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Effects of molecular compositions on crystalline structure and functional properties of rice starches with different amylopectin extra-long chains

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ABSTRACT

The extra-long chain (ELC) of amylopectin influences molecular compositions of starch. In this study, starches were isolated from 22 rice varieties with different ELCs. Molecular compositions of starch were determined, and their relationships with crystalline structure, gelatinization properties, pasting properties, and enzyme hydrolysis were analysed. The results showed that the starches with different ELCs had significantly different structural and functional properties. The ELC was significantly positively related to setback viscosity and negatively related to relative crystallinity, lamellar peak intensity, swelling power, gelatinization enthalpy, and rapidly digestible starch of retrograded starch. The true amylose content was significantly positively related to retrogradation and negatively related to peak viscosity and hydrolysis degree by α-amylase and amyloglucosidase. The short branch-chain of amylopectin was significantly positively related to lamellar peak intensity, swelling power, hydrolysis degree by α-amylase, and rapidly digestible starch of retrograded starch and negatively related to setback viscosity and resistant starch of retrograded starch. The ratio of short to long branch-chain of amylopectin was significantly positively related to swelling power and hydrolysis degree by α-amylase. The principal component analysis and partial least squares discriminant analysis demonstrated that the low-ELC starches were distinguished from the middle- and high-ELC starches, the middle-ELC starches basically clustered together, but the high-ELC starches were highly dispersed. The above results would provide some new information for rice quality breeding and starch applications by changing the ELC in starch.

1. Introduction

Starch consists of two main components: mainly linear and slightly branched amylose and highly branched amylopectin, and is stored as semicrystalline granules in plants. The contents and structures of amylose and amylopectin determine starch properties and influence starch applications in food and nonfood industries (Jane et al., 1999; Koroteeva et al., 2007; Lin et al., 2016a; Schirmer, Höchstötter, Jekle, Arendt, & Becker, 2013). Therefore, it is very important to investigate the contents and structures of amylose and amylopectin.

The contents of amylose and amylopectin in starch are usually measured using the amylose-iodine colorimetry and amylopectin-Concanavalin A precipitation method. However, in fact, it is very difficult to accurately measure the true amylose content (TAC). For amylose-iodine colorimetry method, the branch-chains of amylopectin, especially the long branch-chains, also have iodine binding capacity, leading to an overestimation of amylose (Bates, French, & Rundle, 1943; Lin et al., 2016b; Man et al., 2014). Though the amylopectin-Concanavalin A precipitation method can accurately measure the contents of amylose and amylopectin, their structure information is unavailable (Wang et al., 2018). The gel permeation chromatography (GPC) analysis of debranched starch is thought to be a reliable method

Abbreviations: AAC, apparent amylose content; AAG, *Aspergillus niger* amyloglucosidase; AC, amylose content; AP_S, amylopectin short branch-chain; AP_L, amylopectin long branch-chain; ATR-FTIR, attenuated total reflectance-Fourier transforms infrared; ELC, extra-long chain; GPC, gel permeation chromatography; PCA, principal component analysis; PLS-DA, partial least squares discriminant analysis; PLSR, partial least squares regression; PPA, porcine pancreatic α-amylase; RDS, rapidly digestible starch; RS, resistant starch; RVA, rapid viscosity analysis; SAXS, small-angle X-ray scattering; SDS, slowly digestible starch; TAC, true amylose content; XRD, X-ray powder diffraction

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to evaluate the contents and structures of amylose and amylopectin in starch (Cai et al., 2015; Lin et al., 2016b; Man et al., 2014; Song & Jane, 2000). The GPC profile can show the molecular weight distribution of starch, and be used to measure the amylose, amylopectin short branch-chain (AP_S), and amylopectin long branch-chain (AP_L). However, some amylopectins have extra-long chain (ELC) with similar chain length and characteristics to amylose. When these amylopectins are debranched by isoamylase, the ELC can be detected in the fraction of GPC profile corresponding to where the peak fraction of amylose is detected (Abe et al., 2014; Asai et al., 2014; Fujita et al., 2007; Horibata, Nakamoto, Fuwa, & Inouchi, 2004; Wang et al., 2018). The existence of ELC influences the determination of TAC in starch. The amylose content (AC) containing ELC in debranched starch measured by GPC is usually nominated as apparent amylose content (AAC). The TAC or absolute AC in starch can be obtained by subtracting ELC from AAC through GPC analysis of debranched starch and amylopectin (Abe et al., 2014; Asai et al., 2014; Fujita et al., 2007; Horibata et al., 2004; Wang et al., 2018). Therefore, the analysis of GPC profiles of debranched starch and amylopectin can obtain the molecular compositions of starch including AAC, ELC, TAC, AP_S, and AP_L.

It has been reported that granule-bound starch synthase I is involved in the biosynthesis of ELC of amylopectin in rice (Hanashiro et al., 2008), wheat (Yoo & Jane, 2002), and maize (Yangcheng, Blanco, Gardner, Li, & Jane, 2016). The ELC is considered to be over 170 DP. Starches from different cereal crops or varieties have significantly different structure and content of ELC (Abe et al., 2014; Asai et al., 2014; Hanashiro et al., 2008; Yangcheng et al., 2016; Yoo & Jane, 2002). The ELC influences the pasting and thermal properties, two important characteristics for evaluating rice quality (Hanashiro et al., 2008; Horibata et al., 2004). Amylopectin has generally been thought responsible for starch crystallinity, while amylose disrupts the crystalline packing of amylopectin (Cheetham & Tao, 1998; Pérez & Bertoft, 2010). As an important component of amylopectin, the effects of ELC on starch crystalline structure including crystalline type, ordered structure, and lamellar structure are unclear.

Usually, starch components are divided into amylose and amylopectin, and the AC plays an important role in determining the functional properties of starch (Jane et al., 1999; Kong et al., 2015; Koroteeva et al., 2007; Lin et al., 2016a; Schirmer et al., 2013). Some literature have reported the relationship between functional properties and AC determined by iodine colorimetric method (Chen, Bergman, McClung, Everette, & Tabien, 2017; Chung, Liu, Lee, & Wei, 2011; Park, Kim, Chung, & Shoemaker, 2013), Concanavalin A precipitation method (Cozzolino, Roumeliotis, & Eglinton, 2013; Park et al., 2013), and GPC profile of debranched starch (Cai et al., 2015). As the above review, in fact, the molecular compositions of starch contain AAC, ELC, TAC, AP_S and AP_L due to the existence of ELC. However, to our knowledge, the effects of these molecular compositions on functional properties of starch are seldom reported, and the differences of rice varieties with different ELCs are unclear from starch property point of view.

In this study, 22 rice starches with different ELCs were investigated for their molecular compositions, crystalline structure, gelatinization properties, pasting properties, and enzyme hydrolysis. Our objective was to reveal the interrelationship between the molecular compositions and crystalline structure and functional properties, and demonstrate the similarities and differences among rice varieties with different ELCs based on their starch properties. This study would provide some new information for rice quality breeding and starch applications by changing the ELC in starch.

2. Materials and methods

2.1. Plant materials

Twenty two normal rice varieties of Sidao 785 (SD 785), Zhonghui 8006 (ZH 8006), Jiahe 218 (JH 218), IAPAR 9, Hua 7 (H 7), RA 73, G 297, Minghui 63 (MH 63), Lvhuangzhan (LHZ), Manian (MN), II32-B, Sahe 1134 (SH 1134), Nanjing 11 (NJ 11), Teqing (TQ), CBB 23, Qingluzhan 11 (QLZ 11), G 392, Sanluzhan 7 (SLZ 7), Fengaizhan 1 (FAZ 1), Guichao 2 (GC 2), Tianyou 3611 (TY 3611), and Guinongzhan (GNZ) were grown in the experiment field of Yangzhou University, China in 2016. The varieties of SD 785, JH 218, IAPAR 9, H 7, RA 73, and MN are *japonica* rice, and the others are *indica* rice. Mature seeds were harvested and used to isolate starches.

2.2. Isolation of starch granules and separation of amylopectin

Starch was isolated from mature seeds following the method of Man et al. (2014). The amylopectin was separated and purified from rice starch according to the protocols described by Naguleswaran, Vasanthan, Hoover, and Bressler (2014) with some modifications. Ten milligrams of starch was deproteinized and dissolved in 1.8 mL LiBr/DMSO (w/w, 0.5%) in a ThermoMixer at 80 °C and 350 rpm for 12 h. Dissolved starch was cooled to room temperature and the solution was mixed with 8 mL of absolute ethanol to precipitate starch. The precipitated starch was washed with ethanol again and dried at room temperature for about 10 min. The starch was dispersed and incubated in boiling water (4.5 mL) for 30 min, then cooled to 80 °C and added 0.25 mL of n-butanol and 0.25 mL of isopentanol (3-methyl-1-butanol). The following processes were the same as those in paper of Naguleswaran et al. (2014). The purification of amylopectin was repeated three times.

2.3. Determination of AAC, ELC, TAC, and amylopectin of starch

The AAC, ELC and TAC were determined through GPC chromatograms of isoamylase-debranched starch and amylopectin following the method of Hanashiro et al. (2008) with some modifications. The starch was deproteinized, dispersed, and precipitated following the method described in section 2.2. The precipitated starch and separated amylopectin were debranched using isoamylase following the method of Lin et al. (2016b). The debranched starch and amylopectin were detected with a PL-GPC 220 system (Agilent Technologies UK Limited). The chromatograms of debranched starch and amylopectin were overlaid to normalize the peak area of AP_S and AP_L for determination of AAC and ELC. The value obtained after subtraction of ELC from AAC was equivalent to the TAC of starch (Hanashiro et al., 2008).

2.4. Crystalline structure analysis of starch

The crystalline structure of starch was analysed on an X-ray powder diffractometer (XRD) (D8, Bruker), and the relative crystallinity was measured using the ratio of the crystallinity area to the total diffraction area following the method described by Cai et al. (2015).

2.5. Short-range ordered structure analysis of starch

The short-range ordered structure of starch was analysed using Varian 7000 attenuated total reflectance-Fourier transforms infrared (ATR-FTIR) spectroscopy as described by Man et al. (2013).

2.6. Lamellar structure analysis of starch

The lamellar structure of starch was analysed using a Bruker NanoStar small-angle X-ray scattering (SAXS) instrument following the method of Yuryev et al. (2004). The SAXS data were analysed using DIFFRAC^{plus} NanoFit software, and SAXS spectrum parameters were determined following the simple graphical method (Cai et al., 2014).

2.7. Swelling power and water solubility determination of starch

The swelling power and water solubility of starch were measured at 95 °C following the method of Lin et al. (2016a).