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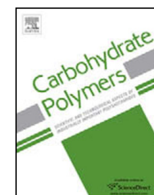

Molecular structure of quinoa starch

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ABSTRACT

Quinoa starch has very small granules with unique properties. However, the molecular structure of quinoa starch remains largely unknown. In this study, composition and amylopectin molecular structure of 9 quinoa starch samples were characterised by chromatographic techniques. In particular, the amylopectin internal molecular structure, represented by φ, β-limit dextrins (LDs), was explored. Great variations in the composition and molecular structures were recorded among samples. Compared with other amylopectins, quinoa amylopectin showed a high ratio of short chain to long chains (mean:14.6) and a high percentage of fingerprint A-chains (A_{fp}) (mean:10.4%). The average chain length, external chain length, and internal chain length of quinoa amylopectin were 16.6, 10.6, and 5.00 glucosyl residues, respectively. Pearson correlation and principal component analysis revealed some inherent correlations among structural parameters and a similarity of different samples. Overall, quinoa amylopectins are structurally similar to that from starches with A-type polymorph such as oat and amaranth starches.

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1. Introduction

Quinoa (*Chenopodium quinoa* Willd.) is a pseudocereal originated from South America. It has attracted much research interest in the last decade for its high nutritional profile (Abugoch, 2009; Wang & Zhu, 2016). Starch is the major component of quinoa seeds and contributes to more than 50% of the dry weight (Lindeboom, Chang, Falk, & Tyler, 2005). Quinoa starch has A-type polymorph and rather small granules (~1–3 μm) with great potential for various food and non-food applications (Wang & Zhu, 2016). The starch is mainly constituted of amylose and amylopectin. Amylose is of linear glucosyl chain connected by α-(1,4) linkage while amylopectin is highly branched by α-(1,6) linkages in a clustered manner (Bertoft, 2013). The structure of amylopectin is closely correlated to the physical properties of starch such as gelatinization properties (Bertoft, Piyachomkwan, Chatakanonda, & Sriroth, 2008; Vamadevan & Bertoft, 2015).

The amylopectin could be debranched by isoamylase and/or pullulanase to obtain the unit chain length distribution (Bertoft, 2004). The unit chains of amylopectin are classified into A-chain (without carrying any other chains), B-chain (carrying other chains via α-(1,6) linkage), and C-chain (carrying the only reducing residue in a single amylopectin molecule) (Peat, Whelan, & Thomas, 1952). Different categories of unit chains have been reported based on the chain length distribution as revealed by various chromatographic techniques (Hizukuri, 1986; Hanashiro, Abe, & Hizukuri, 1996). Through HPSEC (high-performance size exclusion chromatography) analysis, Hizukuri (1986) suggested that the B-chains could be fractioned into B1-, B2-, and B3-chains which involve in one, two, and three clusters, respectively. Alternatively, the unit chains could be sorted into short chains and long chains. Hanashiro et al. (1996), using HPAEC (high performance anion-exchange chromatography), categorized the unit chains into four groups: fa (DP (degree of polymerization) 6–12), fb1 (DP 13–24), fb2 (DP 25–36), and fb3 (DP > 36). Based on the location of non-reducing ends and branch points, the unit chains can be defined as external chains (the chain segments between the non-reducing ends and the branches) and internal chains (the chain segments between two branches) (Bertoft et al., 2008).

Although the unit chain length distribution of amylopectin provides some information on the structure, the internal structure is also important to understand the organization of unit chains in the starch granules (Vamadevan & Bertoft, 2015). For the analysis of amylopectin internal structure, β-amylase and phosphorylase *a* have been applied for the preparations of φ, β-limit dextrins (LDs) (Bertoft, 2004; Bertoft et al., 2008). The external chains are firstly cleaved to 3.5 glucosyl residues from the branch points by phosphorylase *a*. Then, one maltose is released by β-amylase to give the external chain length as 1.5 glucosyl residues (Bertoft, 2004). After debranching of φ, β-LDs, all the maltose molecules are from the A-chains and the rest are of the B-chains (Bertoft, 2004; Bertoft et al., 2008).

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With the help of advanced chromatography instruments such as high performance anion-exchange chromatography coupled with pulsed amperometric detector (HPAEC-PAD), the amylopectin unit chain length distribution as well as the internal parts from various botanical sources have been studied (Annor, Marcone, Bertoft, & Seetharaman, 2014b; Kalinga, Bertoft, Tetlow, Liu, Yada, & Seetharaman, 2014; Laohaphatanaleart, Piyachomkwan, Sriroth, Santisopasri, & Bertoft, 2009; Zhu, Corke, & Bertoft, 2011). Bertoft et al. (2008) investigated a broad range of starches from different origins and defined four groups of amylopectins based on the internal unit chain composition. Group 1 amylopectins have the lowest amounts of long internal chains (B2- and B3-chains). Some A-crystalline type cereal starches such as oat and rye starches belong to this group. Several cereal starches (e.g., waxy maize starch) and some C-crystalline type starches (e.g., sago palm starch) are classified into group 2 for their higher amounts of B2-chains but a similar amount of B3 as compared to those of group 1. With a similar amount of B2-chains to that of group 2, group 3 was defined as those starches having a medium amount of B3-chains and a lower amount of fingerprint B-chains (B_{fp}, the B-chains of DP 3–7). Group 4 was defined as those starches abundant in both B2- and B3-chains (mainly B-crystalline type root and tuber starches such like potato and yam (*Dioscorea esculenta*) starches) (Bertoft et al., 2008).

Although the physicochemical properties of quinoa starch have been extensively studied (Abugoch, 2009; Li, Wang, & Zhu, 2016; Lindeboom et al., 2005), only a few reports focused on the amylopectin structure. Praznik et al. (1999) estimated the molar mass and DP of quinoa starch by HPSEC and suggested that the quinoa starch has a lower packing density than amaranth and maize starches. Tang, Watanabe, and Mitsunaga (2002), using HPSEC, estimated the DP of quinoa amylopectin to be around 6700 and suggested that the quinoa amylopectin has a high ratio of short chains to long chains. There is a lack of systematic analysis on the molecular structure of quinoa starches from different genotypes. In particular, the internal structure of quinoa amylopectin is unknown. The lack of systematic information on the quinoa starch structure seriously hinders the further development of quinoa as a sustainable crop.

Our previous work has characterized the physicochemical properties of quinoa starches from 26 samples (Li et al., 2016). The present work further selected 9 quinoa starches based on the variations in the properties. The composition of these quinoa starches and the fine structure of their amylopectins were characterized using enzymatic and chromatographic techniques. Due to the large number of nomenclatures used, a list of abbreviations is presented (Supplementary Table 1). This study expands the knowledge of the detailed structure of quinoa starch and provides a basis for exploring the structure-property relationships.

2. Materials and methods

2.1. Starches and enzymes

Nine quinoa starches (S3, S6, S14, S22, S26, S15, S24, S17, and S21) were from the 26 samples investigated in a previous work and the selection was based on the results of principal component analysis (PCA) (Li et al., 2016). These 9 quinoa starches differ greatly in the physicochemical properties as revealed by chemometrics (Li et al., 2016). Sample information such as country of origin and grain color is summarized in Supplementary Table 2. Readers are encouraged to refer to the previous report by Li et al. (2016) to gain the background information of these samples. Normal maize starch (Melogel) was kindly provided by Ingredion (Auckland, New Zealand) and was used as a reference throughout the experiments.

Rabbit muscle phosphorylase *a* (EC 2.4.1.1, specific activity ~ 1.2 U/mg) was from Sigma-Aldrich (Deisenhofen, Germany). β-Amylase from barley (EC 3.2.1.2, specific activity ~ 600 U/mg), *Pseudomonas* sp. isoamylase (EC 3.2.1.68, specific activity ~ 280 U/mg), and *Klebsiella planticola* pullulanase (EC 3.2.1.41, specific activity ~ 30 U/mg) were from Megazyme International (Wicklow, Ireland). The given enzyme activities were according to the suppliers.

2.2. Amylose content determined by concanavalin A precipitation-based method

The amylose content (ACC) was measured by concanavalin A (Con A) precipitation-based method using an amylose/amylopectin kit (Megazyme, Wicklow, Ireland) (Gibson, Solah, & McCleary, 1997).

2.3. Gel permeation chromatography of whole starch

The molecular size distribution of quinoa starch was estimated by gel permeation chromatography (GPC) method according to a previous report (Zhu, Bertoft, Källman, Myers, & Seetharaman, 2013). Briefly, the starch was gelatinized in 90% DMSO (dimethyl sulfoxide) in boiling water bath for half an hour before stirring at room temperature for another 12 h for a complete dissolution. The sample was filtered through Whatman™ filter paper No. 1 before loading on a column (1 cm × 40 cm) of Sepharose CL 2B (GE Healthcare, Uppsala, Sweden). The sample was eluted with a NaOH solution (0.05 M) at 0.3 mL/min and collected from 20 min after loading the sample by a Gilson FC 204 fraction collector (Middleton, WI, USA). The volume of each fraction was 0.5 mL. The fractions with odd numbers were analyzed for the carbohydrate content by phenol-sulfuric acid-based method carried out in a 96 well plate as described in Li et al. (2016). The fractions with even numbers were neutralized with 0.05 M HCl solution before adding 0.5 mL iodine solution (2% KI, 0.2% I_2). The wavelength of maximum absorption (λ_{max}) was read from a spectrophotometer (SPECTRONIC™ 200, Thermo Fisher Scientific) (Auckland, New Zealand). The amylose content was represented by the percentage of carbohydrate in the fractions 20–45 out of the total carbohydrate eluted. The apparent amylose content estimated by this method was termed AAM_{2B}.

2.4. Gel permeation chromatography of debranched starch

The starch was debranched and analyzed following a previous description (Zhu et al., 2011) with several modifications. Briefly, starch (2 mg) was dissolved in 50 μL 90% DMSO for 15 min before stirring overnight. Warm water (400 μL) and 50 μL of sodium acetate buffer (pH = 5.5, 0.01 M) were added. After cooling to the room temperature, isoamylase (1 μL) and pullulanase (1 μL) were added to debranch the starch. The reaction was conducted at room temperature for 12 h and terminated by adding 50% (w/w) sodium hydroxide solution to reach a concentration of 2 M. The sample was diluted with water (1.5 mL) before filtering (0.22 μm) and loading on a column (1 cm × 90 cm) of Sepharose CL 6B (GE Healthcare, Uppsala, Sweden). The eluent was 0.5 M NaOH and the elution speed was 0.3 mL/min. The volume of each fraction was 1 mL. The carbohydrate content of each fraction was analyzed as described in Section 2.3. The first peak eluted at void volume (fraction number 34–43) was defined as long chain amylose fraction (LC_{AAM}) while the second peak (fraction number 68–100) was of amylopectin. The adjacent part between the two peaks (fraction number 44–67) was the short unit chains of amylose (SC_{AAM}) (Bertoft et al., 2008). The apparent amylose content calculated from this method was termed AAM_{6B}.

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