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Physicochemical and structural properties of debranched waxy rice, waxy corn and waxy potato starches

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ABSTRACT

Starch gels of waxy rice (WR), waxy corn (WC) and waxy potato (WP) were hydrolyzed with pullulanase, and the products obtained were analyzed for unit chain length distribution and certain physicochemical properties. Average chain lengths of debranched WR, WC and WP starches were 18.2, 19.2 and 25.6, respectively. The debranched starches had a greater ability to form complexes with iodine and possessed higher solubility but lower viscosity compared with their corresponding dispersed native starches. Their complexing abilities with fatty acids (palmitic and butyric acids) were found to be dependent on the unit chain length. Among the three debranched starches, debranched waxy potato starch exhibited the greatest ability to form complexes with iodine and fatty acids, while debranched waxy rice starch had the highest solubility and lowest viscosity. The debranched starches formed stable gels at high concentrations (10–20%) and formed precipitates at concentrations up to 5%.

1. Introduction

Native starches are used in food and non-food applications, in which starch properties such as viscosity, retrogradation, solubility, gelation, gel appearance and texture are the main criteria for choosing an appropriate starch for a certain end-use. In most applications, starch is used in a gelatinized native form, either in cooked or uncooked products. It is well-known that starch is biosynthesized as granules in higher plants and consists of two types of α-D-glucose polymers: amylose and amylopectin. Amylose is a mixture of lightly branched and linear molecules, whereas amylopectin is a much larger molecule with a highly branched structure consisting of about 95% α-1,4 linkages and 4–5% α-1,6linkages (Hizukuri, Abe, & Hanashiro, 2006; Tester, Karkalas, & Qi, 2004). The ratio of amylose to amylopectin in starch varies depending on the botanical source. Generally, normal starches consist of 20–30% amylose and 70–80% amylopectin, whereas waxy starches contain essentially 100% amylopectin.

Starch can be debranched at α-1, 6 linkages by debranching enzymes (e.g. isoamylase and pullulanase) under specific conditions. The debranched products are a mixture of short linear chain glucans with different degrees of polymerization (DP) (Hizukuri et al., 2006; Manners, 1989). For amylose-containing starch (normal starch), both amylose and amylopectin are debranched, producing a mixture of long linear chains derived from amylose with average chain lengths between 350 and 550 (Charoenkul, Uttapap, Pathipanawat, & Takeda, 2006; Morrison & Karkalas, 1990; Tester et al., 2004; Thitipraphunkul, Uttapap, Piyachomkwan, & Takeda, 2003), and short linear chains derived from amylopectin with average chain lengths between 20 and 30 (Charoenkul et al., 2006; Hizukuri et al., 2006; Tester et al., 2004; Thitipraphunkul et al., 2003). On the other hand, only short linear chains are released when waxy starch is debranched, and therefore these chains have a relatively narrower MW distribution (Shi, Cui, Birkett, & Thatcher, 2006). The chain length (CL) distribution of debranched amylopectin is highly related to its crystalline polymorphs (Hizukuri, 1985). In general, amylopectins of A-type

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starches contain a large proportion of short branch chains, whereas those of B-type starches have a larger proportion of long chains (Hanashiro, Abe, & Hizukuri, 1996). The distinct branch CL distributions of amylopectin from A- and B-type starches can affect the functionalities of the debranched products.

Apart from using starch in the native form, debranched starch (DBS) derived from enzyme hydrolysis of gelatinized starch is now recognized as a potential source of natural linear polymers. DBS has a totally different structure from native starch; therefore, their functionalities are supposed to be different. To date, research work on applications of DBS has mainly focused on resistant starch formation (Miao, Jiang, & Zhang, 2009). DBS is also being used as a fat/protein replacer in food products (Chiu & Mason, 1998), as well as a tableting excipient in drug formulation (Arends-Scholte et al., 2000; Shi et al., 2006).

To determine suitable utilizations of these DBSs for industrial purposes, information on their basic properties (structural and physicochemical properties) should be elucidated. So far, there have been many investigations on the molecular structure of DBSs (Cai & Shi, 2010; Cai, Shi, Rong, & Hsiao, 2010; Kurimoto & Sugimoto, 1975; Yotsawimonwat et al., 2008). This study aimed to investigate both the structural and physicochemical properties of DBSs. Waxy-type starches (waxy rice, corn and potato starches) were chosen for the reason that the debranched products obtained would have more uniform unit chain length. Fatty acid-complexing ability, solubility, viscosity and gelation of the DBSs were determined and discussed in relation to unit chain length distribution. Information on these characteristics was also discussed in view of potential industrial applications of DBSs.

2. Materials and methods

2.1. Materials

Waxy rice (RD 8) and waxy corn (Kwpsx 7253) were provided by the Sakon Nakhon Rice Research Center (Sakon Nakhon, Thailand) and the National Corn and Sorghum Research Center (Pak Chong, Thailand), respectively. Waxy potato starch (3.92% amylose content) was acquired from National Starch Food Innovation (Bangkok, Thailand). *Bacillus acidopullulyticus* pullulanase (EC 232-983-9P, ≥400 U/ml), maltoheptaose, and two pullulan standards (P6000 and P12000) were purchased from Sigma–Aldrich (St. Louis, MO). All chemicals used in this experiment were analytical grade.

2.2. Starch isolation

Waxy rice and waxy corn with amylose contents of 0.24% and 3.80%, respectively, were isolated according to the procedures described by Jiranuntakul, Puttanlek, Rungsardthong, Puncha-Arnon, and Uttapap (2011). De-hulled waxy rice grains were steeped in distilled water at 4 °C for 24 h, while corn kernels were steeped in water containing 0.16% sodium hydrogen sulfite at 50 °C for 24 h. The supernatant was discarded, and the steeped waxy rice grains/corn kernels were ground with a blender and then passed through a 63 μm screen. The slurry was kept at 4 °C for 48 h. The supernatant was removed, and the starch cake was re-suspended in 0.35% sodium hydroxide solution and kept at 4 °C for 48 h. The supernatant was decanted and the starch layer was re-slurried with water. The starch slurry was passed through a 63 μm sieve and kept at 4 °C for 48 h. The steps of washing with water were repeated four times until the pH of the starch slurry reached 7, and then it was stored at 4 °C for 48 h. Finally, the supernatant was removed and the starch cake was dried in an oven at 40 °C for 24 h.

2.3. Waxy starch debranching

Starch debranching was carried out according to the method of Yotsawimonwat et al. (2008) with a slight modification. Waxy starch was suspended in 0.05 M acetate buffer, pH 5.0 (10%, w/w). The suspension was cooked in a boiling water bath with stirring for 60 min, followed by autoclaving at 121 °C for 60 min to complete gelatinization. The gel was cooled to 55 °C and hydrolyzed with pullulanase (45 U/g of starch) at 55 °C in a shaking water bath for 20 h. The enzyme was then deactivated with threefold volume of 99% ethanol. The precipitated debranched starch was recovered by filtration with Whatman No.4 filter paper, washed with 95% ethanol three times, dried in an oven at 50 °C for 18 h, and sifted through a 106 μm sieve. Yields of DBSs, based on dry weight basis of initial starch, ranged between 89.9 and 92.3%. Debranched waxy rice, corn and potato starches were denoted as DWRS, DWCS and DWPS, respectively.

2.4. Molecular structure

Average chain length and unit chain distribution of DBSs were determined by high-performance size-exclusion chromatography (HPSEC), according to the procedures described by Jiranuntakul et al. (2011). The HPSEC system consisted of a pump (LC-20AD; Shimadzu, Tokyo, Japan), an injector, and two 30 cm columns connected in series and packed with 5 μm porous silica microspheres (Zorbax PSM 60S; Agilent Technologies, Santa Clara, CA). The temperature of the columns was maintained at 50 °C. The mobile phase was 90% (v/v) dimethyl sulfoxide (DMSO) in water with a 0.5 ml/min flow rate. Debranched samples (4 mg) were individually dispersed in 1 ml of 90% DMSO and heated for 5 min in a boiling water bath. After dispersion, the solution was filtered using 0.45 μm filter paper. A 40 μl aliquot was then injected into the HPSEC system. A calibration curve for the chromatograms was constructed using maltoheptaose and two pullulan standards (P6000 and P12000). The *y*-axis of the chromatogram was converted from the refractive index (RI) value to a molar response using the calibration curve (Yuan, Thompson, & Boyer, 1993). Chain-length distributions were categorized into DP of 6–12, 13–24, 25–36 and ≥37, according to the classification proposed by Hanashiro et al. (1996).

2.5. Fatty acid-complexing ability

2.5.1. Iodine staining index (ISI)

Iodine staining index was used as a tool to quantify and evaluate the iodine binding and fatty acid-complexing abilities of the native starches and DBSs (Kaur & Singh, 2000; Yotsawimonwat et al., 2008). Measurement of ISI was modified from the procedure described for iodine-binding capacity determination by Knutson (1986). Each debranched starch sample (0.25 g dwb) was dispersed in 2.5 ml of 90% DMSO and cooked in a boiling water bath for 30 min, and then 22.5 ml of deionized water was added. For non-debranched starch, the native starch sample (0.25 g dwb) in 25 ml of deionized water was directly cooked in a boiling water bath for 30 min. Then 50 μl of this solution was transferred into a test tube, which was wrapped with aluminum foil for light protection and then incubated with 5 ml of 0.6 mM iodine solution in 10% DMSO for 30 min. The absorbance of the DBS–iodine complex was scanned at wavelengths from 400 to 700 nm at 1 nm intervals to obtain a spectrum. The iodine staining indexes of the DBS–iodine complex was expressed as the absorbances at 460 and 570 nm.

2.5.2. Fatty acid-complexing ability

Fatty acid-binding capacity was determined using the method of Yotsawimonwat et al. (2008) with slight modifications. Twenty-five