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Preparation and slowly digestible properties of β-cyclodextrins (β-CDs)-modified starches

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ABSTRACT

The β-cyclodextrin (β-CD)-, maltosyl-β-CD (Mal-β-CD)- and hydroxypropyl-β-CD (HP-β-CD)-modified rice starches were prepared and their slowly digestible properties were estimated. The results showed that β-CD, Mal-β-CD and HP-β-CD significantly increased the slow digestibility of β-CDs-modified starches ($P < 0.05$). The optimum conditions for the modification were obtained: amylose, 4.76%; free lipids, 0.24%; β-CD, Mal-β-CD and HP-β-CD, 3%; water, 80%; and equilibrium temperature, 25 °C. The maximum yield of slowly digestible starch (SDS) was 52.1% when β-CD was used as a denaturant (β-CD, 3%; water, 80%; and equilibrium temperature, 25 °C). This higher SDS yield was probably attributed to the better compatibility of β-CD and starch molecules. Furthermore, β-CD-, Mal-β-CD- and HP-β-CD-modified starches generated slowly digestible curves during enzymatic digestion and showed the intermediate predicted glycemic indexes (pGI) of 58.7, 69.1 and 70.3, respectively. These findings suggest that the β-CDs-induced modification is one of promising techniques for preparing the SDS products in food and pharmaceutical industries.

1. Introduction

Slowly digestible starch (SDS) provides a sustained supply of glucose that may help control and prevent several diseases, such as cardiovascular diseases (Ells, Seal, Kettlitz, Bal, & Mathers, 2005), type 2 diabetes (Axelsen, Arvidsson, Lonnroth, & Smith, 1999; Seal et al., 2003), and obesity (Wolf, Bauer, George, & Fahey, 1999). It is generally prepared by pullulanase debranching (Guraya, James, & Champagne, 2001; Miao, Jiang, & Zhang, 2009) and starch retrogradation (Park, Baik, & Lim, 2009; Zhang, Hu, Xu, Jin, & Tian, 2011). However, the stability of the SDS products prepared via retrogradation is low, due to the melting temperature of amylopectin re-crystallites less than 70 °C (Tian, Li, Jin, & Xu, 2009).

Recent studies have demonstrated that the hydrophobic section of some lipids is preferentially introduced into the central axis of amylose helix to form an amylose–lipid complex during the interaction of amylose and lipids (Lalush, Bar, Zakaria, Eichler, & Shimoni, 2005; Nebesny, Rosicka, & Tkaczyk, 2005). The formed complex has an unstable V-type crystalline structure and inhibits the formation of B-type re-crystallized starch. The stability of the V-type complex to amylolytic and lipolytic enzymes is also estimated and its melting temperature is above 100 °C (Nebesny et al., 2005). This higher temperature is suitable for protecting SDS from dissociation during food processing. However, the lipid content added during the formation of amylose–lipid complex often is more than 10% that produces lots of additional energies.

β-Cyclodextrins (β-CDs) are cyclic and non-reducing functional oligosaccharides, consisted of D-glucose units with α-1,4-glycosidic bonds in a donut-shaped ring (Lindner & Saenger, 1982). Its aperture can form inclusion complexes with organic and inorganic molecules in aqueous solution due to its hydrophobic core, while its hydrophilic shell outside can interact with the hydroxyls of starch molecules (Tian, Li, Manthey, et al., 2009; Tian, Yang, et al., 2010). For instance, β-CD could generate amylose-β-CD non-inclusion complex and starch-β-CD–lipid complex with amylose and starch (Tian, Li, Manthey, et al., 2009; Tian, Yang, et al., 2010). Both of the complexes showed a part V-type crystalline structure and a melting temperature above than 100 °C (Tian, Li, Jin, & Xu, 2010). These data indicated that β-CDs could be used as denaturants during starch gelatinization to prepare the products rich in SDS.

In this study, starch was first modified by β-CD, HP-β-CD and Mal-β-CD. The modification conditions were optimized using single factor experiment. The hydrolysis rate and the predicted glycemic index (pGI) of the β-CDs-modified starches were also evaluated.

2. Experimental

2.1. Materials

Rice starch was extracted and purified from fresh grain (Shandong Mei-Jing Rice Inc., China) using the procedure described

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by Sodhi and Singh (2003). It contained 0.3% proteins, 1.2% free lipids, and 23.8% amylose that was determined by the spectrophotometric method described by Hoover and Ratnayake (2001). β-Cyclodextrins (β-CD, HP-β-CD and Mal-β-CD) were purchased from Seebio Biotechnology Inc. (Shanghai, China). Porcine pancreas α-amylase (EC 3.2.1.1) and amyloglucosidase (EC 3.2.1.3) were purchased from Wuxi Syder Bio-Products Co. Ltd. (Wuxi, China). All other chemicals and reagents were of analytical grade unless otherwise stated.

2.2. Preparation of β-CDs-modified starches

Three grams of rice starch was mixed with 0%, 1%, 2%, 3%, and 4% of β-CDs (β-CD, HP-β-CD and Mal-β-CD) and dispersed with 50%, 60%, 70%, 80%, and 90% (w/v) of deionized water. The resultant mixtures were heated in boiling water for 30 min, hermetically sealed and equilibrated at 4 °C, 25 °C and 60 °C for 2 h to prepare the β-CDs-modified starches. Each final sample was subjected to drying in an air oven at 60 °C for 5 h and milled to pass through a 100-mesh sieve for analysis.

2.3. In vitro digestibility determination

In vitro digestibility of β-CDs-modified starches was determined according to Englyst, Kingman, and Cummings (1992) with a minor modification. In brief, 200 mg of β-CDs-modified starches was put into the tubes and dissolved in fresh phosphate buffer (0.2 mol/L, pH 5.2, 15 mL). Six glass balls with 10 mm in diameter and 10 mL of the enzyme mixture (porcine pancreas α-amylase and amyloglucosidase) were added in the tubes and horizontally immersed in a shaking-water bath (160 rpm, 37 °C) for starch hydrolysis. Aliquots of the hydrolyzed solution (0.5 mL) were taken out at 20 min and 120 min, respectively. The enzymes remaining in the hydrolyzed solution was deactivated by 4 mL of 95% ethanol. The final SDS yield of the β-CDs-modified starches was estimated according to the following formula:

$$\text{SDS } (\%) = \left[\frac{G_{120} - G_{20}}{TS}\right] \times 0.9 \times 100 \quad (1)$$

where G_{20} and G_{120} represent the content of glucose after the sample hydrolyzed for 20 min and 120 min, respectively. *TS* is the total starch sample used for test. The percentage of hydrolyzed starch was calculated by multiplying a factor of 0.9 with the glucose content.

2.4. Prediction of in vitro glycemic index (pGI) for β-CDs-modified starches

The rate of starch digestion was expressed as the percentage of total starch hydrolyzed at intervals of 0, 30, 60, 90, 120, 150 and 180 min. pGI value of β-CDs-modified starches was estimated by the following equation: pGI = 39.71 + 0.549 HI, described by Goni, Garcia-Alonso, and Saura-Calixto (1997).

2.5. Statistical analysis

The data were expressed as means of triplicate determinations. Statistical significance was assessed with one-way analysis of variance (ANOVA) using ORIGIN 7.5 (OriginLab Inc., USA) for windows program. A probability $P < 0.05$ was considered significant throughout the study.

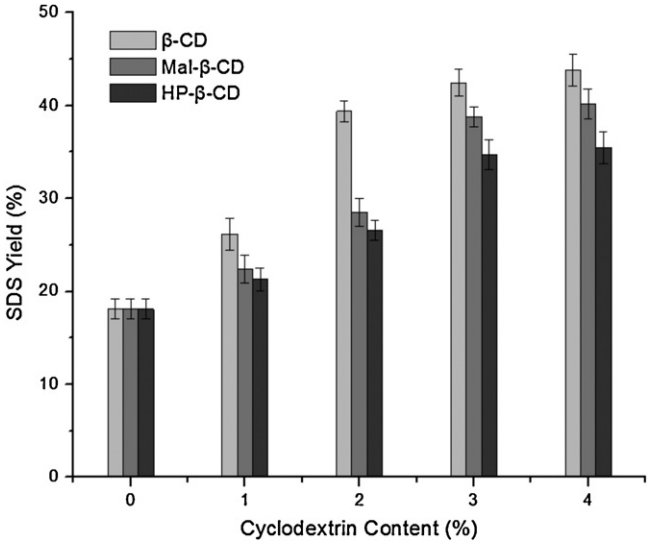

Fig. 1. Effect of β-CD, Mal-β-CD and HP-β-CD on the slow digestibility of β-CDs-modified starches.

3. Results and discussion

3.1. Effect of β-CDs on the slow digestibility of β-CDs-modified starches

The results showed that the β-CDs-modified treatment significantly increased the SDS yield of rice starch (Fig. 1). For instance, 2% of β-CD increased the SDS yield from 18.1% to 39.4%, although the SDS yield remained in a stable level when β-CD was more than 2%. The SDS yield was also increased by Mal-β-CD and HP-β-CD with an optimum amount of 3%. This increase could be interpreted by the fact that β-CDs interacted with amylose or starch molecules via formation of starch-β-CDs non-inclusion complex (Tian, Li, et al., 2010). The stability of the formed non-inclusion complex (part V-type crystalline structure) was lower than that of amylose–lipid complex (V-type crystalline structure) (Tian, Li, et al., 2010). This lower stability could generate more SDS but lower resistant starch (RS). Furthermore, according to the molecular model of amylose-β-CD non-inclusion complex described by Tian, Li, Manthey, et al. (2009), β-CD might accelerate the formation of amylose-β-CD non-inclusion complex easier than derivative β-CDs with branch chains, thus resulting in the higher SDS yield of the β-CD-modified starch.

3.2. Effect of water content on the slow digestibility of β-CDs-modified starches

The results showed that the maximum SDS yield reached 52.1% in the β-CD-modified starch with 80% of water and 3% of β-CD (Fig. 2). This indicated that higher water could promote the gelatinization of rice starch and increase the contact chance of starch and β-CDs molecules. Tian, Li, Manthey, et al. (2009) reported that amylose-β-CD non-inclusion complex only was formed during the cooling process of gelatinized starches. It was, therefore, deduced that the migration rate of starch and β-CDs molecules was decided by an equilibrium of water content and starch/β-CDs concentration.

3.3. Effect of equilibrium temperature on the slow digestibility of β-CDs-modified starches

Fig. 3 reveals that equilibrium temperature fitted for increasing the SDS yield of β-CDs-modified starches is 25 °C and the maximum SDS yield is 52.1% in β-CD-modified starch at this temperature.

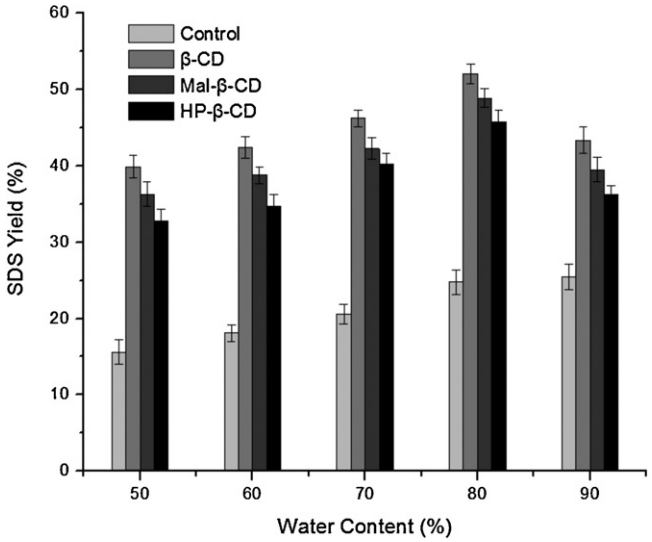

Fig. 2. Effect of water content on the slow digestibility of β-CDs-modified starches (3% of β-CD, Mal-β-CD and HP-β-CD).

Lower temperature could favor the nucleus formation and increase the yield of resistant starch (RS) (Mangala, Udayasankar, & Tharanathan, 1999). Higher temperature could not provide enough driving force for the interaction of starch and cyclodextrin molecules (Tian, Li, Manthey, et al., 2009). Furthermore, compared to Mal-β-CD and HP-β-CD, β-CD showed a better effect for the improvement of SDS yield, since the better compatibility occurred between β-CD and starch molecules (Tian, Li, Manthey, et al., 2009).

3.4. Total hydrolysis rate of β-CDs-modified starches

The results showed that gelatinized starch without modification was rapidly digested by enzymes and the hydrolysis rate reached 75.7% after 30 min, while the hydrolysis rate was significantly reduced by β-CDs (Fig. 4). Furthermore, β-CD-modified starch had a slower hydrolysis rate than Mal-β-CD- and HP-β-CD-modified starches. These results indicated that the digestible process was hindered by formation of starch-β-CDs non-inclusion complex. The formed non-inclusion complex showed a part V-type crystalline

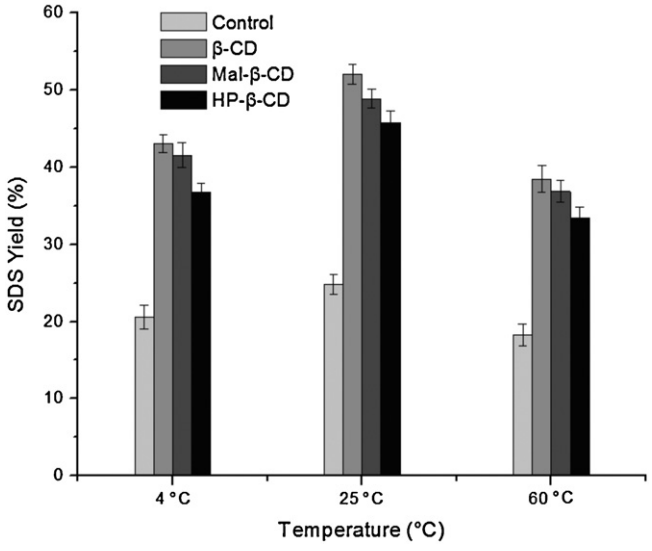

Fig. 3. Effect of equilibrium temperature on the slow digestibility of β-CDs-modified starches (80% of water and 3% of β-CD, Mal-β-CD and HP-β-CD).

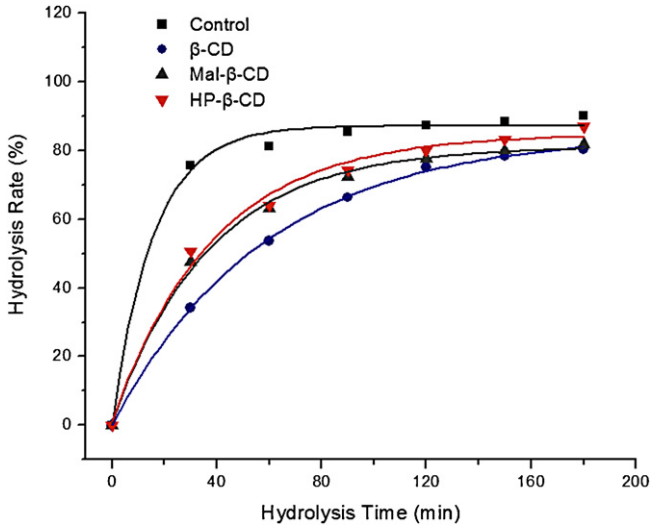

Fig. 4. Total hydrolysis rate of β-CDs-modified starches prepared under the following conditions: 3% of β-CD, Mal-β-CD and HP-β-CD; 80% of water; and equilibrium temperature at 25 °C.

Table 1
Predicted glycemic index (pGI) of the β-CDs-modified starches prepared via following conditions: amylose, 4.76%; free lipids, 0.24%; 3% of β-CD, Mal-β-CD and HP-β-CD; 80% of water; and equilibrium temperature at 25 °C.

Different modification	Predicted glycemic index (pGI)
Control	92.6 ± 1.8 a[a]
β-CD	58.7 ± 2.1 c
Mal-β-CD	69.1 ± 1.3 b
HP-β-CD	70.3 ± 2.5 b

[a] Samples mean with different lowercase letters in the same column are significantly different ($P < 0.05$).

structure that had a weak resistance to enzymes (Nebesny, Rosicka, & Tkaczyk, 2002; Tian, Li, et al., 2010).

3.5. Predicted glycemic index (pGI) of β-CDs-modified starches

The data summarized in Table 1 showed that in vitro pGI was significantly reduced by β-CDs modification. β-CD-modified starch had the lowest pGI value of 58.7. This was partly confirmed by the previous report, indicating that β-CD generated a better compatibility with amylose (Tian, Li, et al., 2010). The stability of amylose-β-CD non-inclusion complex was retained by the major driving force of hydrogen bond, while Van der walls (Vdw) and hydrogen bond were the driving forces for the stability of starch–lipid inclusion complex. These indicated that the amylose-β-CD non-inclusion complex was better suitable for improving the SDS yield, while starch–lipid complex was responsible for the major component of RS (Lehmann & Robin, 2007). Therefore, the β-CDs-modified starches showed the intermediate pGI values for health.

4. Conclusions

This work demonstrated that β-CDs could interact with starch to increase the SDS yield of β-CDs-modified starches. The optimum modification conditions were addressed below: amylose, 4.76%; free lipids, 0.24%; β-CD, Mal-β-CD and HP-β-CD, 3%; water content, 80% and equilibrium temperature, 25 °C. Under the listed conditions, the maximum SDS yield reached 52.1% in the β-CD-modified starch (3% of β-CD). The basic rule for the slow digestibility was mainly attributed to the formation of starch-β-CDs non-inclusion complex that showed a part V-type and a weak resistance to

enzymes. It was also concluded that starch-β-CDs non-inclusion complex was more suitably used for improving the SDS yield than starch–lipid complex. The digestible process of β-CDs-modified starches in a molecular level would be estimated in future work.

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