

Molecular and Gelatinization Properties of Rice Starches from IR24 and Sinandomeng Cultivars¹

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ABSTRACT

Cereal Chem. 78(5):596–602

The differences in pasting properties involving gelatinization and retrogradation of rice starches from IR24 and Sinandomeng cultivars during heating-cooling processes were investigated using a Rapid Visco Analyser (RVA) and a dynamic rheometer. The results were discussed in relation to the molecular structure, actual amylose content (AC), and concentration of the starches. Generally, both starches possessed a comparable AC (≈ 11 wt%), amylose average chain length (CL), iodine absorption properties, and dynamic rheological parameters on heating to 95°C at 10 wt% and on cooling to 10°C at higher concentrations. In contrast to Sinandomeng,

IR24 amylose had a greater proportion of high molecular weight species and number-average degree of polymerization (DP_n). IR24 amylopectin possessed a lower DP_n and greater CL, exterior CL (ECL), and interior CL (ICL). Comparing the results of RVA analysis and dynamic rheology, the gelatinization properties and higher retrogradation tendencies of IR24 starch can be related to the structural properties and depend on starch concentration. In addition, the exponent n of starch concentration for storage moduli at 25°C ($G'_{25} \propto C^n$) increased linearly with increasing AC.

The texture of cooked rice or the pasting and rheological property of rice flour suspensions examined by Brabender viscoamylograph, Rapid Visco Analyser (RVA), or dynamic rheometry (DR) is known to be mainly governed by starch and partially by nonstarch components such as proteins and lipids (Juliano 1985). The physicochemical properties of starches and flours are frequently of interest in predicting the texture or eating quality of cooked rice or other rice products. Amylose content (AC), crude protein content, alkali spreading value, gelatinization temperature (GT) determined by differential scanning calorimetry (DSC), gel consistency, and Instron hardness can be used to evaluate cooked rice quality (Roferos and Juliano 1997). Among these indices, AC plays the most important role in changing the elasticity of starchy systems during early retrogradation and, therefore, the texture of freshly cooked rice (Juliano 1985, 1998).

Nonetheless, these physical indices are usually examined at various sample concentrations and consequently cannot explain the role of molecular structure in starch-containing systems to a great extent. For example, cooked rices with similar AC or GT generally show different cooking and eating qualities (Juliano 1985, 1998; Roferos and Juliano 1997). Two examples are 18% AC IR24 and Sinandomeng rices developed in the Philippines. Freshly cooked rices of both cultivars are preferred by consumer panelists but, after storage, the preference for Sinandomeng is superior to IR24 because the IR24 shows a firmer texture (Roferos and Juliano 1997). The hardening of cooked rice can be mainly attributed to starch retrogradation; therefore, the molecular properties of the starches should be crucial to cooked rice quality, as reported for maize starch (Shi and Seib 1995; Mua and Jackson 1998), waxy maize starch (Würsch and Gumy 1994), and purified rice amylopectin (Lai et al 2000) systems. However, the effects of amylose and amylopectin structures on the starch pasting, gelatinization, and subsequent retrogradation, which are frequently examined by RVA and DR, are seldom clarified by considering the change in starch concentration. Accordingly, the present report deals with the examination of molecular and

physical differences between IR24 and Sinandomeng rice starches. The structural effects on the starch pasting, gelatinization, and retrogradation properties examined by RVA and DR are elucidated to a greater extent, with respect to starch concentration or soluble and granular properties. The potential effects on the texture of cooked rices are also discussed.

MATERIALS AND METHODS

Starch Isolation

IR24 and Sinandomeng cultivars of rice were harvested in the dry season of 1997 in the Philippines. The rice starches were isolated from milled rice by wet milling and a modified alkaline steeping method (Yang et al 1984).

Isolation of Amyloses and Amylopectins

According to the method of Takeda et al (1986), 10 g of rice starch was dissolved in 300 mL of dimethyl sulfoxide (DMSO) (refluxed in boiling water bath for 15 min under nitrogen) followed by precipitation with 300 mL of ethanol (0°C, several hours) and centrifugation (2,700 \times g, 20 min, 4°C). The defatted starch precipitate was redissolved in a hot mixture of 1-butanol, isoamyl alcohol, and water (100, 100, and 1,700 mL, respectively) (refluxed in a boiling water bath, 3 hr, under nitrogen), then gradually cooled to 4°C. The mixture was allowed to stand at 4°C for 48 hr before centrifugation (10,000 \times g, 20 min, 4°C). The crude amylose precipitates from the supernatant containing amylopectins. The crude amylose fraction was purified by repeated (3 \times) dissolution and recrystallization in 10% aqueous 1-butanol (4°C, 24 hr) and ultracentrifugation (10,000 \times g, 20 min, 4°C). The supernatant containing amylopectins was concentrated under vacuum at 40°C to one-third initial volume, followed by precipitation with two volumes of ethanol, filtration on G-2 glass filter, and drying under vacuum at room temperature.

Fractionation and Fine Structure Analysis

Starch was fractionated by gel-permeation chromatography (GPC) on a column (2.6 cm i.d. \times 100 cm high) with Tosoh TSK HW-75F gels and a fraction volume of 5.0 mL. Deionized water containing 0.02% (w/v) sodium azide (Lu et al 1997) was used as the eluent. The flow rate was 40 mL/hr. Starch sample (10 mg) was dissolved in 90% DMSO (1.0 mL), precipitated with ethanol (3.0 mL), and then completely dissolved in hot deionized water (5.0 mL) for GPC analysis. For the purified amylose fraction, a GPC column filled with Tosoh TSK HW-65F gels (2.6 cm i.d. \times 100 cm high) was used. Amylose sample (10 mg) was predispersed in DMSO and then completely dissolved in deionized water (5.0 mL) for GPC measurements. An aqueous solution of 1.0 mM NaOH and 25.0 mM

¹ Presented in part at the AACC 84th Annual Meeting, Kansas City, MO, November 2000.

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NaCl was used as the eluent. The subfraction volume and flow rate were 2.5 and 40 mL/hr, respectively. The chain distribution of an isoamylase-debranched amylopectin fraction was determined on a Tosoh TSK HW-50F column (2.6 cm i.d. × 100 cm height) with 5.0 mL per subfraction at 30 mL/hr. Debranched amylopectin (10 mg) was dissolved in 5.0 mL of deionized water under nitrogen, followed by GPC measurements with an aqueous eluent containing 1 mM NaOH and 25 mM NaCl. All of the above sample solutions were filtered through a 1.0- μ m nylon membrane before GPC measurements at 35°C. The void and eluent volumes of GPC columns were determined using blue dextran (average molecular weight 2×10^6) and D-glucose, respectively (Sigma-Aldrich, St. Louis, MO).

The number-average degree of polymerization (DP_n) of purified amylose and amylopectin fractions and the average chain length (CL) of GPC subfraction were calculated as the molar ratio of total carbohydrate to reducing end contents, measured respectively with phenol-sulfuric acid (Dubois et al 1956) and modified Park-Johnson (Hizukuri et al 1983a) or Somogyi-Nelson (Nelson 1944; Somogyi 1952) methods. The CL values of amylose and amylopectin fractions were examined on samples debranched by isoamylase and pullulanase (for amylose) or only isoamylase (for amylopectin) according to the method described by Hizukuri et al (1981). The average number of chains (NC) per molecule was calculated as DP_n/CL . The average exterior CL (ECL) and interior CL (ICL) were calculated as $ECL = CL \times (\beta\text{-AL}) + 2$ and $ICL = CL - ECL - 1$ (Manners 1989), where $\beta\text{-AL}$ is the β -amylolysis limit (%) determined according to the method of Hizukuri et al (1983b).

TABLE I
Crystallinities, Compositions, and Iodine-Absorption Properties of Rice Starches from IR24 and Sinandomeng Cultivars^a

| Properties | IR24 | Sinandomeng |
|------------------------------------|--------------|--------------|
| Crystallinity (%) | 36.2 | 39.4 |
| Actual amylose content (wt%) | 11.36 ± 0.22 | 10.73 ± 0.15 |
| Damage starch (wt%) | 2.72 ± 0.04 | 4.23 ± 0.11 |
| Crude protein (wt%) | 0.20 ± 0.06 | 0.18 ± 0.04 |
| Crude lipid (wt%) | 0.42 ± 0.09 | 0.41 ± 0.01 |
| Blue values ^b | 0.20 ± 0.01 | 0.16 ± 0.01 |
| λ_{\max} (nm) ^c | 587 ± 1 | 571 ± 2 |

^a Data (except crystallinity) are means ± standard deviations, $n = 3$.

^b Blue values = the absorption intensities of starch-iodine mixture at 680 nm.

^c Maximal absorption wavelengths of starch-iodine mixtures.

TABLE II
Molecular Properties of Starch Fractions from IR24 and Sinandomeng Cultivar^a

| Properties ^b | IR24 | Sinandomeng |
|-------------------------|-------------|-------------|
| Amylose | | |
| DP_n (g.u.) | 690 ± 40 | 613 ± 47 |
| $\beta\text{-AL}$ (%) | 80.0 ± 3.0 | 79.4 ± 3.4 |
| CL (g.u.) | 202 ± 24 | 214 ± 20 |
| NC | 3.4 | 2.9 |
| BV | 1.25 ± 0.01 | 1.36 ± 0.01 |
| λ_{\max} | 651 ± 1 | 648 ± 2 |
| Amylopectin | | |
| DP_n (g.u.) | 5276 ± 36 | 8706 ± 44 |
| $\beta\text{-AL}$ (%) | 58.3 ± 6.3 | 57.7 ± 5.3 |
| CL (g.u.) | 17.2 ± 1.4 | 15.3 ± 0.9 |
| ECL (g.u.) | 12.0 | 10.8 |
| ICL (g.u.) | 4.2 | 3.5 |
| NC | 307 | 569 |
| BV | 0.06 ± 0.01 | 0.05 ± 0.00 |
| λ_{\max} | 533 ± 1 | 533 ± 1 |

^a Data are means ± standard deviations, $n = 3$.

^b DP_n = number-average degree of polymerization, $\beta\text{-AL}$ = β -amylolysis limit, CL = average chain length, NC = DP_n/CL , $ECL = CL \times (\beta\text{-AL}\%) + 2$, $ICL = CL - ECL - 1$, blue values (BV) = the absorption intensities of starch-iodine mixture at 680 nm, and λ_{\max} = maximal absorption wavelengths of starch-iodine mixtures.

Iodine Absorption Property and Chemical Composition

Actual AC of defatted starch was determined with the iodine absorption method (Juliano et al 1981) using various ratios of purified rice amylopectin and amylose to establish a standard curve. Damage starch, crude protein, and lipid contents were determined with the Approved Methods 76-31, 46-11A ($N\% \times 5.95$) and 30-10, respectively (AACC 2000). Blue value (BV, at 680 nm) and the wavelength with maximum absorbance (λ_{\max}) were measured on a solution containing starch component (2.0 mg), iodine (0.40 g), and potassium iodine (4.0 g) in 100 mL of acetate buffer (10 mM and pH 4.8) (Hizukuri et al 1983a).

Gelatinization Properties Measured by DSC

DSC measurements were performed with a Setaram DSC 121 system (Caluire Cedex, France). A portion of starch suspension (25 wt%, ≈ 120 mg) was hermetically sealed in a stainless steel crucible with a stainless steel stopper and aluminum O-ring. The sample was heated from 20 to 120°C at 5°C/min. An empty sealed crucible was used as the reference. The onset (T_o), peak (T_p), and conclusion (T_c) temperatures, as well as enthalpy changes (ΔH in J/g starch) during gelatinization, were means of three replicate measurements.

Rheological Change on Heating-Cooling Process

The pasting property of an 8 wt% starch suspension (25 mL) was measured in a Rapid Visco Analyser (RVA 4D, Newport Scientific Pty., Ltd, Narrabeen, Australia) with an aluminum RVA canister and a paddle rotated at 160 rpm. The temperature program for the sample was 35°C for 1.5 min; heating to 95°C at 6°C/min; 95°C for 4 min; cooling to 35°C at 6°C/min; 35°C for 5 min. Apparent viscosity (cP) was calculated from RVA units (1 RVU ≈ 10 cP).

Dynamic rheological properties during a heating-cooling cycle of starch suspensions at 10–35 wt% were determined using a Carri-Med CSL-100 (TA Instruments Ltd., Surrey, England) with a parallel plate geometry of 20-mm diameter and 1-mm gap. Oscillatory shear mode was used for the temperature sweep: heating from 45 to 95°C at 1°C/min, then cooling to 10°C at 2.5°C/min (Tsai and Lii 2000). A layer of light silicone oil was applied to the exposed edge of the loaded sample to eliminate dehydration. The storage modulus (G'), loss modulus (G''), and $\tan \delta$ (G''/G') of starch suspensions were recorded at a strain of 0.5% and frequency of 1.0 Hz, which are in the linear viscoelastic region examined previously (Lii et al 1995). Data are means of triplicate measurements.

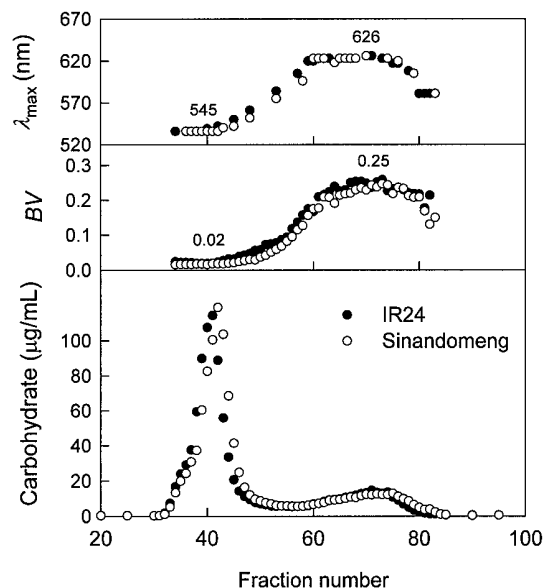


Fig. 1. Gel permeation chromatograms of IR24 and Sinandomeng rice starches fractionated on Tosoh TSK HW-75F (40 mL/hr, 5.0 mL per subfraction, deionized water as eluent). Maximum absorbance (λ_{\max}) and blue value (BV) for bimodal chromatographic peaks of IR24 are indicated.

Powder X-ray Diffraction

A Siemens D 5000 diffractometer (Germany) was operated at the $\text{CuK}\alpha$ wavelength of 0.154 nm, 25 mA, and 35 keV. The spectra over the range of diffraction angles (2θ) = 4.0–30.0° were recorded at a scan rate of 0.02° 2 θ /sec. The spectra were recorded on the starch powders after hydration overnight. From the diffractogram with peaks at 2θ = 15.3°, 17.1°, 18.2°, 20.3°, and 23.5°, apparent crystallinity extent (%) was calculated as the percentage of diffraction peak area to total diffraction area (Cheetham and Tao 1998).

RESULTS AND DISCUSSION

Physicochemical Properties of Starches

The apparent crystallinity extent of IR24 and Sinandomeng starches were 36.2 and 39.4%, respectively (Table I). The IR24 possessed a comparable apparent AC (11.36 wt%), slightly greater BV (0.20) and λ_{max} (587 nm), and lower damage starch content (2.72 wt%) than did the Sinandomeng (AC = 10.73 wt%, BV = 0.16, λ_{max} = 571 nm, and damage starch = 4.23 wt%). The crude protein and lipid contents were equal for both starches (\approx 0.2 and 0.4%, respectively). The AC values of both starches (\approx 11 wt%) are lower than the previous data (18–20 wt%) (Biliaderis et al 1986; Roferos and Juliano 1997), likely due to differences in the cultivated condition of rice (Juliano 1985) and in the standards used for calibration.

Fractionation and Molecular Property

Gel permeation chromatograms of IR24 and Sinandomeng starches on Tosol TSK HW-75F are shown in Fig. 1. The chromatographic peaks for amylopectin and amylose fractions of IR24 starch appeared to show a BV = 0.020 and 0.250 and λ_{max} = 545 and 626 nm, respectively. In contrast to the IR24, these two fractions of Sinandomeng starch showed a somewhat lower BV and λ_{max} values.

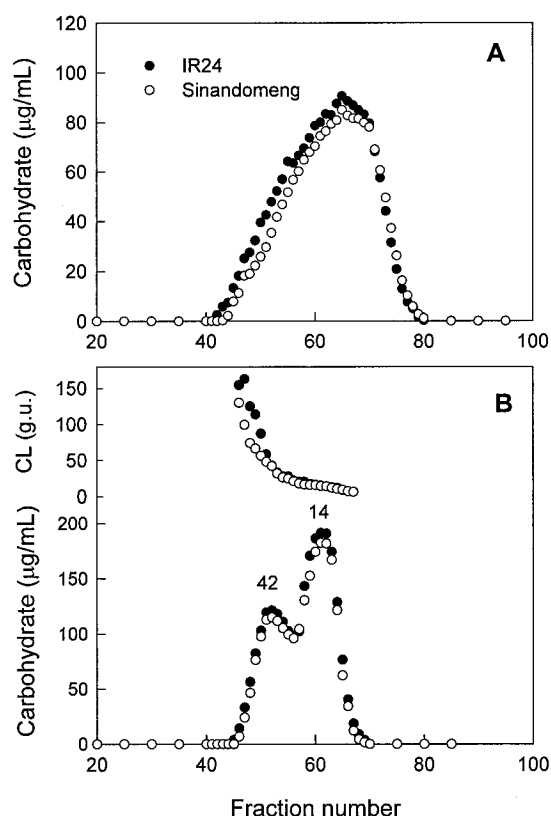


Fig. 2. Gel permeation chromatograms of **A**, IR24 and Sinandomeng amyloses and **B**, debranched amylopectins fractionated on Tosoh TSK HW-65F (40 mL/hr, 2.5 mL per fraction) and HW-50F (30 mL/hr, 5.0 mL per fraction) gels, respectively, both eluted with an aqueous solution containing 1.0 mM NaOH and 25.0 mM NaCl. Numbers indicate chain length (CL) values at chromatographic peaks for both cultivars.

The purified IR24 amylose (Fig. 2A) had a greater proportion of high molecular weight species than did the Sinandomeng. For the debranched amylopectins (Fig. 2B), both cultivars exhibited a similar bimodal distribution peaked at CL = 42 and 14 glucose units (g.u.), and the short-chain (CL \leq 20 g.u.) compositions of 64 wt%. However, the detectable CL values for the long-chain subfraction were notably higher for IR24 (\leq 163 g.u.), in contrast to the Sinandomeng (\leq 130 g.u.). The peak-point CL values of short- and long-chain subfractions for these amylopectins are the same as those for many nonwaxy rice amylopectins, including IR series (Takeda et al 1987; Lu et al 1997), but greater than those for IR29, a waxy rice cultivar (39 and 12 g.u.) (Murugesan et al 1992).

Subfractions with CL ranges of $>$ 55, \approx 20–55, and \leq 20 g.u. by HPLC were previously classified as F1, F2, and F3 (Takeda et al 1987); therefore, the long- and short-chain subfractions in this study can be viewed as F1 + F2 and F3, respectively. The critical CL (20 g.u.) for differentiating short- and long-chain species as well as the short-chain (F3) composition (64 wt%) are the same as those found for 14 cultivars of Taiwanese rice amylopectins (Lu et al 1997). The F3 compositions are within the range reported for the other rice amylopectins of IR series (61–67%) (Takeda et al 1987; Hizukuri et al 1989). Evidently, the IR24 amylopectin appeared to contain a greater amount of extra-long-chain (CL $>$ 100 g.u.) and long-chain species (20 $<$ CL \leq 100 g.u.) (Lu et al 1997) than did the Sinandomeng amylopectin.

The molecular properties of purified amylose and amylopectin fractions from IR24 and Sinandomeng cultivars are listed in Table II.

TABLE III
Pasting and Gelatinization Properties
of IR24 and Sinandomeng Starches^a

| Properties ^b | IR24 | Sinandomeng |
|-------------------------|----------------|----------------|
| RVA | | |
| $T_{o,\eta}$ (°C) | 71.9 \pm 0.2 | 73.0 \pm 0.5 |
| $T_{p,\eta}$ (°C) | 94.3 \pm 0.3 | 95.8 \pm 0.2 |
| P (cP) | 2,627 \pm 24 | 2,321 \pm 16 |
| H (cP) | 1,178 \pm 8 | 1,242 \pm 16 |
| P – H (cP) | 1,449 \pm 31 | 1,080 \pm 31 |
| C (cP) | 2,118 \pm 24 | 2,024 \pm 58 |
| C – H (cP) | 941 \pm 29 | 782 \pm 45 |
| DSC | | |
| T_o (°C) | 63.2 \pm 0.2 | 63.9 \pm 0.1 |
| T_p (°C) | 69.8 \pm 0.2 | 70.7 \pm 0.1 |
| T_c (°C) | 80.0 \pm 0.4 | 80.2 \pm 0.1 |
| ΔH (J/g) | 12.8 \pm 0.2 | 13.1 \pm 0.2 |

^a Data are means \pm standard deviations, n = 3.

^b RVA = Rapid-Visco analysis (8 wt%, 6°C/min); DSC = differential scanning calorimetry (25 wt%, 5°C/min); $T_{o,\eta}$ and $T_{p,\eta}$ = the onset and peak temperatures for rapid viscosity, respectively; P, H, and C = the peak, hot-paste, and cold-paste viscosities, respectively; P – H = breakdown; C – H = setback; T_o , T_p , T_c , and ΔH = the onset, peak, and conclusion temperatures and enthalpy change, respectively, of gelatinization by DSC.

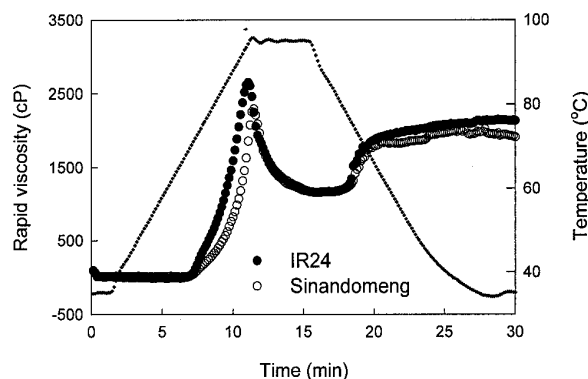


Fig. 3. Rapid viscosity profiles of 8 wt% IR24 and Sinandomeng rice starch suspensions by RVA analysis (heating and cooling rate = 6°C/min, stirring speed = 160 rpm)

The IR24 amylose exhibited a greater average DP_n and NC, comparable CL, β-AL, and λ_{max}, and lower BV compared with the Sinandomeng amylose. For the amylopectins, the IR24 cultivar showed a greater average CL, ECL, and ICL and lower DP_n and NC values than the Sinandomeng. Both amylopectins were similar in β-AL, BV, and λ_{max}. The differences in amylose-DP_n as well as amylopectin-DP_n and CL between IR24 and Sinandomeng can be confirmed by the results of Fig. 2.

For both IR24 and Sinandomeng amyloses, the DP_n values are in the range reported for the other rice amyloses (532–793 g.u.) isolated by autoclaving (Hizukuri et al 1983b). The IR24 amylose also shows a lower DP_n but similar NC compared with the other amyloses of higher AC IR series, including IR32, IR36, IR42, IR48, and IR64 (DP_n = 920–1,040 g.u., NC = 2.3–4.3) (Hizukuri et al 1989). In the case of amylopectins, the IR24 cultivar showed an intermediate DP_n, similar β-AL, and lower CL, BV, and λ_{max} than the higher AC IR series (DP_n = 4,700–15,000 g.u., β-AL = 56–59%, CL = 20–22 g.u., BV = 0.150–0.232, and λ_{max} = 565–575 nm) (Takeda et al 1987; Hizukuri et al 1989).

The iodine absorption properties of starch are concomitantly governed by amylose, intermediate molecules, and the long-chain (especially F1a fraction) composition in amylopectin (Juliano et al 1981; Takeda et al 1987; Hizukuri et al 1989; Radhika Reddy et al 1993). The starches examined contained similar amylose contents; therefore, the iodine reactions may be influenced by amylopectin structure. It is reasonable that, in contrast to Sinandomeng, the IR24 amylopectin had the long-chain species with a higher CL that led to a higher iodine affinity for its parent starch. Accordingly, the extra-long chains (CL > 100 g.u.) in IR24 amylopectin likely play a certain role for iodine affinity, as does the F1a subfraction (CL > 200 g.u.) (Hizukuri et al 1989). However, the result that the BV of IR24 amylose was lower than those of Sinandomeng amylose is inconsistent with that for whole starches (Table I and Fig. 2). This is perhaps due to the higher NC for IR24 amylose (Table II), despite its greater proportion of high molecular weight species (Fig. 2A).

Pasting and Thermal Properties During Gelatinization

The rapid viscosity changes of 8 wt% starch suspensions during RVA measurements are shown in Fig. 3. Clearly, the IR24 starch suspension showed a notably greater viscosity during pasting (at <95°C) and cooling processes as compared with the Sinandomeng. On cooling of both starches, the major increment in viscosity was observed at 80–70°C, rather than at 70–35°C,

due to the formation of hydrogen bonds between starch molecular chains (Tako and Hizukuri 2000). The RVA as well as DSC parameters during gelatinization of these starches examined are listed in Table III. The onset temperature of viscosity increment (T_{o,η}) and the temperature for peak viscosity (T_{p,η}) were lower for IR24 starch than for the Sinandomeng. The IR24 also exhibited a greater peak viscosity (P), breakdown (P – H), cold-paste viscosity (C), and setback (C – H), but lower hot-paste viscosity (H) than the Sinandomeng. As for the DSC parameters during starch gelatinization at 25 wt%, only the T_o and T_p for the IR24 were somewhat different than those for the Sinandomeng. The results wherein IR24 starch had a greater P, P – H, and H, but lower C – H than the Sinandomeng, coincide with those examined at 10 wt% by viscoamylography (Roferos and Juliano 1997). The gelatinization temperatures of IR24 starch differ between this study and a previous report of T_o, T_p, and T_c = 60, 68.7, and 77°C (Biliaderis et al 1986) by ≈3°C.

Dynamic Rheological Change During Heating-Cooling Process

The changes in storage modulus (G') of IR24 and Sinandomeng starch suspensions on heating and subsequent cooling processes are compared in Fig. 4. Typically, the G' at 10 wt% increased during the early heating period (72–87°C) due to granular swelling and decreased thereafter due to disintegration of closed-packed swollen granules (Lii et al 1996). The G' profile on heating sharpened when starch concentration increased to >15 wt%, accompanying with a reduced temperature at which G' maximized (T_{G'max}). This may be attributed to greater compactness between swollen granules at higher starch concentrations. On cooling to <80°C, the G' at 10 wt% increased progressively, in accord with the result of RVA (Fig. 3) and reflecting the interactions between just close-packed swollen granules (Lii et al 1996; Tsai et al 1997) and leaching components (Tsai and Lii 2000). However, the G' increment on cooling was comparatively less notable at higher starch concentrations likely due to limited leaching properties.

The effects of starch concentration on the rheological parameters during the heating-cooling process are indicated in Table IV. When the concentration of IR24 starch increased from 10 to 35 wt%, the onset and peak temperatures of G' increase on heating (T_{o,G'} and T_{G'max}) reduced from 72.5 to 65.1°C and from 86.1 to 68.9°C, respectively, on average. The maximal G' (G'_{max}) and the G' values at 95 and 10°C (G'₉₅ and G'₁₀) rose from 934 to 27,503 Pa, 362 to 6,114 Pa, and 577 to 7,055 Pa, respectively. The tan δ₉₅ decreased from 0.164 to 0.101, contrary to the tan δ₁₀ increasing from 0.087 to 0.137. In the case of Sinandomeng, the T_{o,G'}, T_{G'max}, and tan δ₉₅

TABLE IV
Dynamic Rheological Properties of IR24 and Sinandomeng Starch Suspensions During Heating-Cooling Processes^a

| Properties ^b | Starch Concentration (wt%) | | | | Exponent <i>n</i> ^c |
|-------------------------|----------------------------|---------------|---------------|---------------|--------------------------------|
| | 10 | 15 | 25 | 35 | |
| IR24 | | | | | |
| T _{o,G'} (°C) | 72.5 ± 0.1 | 71.1 ± 0.2 | 67.2 ± 0.1 | 65.1 ± 0.1 | -14.1 |
| T _{G'max} (°C) | 86.1 ± 0.3 | 78.5 ± 0.2 | 71.7 ± 0.1 | 68.9 ± 0.4 | -31.6 |
| G' _{max} (Pa) | 934 ± 36 | 3,234 ± 22 | 9,418 ± 59 | 27,503 ± 1426 | 2.61 |
| G' ₉₅ (Pa) | 362 ± 24 | 804 ± 52 | 2,193 ± 106 | 6,114 ± 217 | 2.21 |
| tan δ ₉₅ | 0.164 ± 0.012 | 0.136 ± 0.003 | 0.114 ± 0.001 | 0.101 ± 0.002 | ... |
| G' ₁₀ (Pa) | 577 ± 11 | 1,016 ± 16 | 2,920 ± 129 | 7,055 ± 358 | 2.08 (2.03) |
| tan δ ₁₀ | 0.087 ± 0.002 | 0.081 ± 0.001 | 0.107 ± 0.003 | 0.137 ± 0.003 | ... |
| Sinandomeng | | | | | |
| T _{o,G'} (°C) | 72.8 ± 0.3 | 70.6 ± 0.1 | 66.6 ± 0.1 | 64.2 ± 0.0 | -16.1 |
| T _{G'max} (°C) | 88.5 ± 0.2 | 78.4 ± 0.5 | 71.5 ± 0.2 | 69.0 ± 0.1 | -35.5 |
| G' _{max} (Pa) | 792 ± 77 | 3,053 ± 352 | 8,867 ± 1084 | 23,693 ± 358 | 2.62 |
| G' ₉₅ (Pa) | 371 ± 31 | 879 ± 110 | 2,621 ± 414 | 6,719 ± 318 | 2.28 |
| tan δ ₉₅ | 0.166 ± 0.007 | 0.138 ± 0.002 | 0.109 ± 0.004 | 0.093 ± 0.001 | ... |
| G' ₁₀ (Pa) | 499 ± 25 | 1,167 ± 91 | 3,008 ± 367 | 7,121 ± 137 | 2.00 (2.05) ^c |
| tan δ ₁₀ | 0.114 ± 0.005 | 0.095 ± 0.001 | 0.108 ± 0.003 | 0.135 ± 0.001 | ... |

^a Heating and cooling rates = 1.0 and 2.5°C/min, respectively. Data are present as mean ± standard deviation, *n* = 3.

^b T_{o,G'} and T_{G'max} = temperatures at which G' started to increase and maximized, respectively; G'_{max}, G'₉₅, and G'₁₀ = the G' maxima and G' values at 95 and 10°C, respectively; tan δ₉₅ and tan δ₁₀ = tan δ values at 95 and 10°C, respectively.

^c Relationship of T ∝ Cⁿ or G' ∝ Cⁿ, where C is starch concentration (wt%). Data in parenthesis are for G'₂₅.

were 64.2, 69.0, and 0.093 at 35 wt%, less than those at 10 wt% by 8.6°C, 19.5°C, and 0.073, respectively. The G'_{max} , G'_{95} , G'_{10} , and $\tan \delta_{10}$ at 35 wt% were greater than those at 10 wt% by 29.9-fold, 18.1-fold, 14.3-fold, and 0.021, respectively. The exponents (n) of concentration dependencies for $T_{o,G'}$ and $T_{G'_{max}}$ ($T \propto C^n$) were lower for IR24 than for Sinandomeng. However, the n values for G'_{max} , G'_{95} , and G'_{10} ($G' \propto C^n$) were similar for both cultivars ($\approx 2.6, 2.2$, and 2.0 , respectively). The n values for G'_{10} were almost the same as for G'_{25} . Generally, the concentration effects on the above rheological parameters tended to be greater for Sinandomeng than for IR24.

By comparing with our previous studies on Kaoshiung Sen (KSS7), Tainung 67 (TNU67), and Taichung waxy 70 (TCW70) rice starches (Lii et al 1995; Tsai et al 1997), the n of $G'_{25} \propto C^n$ follows the sequence of KSS7 (AC = 25.6%, $n = 3.2$) > TNU67 (AC = 14.8%, $n = 2.4$) > IR24 and Sinandomeng (AC = 11.0%, $n = 2.0$) > TCW70 (AC = 1.0%, $n = 1.3$ – 1.4). Interestingly, the n value increased with increasing AC (Fig. 5) in a very good linearity: $n = 0.076 AC + 1.246$ ($r^2 = 0.995$). Because the hardness of freshly cooked rice correlated significantly with AC (Juliano 1998), the n of $G'_{25} \propto C^n$ may closely relate to the hardness of freshly cooked rice. This points to the fact that amylose is the primary factor in governing the retrogradation of gelatinized starch systems after cooling (Miles et al 1985).

The similarity and dissimilarity in the physicochemical properties of the rice starches are summarized in Table V to clarify the structure and physical relationship of starches. The properties that

were similar for IR24 and Sinandomeng included AC, CL, β -AL, λ_{max} of amylose (AM), β -AL, BV, and λ_{max} of amylopectin (AP), T_c and ΔH by DSC, $T_{o,G'}$, G'_{95} , and $\tan \delta_{95}$ at low starch concentrations (10 wt%), and $T_{G'_{max}}$, G'_{10} , and $\tan \delta_{10}$ at high starch concentrations, and the n of $G'_{25} \propto C^n$. The properties in which IR24 predominated over Sinandomeng were BV and λ_{max} of starch, DP_n and NC of AM, CL, ECL, and ICL of AP, pasting parameters P, P-H, C, and C-H, $T_{o,G'}$, and $\tan \delta_{95}$ at high starch concentrations, G'_{max} over the concentration examined, and G'_{10} at a low starch concentration (10 wt%). The properties in which Sinandomeng predominated over IR24 were apparent crystallinity level, BV of AM, the DP_n and NC of AP, pasting parameters $T_{o,\eta}$, $T_{p,\eta}$, and H, T_o and T_p by DSC, $T_{G'_{max}}$ and $\tan \delta_{10}$ at low starch concentrations, and G'_{95} at high starch concentrations.

TABLE V
Comparison of the Physicochemical Properties of Rice Starches from IR24 and Sinandomeng Cultivars

| Properties ^a | Gelatinization and Rheological Properties ^b |
|--------------------------------------|---|
| IR24 \approx Sinandomeng | |
| AC | $T_c, \Delta H$ |
| AM-CL, β -AL, λ_{max} | $T_{o,G'}$ (10 wt%), $T_{G'_{max}}$ (15–35 wt%) |
| AP- β -AL, BV, λ_{max} | G'_{95} (10 wt%), G'_{10} (15–35 wt%), $\tan \delta_{95}$ (10–15 wt%), $\tan \delta_{10}$ (25–35 wt%), n of $G'_{25} \propto C^n$ |
| IR24 > Sinandomeng | |
| Starch-BV, λ_{max} | P, P-H, C, C-H |
| AM- DP_n , NC | $T_{o,G'}$ (15–35 wt%), G'_{max} (10–35 wt%) |
| AP-CL, ECL, ICL | G'_{10} (10 wt%), $\tan \delta_{95}$ (25–35 wt%) |
| IR24 < Sinandomeng | |
| Crystallinity level | $T_{o,\eta}, T_{p,\eta}, H; T_o, T_p$ |
| AM-BV | $T_{G'_{max}}$ (10 wt%), G'_{95} (15–35 wt%) |
| AP- DP_n , NC | $\tan \delta_{10}$ (10–15 wt%) |

^a AC = the actual amylose content, AM = amylose, DP_n = number-average degree of polymerization, β -AL = β -amylolysis limit, CL = average chain length, NC = DP_n/CL , ECL = $CL \times (\beta\text{-AL}\%) + 2$, ICL = $CL - ECL - 1$, blue values (BV) = the absorption intensities of starch-iodine mixture at 680 nm, and λ_{max} = maximal absorption wavelengths of starch-iodine mixtures.

^b T_o, T_p, T_c , and ΔH = the onset, peak, and conclusion temperatures and enthalpy change, respectively, of gelatinization by differential scanning calorimetry; $T_{o,\eta}$ and $T_{p,\eta}$ = the onset and peak temperatures for rapid viscosity, respectively; P, H, and C = the peak, hot-paste, and cold-paste viscosities, respectively; P-H = breakdown; C-H = setback; $T_{o,G'}$ and $T_{G'_{max}}$ = the temperatures at which G' started to increase and maximized, respectively; G'_{max}, G'_{95} , and G'_{10} = the G' maxima and G' values at 95 and 10°C, respectively; $\tan \delta_{95}$ and $\tan \delta_{10}$ = the $\tan \delta$ values at 95 and 10°C, respectively; $G' \propto C^n$, where C is starch concentration (wt%).

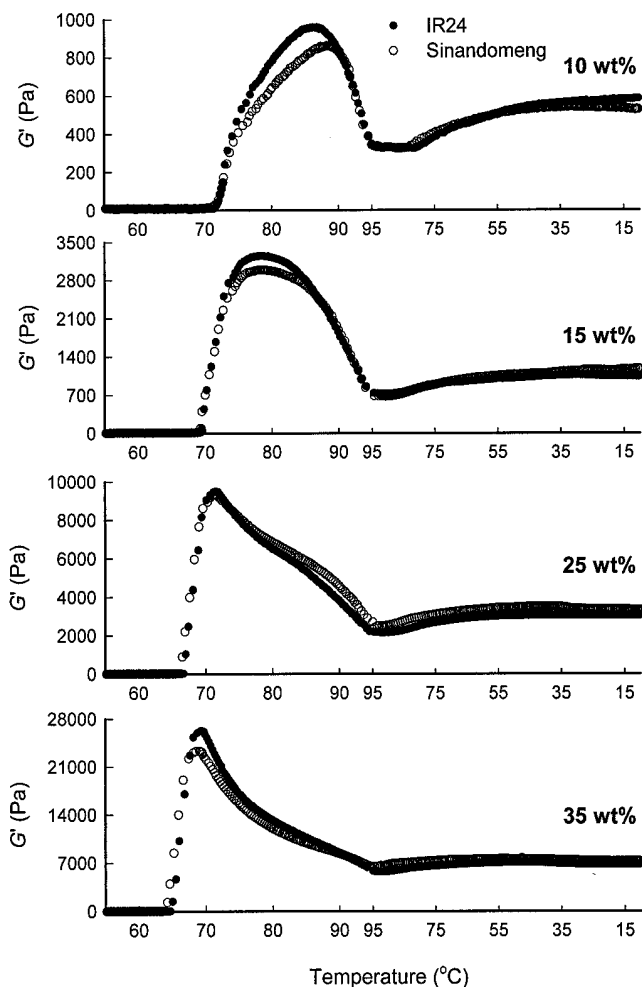


Fig. 4. Developments in storage modulus (G') during heating and subsequent cooling processes of IR24 and Sinandomeng rice starch suspensions at 10–35 wt% (heating rate = 1.0°C/min, cooling rate = 2.5°C/min, frequency = 1 Hz, strain = 0.5%).

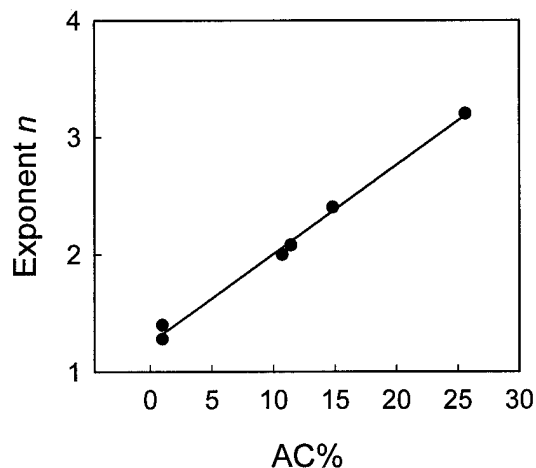


Fig. 5. Relationship between the exponent n of $G'_{25} \propto C^n$ and amylose content (AC) of rice starches from cultivars IR24, Sinandomeng (in this study), KSS7, TNU67, and TCW70 (Lii et al 1995; Tsai et al 1997) (G'_{25} = G' value [Pa] of a gelatinized starch dispersion cooled to 25°C, C = starch concentration [wt%]).

Theoretically, starch granules swell freely with notable leaching and swell quite limitedly with little leaching, respectively, in the 8–10 wt% and 35 wt% systems (Lii et al 1996; Tsai and Lii 2000). The results of the low and high concentration systems are considered with some important molecular factors to facilitate the understanding of the structural effects from amylose and amylopectin. For the 8–10 wt% systems, the gelatinization properties, including the $T_{o,G}$, G'_{95} , and $\tan \delta_{95}$, that analyzed without instrumental interferences follow the same sequence as AC, indicating they likely depend on AC. However, the P, P – H, H, $T_{o,\eta}$, and $T_{p,\eta}$ detected under serious shearing seems to relate with granular structure and therefore with molecular structure. The higher crystallinity level for Sinandomeng starch rather than IR2, may account for its lower P and P – H, and higher $T_{o,\eta}$, $T_{p,\eta}$, H, and $T_{G'_{max}}$ values because of greater granular rigidity and more limited swelling.

When the low concentration systems retrograded on cooling, the C, C – H, G'_{10} , and $\tan \delta_{10}$ depended on molecular structure. Low AC rice starches generally show a hot-water-soluble content comparable to corresponding AC (Lii et al 1996; Tsai et al 1997); therefore, this would be true for IR24 and Sinandomeng starches. Accordingly, the structure of amylose molecules would play an important role in the parameters involving retrogradation. Compared with Sinandomeng, IR24 amylose possessed a higher DP_n , as well as greater proportion of high molecular weight species and had higher C, C – H, G'_{10} , and lower $\tan \delta_{10}$ (more elastic) than its parent starch. These results coincide with the reports on the addition of hot-water-soluble starch components to rice starches (Tsai and Lii 2000) that high molecular weight additives promote the retrogradation of rice starches during cooling and early aging (25°C for 3.5 hr) more effectively than the low molecular weight additives. Nevertheless, the greater CL (CL, ECL, and ICL) of amylopectin would also partially contribute to the retrogradation parameters, especially the long-chain composition of amylopectin (Jane et al 1999; Tako and Hizukuri 2000). Minor differences in amylose CL of between IR24 and Sinandomeng has negligible influences on these properties.

For the 35 wt% starch systems, in which the moisture contents approach those of cooked rice, the $T_{G'_{max}}$, G'_{10} , and $\tan \delta_{10}$ are likely governed by AC, resembling the result on Instron hardness of freshly cooked rice (Roferos and Juliano 1997). However, the G'_{max} , $\tan \delta_{95}$, and G'_{95} that mainly relate to granular rigidity at high concentrations (Tsai et al 1997) appear to be affected by molecular structure. Higher amylose DP_n , amylopectin CL, and DP_n may result in more rigid granules and possibly in hardening of staled cooked rice, like in maize starch (Mua and Jackson 1998). Nonetheless, the structural effects of amylose and amylopectin on starch granular property need to be further investigated in terms of starch concentration and storage period. These results also imply that greater CL, as well as a proportion of long and extra-long chains on amylopectin molecules, can account for the hardening of staled cooked rice for IR24 (Roferos and Juliano 1997) and for some high AC indica rice (Lu et al 1997; Lii et al 1998) because of high retrogradation tendencies (Yuan et al 1993; Würsch and Gumy 1994; Shi and Seib 1995; Lai et al 2000).

CONCLUSIONS

IR24 and Sinandomeng rice starches had a similar AC and their amylose and amylopectin fractions had analogous iodine absorption properties. The starch suspensions of these two cultivars exhibited generally similar dynamic rheological parameters on heating to 95°C at 10 wt% and on cooling to 10°C at high concentrations. In contrast to Sinandomeng, the properties of IR24 starches included higher peak, cold paste, and setback viscosities as well as G'_{10} at low starch concentrations, and G'_{max} over the concentration examined could be linked to its greater amylose- DP_n and amylopectin-CL. The higher amylose NC together with lower apparent crystallinity level, and lower amylopectin- DP_n and NC for IR24 starch may

be responsible for the lower values in pasting and gelatinization temperatures, hot paste viscosity, $\tan \delta_{10}$ at low concentrations, and G'_{95} at high starch concentrations. The n value of $G'_{25} \propto C^n$ on cooling of rice starches increased with increasing AC in excellent linearity and may reflect the hardness of freshly cooked rice. The structural effects of amylose and amylopectin on these properties can be understood to a greater extent by considering the soluble and granular properties. However, the effects of amylose content and starch structure on the rheological, textural, or eating properties of commercial cooked rice products that may experience long-term storage should be studied.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Council, Executive Yuan, Taiwan (NSC-88-2113-M-001-034).

LITERATURE CITED

- AACC. 2000. Approved Methods of the American Association of Cereal Chemists, 10th ed. Methods 76-31, 46-11A, and 30-10. The Association: St. Paul, MN.
- Biliaderis, C. G., Page, C. M., Maurice, T. J., and Juliano, B. O. 1986. Thermal characterization of rice starches: A polymeric approach to phase transitions of granular starch. *J. Agric. Food Chem.* 34:6-14.
- Cheetham, N. W. H., and Tao, L. 1998. Variation in crystalline type with amylose content in maize starch granules: An X-ray powder diffraction study. *Carbohydr. Polym.* 36:277-284.
- Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., and Smith, F. 1956. Colorimetric method for determination of sugars and related substance. *Anal. Chem.* 28:350-356.
- Hizukuri, S., Kaneko, T., and Takeda, Y. 1983a. Measurement of the chain length of amylopectin and its relevance to the origin of crystalline polymorphism of starch granules. *Biochim. Biophys. Acta* 760:188-191.
- Hizukuri, S., Shirasaka, K., and Juliano, B. O. 1983b. Phosphorus and amylose branching in the rice starch granules. *Starch* 35:348-350.
- Hizukuri, S., Takeda, Y., Maruta, N., and Juliano, B. O. 1989. Molecular structures of rice starch. *Carbohydr. Res.* 189:227-235.
- Hizukuri, S., Takeda, Y., Yasuda, M., and Suzuki, A. 1981. Multibranched nature of amylose and the action of debranching enzymes. *Carbohydr. Res.* 94:205-213.
- Jane, J., Chen, Y. Y., Lee, L. F., McPherson, A. E., Wong, K. S., Radosavljevic, M., and Kasemsuwan, T. 1999. Effects of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch. *Cereal Chem.* 76:629-637.
- Juliano, B. O. 1985. Criteria and tests for rice grain qualities. Pages 443-524 in: *Rice: Chemistry and Technology*. B. O. Juliano, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.
- Juliano, B. O. 1998. Varietal impact on rice quality. *Cereal Foods World* 43:207-221.
- Juliano, B. O., Perez, C. M., Blankeney, A. B., Castillo, D. T., Kongseree, N., Laignelet, B., Lapis, E. T., Murty, V. V. S., Paule, C. M., and Webb, B. D. 1981. International cooperative testing on the amylose content of milled rice. *Starch* 33:157-162.
- Lai, V. M. F., Lu, S., and Lii, C.-y. 2000. Molecular characteristics influencing retrogradation kinetics of rice amylopectins. *Cereal Chem.* 77:272-278.
- Lii, C., Lai, V. M. F., Lu, S., and Tsai, M.-L. 1998. Correlation between the physical property, eating quality and the molecular structure of rice-starchy systems. *Zywnosc. Technologia. Jakosc.* (Poland) 4(17):72-86.
- Lii, C., Lai, V. M. F., and Tsai, M.-L. 1996. Studies on starch gelatinization and retrogradation with dynamic rheometry—The influence of starch granular structure and composition. *Zywnosc. Technologia. Jakosc.* (Poland) 2(7):27-53.
- Lii, C., Shao, Y.-Y., and Tseng, K.-H. 1995. Gelation mechanism and rheological properties of rice starch. *Cereal Chem.* 72:393-400.
- Lu, S., Chen, L.-N., and Lii, C. 1997. Correlations between the fine structure, physicochemical properties, and retrogradation of amylopectins from Taiwan rice varieties. *Cereal Chem.* 74:34-39.
- Manners, D. J. 1989. Recent development in our understanding of amylopectin structure. *Carbohydr. Polym.* 11:87-112.
- Miles, M. J., Morris, V. J., Orford, P. D., and Ring, S. G. 1985. The roles of amylose and amylopectin in the gelation and retrogradation of starch. *Carbohydr. Res.* 135:271-281.

- Mua, J. P., and Jackson, D. S. 1998. Retrogradation and gel textural attributes of corn starch amylose and amylopectin fractions. *J. Cereal Sci.* 27:157-166.
- Murugesan, G., Hizukuri, S., Fukuda, M., and Juliano, B. O. 1992. Structure and properties of waxy-rice (IR29) starch during development of the grain. *Carbohydr. Res.* 223:235-242.
- Nelson, N. 1944. A photometric adaptation of the Somogyi method for the determination of glucose. *J. Biol. Chem.* 153:375-378.
- Radhika Reddy, K., Zakiuddin Ali, S., and Bhattacharya, K. R. 1993. The fine structure of rice-starch amylopectin and its relation to the texture of cooked rice. *Carbohydr. Polym.* 22:267-275.
- Roferos, L. T., and Juliano, B. O. 1997. Chemometrics of grain quality of raw and cooked Philippine milled rice. *Phillipp. Agric.* 80:211-236.
- Shi, Y.-C., and Seib, P. A. 1995. Fine structure of maize starches from four *wx*-containing genotypes of the W64A inbred line in relation to gelatinization and retrogradation. *Carbohydr. Polym.* 26:141-147.
- Somogyi, M. 1952. Notes on sugar determination. *J. Biol. Chem.* 195:19-23.
- Takeda, Y., Hizukuri, S., and Juliano, B. O. 1986. Purification and structure of amylose from rice starch. *Carbohydr. Res.* 148:299-308.
- Takeda, Y., Hizukuri, S., and Juliano, B. O. 1987. Structure of rice amylopectins with low and high affinities for iodine. *Carbohydr. Res.* 168:79-88.
- Tako, M., and Hizukuri, S. 2000. Retrogradation mechanism of rice starch. *Cereal Chem.* 77:473-477.
- Tsai, M.-L., Li, C.-F., and Lii, C. 1997. Effects of granular structures on the pasting behaviors of starches. *Cereal Chem.* 74:750-757.
- Tsai, M.-L., and Lii, C. 2000. Effect of hot-water-soluble components on the rheological properties of rice starch. *Starch* 52:44-53.
- Würsch, P., and Gumy, D. 1994. Inhibition of amylopectin retrogradation by partial beta-amyolysis. *Carbohydr. Res.* 256:129-137.
- Yang, C. C., Lai, H. M., and Lii, C. 1984. The modified alkaline steeping method for the isolation of rice starch. *Food Sci. (Taiwan)* 11:158-171.
- Yuan, R. C., Thompson, D. B., and Boyer, C. D. 1993. Fine structure of amylopectin in relation to gelatinization and retrogradation behavior of maize starches from three *wx*-containing genotypes in two inbred lines. *Cereal Chem.* 70:81-89.

[Received February 20, 2001. Accepted May 17, 2001.]