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Relationship between the structure, physicochemical properties and *in vitro* digestibility of rice starches with different amylose contents

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ABSTRACT

The *in vitro* digestibility and molecular and crystalline structures of rice starches (Long-grain, Arborio, Calrose, and Glutinous) differing in amylose content were investigated and the relationship between the structure and *in vitro* digestibility of starch was studied. Long-grain showed the highest amylose content (27.2%), whereas Glutinous showed the lowest amylose content (4.2%). Long-grain had the highest average amylopectin branch chain length (18.8) and proportion (8.7%) of long branch chains (DP ≥ 37), and the lowest proportion (26.9%) of short branch chains (DP 6–12). Among the non-waxy rice starches (Long-grain, Arborio, and Calrose), Calrose had the lowest average chain length (17.7) and the lowest proportion (7.1%) of long branch chains (DP ≥ 37). The relative crystallinity of rice starch followed the order: Glutinous (33.5%) > Calrose (31.4%) > Arborio (31.0%) > Long-grain (29.9%). Long-grain had the highest gelatinization temperature and the lowest gelatinization temperature range, whereas Glutinous showed the highest gelatinization temperature range and gelatinization enthalpy. Arborio had the highest melting enthalpy for amylose–lipid complex among the tested rice starches. Pasting temperature, setback, and final viscosity increased with increasing amylose content, whereas the peak viscosity and breakdown showed negative correlations with amylose content. The rapidly digestible starch (RDS) content of the tested rice starches followed the order: Glutinous (71.4%) > Calrose (52.2%) > Arborio (48.4%) > Long-grain (39.4%). Contrary to this, the slowly digestible starch (SDS) and resistant starch (RS) contents showed an opposite trend compared to RDS. Digestibility (RDS, SDS, and RS) of the rice starches was significantly correlated ($p \leq 0.05$) with amylose content, proportions of DP 6–12 and DP 13–24, relative crystallinity, intensity ratio (of 1047 cm^{-1} to 1022 cm^{-1} from Fourier transform infrared spectroscopy), swelling factor, amylose leaching, onset temperature of gelatinization, gelatinization temperature range, gelatinization enthalpy, pasting temperature, peak viscosity, breakdown, setback, and final viscosity.

1. Introduction

Rice has been a staple food in the world and it is consumed principally as a whole grain. The texture and digestibility of the whole grain are matters of primary importance (Ong & Blanshard, 1995). Different cultivars of waxy and non-waxy rices are usually classified according to their amylose content and gelatinization properties of the extracted starches. Rice starch has been used in various foods and industrial applications as an agent for thickening, gelling and filling, cosmetic dusting powder and photographic paper powder (Champagne, 1996). Rice starch, like other starches, consists of two polysaccharides, amylose and amylopectin. Amylose is an essentially linear molecule of α-(1 → 4)-linked D-glucopyranosyl units with a few branches, whereas amylopectin has large molecular weight and highly branched structures consisting of α-(1 → 4)-linked D-glucopyranosyl units with 5–6% non-randomly distributed α-(1 → 6)-D-glucopyranosyl units (Hizukuri, 1986). These two polymers are organized into a semi-crystalline structure.

The functional properties of rice starch have been influenced by the amylose–amylopectin ratio, the fine structure of amylopectin, and the crystalline structure (Jane et al., 1999; Ong & Blanshard, 1995; Vandeputte, Vermeylen, Geeroms, & Delcour, 2003). An understanding of the relationship between structural characteristics and functional properties of rice starches is very important for optimizing industrial applications and allowing consumer to select

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suitable rice varieties for health benefits. The role of amylose and amylopectin in relation to functional properties of rice starch has been widely studied. Gelatinization temperature increased with high amylose content, and was negatively correlated with the amount of amylopectin short chains (DP 6–12) and positively correlated with amylopectin long branch chains (DP ≥ 37) (Jane et al., 1999; Park, Ibanez, Zhong, & Shoemaker, 2007). Short branch chains of amylopectin destabilize the crystalline lamellar structure, whereas the long branch chains of amylopectin could form longer double helices, which require higher temperatures for complete dissociation. Higher amylose content and proportion of long branch chains in amylopectin increased starch pasting temperature and setback, and decreased peak viscosity and shear thinning (Jane et al., 1999; Park et al., 2007; Patindol, Gu, & Wang, 2009).

Dietary starch has been classified into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) (Englyst, Kingman, & Cummings, 1992). Starch digestion is a highly important metabolic response and the rate and extent of starch digestibility in the small intestine are nutritionally important (Jenkins et al., 1982). A few studies have reported the relationship between molecular structure and starch nutritional fractions with cooked rice starch (Benmoussa, Moldenhauer, & Hamaker, 2007; Sasaki et al., 2009). Higher amylose content has been associated with reduced susceptibility to enzymatic hydrolysis of cooked rice starches, and a lower proportion of shorter chains in amylopectin contributed to the higher resistance to enzymatic digestion (Sasaki et al., 2009). Benmoussa et al. (2007) reported that RVA breakdown of raw rice starches was positively correlated with RDS and negatively correlated with SDS of cooked rice starches. However, there is a lack of information on the relationship between molecular and crystalline structures and *in vitro* starch nutritional fractions (RDS, SDS and RS) in rice starches. Furthermore, no information is available on *in vitro* digestibility and physicochemical properties of rice starches obtained from commonly consumed rice varieties in Canada, including *indica* and *japonica* cultivars.

In this study, molecular structure (apparent amylose content and amylopectin branch chain length distribution), crystalline structure (X-ray diffraction pattern and relative crystallinity for long-range order, and secondary ordered structure in starch granule from FT-IR), as well as physicochemical properties (swelling factor, amylose leaching, thermal characteristics and pasting properties) of rice starches with different amylose contents from four commercial rice varieties were determined. Results obtained from these studies were used to establish correlation between structural characteristics and *in vitro* starch digestibility.

2. Materials and methods

2.1. Materials

Four commercial rice varieties in Canada, Long-grain (*indica* long-grain rice, USA), Calrose (*japonica* medium-grain rice, USA), Arborio (Italian short-grain rice, Italy), and Glutinous (white glutinous rice, Thailand), were obtained from the local grocery store. Rice grains were wet-milled according to the procedure of Chiang and Yeh (2002). Starch was isolated following the alkaline steeping method described by Wang and Wang (2001).

2.2. Apparent amylose content and amylopectin chain length distribution

Apparent amylose content of rice starches was determined by a colorimetric method (Williams, Kuzina, & Hlynka, 1970). Amylopectin branch chain length distributions were analyzed by using high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) (Dionex, Sunnyvale, CA) according to the procedure of Liu, Gu, Donner, Tetlow, and Emes (2007).

2.3. Swelling factor (SF) and amylose leaching (AML)

SF and AML at different temperatures were measured according to the methods of Tester and Morrison (1990) and Chung et al. (2008), respectively.

2.4. X-ray diffraction and relative crystallinity

X-ray diffractograms were obtained with an X-ray diffractometer (RPT 300 PC, Rigaku-Denki Co., Tokyo, Japan). The diffractometer was operated at 40 kV and 100 mA with measurement angle (2θ) of 3–35° and a scan rate of 2.0°/min. The crystallinity of starch was quantitatively calculated following the method of Nara and Komiya (1983) using software (Origin 6.0, Microcal, Northampton, MA).

2.5. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra of rice starches were obtained with a Digilab FTS 7000 spectrometer (Digilab USA, Randolph, MA) equipped with a thermoelectrically cooled deuterated triglycine sulfate (DTGS) detector using an attenuated total reflectance (ATR) accessory following the method of Chung et al. (2008).

2.6. Differential scanning calorimetry (DSC)

Thermal properties of rice starches in the presence of excess water were measured using a differential scanning calorimeter (2920 Modulated DSC, TA Instruments, New Castle, DE). Starch (12 mg, db) was weighed into a high-volume pan with 28 μL of distilled water. The sample pan was sealed, equilibrated at room temperature for 12 h, and then heated from 5 to 180 °C at a heating rate of 10 °C/min.

2.7. Rapid visco-analyser (RVA)

Pasting properties of rice starches were analyzed using a Rapid Visco-Analyser (RVA-4) (Newport Scientific, Warriewood, Australia). Starch slurries (10.7% w/w dsb, 30 g of total weight) were equilibrated at 50 °C for 1 min, heated at 6 °C/min to 95 °C, held at 95 °C for 5 min, cooled at 6 °C/min to 50 °C, and held at 50 °C for 2 min. A constant rotating speed of the paddle (160 rpm) was used.

2.8. Rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS)

The amounts of RDS, SDS and RS were measured by Approved Method 32-40 (AACC, 2000) as modified by Chung et al. (2008). Rice starches (100 mg) were incubated with pancreatin (10 mg, P-1625, Sigma Chemical, St. Louis, MO) and amyloglucosidase (12U, E-AMGDF, 3300 U/mL, Megazyme International Ireland Ltd., Bray, Ireland) in 4 mL of 0.1 M sodium maleate buffer (pH 6.0) at 37 °C with continuous shaking (200 strokes/min) for 0.5, 2 and 16 h. The glucose released at each time was determined using the glucose oxidase–peroxidase assay kit (K-GLUC, Megazyme).

The amount of RDS was obtained by measuring the glucose released after 0.5 h of incubation. The SDS fraction was the starch hydrolyzed between 0.5 and 16 h. The starch that remained unhydrolyzed after 16 h incubation was measured as RS with further treatment by KOH and amyloglucosidase.