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Quinoa starch: Structure, properties, and applications

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ABSTRACT

Quinoa (*Chenopodium quinoa* Willd.) has gained popularity worldwide largely due to the attractive nutritional profile. It also has much potential for food security due to the great genetic diversity. Starch is the main component of quinoa grain and makes up to 70% of the dry matter. The starch plays a crucial role in functional properties of quinoa and related food products. The starch granules are rather small (~1–3 μm) with relatively low amylose contents as compared with most of the other starches. Quinoa amylopectin has significant amounts of short chains and super-long chains. These unique features have generated research interest in using the starch for food and other applications such as creating Pickering emulsions. This review summarizes the present knowledge of the isolation, composition, granular and molecular structures, physicochemical properties, modifications, and applications of quinoa starch. It becomes obvious that this starch has great potential for food and nonfood applications.

1. Introduction

Quinoa (*Chenopodium quinoa* Willd.) of the Chenopodiceae family is native to the Andes, and has been cultivated in the Andean Region for several thousand years (Taylor & Parker, 2002; Fleming & Galwey,1995). Before Spanish colonization of the South America, quinoa had been widely grown as a staple grain crop for its edible seeds (Valencia-Chamorro, 2003). In the late 1970s, quinoa production started to experience a renaissance within South America, not only for domestic consumption but also for export (Fleming & Galwey, 1995). Quinoa cultivation is in the process of rapid expansion outside its traditional cultivated areas with good yields (FAOSTAT, 2017; Wang & Zhu, 2016). World production of quinoa has kept increasing in the period of 1992–2014, exceeding 192 thousand metric tons in 2014 (FAOSTAT, 2017).

Quinoa plays a significant role in food security for its broad genetic diversity and an extraordinary adaptability to a wide range of agro-ecological conditions (Alan, 2011). It can grow from sea level to 4000 m above sea level, at humidity ranging from 40% to 88%, and at temperatures from −4 to 38 °C (Alan, 2011). It has a high tolerance to adverse environmental conditions such as drought and saline environments with low input costs (Jacobsen, 2003). The above-mentioned characteristics make quinoa a strategic crop for providing nutrition and food security in the face of climate change (Ruiz et al., 2014). The genome of quinoa has been recently sequenced, providing the genetic basis for the improvements in agricultural traits and food processing properties of this crop (Jarvis et al., 2017). Quinoa seeds come in a variety of colors ranging from white to red and black (Vega-Galvez et al., 2010). An example of the seed cross-section is presented in Supplementary Fig. 1.

In recent years, there has been renewed interest in quinoa due to its attractive nutritional features. The seed is a source of starch, protein, dietary fiber, fat, minerals, polyphenols, and vitamins (Repo-Carrasco et al., 2003; Espinoza, & Jacobsen, 2003; Ruales et al., 1993; Vega-Galvez et al., 2010). It contains no gluten and can be a gluten-free alternative for persons with celiac disease (Alvarez-Jubete, Arendt, & Gallagher, 2010).

The major component of quinoa seed is starch, which varies from ~30 to 70% of the dry matter (Supplementary Table 1). The quality of quinoa food products can be much affected by the properties of the starch (Wang, Opassathavorn, & Zhu, 2015). Recent research has shown that quinoa starch can be an ingredient for food and non-food applications (Wang & Zhu, 2016). Compared with other starches from maize, potato, and wheat, there is a lack of systematic knowledge of quinoa starch. This limits the further development of this crop and the utilization of the starch. This review summarizes the present knowledge of the isolation, composition, granular and molecular structures, physicochemical properties, modifications, and uses of quinoa starch. Suggestions for the direction to improve the understanding and utilization of this starch are provided.

2. Isolation of quinoa starch

Various milling and soaking approaches have been applied to

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remove the non-starch components of quinoa seeds. The seeds were washed and steeped in water or alkaline solutions before homogenizing in a blender (Araujo-Farro, Podadera, Sobral, & Menegalli, 2010; Wright, Huber, Fairbanks, & Huber, 2002). Alternatively, the seeds were dry-milled into flour before soaking in solutions (Li, Wang, & Zhu, 2016; Mundigler, 1998; Watanabe, Peng, Tang, & Mitsunaga, 2007). It should be noted that too harsh dry-milling conditions may induce damages to starch granules (Li & Zhu, 2017c; Qian & Kuhn,1999). The solution used to soak the seeds or flour could be deionized water or solution containing sodium hydroxide, sodium bisulfite, sodium dodecyl sulfate (SDS), or sodium acetate to remove the other components such as proteins, lipids, saponins, and fibers (Atwell, Patrick, Johnson, & Glass, 1983; Li et al., 2016; Srichuwong et al., 2017; Araujo-Farro et al., 2010). The enzymatic treatment is effective in starch purification but the cost is high, which may not be suitable for large sample preparation. The soaking time varied from 5 min to 1 week among different studies (Atwell et al., 1983; Steffolani, León, & Pérez, 2013). Long soaking may give rise to microbial issues, whereas the altered pH may induce damage to starch granules (Lim, Lee, Shin, & Lim, 1999).

After soaking, the suspension was filtered and the starch in filtrate was recovered by centrifuge. High centrifugation speed ($> 2000 \times g$) was applied to increase the recovery of starch due to the small granule size (Li et al., 2016; Lindeboom, Chang, Falk, & Tyler, 2005; Steffolani et al., 2013). The starch cake was re-suspended in water to further remove the non-starch components and chemical reagents added. It should be noted that residue of the reagents, if not washed off probably, may affect the physicochemical properties of starch such as enzyme susceptibility (Zhang & Hamaker, 1999).

The starch yield was in range of 30–53.3% (Jan, Panesar, Rana, & Singh, 2017; Wright et al., 2002). The purity was from 93% to 99% (Jan et al., 2017; Mundigler, 1998; Srichuwong et al., 2017). The quinoa starch isolations were mainly carried out at laboratory-scale and there appears to be no reports on industrial isolations of this starch.

3. Chemical composition of quinoa starch

Starch is mainly composed of two kinds of biopolymers: the linear amylose and the branched amylopectin (Pérez & Bertoft, 2010). The amylose contents of quinoa starch have been measured by a range of methods based on iodine binding-spectrophotometry/potentiometry, concanavalin A (Con A) precipitation, and size exclusion chromatography (SEC) (Table 1). Amylose content estimated by iodine binding-based methods ranged from 0.3% to 27.7% (Table 1). It is notable that the amylose content calculated by subtracting the influence from amylopectin was significantly lower (7.1%) than that calculated from the whole starch (25.4%) (Tang, Watanabe, & Mitsunaga, 2002). Such a difference could be due to the fact that the long-chain fraction of quinoa amylopectin also complex with iodine, causing an overestimation of amylose content (Tang et al., 2002; Vilaplana et al., 2012). The lipids of starch granules may affect the amylose content measured by iodine-binding based method by forming amylose-lipid inclusion complexes (Srichuwong & Jane, 2007). Thus, the iodine binding method should be employed together with other methods for the estimation of amylose content in quinoa starch.

The amylose contents estimated from SEC of whole starch were 4–10.9% (Table 1). The values seem to be lower than those estimated by SEC of debranched whole starch which ranged from 3.5 to 27.0% (Table 1). The presence of long unit chains of amylopectin may affect the amylose content estimated from debranched whole starch (Li & Zhu, 2017b).

The Con A binding based method has been also used for quantifying the amylose content of quinoa starch (Gibson, Solah, & McCleary, 1997). Only the branched polysaccharides could form precipitates with Con A (Goldstein, Hollerman, & Merrick, 1965). Apart from amylopectin, branched amylose may also get precipitated in this process. Although the amylose content estimated by this method has been reported as high as 19.7%, the majority of the studies reported a value of less than 10% (Table 1). The lower amylose content estimated by this method may due to the over-estimation in the value from the iodine binding and SEC of debranched whole starch based methods or underestimation of Con A method caused by amylose precipitation.

The isolated starch contains minor components such as protein, lipid, ash, and fiber (Table 1). The majorities of the studies reported the values of the minor components being less than 0.5% (Table 1). High contents of minor components suggest an insufficient purification of starch. It should be borne in mind that these minor components, though small in quantity, may have effects on the functional properties of starch (Srichuwong & Jane, 2007).

4. Structure of quinoa starch

4.1. Morphology

Various techniques such as light microscope (LM), scanning electron microscope (SEM), transmission electron microscopy (TEM), Coulter Counter (CC), and laser light diffraction (LLD) have been employed to study the morphology of quinoa starch granules (Supplementary Table 2). The individual starch granules could be released during the isolation process (Atwell et al., 1983; Qian & Kuhn, 1999). The size of quinoa granule was mostly in the range of 0.4–2.0 μm, which was smaller than that of most starches from other botanical origins (Supplementary Table 2). The shape of quinoa starch was polygonal, angular, and irregular. The diversities in both the shape and size of single quinoa starch granule are relatively small (Lindeboom, Chang, & Tyler, 2004; Li & Zhu, 2017a). Light microscopy, limited in the resolution capacity, should not be used to study the details of quinoa starch granules. TEM analysis showed that quinoa starch granule had a homogeneous outer layer with a high density and a hilum with a low density (Supplementary Fig. 2) (Tang et al., 2002).

Quinoa starch may present as aggregations (Supplementary Table 2). These spherical or oblong shaped aggregates were between 10–30 μm in size with 14,000–20,000 single starch granules (Fig. 1) (Ando et al., 2002; Lorenz, 1990; Ruales & Nair, 1994; Srichuwong et al., 2017). It should be noted that these aggregates may give rise to the artefacts of granule size distribution data. The formation of these aggregates may be largely due to the presence of protein because adding pepsin facilitated their disaggregation (Atwell et al., 1983; Ruales & Nair, 1994).

4.2. Crystallinity

Quinoa starch has an A-type polymorph (Supplementary Table 3). The degree of crystallinity of quinoa starch ranged between 21.5–43.0% (Supplementary Table 3). The value from peak fitting method (the area ratio between crystalline peak and total peak) appeared to be higher than those calculated from the ratio of crystalline area (separated by a smooth line in spectrum) and total areas. The degree of crystallinity of quinoa starch has been reported to be lower than amaranth, garden orache, and normal maize starches and higher than barley, adzuki, and kañiwa starches (Qian & Kuhn, 1999; Steffolani et al., 2013; Tang et al., 2002; Wright et al., 2002). Such differences may be due to the differences in the chemical structure and composition of starches (Pérez & Bertoft, 2010). The quinoa starch has been reported to have a significant amount of A_{fp}-chains which could contribute to the defects in crystalline lamella and a low degree of crystallinity in quinoa starch. The peak around 0.44 nm (d-spacing) in wide-angle X-ray diffraction (XRD) spectrum is characteristic of amylose-lipid inclusion complexes. This peak is not significant for quinoa starch, indicating that the starch had a low level of amylose-lipid complexation (Tang et al., 2002).

The nature of quinoa starch crystallinity can be probed by techniques other than XRD, such as solid-state nuclear magnetic resonance