# Characterization of Quinoa Starch<sup>1</sup>

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### **ABSTRACT**

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Quinoa (Chenopodium quinoa Willd.) is a cereal crop grown in the mountainous regions of South America. Starch was extracted by two extraction schemes that varied primarily in the amount of agitation. The harsher treatment yielded polygonal granules  $1-2.5~\mu m$  in diameter that gelatinized from 57 to 64°C. Analysis of the components indicated 11% amylose, a  $\overline{CL}$  of 27, and a bimodal distribution of amylopectin chain

lengths. Differential scanning colorimetry data indicated a heat of gelatinization of  $4.03\,\mathrm{cal/g}$  of dry starch. Scanning electron microscopy of the products of a milder isolation treatment revealed primarily a large oval species composed of hundreds of the individual granules. Light microscopy of thin-sectioned quinoa seeds indicated that several of these composite aggregates exist within each endosperm cell.

Quinoa is a native American crop that has been cultivated for centuries. Recently, interest was renewed in quinoa as a valuable food source<sup>4</sup> due to its versatility, growth requirements, and recent findings concerning the nutritive value of its protein (Mahoney et al 1975). Although Wolf et al (1950) compared some traits of quinoa starch to related cereal starches, an in-depth characterization, which was the objective of this work, was not previously reported.

## MATERIALS AND METHODS

## Starch Isolation

Mild Treatment (Crude Preparation). This procedure was based on those of Banks and Greenwood (1975) and Badenheuzen (1964). Quinoa seeds (400 g) were steeped in 1 L of  $0.1\,M$  acetate buffer (pH 6.5,  $0.01\,M$  HgCl<sub>2</sub>) under refrigeration overnight. Subsamples (approximately 80 g) were added to a Waring Blendor and agitated for 2 min. The resultant slurries were sieved through a series of sieves, the last being a U.S. standard no. 400. The combined suspensions were then centrifuged  $(2,000\times g,15\,\text{min})$  and yielded three layers: a thin white layer on top, a large grey layer, and an obviously impure dark layer on the bottom. After the bottom layer was discarded, the preparation was resuspended in distilled water. This centrifugation process was repeated five times to remove the dark layer and ionic impurities. Because segregating the top layer was exceedingly difficult, the entire preparation was dried and defatted in methanol.

Rigorous Treatment (Pure Preparation). This isolation scheme was identical to the above, except that the seeds were steeped for one week and agitated in a Waring Blendor for 10 min. The top white layer predominated and was the only one retained during centrifugation.

## Particle Size Analysis

The samples were dispersed in 4% NaCl and mixed in a Vortex mixer before analysis. Particle size distributions were obtained using a model TA-2 Coulter Counter. A 19- $\mu$ m aperture was used for the pure preparation, and multiaperture analysis (19, 280  $\mu$ m) was required for the crude preparation.

## Microscopy

Samples were dried at  $70^{\circ}$ C for 4 hr, immersed in liquid  $N_2$  for 5 min, and fractured. Specimens were glued on specimen stubs using

silver conducting tape and coated with gold-palladium. Scanning electron micrographs (SEM) were obtained using a JEOL 35 scanning electron microscope. Light magnification micrographs of endosperm sections were obtained using a Zeiss Universal microscope at  $\times 165$  magnification.

## Analysis of the Pure Preparation

The gelatinization range was obtained by viewing a 1% water dispersion that was heated at a rate of 1°C/min in an apparatus containing a heating element, a stirrer, and a calibrated thermometer. Aliquots were removed and viewed at 1°C intervals under polarized light at ×800 magnification. Amylose content was determined by the method of Juliano (1971) with previously obtained amylose and amylopectin standards (Atwell et al 1980). Differential scanning calorimetry (DSC) was performed on weighed samples (~5 mg) with an amount of water equal to twice

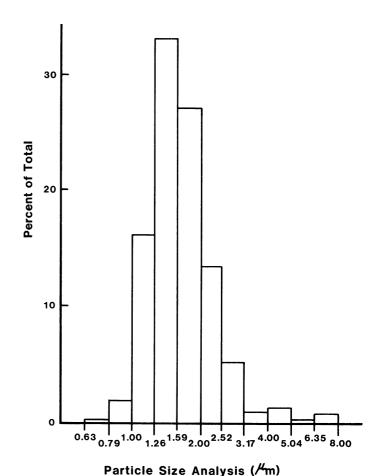


Fig. 1. Particle size distribution of pure quinoa starch preparation.

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<sup>&</sup>lt;sup>4</sup>R. W. Glass and L. A. Johnson. The revival of quinoa (*Chenopodium quinoa*, Willd.) as a food crop. Presented at the 64th Annual Meeting of the AACC, Washington, DC, October, 1979.

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the sample weight, in sealed aluminum pans that were equilibrated at room temperature for 16 hr. Thermograms were run at a heating rate of 5°C/min and a sensitivity of 0.5 mcal/sec on a Perkin-Elmer DSC-2 instrument. X-ray analysis was performed on a Seimens D500 diffractometer. The chain profile of quinoa starch was obtained by debranching with pullulanase and subjecting the digest to gel filtration on Bio-Gel P-10 as previously described (Atwell et al 1980). Total starch in effluent fractions was estimated by the glucoamylase-glucose\_oxidase method (Southgate 1976). The average chain length (CL) of the debranched starch was obtained as described by Lii and Lineback (1977) with the following modifications. Pullulanase was used to debranch, and the

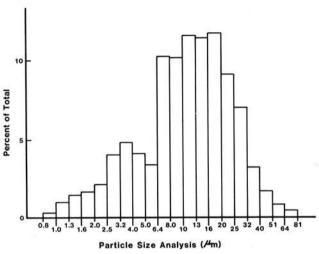


Fig. 2. Particle size distribution of crude quinoa starch preparation.

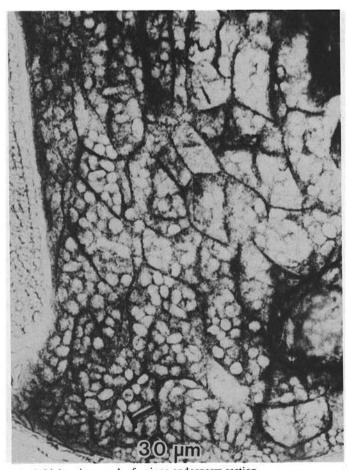


Fig. 3. Light micrograph of quinoa endosperm section.

glucoamylase-glucose oxidase method was used to determine the total starch in the sample. Amylograms were obtained by heating 8% aqueous dispersions from 35 to 95°C at a rate of 1.5°C/min, holding the paste at 95°C for 1 hr, and cooling it from 95 to 35°C at a rate of 1.5°C/min.

## RESULTS AND DISCUSSION

Figures 1 and 2 show particle size distributions of the pure and crude quinoa starch preparations, respectively. The pure preparation exhibits a normal distribution of sizes centered at about 1.5  $\mu$ m, whereas the crude preparation contains particles ranging from 0.8  $\mu$ m to more than 80  $\mu$ m in diameter. In the early stages of this research, the distribution of particle sizes in the crude preparation was considered analogous to the bimodal distribution of wheat starch granules. This was discounted when the crude sample was viewed using light microscopy (Fig. 3) and scanning electron microscopy (Fig. 4). Regularly formed compound starch aggregate was clearly present and had approximately the same dimensions as the major peak of Fig. 2. The possiblity that these aggregates were isolated, intact cells was disproven with light micrographs of thin-sectioned quinoa endosperm. Figure 5 shows that this composite species occurs within the cell.

Purity analysis yielded 0.11% protein and 0.04% ash for the pure preparation and 7.11% protein and 0.50% ash for the crude preparation. Consequently, further analyses were performed exclusively on the pure preparation. These are summarized in Table I. Quinoa starch exhibits the A X-ray diffraction pattern common to native cereal starches. DSC analysis indicates an onset temperature of 50.6°C and a ΔHg of 4.0 cal/g starch. This is very similar to the results reported by Wooten and Bamunuarchchi (1979) for wheat starch using a similar DSC method. The loss of birefringence of quinoa starch as determined by polarized light microscopy also yields a gelatinization range similar to wheat (Lii and Lineback 1977).

Although quinoa starch loses birefringence at approximately the same temperature as wheat starch, the pasting properties are considerably different. The amylograms of quinoa starch and wheat starch display substantially different viscosities at equal starch concentrations (Table I). The first measurable viscosity of

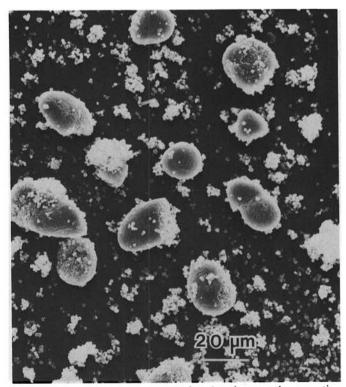


Fig. 4. Scanning electron micrograph of crude quinoa starch preparation.

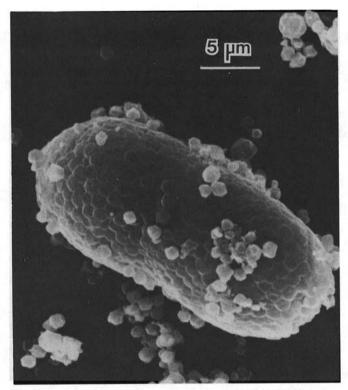


Fig. 5. Scanning electron micrograph of quinoa starch aggregate.

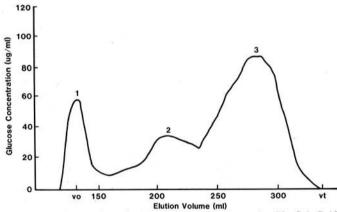


Fig. 6. Chain profile of debranched quinoa starch (Bio-Gel P-10 chromatogram).

the quinoa amylogram coincides with the temperature at which birefringence is lost. This may be attributable to a swelling of granule size concomitant with gelatinization. Throughout the curves, quinoa starch exhibits a higher viscosity than wheat starch. No loss in viscosity occurs for quinoa starch. The cooling portions of the curves indicate a comparable rate of increase in viscosity.

Further analysis of quinoa starch indicates that it has 11% amylose content, which is low in comparison to most normal cereal starches. It is comparable, however, to some varieties of rice, as reported by Williams et al (1958), who used the same procedure.

TABLE I Characterization of Ouinoa Starch

Analysis	Range	
Gelatinization	57-64° C	
Differential scanning calorimetr	у	
T onset	50.6 ± 1.8°C	
T complete	$87.8 \pm 1.4^{\circ}$ C	
ΔH gelatinization	$4.0 \pm 0.8 \text{ cal/g}$	
Amylograph viscosities <sup>a</sup>		
Initial	60°C	
At 95°C	570 BU <sup>b</sup>	
After 60 min at 95°C	790 BU	
After cooling to 35°C	1,200 BU	
X-ray diffraction pattern	Α	
Amylose content	$11.0\pm0.2\%$	
Average chain length	$27.0 \pm 2.6$	

<sup>&</sup>lt;sup>a</sup>For wheat starch: initial viscosity, 84°C; at 95°C, 210 BU; after 60 min at 95°C, 180 BU; after cooling to 35°C, 660 BU.

The  $\overline{C}L$  of 27.0 and the chain profile of debranched quinoa starch (Fig. 6) indicate that the amylopectin component is probably of similar structure to the amylopectin from other sources (Lii and Lineback 1977). Peak 1 in Fig. 6 corresponds to the amylose in the debranched quinoa starch mixture, whereas peaks 2 and 3 correspond to the long and short chains of the amylopectin component, respectively. The small size of peak 1 (amylose) relative to the size of combined peaks 2 and 3 (amylopectin) adds further substantiation to the small amount of amylose determined.

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<sup>&</sup>lt;sup>b</sup>Brabender units.