Note

Molecular Structural Characteristics of Quinoa Starch

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The structural properties of starches isolated from five quinoa lines were characterized. All quinoa starches used in the study exhibited the A-type of diffraction pattern. The starches were waxy, with low amylose contents (5.2 to 10.9%) and high degrees of relative crystallinity (39.0 to 43.0%). Quinoa amylose molecules had a large number of branched chains, and the λ max (maximum absorption wavelength) and BV (blue value at 680 nm) of quinoa amylose molecules were low compared to barley amylose molecules. On the other hand, quinoa amylopectin molecules had a large proportion of LC (longest chain) with a high λ max and BV. These structural characteristics of quinoa starches suggested that quinoa could be used as a novel food source.

Keywords: molecular structure, quinoa, starch

Introduction

Quinoa (*Chenopodium quinoa* Willd) is a pseudocereal native to South America. Recently, it has attracted renewed attention because of the high nutritional value of its protein and its suppressive effect on increased blood pressure (Ranhotra *et al.*, 1993; Ogawa *et al.*, 2001). Quinoa protein has a high level of lysine, and its amino acid score is higher than that of cereals such as rice and wheat (Watanabe *et al.*, 2003). Furthermore, quinoa protein contains significant amounts of albumin and globulin, and, unlike most cereals, has little prolamin and glutelin (Watanabe *et al.*, 2003). This suggests that quinoa could be used as an alternative for individuals allergic to cereals. Starch is the major component of quinoa, comprising 60% of the seeds (Ando *et al.*, 2002). Thus, it is important to elucidate starch characteristics in order to utilize quinoa as a food source. There are various reports on quinoa starch (Atwell *et al.*, 1983; Ahamed *et al.*, 1996). Recently, Lindeboom *et al.* (2005) have reported on differences in functional and physicochemical characteristics, including gelatinization, retrogradation, pasting and swelling properties, among the starches isolated from eight quinoa lines. However, a comparison of the structural properties such as the degree of polymerization, chain-length distribution and crystallinity among starches from different varieties has not yet been reported. Thus, the molecular structural properties of starches from five quinoa lines were investigated and compared with those of other plant species to discuss the effective utilization of quinoa as a food source in this study.

Materials and Methods

Materials Five quinoa lines (Real, Sajama, Kanccola, Blanca, Rosada) were obtained from Asai Co. Ltd. (Nagoya, Japan).

Starch isolation Quinoa seeds were powdered with an electric mill. Starch was isolated from the powdered seeds by the alkali method (Takeda *et al.*, 1999). Amylose and amylopectin were prepared from the isolated starches according to the method of Takeda *et al.* (1986).

X ray diffraction of starch granules X-ray diffraction was performed using a Rint-2500 X-ray diffractometer (Rigaku Denki Co. Ltd., Tokyo, Japan) operating at 40 kV and 80 mA. Diffractograms were obtained from 4° 2θ to 40° 2θ with a scanning speed of $8^\circ/\text{min}$ and a scanning step of 0.02° 2θ . The degree of relative crystallinity for the starch granules was calculated as the ratio of the areas of crystalline to amorphous regions on the X-ray diffractograms using Hermans' method (Nara *et al.*, 1978).

Analysis of fine structures of starches Iodine absorption spectra were measured by the method described previously (Takeda *et al.*, 1983). The number-average degrees of polymerization (DP_n) in the amylose and amylopectin molecules were determined by the modified Park-Johnson method (Hizuruki *et al.*, 1981). The average chain length (CL) was determined by the same method after isoamylolysis of the molecules (Tang *et al.*, 2001a, b). The average number of chains per molecule (NC) was the value of ((DP_n/CL)-1) (Tang *et al.*, 2001a).

Chain-length distribution in the amylose and amylopectin molecules was analyzed on two sequentially linked columns (TSK gel G3000SW + TSK gel G2000SW, 7.5 mm $\times$ 60 cm) at 35°C using the Shimazu LC-6A system equipped with Shimazu RID-2A and Shimazu C-R6A (Shimazu Co. Ltd., Kyoto, Japan) as reported previously (Tang *et al.*, 2001a, b). The total carbohydrate amount was deter-

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mined by the phenol-sulfuric acid method (Dobois *et al.*, 1956).

Results

X-ray diffraction of starch granules Figure 1 shows the X-ray diffraction patterns of starch granules from the five quinoa lines. The starch granules exhibited the A-type of diffraction pattern common to most cereal starches (Atwell *et al.*, 1983; Zobel 1988). The degrees of relative crystallinity of the starch granules were 39.0, 41.2, 42.8, 40.0, and 43.0% for Real, Sajama, Kanccola, Blanca, and Rosada, respectively.

Properties of amylose and amylopectin molecules The properties of the amylose and amylopectin molecules from the five quinoa lines are presented in Tables 1 and 2. The λ max (maximum absorption wavelength) and BV (blue value at 680 nm) of the amylose molecules were 648 to 650 nm and 0.998 to 1.101, respectively. The DPn and CL of the amylose molecules were 822 to 1054 and 98 to 119, suggesting that quinoa amylose had a number of branched chains (NC=6 to 9). On the other hand, the λ max and BV of the amylopectin molecules were 589 to 590 nm and 0.190 to 0.210, respectively. The DPn and CL were 3403 to 4752 and 18 to 20.

The chain-length distribution of the amyloses is shown in Fig. 2. The amylose molecules contained C-chains (CC) which characterize the molecular structure of amylose (Takeda *et al.*, 1986). However, short chains were also found in the amylose molecules from quinoa starches. This result suggested that the quinoa amylose molecule had branched chains. Figure 3 shows the chain-length distribution of the amylopectins. The longest chains (LC) were found in the amylopectin molecules.

The carbohydrate proportion (weight%) of LC was 15.4 to 19.9%. The value was higher than that of barley amylopectin molecules (Tang *et al.*, 2001a, b). The major peaks were divided into four fractions, F.1 to F.4. F.1 was

Fig. 1. X-ray diffraction patterns of quinoa starch granules. A, Real; B, Sajama; C, Kanccola; D, Blanca; E, Rosada.

Table 1. Properties of amylose molecules from quinoa starches.

Variety	λ_{max}^a	BV ^b	DPn ^c	CL ^d	NC ^e
Real	649	1.047	1054	115	8
Sajama	648	0.998	910	99	8
Kanccola	650	1.035	989	98	9
Blanca	649	1.101	864	119	6
Rosada	648	1.083	822	112	6

Values represent the mean of three separate measurements.

^aMaximum absorption wavelength (nm), ^bBlue value at 680 nm, ^cNumber-average degrees of polymerization, ^dAverage chain-length, ^eAverage number of chains per molecule.

Table 2. Properties of amylopectin molecules from quinoa starches.

Variety	λ_{max}^a	BV ^b	DPn ^c	CL ^d	NC ^e
Real	590	0.196	4752	20	227
Sajama	590	0.190	4380	20	215
Kanccola	589	0.194	4199	19	216
Blanca	590	0.203	3403	18	172
Rosada	590	0.210	4300	19	217

Values represent the mean of three separate measurements.

^aMaximum absorption wavelength (nm), ^bBlue value at 680 nm, ^cNumber-average degrees of polymerization, ^dAverage chain-length, ^eAverage number of chains per molecule.

Fig. 2. Elution profiles of isoamylase-debranched amyloses from gel-permeation HPLC.
CC, C-chain; A, Real; B, Sajama; C, Kanccola; D, Blanca; E, Rosada.

the long chain fraction, and F.2 to F.4 were the short chain fractions (Tang *et al.*, 2001a). The average degrees of polymerization of short chains (F.2, F.3, and F.4) were 14.9, 14.9, 15.4, 16.3, and 16.6 for Real, Sajama, Kanccola, Blanca, and Rosada, respectively. The ratios (molar%) of the short chain fraction (F.2, F.3, and F.4) per long chain fraction (F.1) were 13.9, 14.4, 15.4, 9.7, and 13.3 for the five lines, respectively. It was shown that the average number of short chains per cluster of quinoa amylopectin molecules was 10 to 16.

Discussion

Quinoa starch exhibited an A-type of X-ray diffraction pattern (Fig. 1). The degrees of relative crystallinity were 39.0 to 43.0%. Jenkins and Donald (1995) reported that amylose disrupted the structure order within the amylopectin crystallites. Thus, the crystallinity of starch is associated with amylose content. The relative crystallinity of quinoa starch was higher than that of normal barley starch, and similar to that of waxy barley starch (Tang *et al.*, 2002). The amylose content of quinoa starches has been reported to range from 3.0 to 20.0% (Atwell *et al.*, 1983; Lindeboom *et al.*, 2005). The amylose content of

Fig. 3. Elution profiles of isoamylase-debranched amylopectins from gel-permeation HPLC.

—, R.i. response; ●, degrees of polymerization; LC, the longest chain; F.1, fraction 1; F.2, fraction 2; F.3, fraction 3; F.4, fraction 4; A, Real; B, Sajama; C, Kanccola; D, Blanca; E, Rosada.

starches from the five quinoa lines used in this study was 5.2 to 10.9% (unpublished results), lower than those of normal corn and barley starches, but similar to that of waxy barley starches, and higher than that of waxy corn starches (Tang *et al.*, 2002; Lindeboom *et al.*, 2005). These results showed that no lines with high amylose starch were found among cultivated quinoa, as reported by Lindeboom *et al.* (2005). The λ max and BV of quinoa amylose (Table 1) were lower than those of barley amylose (Tang *et al.*, 2001a, b). Amylose molecules are composed of linearly linked long glucose polymers, whereas amylopectin molecules have many branched chains of short glucose polymers. Therefore, the λ max and BV of amylose are higher than those of amylopectin. Quinoa amylose had a large number of branched chains (Table 1, Fig. 2) compared to barley amylose (Tang *et al.*, 2001a). It was suggested that the low λ max and BV of quinoa amylose molecules resulted from the presence of the branched chains. On the other hand, the λ max and BV of quinoa amylopectin (Table 2) were higher than those of

barley amylopectin (Tang *et al.*, 2001a, b). Takeda and Hizukuri (1987) reported that rice amylopectins containing a large proportion of LC showed high λ max and BV in a comparison between indica and japonica rice. These results suggest that quinoa amylopectin has a large proportion of LC (Fig. 3) which result in the high values.

The physicochemical properties of starches from various quinoa lines were investigated (Lindeboom *et al.*, 2005). The swelling power of quinoa starches was similar to that of barley and wheat starches (Tang *et al.*, 2002; Tang *et al.*, 2005). However, the freeze thaw stability of quinoa starches was higher than that of barley and wheat starches (Tang *et al.*, 2004; Tang *et al.*, 2005), and the gelatinization onset and peak temperatures of quinoa starches were lower than those of barley starches (Tang *et al.*, 2002). Quinoa starch had different physicochemical and structural properties from barley and wheat starches. Additionally, it was reported that amylopectins with LC were subjected to rapid retrogradation (Takeda and Hizukuri, 1987). These results suggested that quinoa starch was tolerant of freeze thaw, and subjected to rapid retrogradation. Thus, quinoa could be used as a novel food source.

References

- Ahamed, N.T., Singhai, R.S., Kulkarni, P.R. and Pal, M. (1996). Physicochemical and functional properties of *Chenopodium quinoa* starch. *Carbohydr. Poly.*, **31**, 99–103.
- Ando, H., Chen, Y.C., Tang, H., Shimizu, M., Watanabe, K. and Mitsunaga, T. (2002). Food components in fractions of quinoa seed. *Food Sci. Technol. Res.*, **8**, 80–84.
- Atwell, W.A., Patrick, B.M., Johnson, L.A. and Glass R.W. (1983). Characterization of quinoa starch. *Cereal Chem.*, **60**, 9–11.
- Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956). Colorimetric method for determination of sugars and related substances. *Anal. Chem.*, **28**, 350–356.
- Hizukuri, S., Takeda, Y., Yasuda, M. and Suzuki, A. (1981). Multi-branched nature of amylose and the action of debranching enzymes. *Carbohydr. Res.*, **94**, 205–213.
- Jenkins, P.J. and Donald, A.M. (1995). The influence of amylase on starch granule structure. *Inter. J. Biol. Macromolec.*, **17**, 315–321.
- Lindeboom, N., Chang, P.R., Falk, K.C. and Tyler, R.T. (2005). Characteristics of starch from eight quinoa lines. *Cereal Chem.*, **82**, 216–222.
- Nara, S., Mori, A. and Komiya, T. (1978). Study on relative crystallinity of moist potato starch. *Starch*, **30**, 111–114.
- Ogawa, H., Watanabe, K., Mitsunaga, T. and Meguro, T. (2001). Effect of quinoa on blood pressure and lipid metabolism in diet-induced hyperlipidemic spontaneously hypertensive rats (SHR). *J. Jpn. Soc. Nutr. Food Sci.*, **54**, 221–227.
- Ranhotra, G.S., Gelroth, J.A., Glaser, B.K., Lorenz, K.J. and Johnson, D.L. (1993). Composition and protein nutritional quality of quinoa. *Cereal Chem.*, **70**, 303–305.
- Takeda, C., Takeda, Y. and Hizukuri, S. (1983). Physicochemical properties of lily starch. *Cereal Chem.*, **60**, 212–216.
- Takeda, Y., Hizukuri, S. and Juliano, B.O. (1986). Purification and structure of amylose from rice starch. *Carbohydr. Res.*, **148**, 299–308.
- Takeda, Y. and Hizukuri, S. (1987). Structures of rice amylopectins with low and high affinities for iodine. *Carbohydr. Res.*, **168**, 79–88.
- Takeda, Y., Takeda, C., Mizukami, H. and Hanasuiro, I. (1999). Structures of large, medium and small starch granules of barley grain. *Carbohydr. Poly.*, **38**, 109–114.
- Tang, H., Ando, H., Watanabe, K., Takeda, Y. and Mitsunaga, T. (2001a). Fine structures of amylose and amylopectin from large medium and small waxy barley starch granules. *Cereal Chem.*, **78**, 111–115.
- Tang, H., Ando, H., Watanabe, K., Takeda, Y. and Mitsunaga, T. (2001b). Physicochemical properties and structure of large, medium and small granule starches in fractions of normal barley endosperm. *Carbohydr. Res.*, **330**, 241–248.
- Tang, H., Watanabe, K. and Mitsunaga, T. (2002). Structure and functionality of large, medium and small granule starches in normal and waxy barley endosperms. *Carbohydr. Poly.*, **49**, 217–224.
- Tang, H., Mitsunaga, T. and Kawamura, Y. (2004). Relationship between functionality and structure in barley starches. *Carbohydr. Poly.*, **57**, 145–152.
- Tang, H., Mitsunaga, T. and Kawamura, Y. (2005). Functionality of starch granules in milling fractions of normal wheat grain. *Carbohydr. Poly.*, **59**, 11–17.
- Watanabe, K., Ibuki, A., Chen, Y.C., Kawamura, Y. and Mitsunaga, T. (2003). Composition of quinoa protein fractions. *J. Jpn. Soc. Food Sci. Technol.*, **50**, 546–549.
- Zobel, H.F. (1988). Starch crystal transformations and their industrial importance. *Starch*, **40**, 1–7.