Preparation of Granular Cold-Water-Soluble Starches by Alcoholic-Alkaline Treatment[1]

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ABSTRACT

Granular cold-water-soluble starches were prepared by an alcoholic-alkaline treatment. Native starches were treated with mixtures of ethanol and NaOH solution to swell starch granules. The treated starches were then neutralized with HCl, washed, and dried at 80°C for 3 hr. The method was effective with a wide variety of starches, including normal, high-amylose, and waxy starches. The efficacy of the method depended mainly on starch variety, concentration of ethanol and NaOH, and reaction temperature. Different reaction conditions gave products different properties. Lesser concentrations of ethanol, greater concentrations of NaOH, or higher reaction temperatures gave the resulting starches better cold-water solubility. The resulting starches displayed cold-water solubility of ~70–90%. A trace amount of small molecules, mainly amylose, was leached out in the supernatant during the preparation. Total weight losses were ~0.01, 0.4, and 1.9% for waxy maize, normal maize, and high-amylose maize starches, respectively.

Cold-water-soluble starches, which provide important functional properties to many instant foods, are being developed to expand the usefulness of starch for industrial applications. Pregelatinized starch is an example. Traditional methods of preparing pregelatinized starches include drum drying, extrusion, and cooking followed by spray drying (Powell 1967). However, compared with cook-up starches, pregelatinized starches showed more graininess, less sheen, and less flexibility to processing conditions. Therefore, the textures of instant foods made with pregelatinized starches cannot match the quality of those made with cook-up starches.

In the past decades, efforts have been made to develop granular starches that will dissolve or swell in cold water. Granular cold-water-soluble (GCWS) starches exhibit a smooth texture and have properties similar to those of cook-up starches. Pitchon et al (1981) described a process for preparing GCWS starch using a spray-dryer fitted with two fluid nozzles. The starch slurry was atomized into an enclosed chamber from one of the nozzles, and steam was injected into the chamber from the other nozzle at the same time to cook the starch. The cooked starch granules were moving rapidly and left the chamber in a subsequent spray-drying process. The starch granules with indented spheres swelled upon rehydration. GCWS starches were also produced by subjecting normal starch, slurried in aqueous alcohol, to high-temperature and high-pressure conditions (Eastman and Moore 1984, Jane et al 1986). The resulting GCWS starch exhibited at least 50% cold-water solubility. The method did not convert waxy starch into GCWS starch because waxy starch tended to gelatinize during the treatment. However, Eastman (1987) successfully conducted a similar treatment with a starch composition including at least two starches: waxy and normal starches. Rajagopalan and Seib (1991, 1992) described a method of preparing GCWS starches by heating a starch slurry in a mixture of water and polyhydric alcohol at atmospheric pressure. The resulting products have cold-water solubilities of 70–95%.

However, these methods cannot be applied to high-amylose or waxy starch alone. Recently, Jane and Seib (1991) proposed an alcoholic-alkaline treatment for preparing GCWS starches that was applicable to waxy and high-amylose starches. The method treats starches with mixtures of ethanol and alkali, primarily NaOH, to swell starch granules. The treated starches are then neutralized with HCl, washed, and dried at 80°C.

Objectives of this study were to investigate mechanisms of the alcoholic-alkaline treatments and to improve the method for industrial application. Parameters of alcohol, alkali concentrations, and temperature effects were also studied.

MATERIALS AND METHODS

Materials

Normal maize starch was purchased from Sigma Chemical Company (St. Louis, MO). Waxy maize starch was a gift of American Maize-Products Company (Hammond, IN). High-amylose maize starches (Hylon V [HA5] and Hylon VII [HA7]) were gifts of National Starch and Chemical Company (Bridgewater, NJ). Crystalline *Pseudomonas* isoamylase (EC 3.2.1.68) was a product of Hayashibara Shoji, Inc. (Okayama, Japan). The enzyme was used without further purification. Other chemicals were all reagent grade and were used without further treatment.

Preparation of GCWS Starches

GCWS starches were prepared by treating starches with mixtures of ethanol and NaOH solution (3*M*) at different proportions and at different temperatures, 25 and 35°C. Amylose intertwines with amylopectin (Jane et al 1992, Jane et al 1986) and preserves the integrity of starch granules. Without amylose, waxy starch is fragile and tends to disperse during processing. Therefore, different processes were developed for waxy starch and other starches (normal, HA5, and HA7).

GCWS normal maize, HA5, and HA7 starches. Starches (100 g, dsb) were suspended in 400–700 g of ethanol solution (40%, w/w) in a 3,000-ml beaker equipped with a mechanical stirrer. NaOH solution (3*M*, 220–500 g) was weighed and added at ~4 g/min. The mixtures were then allowed to stand for 15 min with gentle stirring. Additional ethanol solution (40%, w/w) was added slowly to the starch suspension. After 10 min of stirring, the slurry was left at room temperature until the starch granules were settled on the bottom. The supernatant was carefully separated and subjected to analyses of total soluble starch and molecular size distribution of the soluble starch. Fresh ethanol solution (40%, w/w) was used to wash the starch. After being washed, the starch was resuspended in aqueous ethanol solution (40%, w/w) and neutralized with HCl (3*M* in absolute ethanol). The neutralized starch was washed with ethanol solutions of 60 and 95%. It was then dehydrated with absolute ethanol and dried in an oven at 80°C for 3 hr. The dried starch was sieved with a 212-μm screen and stored in a screw-capped bottle at room temperature for

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further analyses.

GCWS waxy maize starch. Starch (100 g, dsb) was suspended in 400–700 g of absolute ethanol in a 3,000-ml beaker equipped with a mechanical stirrer. After addition of 200 g of aqueous NaOH (3*M*) solution, 100 g of ethanol solution (80%, w/w) was added, and an additional 120 g of NaOH solution (3*M*) was slowly added. The mixture was stirred for 15 min, and additional ethanol solution (80%, w/w) was added slowly. The slurry was allowed to stand for another 10 min with gentle stirring and then washed. The modified starch was collected and washed with ethanol solution (80%, w/w). After being resuspended in sufficient ethanol solution (80%, w/w) and neutralized with HCl (3*M* in absolute ethanol), the starch was rinsed with 95% ethanol solution, dehydrated with absolute ethanol, and dried in an oven at 80°C for 3 hr. The dried starch was sieved with a 212-μm screen and stored in a screw-capped bottle at room temperature for further analyses.

Different treatments with varied concentrations of alkali and alcohol were used to investigate the effects of those parameters on the properties of the GCWS starches. A summary of the treatments is listed in Table I. Reaction temperatures were set at 25 or 35°C to investigate the temperature effect on the preparation of GCWS starches.

Gel-Permeation Chromatography

The supernatant from the preparation process was neutralized and concentrated. Total carbohydrate content of the concentrate was determined (Dubois et al 1956). Molecular weight of the soluble starch in the supernatant was determined by gel-permeation chromatography (GPC) (Jane and Chen 1992). The samples were solubilized by using dimethyl sulfoxide (DMSO, 90%), precipitated with alcohol, redissolved in boiling water, and injected into a 2.6 × 80-cm column packed with Sepharose CL-2B gel (Pharmacia Inc., Piscataway, NJ). Samples were eluted in ascending direction. Distilled water containing 25 m*M* NaCl and 1 m*M* NaOH was used as an eluant at a flow rate of 30 ml/hr. Fractions of 4.8 ml per cup were collected and analyzed for total carbohydrate (Dubois et al 1956) and blue value (Juliano 1971) using an Autoanalyzer II (Technicon Instruments Corp., Elmsford, NY).

Isoamylase Debranching Reaction of Soluble Starch

An adequate amount of the supernatant concentrate was subjected to an isoamylase debranching reaction by the method reported by Jane and Chen (1992). Molecular size distribution of the soluble starch before and after the enzyme treatment was determined by GPC (Bio-Gel P-6 column) (Jane and Chen 1992).

Cold-Water Solubility

Cold-water solubility of the GCWS starch was determined by the method of Eastman and Moore (1984). Distilled water (100 ml) was precisely measured and transferred into a blender jar (Hamilton Beach model 609-4). A starch sample (1 g, dsb) was carefully weighed and added into the blender operated at a low speed. After all the sample had been added, the blender was switched to a high speed for 2 min. The starch suspension was then transferred to a 250-ml centrifuge bottle and centrifuged at 1,200 × *g* for 15 min. A 25-ml aliquot of the supernatant was transferred to a tared petri dish and dried in an oven at 110°C for 4 hr. The cold-water solubility was calculated by the equation:

$$\text{CWS (\%)} = \frac{\text{grams of solids in supernatant} \times 4}{\text{grams of sample}} \times 100\%$$

Fractionation of Amylopectins of HA5 and HA7 Starches

Starch samples (7.5 g) wetted with distilled water (12.5 ml) were dissolved in DMSO (112.5 ml). The solution was heated at 96°C for 1 hr with constant stirring and was stirred for additional 24 hr at room temperature. The dissolved starch was then precipitated with ethanol, redispersed in distilled water to make a 1.33% aqueous solution, and fractionated (Schoch 1942, Jane and Chen 1992). The fractionated amylopectin was subjected to a debranching reaction by isoamylase as described earlier.

Amylopectin Branch Chain-Length

Branch chain-length of the debranched amylopectins were analyzed by GPC (Bio-Gel P-6 column) (Jane and Chen 1992) and high-performance anion-exchange chromatography (HPAEC) (DX-300 system, Dionex, Sunnyvale, CA) equipped with a pulsed amperometric detector (PAD). The HPAEC system consists of an amperometric flow-through cell with a gold working electrode and a silver-silver chloride reference electrode and a potentiostat. The debranched sample solution was filtered through a 0.45-μm membrane (Supor 450, Gelman Sciences, Ann Arbor, MI). The filtrate (25 μl) was injected and analyzed. A Dionex CarboPac PA1 column (4 × 250 mm) with a guard column was used for the analysis. The pulsed potentials and durations were $E_1 = 0.05$ V ($t_1 = 480$ msec); $E_2 = 0.60$ V ($t_2 = 120$ msec); and $E_3 = -0.60$ V ($t_3 = 60$ msec) at range 2 (sampling periods, 200 msec). The eluant gradient (flow rate 1 ml/min) was: 75% of A and 25% of B at 0 min, and 100% of B at 70 min. Elueat A (150 m*M* sodium hydroxide solution) and eluant B (150 m*M* sodium hydroxide in 500 m*M* sodium acetate solution) were degassed by a Dionex degas module with helium gas. The system was equilibrated with 75% of eluant A and 25% of eluant B for 10 min. Total running time for collecting data was 80 min.

Scanning Electron Microscopy

Scanning electron micrographs were taken by a JEOL JSM-35 scanning electron microscope (JEOL Ltd., Tokyo, Japan). The starch sample was sprinkled on metallic tape (3M, St. Paul, MN) mounted on a brass disc and coated with platinum-palladium alloy (60:40).

RESULTS AND DISCUSSION

Cold-water solubility of the GCWS starch was dependent upon starch variety. Results showed that the cold-water solubilities of

TABLE I
Alcoholic-Alkaline Treatments for Preparing Granular Cold-Water-Soluble Starches

	Proportions (w/w)			
Treatment	Starch (dsb)	H_2O	100% EtOH	3*M* NaOH
A1	1.0	4.2	2.8	3.5
A2	1.0	4.2	2.8	4.5
A3	1.0	4.2	2.8	5.0
B	1.0	2.8	4.2	5.0
C	1.0	0.0	7.0	3.2
D1	1.0	2.4	1.6	2.2
D2	1.0	2.4	1.6	5.0

TABLE II
Cold-Water Solubility of Granular Cold-Water-Soluble Starches Prepared Under Various Conditions

Starch	Alcoholic-Alkaline Treatment	Reaction Temperature (°C)	Cold-Water Solubility (%)[a]
Waxy maize	A3	25	Gelatinized
Normal maize	A3	25	22.5 ± 3.5
HA5	A3	25	90.3 ± 2.1
HA7	A3	25	50.0 ± 2.0
Normal maize	B	25	11.7 ± 3.1
HA5	B	25	78.3 ± 2.5
HA7	B	25	37.0 ± 3.6
Normal maize	A3	35	84.3 ± 0.4
HA5	A3	35	93.3 ± 2.4
HA7	A3	35	78.1 ± 1.6
Waxy maize	C	25	93.7 ± 2.8
Normal maize	D1	25	41.9 ± 2.3
Normal maize	D2	25	60.4 ± 2.4

[a] Data shown as mean ± standard deviation of duplicate samples.

the GCWS normal maize, HA5, and HA7 starches were ~84, 93, and 78%, respectively, for the A3 treatment (35°C; 7× 40% ethanol solution and 5× of 3*M* NaOH solution) (Table II). The solubility difference could be attributed to the differences in amylose contents, which were 28, 54, and 68%, respectively, for normal maize, HA5, and HA7 (Lineback 1984, Takeda et al 1989) and to different crystalline structures of the starches.

Amylose was reported to intertwine with amylopectin to prevent dispersion of starch granules during heating in aqueous alcohol solution (Lindqvist 1979, Jane et al 1986). Jane et al (1992) and Kasemsuwan and Jane (1994) also reported that amylose interspersed among amylopectin in normal starch granules. Banks et al (1973) reported that the forces holding the molecules within the starch granule tend to increase as the apparent amylose content increases. As a result, waxy maize starch, containing no amylose and having short branch-chains, dispersed during the A3 treatment at 25°C (Table II). Normal maize starch, consisting of 28% amylose, retained its granular structure throughout the process.

At 25°C, both of the GCWS high-amylose starches (HA5 and HA7) exhibited greater cold-water solubilities (90 and 50%, respectively) than did GCWS normal maize starch (22%) prepared by the same treatment (Table II). This could be attributed to their crystalline structures. It is well documented that the crystalline structure of A-type starches has a close-packed arrangement, whereas that of B-type starches has space in the unit cell (Sarko and Wu 1978, Imberty and Pérez 1988). Therefore, the structure of the A-type starches is more stable and more resistant to the treatment (Gidley 1987, Zobel 1992, Lii and Lee 1993). Consequently, at a given condition, GCWS starch prepared from normal maize starch that has an A-type crystalline structure has a lesser cold-water solubility than those prepared from high-amylose maize starches.

The solubility of GCWS HA7 was less than that of GCWS HA5. The difference of cold-water solubility between the two starches was of interest. Molecular structures of both starches were investigated to reveal mechanisms of the solubility difference. Branch chain-length distributions of both HA5 and HA7 amylopectins after isoamylase treatment were analyzed by GPC (Bio-Gel P-6 column) (Fig. 1) and HPAEC with a PAD detector (Fig. 2). HPAEC peaks of chain-length ≤ DP 7 were identified by comparison with known standards; peaks of > DP 7 were counted as higher homologes (Suzuki et al 1992). The profile showed that HA5 had more long branch-chains than did HA7. Long branch chains contributed to a B-type X-ray diffraction pattern (Hizukuri et al 1983, Hizukuri 1985). Because HA5 starch has long branch-chains, it should have a more favorable crystalline structure for conversion during the treatment, and it did demonstrate a greater cold-water solubility greater than that of GCWS HA7 starch.

Cold-water solubility of the GCWS starch varied with the concentration of ethanol in the reaction mixture. The cold-water solubility of the GCWS starches decreased from 23 to 12% (Table II) when normal maize starch was subjected to A3 and B treatments, where the ethanol concentration increased from 2.8× to 4.2× (equivalent to 40–60% alcohol, w/w, at 25°C). Similar trends were also found in GCWS HA5 and HA7 starches, which decreased from 90 to 78% and from 50 to 37%, respectively. High concentrations of ethanol in the reaction mixture restricted granule swelling and retarded dissociation of the native, double-helical structure. Consequently, the cold-water solubility of the GCWS starches decreased.

Alkalinity of the reaction mixture was another important factor for the cold-water solubility of the GCWS starches. Results showed that, while other conditions were held constant, treatments with a greater volume of NaOH solution (3*M*) produced GCWS starches with a greater cold-water solubility (Table II). When normal maize starch was subjected to the D1 treatment at 25°C, in which 4× of 40% ethanol solution and 2.2× of 3*M* NaOH solution were used, the cold-water solubility of the resulting GCWS starch was ~42%. However, with the D2 treatment, in which alkaline solution was increased from 2.2× to 5.0×, the cold-water solubility increased to 60%. Similar effects were found with the samples produced at 35°C. All these effects may be attributed to the extent of starch swelling during the treatment. Treatments with greater NaOH concentrations increased the swelling of the granules (Leach 1965, Lancaster and Conway 1968). Therefore, the resulting GCWS starches had a greater cold-water solubility.

Raising the reaction temperature had a progressive effect on the cold-water solubility of the GCWS starches (Table II). Lancaster and Conway (1968) reported an exponential relationship between temperature and the swelling rate of starch granules in NaOH solution. When starch granules swell to a greater extent,

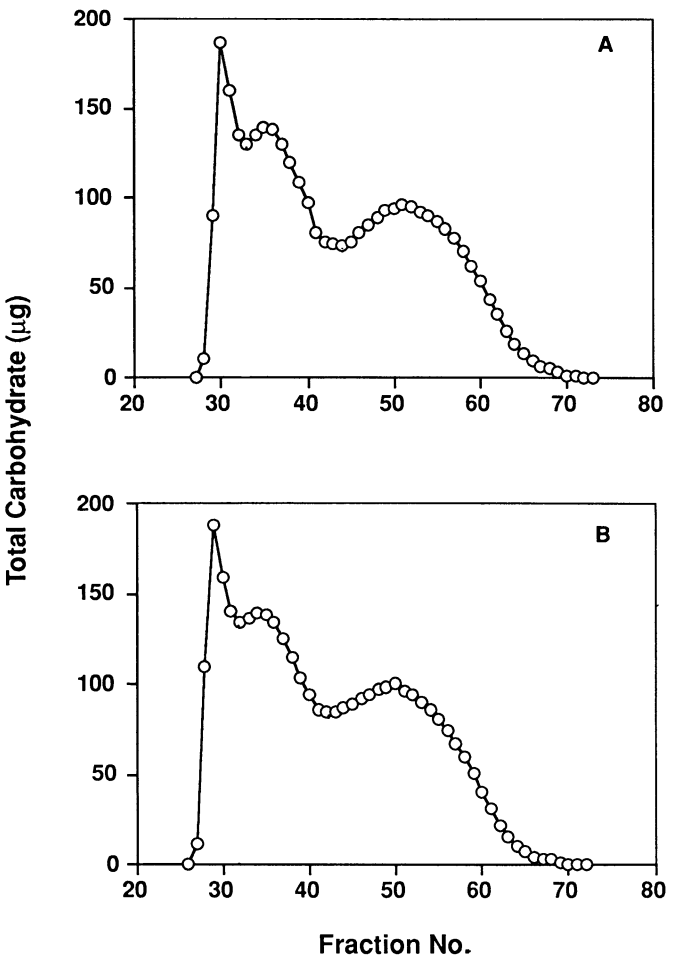

Fig. 1. Branch chain-length of the debranched HA5 (**A**) and HA7 (**B**) amylopectins analyzed by gel-permeation chromatography (Bio-Gel P-6 column; eluant, deionized water; flow rate, 21 ml/hr).

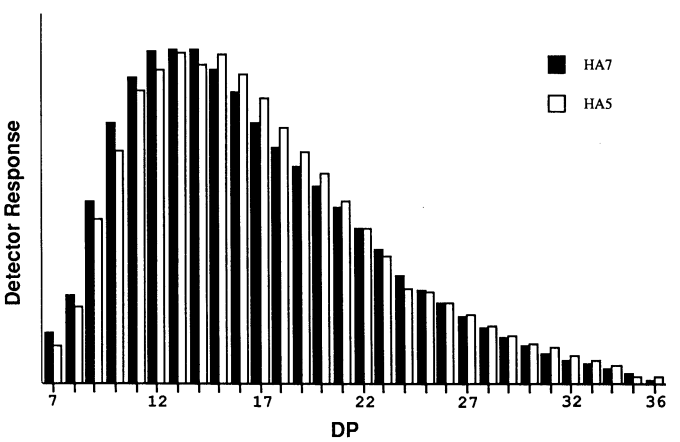

Fig. 2. Branch chain-length of the debranched HA5 and HA7 amylopectins analyzed by high-performance anion-exchange chromatography.

the cold-water solubility of the starch increases. When reaction temperature increased from 25 to 35°C, the solubility of normal maize starch treated with the A treatment increased from 23 to 84%, whereas the temperature effect on the solubility of high-amylose starches was much less. It may be attributed to the relatively low gelatinization temperature of normal maize starch (64–75°C) compared with those of high-amylose starches (69–105°C). Therefore, normal maize starch has a prompt response to temperature increase.

Scanning electron micrographs (Figs. 3 and 4) showed that granules of GCWS starches prepared by the alcoholic-alkaline treatment remained intact and were larger than those of the original native granules. The GCWS starch granules also showed indented appearances. This seemed to result from a granular structure change during the treatment. The GCWS waxy starch displayed highly indented granules. In contrast, the GCWS normal maize, HA5, and HA7 starches displayed less indentation. The difference could be attributed to the amylose content. Amylose served as a connector to hold the starch granules during the treatment (Lindqvist 1979, Jane et al 1986, Jane et al 1993). According to Tester and Morrison (1990), swelling is primarily a property of amylopectin. Therefore, waxy starch, with high amylopectin content (>99%), swelled much more than other starches during the treatment, and the surface of the granules had more dimples. Under a light microscope, it was observed that large granules swelled promptly during the alcoholic-alkaline treatments, whereas small granules were more resistant to swelling under the same reaction conditions.

During preparation, a small amount of soluble starch was leached out in the supernatant. Total weight losses of the soluble starches were 0.01, 0.4, and 1.9% for waxy maize, normal maize, and high-amylose maize starches, respectively. A GPC study on Sepharose CL-2B gel (Jane and Chen 1992) showed that the soluble starches were mainly small, linear molecules that displayed a high blue value (Fig. 5); the molecular size of the soluble starch was $\sim 1.02 \times 10^4$ Da. GPC on Bio-Gel P-6 of the soluble starch before and after the isoamylase hydrolysis showed a slight decrease at the peak and an increase at a shoulder as a result of debranching (Fig. 6), which indicated that the soluble starch had a slightly branched structure.

CONCLUSIONS

GCWS starches can be prepared by an alcoholic-alkaline treatment. Various reaction conditions were applied to different starches. Results showed that treatments at a lesser concentration of ethanol, a greater concentration of NaOH, and a higher reaction temperature produced GCWS starches with greater cold-water solubilities. When amylose contents of starches were above a certain level (~30%), such as those of HA5 and HA7 in this study, the influence of crystalline structure of starches became dominant. Normal maize starch (A-type) is more stable than HA5 and HA7 starches (B-type) at conditions given in this study.

The method is especially useful for preparing GCWS waxy and high-amylose starches. This will improve the use of waxy or high-amylose starch in instant foods.

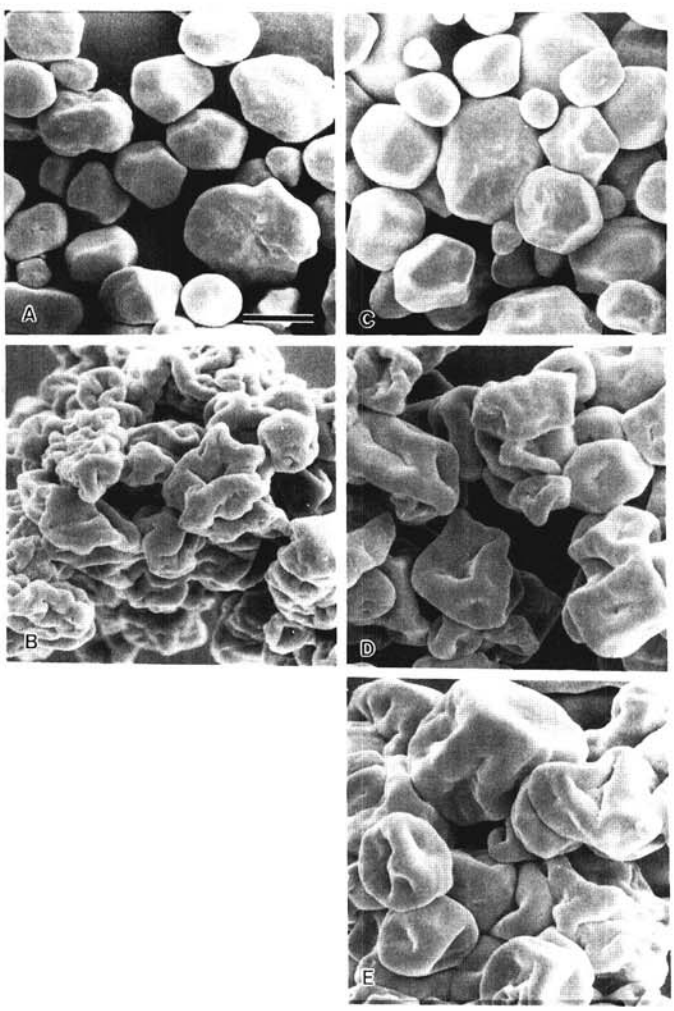

Fig. 3. Scanning electron micrographs of granular cold-water-soluble (GCWS) starches. **A,** native waxy maize; **B,** GCWS waxy maize; **C,** native normal maize; **D,** GCWS normal maize after A3 treatment at 25°C; **E,** GCWS normal maize after A3 treatment at 35°C. Size bar = 10 μm.

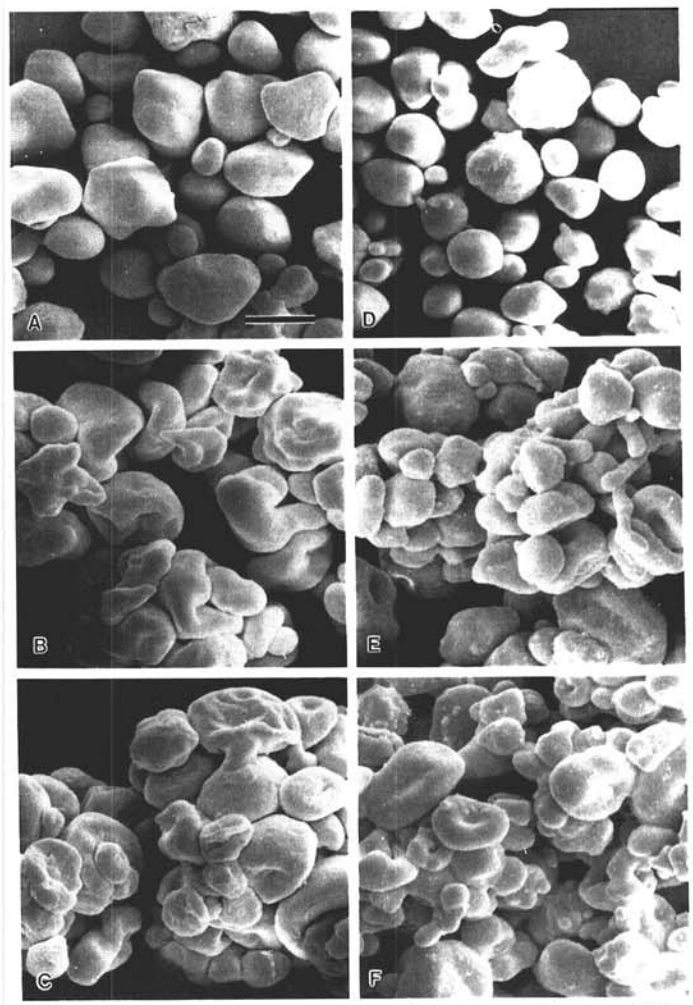

Fig. 4. Scanning electron micrographs of granular cold-water-soluble (GCWS) starches. **A,** native HA5; **B,** GCWS HA5 after A3 treatment at 25°C; **C,** GCWS HA5 after A3 treatment at 35°C; **D,** native HA7; **E,** GCWS HA7 after A3 treatment at 25°C; *F,* GCWS HA7 after A3 treatment at 35°C. Size bar = 10 μm.

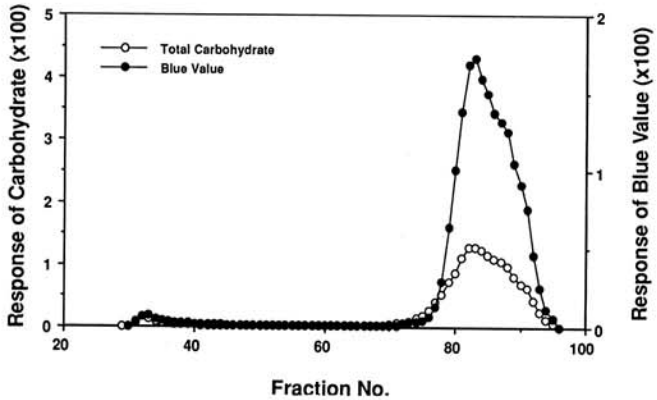

Fig. 5. Gel-permeation chromatography (Sepharose CL-2B) shows soluble starches leached in the supernatant during the preparation of granular cold-water-soluble starches.

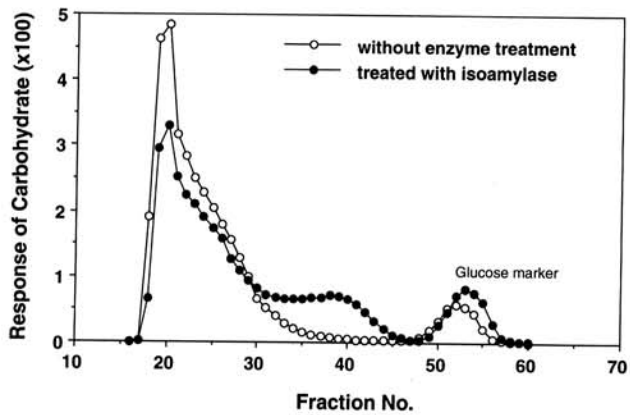

Fig. 6. Gel-permeation chromatography (Bio-Gel P-6) of soluble starches before and after isoamylase hydrolysis.

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