Comparison of Yield and Properties of Amaranth Starches Using Wet and Dry-Wet Milling Processes¹

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ABSTRACT

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Starches from two amaranth grains (Amaranthus hypochondriacus imesA. hybridus [K-343] and A. cruentus [K-283]) were isolated using a traditional wet-milling process and two dry-wet milling methods. The drywet methods included either a three-step or five-step abrasive milling (5-min each, in a modified barley pearler) followed by a short wet-milling to obtain starch-rich perisperm fractions. Protein content was not significantly different among starches isolated with these methods. The starch yield of the dry-wet milling was \sim 5.2% higher than that of the traditional wet-milling process. The properties of the isolated amaranth starches were

compared to those of several commercial starches. The peak viscosity of amaranth starches was lower than that of potato and waxy corn starches, but higher than that of wheat and corn starches. The amaranth starches also showed high stability during the cooking cycle. The damaged starch values of the dry-wet milled and freeze-dried starch were higher than those of the wet-milled starch; viscosity and enthalpy of gelatinization were reduced, and clarity of the cold paste was increased. The A. cruentus starch used in this study had thermal properties, apparent viscosity, and intrinsic viscosity similar to that of waxy corn starch.

Amaranth grain contains protein, lysine, fat, fiber, ash, and minerals (most notably sodium and calcium) in higher amounts than in common cereal grains. The grain is high in fiber and low in saturated fats (Carlsson 1979, Becker et al 1981). Amaranth starch is stored in the perisperm of the seeds. Amaranth starch granules are small $(1-3 \mu m \text{ diameter})$ and spherical or polygonal in shape (Saunders and Becker 1984, Irving and Becker 1985). Amaranth contains 48-62% starch and the amylose content varies (Saunders and Becker 1984). Sugimoto et al (1981) and Becker et al (1981) reported that Amaranthus hypochondriacus has amylose content averaging 7%. Starch from Amaranthus species has been reported as completely nonglutinous or nonwaxy and waxy type (Okuno and Sakaguchi 1981).

Betschart et al (1981) used a modified Strong-Scott barley pearler to separate amaranth into seed coat (hull)-germ and perisperm fractions. The hull-germ fraction could be used as a nutrient-rich ingredient similar to cereal grain brans. The perisperm fraction could be milled for flour or starting material for the isolation of starch granules. Amaranth starch can be used as a food ingredient in gravies, salad dressings, or in a variety of drinks as thickeners. At the present time, amaranth is used as a whole seed ingredient in cereal-based foods.

The objectives of this study were to isolate amaranth starch using a traditional wet-milling process and compare the results to those obtained by removal of the hull-germ outer layers with an abrasive milling followed by a modified short wet-milling. Some chemical and physical properties of amaranth starches were investigated.

MATERIALS AND METHODS

Seed Materials

Two amaranth cultivars were used, K-343 Mercado × Prima type (A. hypochondriacus X A. hybridus) (Amaranth Resources, Inc., Bricelyn, MN) and K-283 (A. cruentus) (Nu-World Amaranth, Inc., Naperville, IL). The names were abbreviated A. hypo. × hyb. and A. cruentus, respectively. Unmodified, commer-

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cial common, waxy, and high-amylose corn starches (American Maize Products, Hammond, IN); wheat and rice starches (Sigma, St. Louis, MO); and potato starches (Roquette, Gurnee, IL) were also used in the experiments to compare starch properties.

Starch Isolation

Method A (wet milling). The wet-milling method was based on the procedure of Rayas-Duarte and Rupnow (1993). Amaranth seeds (250 g) were steeped in 1 L of 0.05% sodium metabisulfite for 20 hr at 50°C. The seeds were washed, blended, and screened through U.S. standard sieves (No. 40, 100, 200, and 230, 425-, 150-, 74-, and 63- μ m, respectively). Protein was extracted with 0.2% NaOH solution and centrifuged at $1,000 \times g$ for 20 min.

Methods B and C (dry-wet milling). Abrasive milling procedures were followed by a modified short wet-milling. Amaranth seeds (250 g) were abraded three times (3×) for Method B and five times (5×) for Method C. The 5-min abrasions were performed in a modified Strong-Scott barley pearler, as described by Betschart et al (1981), using an aluminum sheet instead of a stainless steel liner. Following the abrasion step, the abraded perisperm fraction was steeped in distilled water (1:2, w/v) for 4 hr at 50°C to mellow the perisperm and toughen the residual hull (seed coat) and germ. The steeping water and perisperm were blended for 5 min. Starch slurry was screened through a U.S. No. 230 (63- μ m) sieve and centrifuged at 1,000 \times g for 20 min. The supernatant was discarded, and the sediment was slurried in 0.2% NaOH for 1 hr and centrifuged. The supernatant was discarded, and the top yellowish layer of protein was removed. The white starch layer was resuspended in distilled water and centrifuged as described above. The sediment was resuspended in distilled water, adjusted to pH 6.5-7.0 with diluted HCl, and centrifuged. The supernatant was discarded. The sediment was suspended in ~500 ml of distilled water (to facilitate handling) and freeze-dried or vacuum-filtered and air-dried under a fume hood.

Light Microscopy

After milling, the whole amaranth grain and the perisperm fractions were examined using light microscopy (40×, Nikon Microflex model AFM, Beany, CT).

Scanning Electron Microscopy

The starch samples were mounted on aluminum stubs with double-sticky tape and coated with gold-palladium (SCD 030 Balzers sputter coater, JOEL, Peabody, MA). The samples were visualized and photographed by scanning electron microscopy (JSM-35, JOEL). The size of starch granules was estimated by

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hand-measuring the diameter of one side of the polygon. A total of 40 randomly chosen granules were measured from four photomicrographs.

Chemical Analyses

Moisture, ash, protein, and oil contents were determined according to AACC methods 44-15A, 08-01, 46-13, and 30-25 (AACC 1983). Amylose content of defatted starch samples was estimated using the method of Williams et al (1970). Damaged and total starch were estimated in duplicate samples using a MegaZyme assay kit (Warriewood, Sydney, Australia) according to the method developed by Gibson et al (1992).

Thermal Properties

Thermal properties of starches were determined in two independently isolated starch samples (duplicates), using a differential scanning calorimeter (DSC, Perkin Elmer DSC7, Norwalk, CT) equipped with TAC 7/3 instrument controller and 3700 data station. Indium and deionized water were used as standards to calibrate the instrument. Starch samples (3-5 mg) were weighed into DSC aluminum pans, and deionized water was added with a microsyringe to yield starch-water ratio of 1:2. After sealing, the pan was allowed to equilibrate for 1 hr, and scanned at a rate 5°C/min. An empty pan was used as a reference. Thermal transitions of starch were defined in terms of onset (T_0) , peak (T_p) , and end gelatinization (T_e) temperatures (°C), and enthalpy of gelatinization (ΔH , J/g).

Apparent Viscosity

Apparent viscosity of starches was determined using a Brookfield viscometer (model RVT, Stoughton, MA). The starch slurry (5%, db) was cooked in a boiling water bath for 15 min and cooled to 25°C. Cold paste viscosity was determined using spindle No. 3 at 25°C, at five shear rate speeds: 5, 10, 20, 50, and 100 rpm. The stability of the paste viscosity at 50 rpm was observed at 1, 2, 3, 4, 5, 8, 10, 15, 20, and 30 min.

Intrinsic Viscosity

Intrinsic viscosity was determined at 25°C using the method of Leach (1963) for extrapolation of reduced viscosity versus specific viscosity.

Flow times of four different dilutions (0.20, 0.25, 0.33, and 0.50%) were measured at 25°C with a Ubbelohde viscometer (Cannon-Fenske, State College, PA) with a capillary size of 50. A Temp-Trol viscosity bath (Precision Scientific, Chicago, IL) was used along with an automatic viscosity timer (Wescan Instruments, Santa Clara, CA).

Pasting Properties

Brabender Visco-Amylograph. Starch-pasting properties of a 6% (db) slurry were measured with the Brabender Visco-Amylograph (model E, C.W. Brabender Instruments, South Hackensack, NJ). Starch (30 g, db) was suspended in 500 ml of deionized water. The pH was adjusted to 5.0-6.0 with 0.05N HCl. The suspension was heated at 25-95°C, held at 95°C for 15 min, and cooled to 50°C (Tipples et al 1980).

Rapid Visco Analyzer. Starch-pasting properties of a 6% (db) slurry were also measured with a Rapid Visco Analyzer (RVA-3C, Newport Scientific, Sydney, Australia). Starch (1.68 g, db) was suspended in deionized water. The pH was adjusted to 5.0-6.0 with diluted HCl. The total weight was adjusted to 28 g using distilled water. Sample temperature was equilibrated to 30°C (2 min), heated for 8 min to a maximum temperature of 95°C, and then cooled for 8 min to 50°C.

Cold Paste Clarity

After determining pasting properties with the RVA, pastes of amaranth, waxy corn, and rice starches were transferred to disposable cuvettes and cooled to room temperature (25°C). Absorbance at 720 nm was used to estimate cold paste clarity (Wrolstad 1976).

Statistical Analysis.

Analysis of variance was used to determine differences in mean values from replicate runs of each treatment (SAS 1990).

RESULTS AND DISCUSSION

Microscopic Analyses

Method C (abraded 5×) removed most of the germ ring from the samples. Similar results were reported by Betschart et al (1981) with an A. cruentus cultivar. The amaranth starch granules had an average diameter of 1 μ m and a polygonal shape similar to that of other amaranth cultivars (Saunders and Becker 1984, Irving and Becker 1985).

Starch Isolation and Chemical Analyses

Whole grain flour of A. cruentus had higher protein and ash content but lower oil content than that of A. hypo. \times hyb. (Table I). Total starch and amylose content of the two amaranth varieties used in this study did not differ significantly (P > 0.05).

Yield, ash, and protein content of the perisperm and hull-germ fractions are shown in Table II. Seeds from Method C (abraded 5×) showed significantly lower perisperm and higher hull-germ yield than seeds from Method B (abraded 3×). The results confirmed the effectiveness of an abrasive milling method in obtaining two fractions: a starch-rich perisperm fraction, and a protein/oil-rich hull-germ fraction. The average reduction of protein in the perisperm fraction was from 15.5 to 2.9% (Table II). Wet milling can be used to remove the residual protein, reducing steeping time and amount of water used. The dry-wet milling was designed to steep starch fractions instead of whole grains. Overall, the dry-wet milling method was faster; the mass weight was reduced 56-63% (Table II). This may represent important savings in the production of large amounts of amaranth starch. In wet milling, large amounts of water are used to isolate the starch in the centrifuging and sieving steps (laboratory extraction) and hydrocyclones (industrial extraction).

Among the advantages of Methods B and C over Method A are shorter steeping times (4 hr vs. 20 hr), fewer sieving steps to remove fiber (1 vs. 4), and the elimination of sodium metabisulfite. The perisperm fraction contained mostly starch. The increase of abrasive milling steps from 3 to 5 decreased the yield of the perisperm fraction, but significantly reduced the ash and protein content (Table II). Method B (3× abrasion) yielded higher ash and protein from A. hypo. \times hyb. than from A. cruentus. However, Method C (5× abrasions), yielded perisperm fractions that did not differ in ash and protein content (Table II).

TABLE I Chemical Analyses (%) of Whole Amaranth Flours^a

Whole Grain Flour	Protein ^b	Oil ^b	Ash ^b	Amylose	Total Starch ^e
$A. hypo. \times hyb.$	$14.02 \pm 0.07 \text{ b}$	$9.5 \pm 0.00 \text{ a}$	2.24 ± 0.01 b	4.53 ± 0.05	63.7 ± 1.45
A. cruentus	$16.89 \pm 0.00 \text{ a}$	$7.9 \pm 0.01 \text{ b}$	3.46 ± 0.01 a	5.69 ± 0.10	60.4 ± 0.85
$PR > F^d$	0.0005	0.001	0.0001	0.06	0.779

^a Means within column with different letters differ significantly at P < 0.05.

^bMeans of 2 replicates \pm standard error, dry basis.

Means of 3 replicates \pm standard error, dry basis.

^dP value of the F test.

Ash content was lower (P < 0.05) in Methods B and C (drywet milled starches) than it was in Method A (wet-milled starch) (Table III). Protein content of starch was similar (P > 0.05) among isolation methods and cultivars. Starch recovery from the grain and yield of total starch from the two amaranth cultivars (Table III) did not differ significantly. The starch yield of Method C (dry-wet milling) was 5.2% higher than that of the wet milling. However, starch yield of Methods B and C, (dry-wet milled, abraded $3 \times$ and $5 \times$, respectively) did not differ significantly. Using Method A (wet-milled starch), starch yields were 32.2 and 30.4%, respectively, for A. hypo. \times hyb. and A. cruentus. Similar values

TABLE II
Comparison of Yield, Ash, and Protein (%) of Dry Milling Fractions of
Amaranth Using a Strong Scott Barley Pearler

Fraction	Yield ^a	Ash ^b	Protein ^c
$A. hypo. \times hyb.$			
Perisperm			
Method B ^d	61.8 ± 0.5	0.89 ± 0.06	4.81 ± 0.15
Method C ^e	55.9 ± 0.9	0.38 ± 0.00	3.04 ± 0.03
Hull-germ			
Method B	23.6 ± 0.7	8.40 ± 0.02	36.26 ± 0.26
Method C	29.9 ± 0.7	7.84 ± 0.30	35.83 ± 0.52
A. cruentus			
Perisperm			
Method B	62.7 ± 0.4	0.59 ± 0.03	4.07 ± 0.22
Method C	57.8 ± 0.4	0.37 ± 0.02	2.70 ± 0.25
Hull-germ			
Method B	25.1 ± 0.6	8.55 ± 0.23	39.65 ± 0.01
Method C	29.6 ± 0.2	8.12 ± 0.09	38.64 ± 0.42
Effect of Method and Fracti	on		
Perisperm × Method B	62.2	0.77	4.56
× Method C	56.8	0.38	2.87
Hull-Germ × Method B	24.3	8.46	37.23
× Method C	29.7	8.03	36.53
$PR > F^f$	0.0001	0.1623	0.8874

^a Means of 6 replicates ± standard error, dry basis.

for a wet-milling method have been reported for A. hypochon-driacus (Paredes-Lopez et al 1989).

The composition of wet-milled and air-dried starches isolated from the two amaranth cultivars using Method A was compared with that of a commercial waxy corn starch (Table IV). Ash content in two cultivars was similar, while the protein content was 13-20% lower than that of the commercial waxy corn. The amylose content of the amaranth starches was low (5.8% for A. hypo. \times hyb. and 6.8% for A. cruentus), which is probably typical of all commercial amaranth grains in the United States. Total starch and oil content were not significantly different. Intrinsic viscosity of the two amaranth starches was similar; however, the values of A. hypo \times hyb. starch were lower than that of waxy corn starch, which suggested that the waxy corn starch may have a higher molecular weight.

Pasting Properties

Brabender Visco-Amylograph. The amylographs of 6% (db) slurries for two amaranth starch samples of A. hypo. \times hyb. isolated using Method A (wet-milled) and Method C (abraded 5×) (samples I and II, respectively), as well as three commercial starches are shown in Figure 1. Pasting temperature reflects the ease of cooking of the starch. Potato starch had the lowest initial pasting temperature; wheat starch had the highest. The wheat starch profile had an unusually high initial pasting temperature, which may be due to the lower (6%) slurry concentration used. A 9% concentration is generally used for wheat starch. Pasting viscosity rapidly increases with the concentration (Mazurs et al 1957). For direct comparison of pasting properties, the 6% concentration was used for all the starches in this study. The pasting temperature of amaranth starches were higher than that of potato starch and lower than those of waxy corn, corn, and wheat starches.

Peak viscosity of amaranth starch sample I (wet-milled amaranth starch) was lower than peak viscosity of potato and waxy corn starch and higher than that of wheat starch (Fig. 1). A decrease in the pasting profile viscosity was observed in sample II (dry-wet milling). A decrease of viscosity after heating to 95°C reflects the fragility of the swollen granules that first swell and then break down under continuous stirring (Tipples et al 1980). Amaranth, corn, and wheat starches showed a small decrease in viscosity, suggesting a greater stability of starch granules against

TABLE III Comparison of Ash, Protein, and Yield (%) of Amaranth Starch Fractions Using Different Isolation Methods

Fraction	Ash ^a	Protein ^b	Starch Recovery from Whole Grain ^c	Starch Yield from Total Starch ^c
$A. hypo. \times hyb.$				
Method A ^d	0.38 ± 0.10	0.02 ± 0.00	32.2 ± 1.25	50.6 ± 2.0
Method Be	0.13 ± 0.04	0.06 ± 0.02	34.4 ± 1.12	54.1 ± 1.7
Method Cf	0.11 ± 0.0	0.04 ± 0.01	37.4 ± 1.59	58.7 ± 2.5
A. cruentus				
Method A	0.14 ± 0.04	0.05 ± 0.02	30.4 ± 1.81	50.4 ± 3.0
Method B	0.11 ± 0.04	0.02 ± 0.01	39.3 ± 1.56	65.1 ± 2.6
Method C	0.08 ± 0.07	0.02 ± 0.00	34.8 ± 1.06	57.6 ± 1.8
Effect of Cultivar				
A. hypo. \times hyb.	0.22	0.04	34.8	54.7
A. cruentus	0.11	0.03	34.2	56.6
$PR > F^{f}$	0.0993	0.5151	0.5017	0.4682
Effect of Isolation Method				
Method A	0.30 a	0.03	31.6 b ^g	50.5 b
Method B	0.12 b	0.04	35.7 a	56.8 a
Method C	0.10 b	0.03	36.2 a	58.2 a
$PR > F^h$	0.0169	0.7197	0.0085	0.0083

^aMeans of 4 replicates ± standard error, dry basis.

^bMeans of 2 replicates \pm standard error, dry basis.

^c Means of 3 replicates ± standard error, dry basis.

^dAbraded three times.

^e Abraded five times.

P value of the F test.

^bMeans of 3 replicates \pm standard error, dry basis.

 $^{^{\}circ}$ Means of 5 replicates \pm standard error, dry basis.

dStarch isolated by wet-milling method.

^eStarch isolated by dry-wet milling and abraded 3×.

Starch isolated by dry-wet milling, abraded 5×.

^gMeans within column with different letters differs significantly at P < 0.05.

 $^{^{\}rm h}P$ value of the F list.

mechanical shear when compared to waxy corn and potato starches. After cooking for 15 min at 95°C, the viscosity of the amaranth starch samples was relatively stable, showing a small breakdown of the paste viscosity during cooking. Waxy corn and potato starch showed a marked thinning of the paste viscosity during the cooking period.

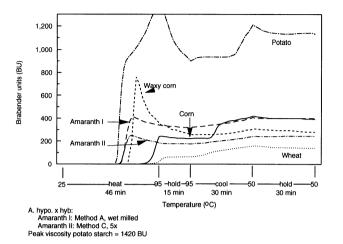


Fig. 1. Pasting curves of 6% (db) slurries for two amaranth starches and three commercial starches determined using the Brabender Visco-Amylograph.

A comparison of pasting properties of the two amaranth cultivars isolated by the three different isolation methods is shown in Table V. Peak viscosity, maximum setback viscosity, and peak temperatures of the samples were similar (P < 0.05). A. cruentus had a an average pasting temperature of 69.6° C, which was significantly higher (P < 0.05) than the average pasting temperature of A. hypo \times hyb. (67.1° C). Isolation method affected peak and setback viscosities, but it did not affect pasting and peak temperatures (Table V). Starch isolated by Methods A and B from both varieties had higher peak and maximum setback viscosities than starch isolated by Method C.

The paste viscosity of starch isolated by Method C was significantly lower for both cultivars. Method C produced a higher percentage of damaged starch (Table VI) due to mechanical damage during the abrading process, which may have affected the viscosity. However, there was no significant correlation between peak viscosity (from the Brabender Visco-Amylograph) and damaged starch (P < 0.05). Damaged starch granules absorb more water at a higher rate than native starch granules.

Peak viscosity of starches from wet-milled A. hypo \times hyb. (420 BU) and A. cruentus (423 BU) were lower than reported values for A. cruentus I and A. cruentus II and A. hypo \times hyb. (1,090, 1,115, and 1,080 BU, respectively) (Stone and Lorenz 1984). Those values were based on a starch slurry with a higher concentration (9%) than the 6% concentration used in this experiment. However, A. hypo \times hyb. and A. cruentus starches at 6% concentration had higher peak viscosity than the A. hypochondriacus (320 BU) at 9% concentration reported by Becker et al (1981). Peak viscosities of the two amaranth starches reported here are

TABLE IV
Chemical Analyses of Two Amaranth Cultivars and a Commercial Waxy Corn Starch

Fraction (%)	A. hypo. \times hyb.	A. cruentus	Waxy Corn	PR > F ^a
Ash ^b	$0.22 \pm 0.03~\mathrm{a^c}$	$0.12 \pm 0.06 \text{ ab}$	$0.02 \pm 0.01 \text{ b}$	0.0587
Protein ^d	$0.02\pm0.00~\mathrm{c}$	$0.03 \pm 0.00 \text{ b}$	$0.15 \pm 0.00 \text{ a}$	0.0001
Amylose ^e	$5.79 \pm 0.02 \text{ a}$	$6.81 \pm 0.08 \text{ a}$	$4.59 \pm 0.08 \text{ b}$	0.0001
Total starche	97.3 ± 2.21	97.5 ± 2.61	•••	0.953
Oil ^f	1.40 ± 0.02	1.23 ± 0.05	•••	0.872
Intrinsic viscosity	$1.13 \pm 0.19 \text{ b}$	$1.53 \pm 0.17 \text{ ab}$	$1.86 \pm 0.23 \text{ a}$	0.0001

^a P value of the F test.

TABLE V
Pasting Properties of Amaranth Starches from Different Isolation Methods Using Brabender Visco-Amylograph in a 6% Slurry (db)^{a,b}

Fraction	Peak Viscosity (BU)	Maximum Setback Viscosity (BU)	Pasting Temperature (°C)	Peak Temperature (°C)		
$A. hypo. \times hyb.$						
Method A ^c	$420 \pm 35 \text{ a}$	$390 \pm 25 \text{ a}$	$67.5 \pm 0.5 \text{ b}$	76.5 ± 0.5		
Method B ^d	$428\pm8~a$	$415 \pm 5 a$	$67.0 \pm 0.0 \text{ b}$	77.5 ± 0.5		
Method C ^c	253 ± 2 b	$247 \pm 2 c$	$66.7 \pm 0.3 \text{ b}$	74.3 ± 0.3		
A. cruentus						
Method A	$423 \pm 17 \text{ a}$	$415 \pm 7 a$	$69.3 \pm 1.3 \text{ ab}$	77.0 ± 1.5		
Method B	$425 \pm 20 \text{ a}$	$405 \pm 0 a$	$68.3 \pm 0.3 \text{ b}$	75.0 ± 0.0		
Method C	$302 \pm 7 \text{ b}$	$313 \pm 13 b$	$71.5 \pm 0.5 a$	78.0 ± 0.0		
$PR > F^f$	0.0005	0.0001	0.0188	0.0908		
Effect of Isolation Method						
Method A	422 a	403 a	68.4	76.7		
Method B	426 a	410 a	67.6	76.2		
Method C	273 b	273 Ь	68.6	75.8		
PR > F	0.0001	0.0001	0.4522	0.7391		

^a Means of 2 replicates ± standard error, dry basis.

^bMeans of 4 replicates ± standard error, dry basis.

^c Means within row with different letters differ significantly at P < 0.05.

^dMeans of 3 replicates \pm standard error, dry basis; amaranth (N \times 5.85), waxy corn (N \times 6.25).

 $^{^{\}circ}$ Means of 3 replicates \pm standard error, dry basis.

f Means of 2 replicates ± standard error, dry basis.

^bMeans within column with different letters differ significantly at P < 0.05.

Starch isolated by wet-milling method.

dStarch isolated by dry-wet milling, abraded 3×.

Starch isolated by dry-wet milling, abraded 5×.

P value of the F test.

lower than the 520 BU for A. paniculatus reported by Singhal and Kulkarni (1991). Again, this was due to concentration differences: 6% in this experiment compared to the 7% concentration used for A. paniculatus, a different variety of amaranth.

Rapid Visco-Analyzer

Pasting properties of amaranth and commercial starches measured by the RVA are shown in Figure 2. The RVA and Visco-Amylograph patterns were similar (Figs. 1 and 2). However, the peaks were sharper and better defined in the RVA graph. Viscosity breakdown in the RVA was faster because the shear rate was higher than that of the Visco-Amylograph. Pannozo and McCormick (1993) speculated that the larger surface area of the RVA paddle may exert higher shear force than the pin arrangement in the Visco-Amylograph.

The pasting and peak temperatures of RVA were higher than those obtained with Visco-Amylograph. This may be the effect of the heating and cooling rates, which were faster in the RVA than in the Visco-Amylograph. Similar RVA curves were obtained for both amaranth starches (Fig. 2). Cultivar and isolation method affected all measurements: peak viscosity, maximum setback viscosity, pasting temperature, and peak temperature. Drying method affected peak viscosity, maximum setback viscosity, and peak temperature, but did not affect pasting temperature. The isolation method did not affect the pasting temperature in the Visco-Amylograph (Table V), but it did affect the RVA results (Table VII).

A. cruentus had higher peak viscosity, maximum setback viscosity, pasting temperature, and peak temperature than A. hypo \times hyb. (Table VII). Starch isolated by Method A provided the highest viscosity, pasting temperature, and peak temperature. Viscosity (peak and maximum setback), pasting temperature, and peak temperature of starch isolated by Methods B and C did not differ significantly in the RVA results. In contrast, the Visco-Amylograph profiles for peak and maximum setback viscosity were the same for Methods A and B, but different for Method C (Table V).

The differences in the amount of damaged starch (Table VI) could explain the lower viscosity values from Methods B and C. The amount of damaged starch was influenced by cultivar and isolation method. Method C caused more damage than Method B. Wet milling of starch reduced mechanical damage to the granules. An increase in the number of abrasion steps (3-5) increased the level of damaged starch, which affected the viscosity. There was a linear correlation (P < 0.01) between peak viscosity determined by RVA and the level of damaged starch (R = 0.5158, R = 78). More damaged starch resulted in lower viscosity in the RVA tests. Table VI shows more damaged starch

TABLE VI

Analysis of Variance of Factors (Cultivar, Isolation, and Drying

Method) of Damaged Starch and Paste Clarity of Amaranth Starches

Factor	Damaged Starch (%)	Paste Clarity
Effect of cultivar		
A. hypo. \times hyb.	0.88 a	1.17 a
A. cruentus	0.64 b	0.37 Ь
$PR > F^b$	0.0001	0.0001
Effect of Isolation Method		
Method A ^c	0.49 c	1.18 a
Method B ^d	0.79 Ь	0.62 b
Method C ^e	0.97 a	0.35 c
PR > F	0.0001	0.0001
Effect of Drying Method		
Air-drying	0.70 b	0.81 a
Freeze-drying	0.82 a	0.61 b
PR > F	0.0001	0.0001

^a Means within column and same factor differed significantly at P < 0.05.

was caused by freeze-drying than by air-drying. This might be the effect of the change of the original arrangement of water molecules within the amylose and amylopectin molecules during freeze-drying.

The plot of peak viscosity of amaranth starches using the RVA and Visco-Amylograph showed that the correlation of peak viscosity of the two amaranth samples differed (P < 0.01) and the linear correlation coefficient for the relationship was high (R = 0.9055, n = 17).

Cold Paste Clarity

A. cruentus gave a clearer cold paste than did A. hypo \times hyb. (Table VI). Paste clarity values for Method C were higher than those from Methods B or A) (Table VI). Freeze-dried starches yielded clearer cold paste than air-dried starches. These differences may be due to the effect of damaged starch. Highly damaged starches resulted in clearer pastes. Meuser et al (1978) reported that increased ball-milling time of corn starch increased its solubility by producing highly damaged starch.

Cold paste of A. cruentus had a clarity similar to that of waxy corn. The cold paste of A. $hypo \times hyb$. was opaque, except for the starches isolated by Method C. Singhal and Kulkarni

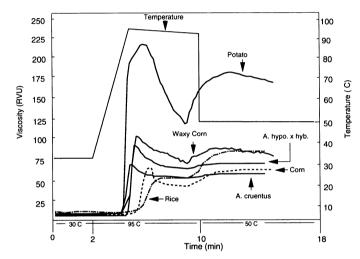


Fig. 2. Pasting properties of 6% (db) slurries for two amaranth starches and five commercial starches determined using the Rapid Visco-Analyzer

TABLE VII

Analysis of Variance of Factors (Cultivar, Isolation Method, and Drying Method) of Amaranth Starch Pasting Profiles
Using Rapid-Visco Analyzer in a 6% Slurry (db)^a

Factors	Peak Viscosity (RVU)	Maximum Setback Viscosity (RVU)	Pasting Temperature (°C)	Peak Temperature (°C)
Effect of cultivar				
A. hypo. \times hyb. a	59.0 b	50.9 b	78.4 b	90.7 b
A. cruentus a	69.7 a	59.6 a	82.3 a	92.9 a
$PR > F^b$	0.0121	0.0020	0.0001	0.0001
Effect of Isolation F	actor			
Method A ^c	75.2 a	62.1 a	81.5 a	92.6 a
Method B ^d	60.3 b	54.3 b	80.5 b	91.5 b
Method C ^e	59.8 b	51.7 b	80.2 b	91.9 ab
PR > F	0.0115	0.0055	0.0001	0.0178
Effect of Drying Me	thod			
Air-drying	74.5 a	63.1 a	81.1	92.7 a
Freeze-drying	52.6 a	46.4 b	80.1	91.2 b
PR > F	0.0001	0.0001	0.3964	0.0018

^a Means within row and same factor differ significantly at P < 0.05.

^bP value of the F test.

^cStarch isolation by wet-milling method.

^dStarch isolated by dry-wet milling, abraded 3×.

^eStarch isolated by dry-wet milling, abraded 5×.

 $^{^{\}rm b}P$ value of the F test.

^cStarch isolated by wet-milling method.

^dStarch isolated by dry-wet milling, abraded 3×.

^cStarch isolated by dry-wet milling, abraded 5×.

(1990) reported that A. paniculatus starch (0.5-5.0% concentration) had lower paste clarity than corn starch.

Thermal Properties

Thermal properties of two wet-milled (Method A) amaranth starches and five commercial starches are shown in Table VIII. The ΔH (20.2 J/g) of A. hypo \times hyb. was higher (P < 0.05) than that of A. cruentus (11.7 J/g). The $T_{\rm o}$, $T_{\rm p}$, and $T_{\rm e}$ of A. hypo \times hyb. were lower than those of A. cruentus.

Isolation method affected the ΔH , $T_{\rm o}$, and $T_{\rm p}$ (Table IX). Method A caused a higher ΔH and $T_{\rm p}$ than Methods B and C.

Drying method affected ΔH but not T_0 , T_p , and T_e . Values reported for A. hypochondriacus were: ΔH (1-3.4 cal/g); T_0 (59-68°C); T_p (67-75°C), and T_e (76-82°C) (Tomita et al 1981, Konishi et al 1985, Barba de la Rosa et al 1989). Values reported for A. caudatus were: ΔH (1.2-1.6 cal/g), T_0 (56-57°C), and T_e (63-65°C) (Tomita et al 1981, Konishi et al 1985). The ΔH (4.8 cal/g) of A. hypo \times hyb. starch from wet milling was higher

than that reported in the literature for A. hypochondriacus starch (Tomita et al 1981, Konishi et al 1985, Barba de la Rosa et al 1989); the gelatinization temperatures were within range. However, the values for ΔH , $T_{\rm o}$, $T_{\rm p}$, and $T_{\rm e}$ were higher for A. hypo \times hyb. than for A. cruentus. ΔH , $T_{\rm p}$, and $T_{\rm e}$ values of A. cruentus are within the range of data reported. However, $T_{\rm o}$ of the same starch type was higher.

Apparent Viscosity

Apparent viscosity of the starch from the two amaranth cultivars and that of the waxy corn decreased when shear rate increased from 5 to 10, 20, 50, and 100 rpm (Table X). This typical decrease in viscosity with an increase in rotational speed indicates shear thinning behavior. Paste viscosities of both amaranth starches had more stability than that of waxy corn. However, the cold paste viscosity of A. cruentus was higher (P < 0.01) than that of A. hypo \times hyb. (Table X), but lower than that of waxy corn. Singhal and Kulkarni (1990) reported a higher viscosity for A.

TABLE VIII
Comparison of Thermal Properties of Amaranth and Commercial Starches^a

Starch	$\Delta H \ ({f J/g})$	ΔH^{b} (cal/g)	<i>T</i> _o (°C)	Т _р (°С)	T _e (°C)
A. hypo. \times hyb. c	$20.2 \pm 0.6 \text{ a}$	4.8	$63.3 \pm 0.1 \text{ c}$	$67.8 \pm 0.1 \text{ b}$	$75.9 \pm 1.7 \text{ bc}$
A. cruentus ^c	$11.7 \pm 0.6 \text{ cb}$	2.8	$69.1 \pm 0.1 a$	$72.0 \pm 0.2 \text{ a}$	$79.3 \pm 3.0 \text{ ab}$
Waxy corn	$11.2 \pm 0.6 \text{ cd}$	2.7	$68.6 \pm 0.1 \text{ ab}$	$73.5 \pm 0.1 \text{ a}$	$82.2 \pm 2.5 \text{ a}$
Corn	$9.4\pm0.7~\mathrm{d}$	2.2	$67.6 \pm 0.3 \text{ b}$	$72.1 \pm 0.1 \text{ a}$	79.1 ± 0.7 ab
Rice	$18.9 \pm 0.4 a$	4.5	$57.3 \pm 0.7 d$	$74.6 \pm 1.8 \text{ a}$	$81.0 \pm 2.5 \text{ ab}$
Potato	$13.7 \pm 0.5 \text{ b}$	3.3	$63.1 \pm 0.2 \text{ c}$	$66.5 \pm 0.1 \text{ b}$	$72.3 \pm 0.0 \text{ cd}$
Wheat	$5.2 \pm 0.7 \text{ e}$	1.2	$62.2 \pm 0.6 \text{ c}$	$66.1 \pm 0.4 \text{ b}$	$69.3 \pm 0.4 \mathrm{d}$
$\frac{PR > F^d}{}$	0.0001	• • •	0.0001	0.0009	0.0079

^a Means of 2 replicates \pm standard error. Means within column with different letters differ significantly at P < 0.01.

TABLE IX
Analysis of Variance of Factors (Cultivar, Isolation Method, and
Drying Method) for Thermal Properties of Amaranth Starches^a

Factor	ΔH (J/g)	(°C)	T _p (°C)	T _e (°C)	
Effect of cultivar					
A. hypo. \times hyb.	18.1 a	61.7 b	66.7 b	75.5 b	
A. cruentus	9.8 b	69.1 a	72.3 a	80.1 a	
$PR > F^b$	0.0001	0.0001	0.0001	0.0001	
Effect of Isolation Method					
Method A ^c	15.7 a	66.8 ab	70.5 a	78.9	
Method B ^d	13.7 b	64.9 ab	69.2 b	77.9	
Method C ^e	12.8 b	64.7 b	68.9 b	76.8	
PR > F	0.01	0.0016	0.0119	0.1927	
Effect of Drying Method					
Air-drying	15.3 a	65.6	69.7	77.6	
Freeze-drying	12.7 b	65.1	69.3	78.0	
PR > F	0.0002	0.6285	0.663	0.4245	

^a Means within column and same factor differ significantly at P < 0.05.

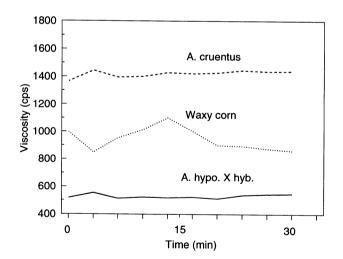


Fig. 3. Cold paste viscosity of 5% (db) slurries for two amaranth starches and waxy corn starch determined using a Brookfield viscometer with spindle No. 3, at 25°C, at 50 rpm.

TABLE X

Effect of Mechanical Shear on the Cold Paste Viscosity (25°C) of Amaranth and Waxy Corn Starches Using Brookfield Viscometer

	Viscosity, cps ^b					
Starch	5 rpm	10 rpm	20 rpm	50 rpm	100 rpm	
A. hypo. \times hyb.	$2,400 \pm 577$	$1,458 \pm 297$	893 ± 17	513 ± 95	338 ± 61	
A. cruentus	$4,913 \pm 366$	$3,103 \pm 205$	$2,102 \pm 138$	1.230 ± 82	848 ± 62	
Waxy corn	$5,647 \pm 451$	$3,523 \pm 448$	$2,155 \pm 285$	1.189 ± 169	768 ± 130	
Accuracy of viscometer	± 325	± 225	± 175	± 145	± 135	

^a Means of 4 replicates ± standard error.

 $^{^{}b}1 \text{ cal} = 4.184 \text{ J (Voet and Voet 1990)}.$

^c Method A (wet milling) and air-dried starches.

^dP value of the F test.

^bP value of the F test.

^cStarch isolated by wet milling method.

dStarch isolated by dry-wet milling abraded 3×.

^eStarch isolated by dry-wet milling, abraded 5×.

^bBrookfield Viscometer RVT model, using spindle No. 3.

paniculatas than for corn starch at 5% concentration using spindle No. 2 at 50 rpm.

The paste viscosity at 5% (dwb) of the two amaranth starch samples and waxy corn starch, at constant rate (50 rpm) and temperature (25°C), showed a higher viscosity for the A. cruentus (Fig. 3). A. $hypo \times hyb$. starch had the lowest viscosity. Both amaranth starch samples showed stability during the 30-min test.

CONCLUSIONS

Dry-wet milling gave a higher starch yield and required less time to isolate starch than wet milling. The dry-wet milled starches had lower viscosity and enthalpy, showed more damaged starch, and formed clearer pastes than wet-milled starches. The clearer pastes may be a useful property for specific applications.

Dry-wet milled starch isolated by Methods B and C provided similar starch yield, starch purity, pasting properties (RVA), and thermal properties. However, Method B used less energy and time than Method C.

The two cultivars of amaranth showed different properties. A. cruentus had thermal properties, intrinsic viscosity, apparent viscosity, and clarity of cold paste that were similar to that of waxy corn starch. The properties of A. $hypo \times hyb$. differed significantly from that of waxy corn.

LITERATURE CITED

- AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1983. Approved Methods of the AACC, 8th ed. Method 08-01, approved April 1961, revised October 1981; Method 30-25, approved April 1961, revised October 1976, October 1981, October 1991; Method 44-15A, approved October 1975, revised October 1981; Method 46-13, approved October 1976, reviewed October 1982, revised October 1986. The Association: St. Paul, MN.
- BARBA DE LA ROSA, A. P., PAREDES-LÓPEZ, O., CÁRABEZ-TREJO, A., and ORDORICA-FALOMIR, C. 1989. Enzymatic hydrolysis of amaranth flour—Differential scanning calorimetry and scanning electron microscopy studies. Starch/Staerke 41:424.
- BECKER, R., WHEELER, E. L., LORENZ, K., STAFFORD, A. E., GROSJEAN, O. K., BETSCHART, A. A., and SAUNDERS, R. M. 1981. A compositional study of amaranth grain. J. Food Sci. 46:1175.
- BETSCHART, A. A., IRVING, D. W., SHEPHERD, A. D., and SAUNDERS, R. M. 1981. Amaranthus cruentus: Milling characteristics, distribution of nutrients within seed components, and the effects of temperature on nutritional quality. J. Food Sci. 46:1181.
- CARLSSON, R. 1979. Quantity and quality of *Amaranthus* grain from plant in temperature, cold and hot, and subtropical climates. A review. Rodale Press: Emmaus, PA.
- GIBSON, T. S., AL QUALLA, H., and McCLEARY, B. V. 1992. An improved enzymatic method for the measurement of starch damage in wheat flour. J. Cereal Sci. 15:15.
- IRVING, D. W., and BECKER, R. 1985. Seed structure and composition

- of potential new crops. Food Microstructure 4:43.
- KONISHI, Y., NOJIMA, H., OKUNO, K., ASAOKA, M., and FUWA, H. 1985. Characterization of starch granules from waxy, nonwaxy, and hybrid seeds of *Amaranthus hypochondriacus* L. Agric. Biol. Chem. 49:1965
- LEACH, H. W. 1963. Determination of intrinsic viscosity of starches. Cereal Chem. 40:593.
- MAZURS, E. G., SCHOCH, T. J., and KITE, F. E. 1957. Graphical analysis of the Brabender viscosity curves of various starches. Cereal Chem. 34:141.
- MEUSER, F., KLINGLER, R. W., and NIEDIEK, E. A. 1978. Characterization of mechanically modified starch. Starch/Starcke 30:376.
- OKUNO, K., and SAKAGUCHI, S. 1981. Glutinous and non-glutinous starches in perisperm of grain amaranths. Cereal Res. Comm. 9:305.
- PANOZZO, J. F., and McCORMICK, K. M. 1993. The rapid viscoanalyzer as a method of testing for noodle quality in wheat breeding program. J. Cereal Sci. 17:25.
- PAREDES-LÓPEZ, O., SCHEVENIN, M. L., HERNÁNDEZ-LÓPEZ, D., and CÁRABEZ-TREJO, A. 1989. Amaranth starch—Isolation and partial characterization. Starch/Staerke 41:205.
- RAYAS-DUARTE, P., and RUPNOW, J. H. 1993. Effect of gamma irradiation on some physical properties of dry bean (*Phaseolus vulgaris*) starch. J. Food Sci. 58(2):389.
- SAS. 1990. SAS/STAT User's guide, Version 6, 4th ed., Vol. 2, SAS Institute: Cary, NC.
- SAUNDERS, R. M., and BECKER, R. 1984. Amaranthus: A potential food and feed resource. Page 357 in: Advances in Cereal Science Technology, Vol 5. Y. Pomeranz, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.
- SINGHAL, R. S., and KULKARNI, P. R. 1990. Some properties of *Amaranthus paniculatus* (Rajgeera) starch pastes. Starch Staerke 42:5 SINGHAL, R. S., and KULKARNI, P. R. 1991. Studies on cross-linked *A. paniculatus* (Rajgeera) starch. Starch/Staerke 43:15.
- STONE, L. A., and LORENZ, K. 1984. The starch of *Amaranthus*—Physico-chemical properties and functional characteristics. Starch/Staerke 36:232
- SUGIMOTO, Y., YAMADA, K., SAKAMOTO, S., and FUWA, H. 1981. Some properties of normal and waxy-type starches of *Amaranthus hypochondriacus* L. Starch/Staerke. 33:112.
- TIPPLES, K. H., D'APPOLONIA, B. L., DIRKS, B. M., HERT, R. F., KITE, F. E., MATSUO, R. R., PATTON, J., RANUM, P., SHUEY, W. C., and WEBB, B. D. 1980. Uses and Applications. Page 12 in: The Amylograph Handbook. W. C. Shuey and K. Tipples, eds. Am. Assoc. Cereal Chem.: St. Paul, MN.
- TOMITA, Y., SUGIMOTO, Y., SAKAMOTO, S., and FUWA, H. 1981. Some properties of starches of grain amaranths and several millets. J. Nutr. Sci. Vitaminol. 27:471.
- VOET, D., and VOET, J. G. 1990. Thermodynamic principles: A review. Page 42 in: Biochemistry. John Wiley & Sons: New York.
- WILLIAMS, P. C., KUZINA, F. D., and HLYNKA, L. 1970. A rapid colorimetric procedure for estimating the amylose content of starches and flour. Cereal Chem. 47:411.
- WROLSTAD, R. E. 1976. Color and pigment analyses in fruit products. Stn. Bull. 624. Agric. Exp. Stn, Oregon State University: Corvallis, OR.

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