Effects of Lipid and Protein Removal on Starch Gelatinization in Whole Grain Milled Rice

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ABSTRACT

Treatment of long-, medium-, and short-grain, and very low amylose varieties of whole grain milled rice with the lipid solvents hexane or chloroform-methanol or the proteolytic enzyme Pronase caused significant changes to occur in starch gelatinization parameters measured by differential scanning calorimetry. Upon examination of the treated kernels by scanning electron microscopy, extensive fissure formation in the kernels was evident. Similar structural changes were noted in milled rice soaked in water for 30 min. The starch gelatinization curves for the soaked kernels resembled those for the lipid-solvent-treated kernels but not for the Pronase-treated kernels. However, fissure formation and modification of the kernel surface was more extensive in the Pronase-treated rice. We concluded that the alteration of kernel structure in intact milled rice increased water availability to the starch granules, which produced significant changes in starch gelatinization. Removal of rice lipid or rice protein per se appeared to have only a minor, but measurable, effect on starch gelatinization.

The thermal properties of rice starch and rice flour have been studied by several investigators using differential scanning calorimetry (DSC) (Russell and Juliano 1983; Nakazawa et al 1984a,b; Maurice et al 1985; Biliaderis et al 1986a,b; Chungcharoen and Lund 1987; Chang and Liu 1988). Modern calorimeters provide a sensitive, direct, and dependable method for assessing rice starch gelatinization under a variety of experimental conditions, including different moisture levels (Maurice et al 1985, Biliaderis et al 1986b, Chungcharoen and Lund 1987, Chang and Liu 1988), the addition of purified lipids (Biliaderis et al 1986a), or the addition of different sugars and salts to the starch or flour suspensions (Chungcharoen and Lund 1987, Chang and Liu 1988). All of these treatments have their own characteristic influence on starch gelatinization and provide valuable information on the potential behavior of starch in specific rice foods containing these additives.

Rice is consumed largely in the cooked, whole grain form (James and McCaskill 1983). However, because of the technical difficulties in measuring starch gelatinization in cooked, whole grain rice, very little is known about the thermal properties of rice starch during cooking. Extrapolation of calorimetric data from studies of purified starch or rice flour can be misleading because starch in an intact food system can behave differently from starch in an isolated state. Recently, however, we (Normand and Marshall 1989) reported DSC thermal curves for representative long-, medium-, and short-grain, and very low amylose varieties of whole grain milled rice and compared them to thermal curves for milled rice flour of the same varieties. Significant differences were observed between intact kernels and flour samples for gelatinization temperatures and gelatinization enthalpies within each variety. These differences persisted at zero heating rate, where heat transfer effects within the kernels were eliminated. We concluded that the structural integrity of the kernel played an important role in determining the thermal parameters of starch gelatinization.

To support this conclusion, this study was designed to investigate whether specific structural changes in the intact kernel brought about by the removal of lipids or protein from whole grain milled rice had an effect on starch gelatinization.

MATERIALS AND METHODS

Materials

The procurement of rough rice samples and preparation of milled rice from the varieties Lemont (long-grain), Mars (medium-grain), S-201 (short-grain), and Calmochi (very low amylose) were described previously (Normand and Marshall, 1989). Solvents used for lipid extraction of milled rice and milled rice flour were reagent grade. Pronase was purchased from Sigma Chemical Co. (St. Louis, MO).

Methods

The preparation of samples for thermal analysis, a description of the calorimeter, development of the thermal curves, and calculation of the thermal parameters were described previously (Normand and Marshall 1989). For our specific studies, thermal data was collected at 10-sec intervals at a scan rate of 1.0°C/min over the temperature range of 20–110°C. Data acquisition was terminated at 110°C because of the maximum temperature limitations placed on the calorimeter by the manufacturer.

Starch gelatinization under some experimental conditions resulted in a complex endotherm consisting of two distinct peaks of unequal magnitude (e.g., Fig. 1, curve 2, all varieties). Since we were measuring only one thermal event, namely starch gelatinization, we assigned only one peak gelatinization temperature (T_p) to characterize that event. T_p values were assigned to these thermal curves based on the temperature at which the greatest value for the heat flow (mJ/sec) occurred.

The removal of surface lipids from whole kernel milled rice was accomplished by the method of Hogan and Deobald (1961). Nonstarch lipid was extracted from rice flour using AACC method

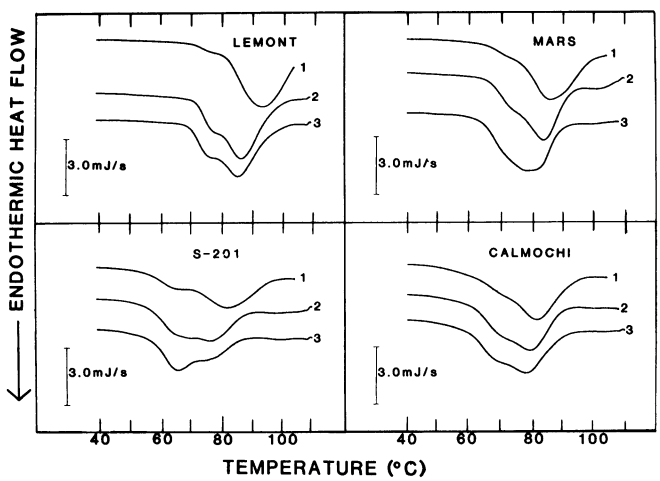

Fig. 1. Differential scanning calorimetry thermal curves of different whole grain milled rice varieties: untreated (curve 1), hexane-treated (curve 2), and chloroform-methanol-treated (curve 3). The water content of all samples was 70% (w/w), and the heating rate of the calorimeter was 1.0°C/min.

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30-25 (AACC, 1983). The lipid-extraction solvents, hexane and chloroform-methanol (C-M) (2:1, v/v), were used in place of petroleum ether as originally described by Hogan and Deobald (1961). The percent of extractable lipid for whole grain milled rice was based on the percent of nonstarch lipid removed from the same quantity of rice flour by C-M treatment. Both hexane and C-M were selected as lipid solvents to compare the thermal properties of rice with only a portion of the lipid removed (hexane treatment) to those of rice with most of the lipid extracted (C-M treatment).

Soaking of whole kernel milled rice was accomplished by adding about 20 g of milled rice to an excess of distilled water. The rice was allowed to soak for 30 min, and the excess water was removed. The moist kernels were dried on an absorbent towel for 24 hr.

Protein was extracted from whole grain milled rice and rice flour by the method of Maningat and Juliano (1980). Both kernels and flour were treated with 0.2% Pronase (4,000 units per gram) in 0.03*M* phosphate buffer, pH 7.4, or treated with buffer without Pronase to establish a buffer-treated sample. Protein (N × 5.95) was determined using AACC method 46-11 (AACC, 1983).

All lipid- and protein-extracted and water-soaked kernels were air dried to a moisture content of 12%.

For scanning electron microscopy (SEM), rice grains were attached to aluminum sample stubs with double adhesive tabs. Since the rice was already dry, no fixation and dehydration processes were used. Some grains were split apart at a deep fissure and mounted so that the broken inner surface could be examined. Prepared stubs were sputter-coated with gold/palladium to prevent charging in the electron beam. The thickness of the gold/palladium coating was about 20 nm. On samples with deep fissures, the thickness was about 40 nm since these kernels were coated twice to get the coating into the fissures. Stubs were placed in the sample chamber of a Hitachi S-510 scanning electron microscope and observed at 5- and 10-kV accelerating voltage.

RESULTS

Thermal Properties of Solvent-Extracted Rice

The effects of solvent extraction on starch gelatinization in the different varieties of whole grain milled rice are depicted in Fig. 1. The thermal curves for solvent-treated kernels (curves 2 and 3) show considerable differences from those of the nontreated controls (curve 1) for each variety examined. For Mars and S-201, differences exist between hexane and C-M treatments. In every variety, the low temperature shoulder (LTS) of the gelatinization endotherm in the control became much more pronounced after lipid extraction. Following C-M treatment of S-201, the gelatinization endotherm of this sample corresponded to the control LTS (curve 1) and was followed by a high temperature shoulder (HTS) (curve 3).

Table I lists the thermal parameters calculated from the thermal curves in Fig. 1 and also lists the percentages of lipid extracted from the kernels. C-M extracted two to three times more lipid from the kernels than did hexane. In fact, in rice flour, hexane removed only 39–62% of the nonstarch lipid, depending on the particular variety. In contrast, C-M removed virtually all the nonstarch lipid from the flour, which was 0.8–0.9% (db) for Lemont, Mars, and S-201 and 1.2% (db) for Calmochi. The absence of complete lipid extraction with C-M in the kernels could be due to the lack of complete penetration of the solvent.

Gelatinization onset temperatures (T_o) between control and solvent-extracted samples were similar in Mars and S-201 and slightly lower in Lemont and Calmochi for solvent-extracted kernels. Differences in T_p values between control and solvent-treated kernels varied from 3.4°C for Calmochi to 17.4°C for S-201. Although C-M extracted much more lipid than hexane, only T_p values in Mars and S-201 showed a difference between these two treatments. Changes in gelatinization conclusion temperatures (T_c) generally reflected the change in T_p values for the same variety and varied from 5.6°C for Calmochi to 11.7°C for S-201. Differences in T_c for Lemont could not be determined because no concluding baseline was observed in the control.

The gelatinization enthalpies (ΔH) decreased for Mars and S-201 upon solvent treatment, but no significant change was observed for Calmochi. ΔH values showed no consistent pattern when varieties were compared with each other. ΔH appeared to be influenced more by specific variety than by specific treatment. In Mars and S-201, treatment of milled rice with hexane or C-M reduced the amount of energy required to gelatinize the starch when compared to energy required for nontreated kernels.

Characterization of Hexane- or C-M-Treated and Water-Soaked Rice

The results described above clearly show changes in starch gelatinization arising from hexane or C-M treatment of the kernels. Solvent extraction not only removed lipid from the kernels, but also produced visible fissures on the surface of the grains. To detail the extent of kernel cracking, solvent-treated kernels were examined by SEM. Figure 2 shows surface details of representative Lemont kernels. The size and extent of kernel cracking varied somewhat within each variety, but the appearance of the fissures was generally as seen in Fig. 2. A nontreated Lemont kernel (Fig. 2A) showed only a minor amount of surface fractur-

TABLE I
Extractable Lipid[a] and Thermal Parameters[b] of Whole Grain Milled Rice[c] Extracted with Hexane or Chloroform-Methanol (C-M)

Rice Variety	Treatment	Extractable Lipid (%)	Gelatinization Temperatures[d] (°C)			Enthalpy, ΔH (J/g)
			T_o	T_p	T_c	
Lemont	None	0	72.7 ± 0.2	93.5 ± 0.5	ND[e]	ND
	Hexane	30 ± 3	71.6 ± 0.5	86.5 ± 0.7	97.1 ± 1.3	14.3 ± 0.4
	C-M	78 ± 1	70.0 ± 0.6	85.7 ± 0.8	95.9 ± 1.3	15.1 ± 0.7
Mars	None	0	64.0 ± 0.6	86.4 ± 0.7	98.1 ± 2.7	15.8 ± 0.0
	Hexane	33 ± 1	65.1 ± 0.8	83.0 ± 0.9	90.6 ± 1.0	13.1 ± 0.5
	C-M	86 ± 0	64.0 ± 0.6	79.0 ± 0.6	88.5 ± 0.2	14.1 ± 0.5
S-201	None	0	55.4 ± 0.7	82.6 ± 0.4	97.6 ± 0.8	13.3 ± 0.1
	Hexane	26 ± 1	56.9 ± 0.8	70.0 ± 4.7	87.0 ± 0.4	11.4 ± 0.5
	C-M	74 ± 1	55.8 ± 1.3	65.2 ± 0.4	85.9 ± 0.5	11.2 ± 1.0
Calmochi	None	0	60.5 ± 0.5	81.7 ± 0.3	93.5 ± 0.5	14.9 ± 0.4
	Hexane	46 ± 2	58.1 ± 0.3	78.3 ± 0.8	87.9 ± 0.6	14.5 ± 0.7
	C-M	87 ± 1	56.6 ± 1.1	77.8 ± 1.0	88.8 ± 1.0	15.1 ± 0.7

[a] Dry weight basis; percent of lipid extracted was based on the total lipid values from C-M-extracted flour samples for each variety; values are means ± standard errors of the means of duplicate determinations.
[b] Values are means ± standard errors of the means of triplicate determinations.
[c] Moisture content of calorimeter samples was 70%.
[d] T_o = onset temperature, T_p = peak gelatinization temperature, T_c = conclusion temperature.
[e] Not determined due to absence of concluding baseline.

ing. Extensive radial and transverse fractures were observed in both hexane-treated and C-M-treated kernels (Figs. 2B and C, respectively). Cracking of kernels generally appeared more extensive in the C-M-extracted samples. Fissures in some C-M-extracted rice grains extended to the kernel center, and a few went completely through the kernel (electron micrographs not shown). The kernel could be separated by hand at these deep fissures to reveal the fractured cross-sectional surface. To determine whether kernel cracking by itself could cause the considerable changes in starch gelatinization observed in Fig. 1, rice grains were soaked in distilled water and then air dried. This method is known to cause transverse fissures to form in rice kernels (Desikachar and Subrahmanyan 1961). An electron micrograph of a typical Lemont kernel subjected to soaking, followed by air drying, is shown in Fig. 2D. Transverse fissures, with a small amount of radial cracking, were seen. The depth of fissure penetration was similar to that in the solvent-treated kernels.

Comparison of Thermal Properties for Hexane- or C-M-Extracted and Water-Soaked Rice

Experiments were conducted to compare the starch gelatinization profiles of untreated milled rice, rice soaked in water, and rice treated with C-M. The results for the Lemont variety, which were representative of the other varieties, are given in Fig. 3. Starch gelatinization for the control (curve 1) was considerably different than starch gelatinization in soaked (curve 2) and solvent-treated (curve 3) samples. However, soaked and C-M-treated milled rice gave similar thermal curves. The data in Table II show a small decrease in T_o and T_p upon C-M treatment, and the ΔH of the C-M sample was slightly higher than the ΔH of the soaked kernels. Since less than 5% of the nonstarch lipid was removed during soaking, these results suggest that the major determinant altering the starch gelatinization profile is the formation of deep fissures in the kernels, and that the removal of nonstarch lipid from the kernel appears to play only a minor role in influencing starch gelatinization. Additional support for this argument comes from experiments we conducted to show the effect of solvent extraction on starch gelatinization in rice flour. The use of rice flour eliminates structural effects due to kernel integrity, and any differences in starch gelatinization parameters between treated and nontreated samples would be caused by the treatment. Extraction of nonstarch lipid with hexane had generally no effect on the T_o, T_p, or ΔH values in rice flour from the four rice varieties, as compared to these values in the nontreated samples, but extraction with C-M generally decreased T_o and T_p by 1–2°C and increased ΔH by 0.4–1.0 J/g compared to control rice flour (data not shown). These data emphasize the minor, but measurable, effect of lipid extraction on starch gelatinization.

Thermal Properties of Pronase-Treated Rice

To determine the effect of protein removal on starch gelatinization in whole kernel milled rice, milled rice was exposed to Pronase digestion. The results of this treatment are given in Fig. 4. A comparison between nontreated (curve 1) and Pronase-treated (curve 3) samples shows a considerable change in the gelatinization profiles after Pronase treatment in all varieties. However, the effect of Pronase can be directly compared only between curves 2 and 3, where buffer-treated samples are matched with Pronase-treated samples. The only difference between these samples is the absence of enzyme in the buffer. As Fig. 4 clearly shows, Pronase treatment modified the gelatinization profiles to the greatest extent in Lemont and Mars and to a lesser extent in S-201 and Calmochi when compared to the buffer-treated

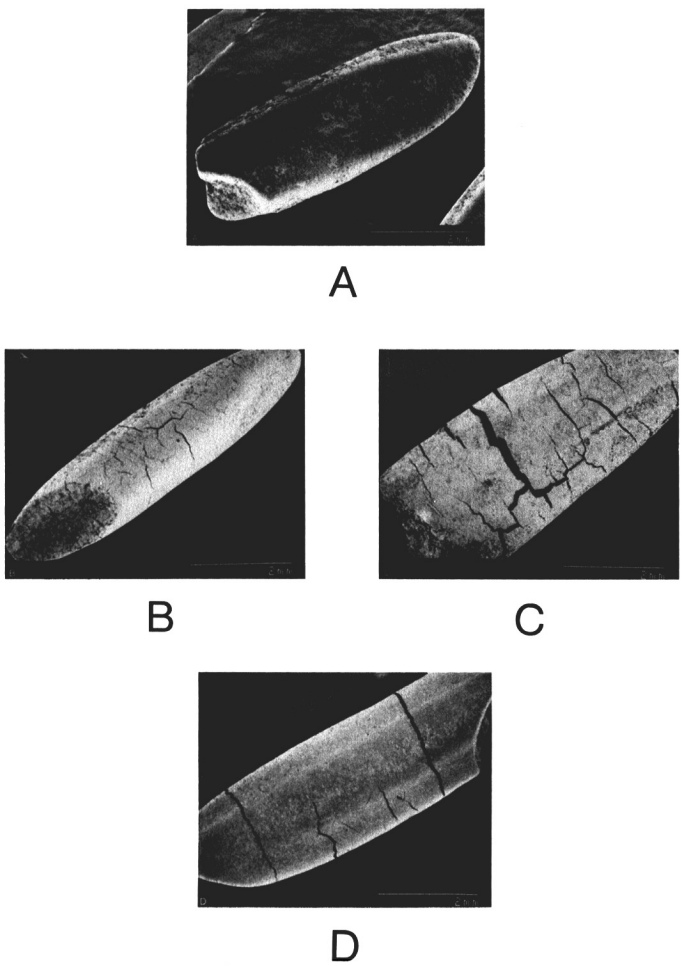

Fig. 2. Scanning electron micrographs of Lemont whole grain milled rice: **A,** untreated; **B,** hexane-treated; **C,** chloroform-methanol-treated; **D,** soaked in water. Accelerating voltage used was 5 kV.

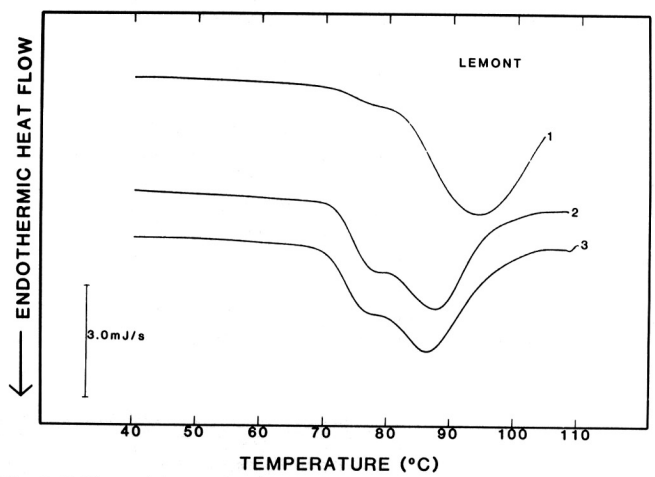

Fig. 3. Differential scanning calorimetry thermal curves of Lemont whole grain milled rice: untreated (curve 1), soaked in water (curve 2), and chloroform-methanol-treated (curve 3). The water content of all samples was 70% (w/w), and the heating rate of the calorimeter was 1.0°C/min.

TABLE II
Thermal Parameters[a] of Lemont Whole Grain Milled Rice[b] Soaked in Water or Treated with Chloroform-Methanol (C-M)

Treatment	Gelatinization Temperatures[c] (°C)			Enthalpy, ΔH (J/g)
	T_o	T_p	T_c	
None	71.2 ± 0.2	93.0 ± 0.5	ND[d]	ND
Soaked	71.4 ± 0.1	86.8 ± 0.2	95.2 ± 0.4	13.6 ± 0.8
C-M	70.0 ± 0.6	85.7 ± 0.8	95.9 ± 1.3	15.1 ± 0.7

[a] Values are the means ± standard errors of the means of duplicate determinations.
[b] Moisture content of calorimeter samples was 70%.
[c] T_o = onset temperature, T_p = peak gelatinization temperature, T_c = conclusion temperature.
[d] Not determined due to absence of concluding baseline.

control.

Starch gelatinization parameters for these samples are given in Table III, along with the percent protein extracted from samples treated with buffer and with buffer plus Pronase. The addition of buffer without Pronase also removed some protein, more so in Mars and Calmochi than in Lemont and S-201. The actual percent of total protein removed by Pronase treatment varied from about 50% for Lemont to about 63% for S-201. The total protein in the kernels varied from 6.0 to 7.6% (db) depending on the variety.

Although the thermal curves in Fig. 4 were greatly different within a specific variety, their T_o values were similar. However, large changes were observed in T_p for each variety. In Mars, S-201, and Calmochi, treating the grains with buffer increased the size of the LTS on the gelatinization endotherm to the point where it could now be used to calculate T_p for the entire endotherm. As a result, differences in T_p between control and buffer-treated samples were increased 12.3°C in Mars and 14.7°C in S-201. T_c values were markedly reduced in Mars, S-201, and Calmochi as the result of exposure to buffer. Differences ranged from 6.8°C in Calmochi to 12.3°C in S-201. In Lemont, buffer treatment increased the size of the LTS, but it remained a shoulder on the endotherm.

When buffer- and Pronase-treated samples were compared, the effect of Pronase was most apparent in the Lemont and Calmochi varieties, judging by the changes in T_p. In Lemont, Pronase treatment produced a major change in the gelatinization endotherm, which resulted in a large decrease in T_p. T_p decreased by 7.7°C in Lemont but increased by 7.0°C in Calmochi. The increase in T_p for Calmochi is inconsistent with the other three varieties and results from the difficulty in distinguishing between peak and shoulder for both buffer- (curve 2) and Pronase- (curve 3) treated samples. Although changes were observed in T_p, T_c values for these varieties were unchanged in Calmochi and only slightly decreased in Lemont. T_p and T_c parameters for Mars and S-201 were essentially unchanged by the removal of 62.7 and 57.2% protein, respectively. The T_p values for Pronase-treated samples of each variety were similar to the T_p values obtained for starch gelatinization in rice flour for that particular variety (Normand and Marshall 1989), even though the general shapes of the endotherms were different. This observation strongly suggests that the LTS seen in nontreated milled rice can develop, with Pronase treatment, into an endotherm with a T_p comparable to that of the gelatinization endotherm seen in rice flour samples (Normand and Marshall 1989).

ΔH values among the control and experimental samples within a given variety varied according to the specific variety (Table III). In Mars, ΔH increased, but in S-201 and Calmochi, a decrease was seen in the buffer- and Pronase-treated kernels compared to the control. Apparently ΔH is dependent on variety but independent of the specific treatment. In any case, the changes in ΔH were not large.

Characterization of Pronase-Treated Rice

As discussed for the solvent-treated samples described earlier, the considerable changes observed for starch gelatinization in Pronase-treated samples could be due to either removal of protein or modification of kernel integrity. Overall, buffer or Pronase treatment had the greatest effect on starch gelatinization in Lemont. As with previous treatments (Fig. 2), buffer or Pronase produced visible fissures in the kernels. To provide a detailed view of the cracks, Lemont kernels were examined by SEM. Figure 5 shows representative electron micrographs. Fissures were seen in the buffer-treated (Fig. 5B) and Pronase-treated (Fig. 5C) samples but not in the nontreated kernel (Fig. 5A). By far the most extensive cracking was observed in the Pronase-treated sample. In addition to fissure formation, the surface of the Pronase-treated sample was marked by numerous pits, possibly due to the removal of protein-rich regions on or near the surface of the kernel (Bechtel and Pomeranz 1978).

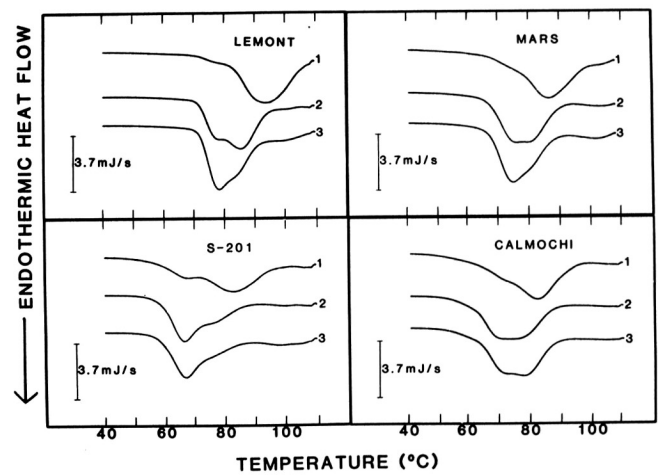

Fig. 4. Differential scanning calorimetry thermal curves of different whole grain milled rice varieties: untreated (curve 1), buffer-treated (curve 2), and Pronase-treated (curve 3). The water content of all samples was 70% (w/w), and the heating rate of the calorimeter was 1.0°C/min.

TABLE III
Extractable Protein[a] and Thermal Parameters[b] of Whole Grain Milled Rice[c] Treated with Buffer (B) or Buffer with Pronase (B + P)

Rice Variety	Treatment	Extractable Protein (%)	Gelatinization Temperatures[d] (°C)			Enthalpy, ΔH (J/g)
			T_o	T_p	T_c	
Lemont	None	0	70.6 ± 0.6	92.7 ± 0.2	ND[e]	ND
	B	3 ± 1	72.0 ± 0.2	85.1 ± 0.4	93.3 ± 0.2	13.8 ± 0.1
	B + P	53 ± 7	70.9 ± 1.1	77.4 ± 0.2	90.9 ± 0.6	13.5 ± 0.3
Mars	None	0	65.7 ± 0.1	85.5 ± 0.3	98.3 ± 1.5	12.4 ± 0.2
	B	11 ± 2	65.4 ± 0.5	73.2 ± 0.4	89.1 ± 0.8	13.3 ± 0.1
	B + P	62 ± 6	66.3 ± 0.3	73.4 ± 0.1	88.1 ± 0.4	13.4 ± 0.5
S-201	None	0	56.2 ± 1.7	79.9 ± 2.5	96.7 ± 5.2	12.8 ± 0.9
	B	2 ± 0	57.6 ± 0.0	65.2 ± 0.3	84.4 ± 1.6	12.0 ± 0.2
	B + P	64 ± 7	57.5 ± 0.2	66.0 ± 0.6	83.7 ± 0.3	11.4 ± 0.7
Calmochi	None	0	58.1 ± 0.1	81.2 ± 0.1	93.3 ± 1.2	15.9 ± 0.0
	B	12 ± 4	60.1 ± 0.6	69.5 ± 0.1	86.5 ± 0.4	15.1 ± 0.3
	B + P	69 ± 4	60.6 ± 1.1	76.5 ± 0.1	86.8 ± 0.1	15.3 ± 0.1

[a] Dry weight basis; actual percent of protein removed by Pronase treatment can be obtained by subtracting the protein removed by buffer wash only; values are means ± standard errors of the means of duplicate determinations.
[b] Values are means ± standard errors of the means of duplicate determinations.
[c] Moisture content of calorimeter samples was 70%.
[d] T_o = onset temperature, T_p = peak gelatinization temperature, T_c = conclusion temperature.
[e] Not determined due to absence of concluding baseline.

Comparison of Pronase-Treated and Water-Soaked Rice

Since both buffer and buffer with Pronase modified the structural integrity of the kernel, we wanted to compare these thermal curves to thermal curves generated from soaking rice, from which less than 5% of the protein was removed. Figure 6 shows that the thermal curve for soaked rice (curve 2) was similar to the thermal curve for buffer-treated rice (curve 3). In both samples, less than 5% protein was removed, and neither sample exhibited the extensive cracking present in the Pronase-treated kernels. Therefore, fissure formation caused by buffer resulted in the marked changes in starch gelatinization seen in the buffer-treated samples. However, the gelatinization endotherm for Pronase-treated Lemont kernels (curve 4) was different from curves 2 and 3. We can conclude that Pronase treatment had a pronounced effect on the shape of the gelatinization endotherm, which was highlighted by the large decrease in T_p. We cannot definitively state the reason for the effect. Since Pronase-treated kernels were extensively cracked and pitted, the additional modification of kernel structure could have caused further change in the starch gelatinization profile. Evidence to support this statement can be obtained by comparing gelatinization parameters for nontreated and Pronase-treated Lemont rice flour. Pronase treatment of the flour removed about 75% of the total protein, but T_o and T_p values decreased less than 1°C compared to those of nontreated flour (data not shown). Protein removal did increase the ΔH from 10.7 J/g in the control to 12.5 J/g in the Pronase-treated flour. Treatment of rice kernels with either organic solvents or proteolytic enzyme appeared to cause a small reduction in T_o and T_p and a small increase in ΔH. The reason for these minor but consistent changes in gelatinization parameters is not known.

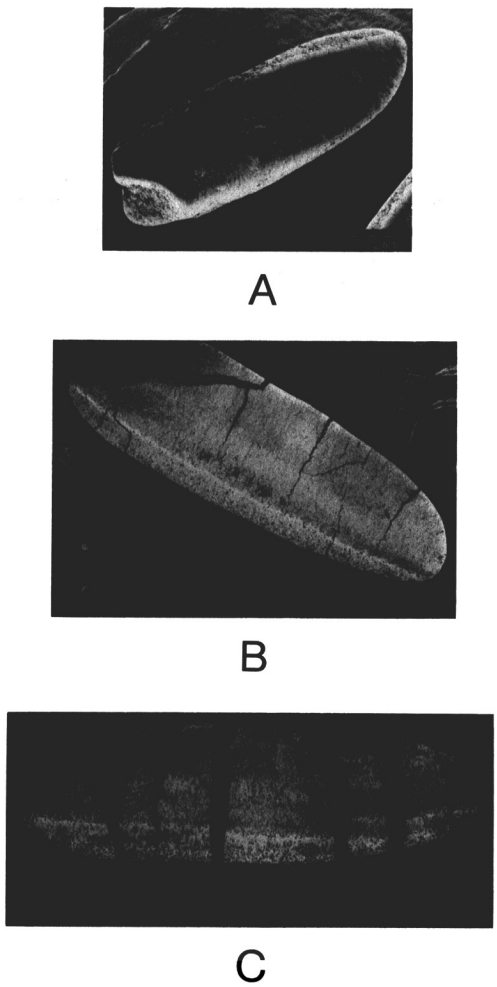

Fig. 5. Scanning electron micrographs of Lemont whole grain milled rice: **A,** untreated; **B,** buffer-treated; **C,** Pronase-treated. Accelerating voltage used was 5 kV.

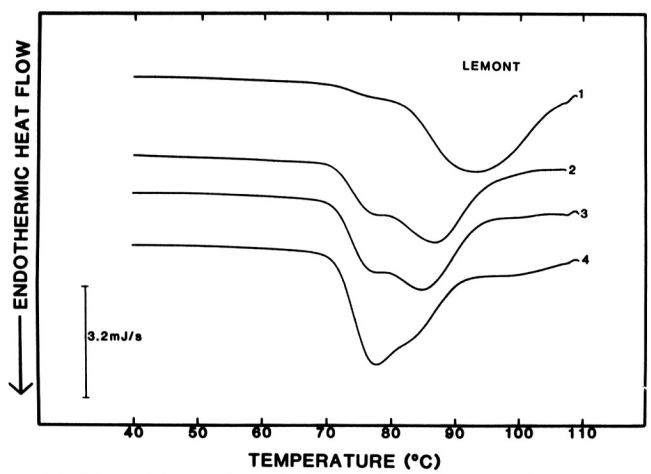

Fig. 6. Differential scanning calorimetry thermal curves of Lemont whole grain milled rice: untreated (curve 1), soaked in water (curve 2), buffer-treated (curve 3), and Pronase-treated (curve 4). The water content of all samples was 70% (w/w), and the heating rate of the calorimeter was 1.0°C/min.

DISCUSSION

The results presented in this article indicate that perturbations (fissures, pits) in the structure of milled rice kernels can lead to significant changes in the shape of the starch gelatinization endotherm and the thermal parameters associated with the endotherms. The methods used to alter the kernel structure, i.e., exposure to organic or aqueous solvents or proteolytic enzymes, may not be as important as the fact that the structure was modified. Normand and Marshall (1989) suggested that milled rice kernels are organized into two "compartments," one easily accessible and one less readily accessible to water penetration upon heating. These compartments may be separated by natural barriers within the kernel, such as cell wall components, that control water penetration to the starch granules. Water is required for starch gelatinization. The higher gelatinization temperature observed in intact kernels compared to flour (Normand and Marshall 1989) is due to the lack of water around most of the starch granules in the kernel. Increased gelatinization temperatures in rice starch were observed by Biliaderis et al (1986b) when limited water was added to the DSC sample pan. In contrast, Normand and Marshall (1989) provided sufficient water to their DSC ampoules, but water to the starch was limited by structural components of the kernel.

In the present study, many of the fissures determined by SEM for soaked or solvent-treated kernels (Fig. 2) and buffer- or Pronase-treated kernels (Fig. 5) extend into the center of the rice grains and would allow water to conveniently and rapidly enter the kernel interior, particularly upon heating of the sample. Therefore, the population of starch granules more easily accessible to water would be increased. This population appears to be associated with the LTS seen in the gelatinization endotherm for all the nontreated milled rice varieties examined.

Our results also provide a better understanding of the complex gelatinization endotherms first observed in an earlier study by Normand and Marshall (1989). In this study, when starch gelatinization in treated and nontreated milled rice was examined by DSC, we always observed a complex endotherm consisting of two distinct parts, an LTS and an HTS, which can change size relative to one another. Our present results show that the position of each portion remains constant, since they all have similar T_o values within a given rice variety. As LTS increases in size to the point where it represents the gelatinization peak, as seen, for example, in Pronase-treated Lemont kernels, its T_o and T_p values correspond to those found in flour samples of the same variety (Normand and Marshall 1989). Therefore, we believe that the low-temperature portion consists of starch granules having water accessibility equivalent to that of granules

found in flour, which means they are highly accessible to water. The T_p and T_c values of the high-temperature portion of the gelatinization endotherm are generally sensitive to disruption of kernel structure. Changes in starch gelatinization occur as fissures create water passages and increase water accessibility to the granules, thereby reducing the size of the granule population that possesses low water accessibility. That part of the endotherm contributed by granules with low water accessibility is thus diminished. As the number of more accessible granules increases and the number of less accessible granules decreases, the thermal characteristics of the rice grains change.

On the basis of the results of this study, DSC can provide a sensitive method to determine changes in rice kernel structure and qualitatively estimate the extent of the changes. The part of the kernel structure that provides control of water penetration to the starch granules has not yet been identified. Experiments are underway to locate this structure(s) within the kernel by using abrasive milling to selectively remove material from the kernel surface and by monitoring related changes in starch gelatinization with DSC.

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