared by method II (incubated at 50 °C) and revealed that the teff starch modified with stearic acid has a promising application in foods for better mouthfeel. Chang et al. (2013) investigated

Abbreviations: NC, normal cornstarch; LA, lauric acid; NC–LA complex, normal cornstarch–lauric acid complex; TLs, total lipids content; FLs, free lipids content; CLs, complexed lipids content; CLSM, confocal laser scanning microscopy; XRD, X-ray diffraction; DSC, differential scanning calorimetry; T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH, enthalpy change.

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the effects of amylose content, lauric acid and incubation temperature on the physicochemical properties of swelled maize starch–lauric acid complex prepared by method I. However, the effects of different modes of adding fatty acids on the properties of swollen V-amylose complex still have not been investigated.

Eliasson (1985) reported that complexation between leached amylose and glyceryl monostearate leads to the formation of an insoluble film on the granule surface, which delays water transport into the granules, preventing further leaching of amylose and thus decreases the swelling. However, researchers today still doubted the location of the V-amylose complex formation. The effects of the modes of adding fatty acid on the V-amylose complex distribution and digestibility of swelled starch–fatty acid complex, to the best of our knowledge, have not been investigated so far.

The objective of this paper was, therefore, to reveal the influence of the modes of adding fatty acid and incubation temperature on the location of the V-amylose complex and digestibility of the swelled normal cornstarch–lauric acid complex.

2. Materials and methods

2.1. Materials

Normal cornstarch (NC) was obtained from COFOO Biochemical Energy Co. (Yushu, China). Pancreatin from porcine pancreas (Cat. No. P7545, activity 8 × USP), amyloglucosidase (Cat. No. A7095, activity 300 unit/mL) and Nile Red (Cat. No. 72485) were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). The other chemicals used in this study were all analytical grade.

2.2. Preparation of starch–lipid complexes

2.2.1. Heating prior to the addition of lauric acid (LA) to the starch slurry (method I)

Starch–lipid complex prepared by method I was referenced to our previous study (Chang et al., 2013). Starch slurry (40 g, 10%, w/w, dry starch base, dsb) was cooked in a water bath at predetermined temperatures 60 °C, 65 °C, and 70 °C (below pasting temperature) with vigorous stirring for 60 min. The pasting temperature of NC was recorded at 78.7 °C (according to the result of Brabender analysis). And then LA (6 g, 15%, w/w, dsb), dissolved in ethanol (15 g, 35%, w/w), was added to the swelled starch dispersions. The final mixture was continuously heated at the determined temperature for an additional 60 min with vigorous stirring.

2.2.2. Heating after the addition of LA to starch slurry (method II)

The LA (6 g, 15%, w/w, dsb), dissolved in ethanol (15 g, 35%, w/w), was added to the starch slurry (40 g, 10%, w/w, dsb) before heating. The mixtures were cooked in a water bath at the predetermined temperatures 60 °C, 65 °C, and 70 °C with vigorous stirring for 120 min.

All the samples (prepared by method I and method II) were cooled to 25 °C and recovered by centrifugation (1500 g, 20 min) and washed with 50% water–ethanol mixture. The final resulting precipitates (starch–LA complex) were dried at 40 °C overnight and ground to fine powder.

2.3. Lipid content

Lipids in starch granules consist of free lipids and complexed lipids (namely, complexed lipids = total lipids − free lipids). The lipid content was determined according to a previous report (Eerlingen et al., 1994). Free lipids (FLs) were Soxhlet extracted with petroleum ether at 50 °C for 10 h. Total lipids (TLs) content was determined after acid hydrolysis. Approximately 2.00 g starch was accurately weighed and suspended in 20 mL water. HCl (30 mL, 8.0 N) was added, and the mixture was heated in a boiling water bath for 25 min. After the addition of 50.0 mL of distilled water, the mixture was filtered through paper and washed with distilled water until the filtrate was neutral. The filter paper with the residue was dried at 40 °C overnight, and then transferred to a defatted extraction thimble. The dried samples were Soxhlet extracted with petroleum ether at 50 °C for 10 h. The recipients with the extracted fat were then dried at 105 °C to constant weight. All samples were performed in duplicate.

2.4. Light microscopy

Light microscopy was performed using an Olympus BX-51 light microscope (Tokyo, Japan) with normal and polarized light. A defined amount of starch powder was thinly spread onto a microscope glass slide and dispersed in a drop of a mixture of water: glycerol (1:1). The dispersed starch was gently covered with a cover slip. The images were recorded at 500× magnification.

2.5. CLSM

Approximately 20 mg of sample was dispersed in 1 mL of freshly made Nile Red solution (1 g/L in ethanol). The reaction mixture was left overnight in a dark cold room for 24 h. The mixture was centrifuged and siphoned off the supernatants. The dyed starch granules were then viewed with a TCS SP5 Confocal Laser Scanning Microscope equipped with an Argon ion laser (Leica, Wetzlar, Germany). The details of the Leica objective lens used were 100×/1.4 oil (100: the magnification times of objective lens; 1.4: the numerical aperture of objective lens, oil means oil immersion lens). The excitation spectrum for Nile Red was 488 nm.

2.6. Wide angle X-ray diffraction

The formation of V-amylose complex was verified by measuring the X-ray diffraction. Starch samples were equilibrated in a chamber with 100% relative humidity at 25 °C for 24 h. The X-ray diffractometer (D8 Advance, Bruker, Germany) was operated at 40 kV and 40 mA with Cu Kα radiation ($\lambda = 0.154$ nm). The starch powder was packed tightly in a rectangular glass cell and scanned over the range 4–35 Bragg angles in steps of 2°/min at room temperature. The relative crystallinity of the starch was calculated using the following equation according to a previous report (Hermans and Weidinger, 1948):

$$\text{Relative crystallinity}(\%) = 100\text{Ac}/(\text{Ac} + \text{Aa}), \quad (1)$$

where Ac is the crystalline area on the X-ray diffractogram, and Aa is the amorphous area.

2.7. Differential scanning calorimetry

The thermal properties of starches were analyzed by using a differential scanning calorimeter (DSC-8000, Perkin–Elmer, USA) with an intra cooler. An empty stainless steel pan was used as the reference, and indium was used for calibration. Complex samples (accurately 2–5 mg, dsb) were mixed with distilled water (moisture content 75%), and hermetically sealed in stainless steel pans (PE No. BO 182901). The thermal properties were investigated according to previous studies with modifications (Hasjim et al., 2010; Zhang et al., 2012). The mixture was equilibrated for 1 h at room temperature and then the samples were scanned from 10 °C to 150 °C at a rate of 10 °C/min. Calculated values for onset temperature (T_o), peak temperature (T_p) and enthalpy (ΔH) were recorded