

Starch fine structure and physicochemical properties of specialty rice for canning

James A. Patindol^a, Blanca C. Gonzalez^a, Ya-Jane Wang^{a,*}, Anna M. McClung^b

^aDepartment of Food Science, University of Arkansas, Fayetteville, AR 72704, USA

^bUSDA-ARS Rice Research Unit, Beaumont, TX 77713, USA

Received 20 January 2006; received in revised form 10 August 2006; accepted 28 August 2006

Abstract

The long-grain, specialty rice cultivars, Bolivar, Cheniere, Dixiebelle, and L-205 are used for wet-pack canning. These cultivars have similar apparent amylose content but showed differences in canning, pasting, and gelatinization properties. Starch fine structures were analyzed to rationalize observed differences in functionality. Cheniere amylopectin had the lowest weight-average molar mass (M_w), shortest average chain length (CL), smallest z -average radius of gyration (R_z), lowest proportion of long chains (DP 37–65), and highest polydispersity; while its amylose had the largest M_w and R_z . These structural features were associated with more leached solids in the canning broth, lower volume expansion, lower peak and final viscosity, and lower gelatinization temperature and enthalpy. Bolivar amylopectin had the largest M_w , longest average CL, largest R_z , highest proportion of long chains (DP 25–65), and lowest proportion of short chains (DP 6–12); while its amylose had the smallest M_w and lowest polydispersity. These structures were associated with lower levels of leached solids, higher volume expansion, and higher peak and final viscosity. L-205 was similar to Bolivar in most structural and functional properties; those of Dixiebelle were either comparable to Bolivar or intermediate to Bolivar and Cheniere. These findings point to the importance of the molar mass of amylopectin and the proportion of long and short chains on the canning stability of rice. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Specialty rice; Canning; Starch structure; Amylopectin; Amylose

1. Introduction

There is an increasing demand for thermally processed or canned rice products for soups, puddings, and dinners. Such products are of primary importance as a convenience food for the prevailing fast-paced urban lifestyle, for people in a military or space mission, in evacuation centers in times of disasters, and in other situations where cooking facilities are limited or unavailable. In the United States, canned rice products are usually processed by the wet-pack

procedure starting with parboiled rice (Alary et al., 1977; Burns and Gerdes, 1985; Juliano and Hicks, 1996; Sharp et al., 1981; Webb, 1979). Wet-pack canning subjects rice to some severe processing steps that generally involve precooking (or blanching), draining and washing in cold water, adding the blanched rice, broth and other ingredients to cans, sealing, and retorting the sealed cans (Burns and Gerdes, 1985; Webb, 1979). Hence, rice breeders select lines and varieties for canning based on their ability to withstand these severe processing conditions. On canning, the kernels should remain separate and non-cohesive, with resistance to longitudinal splitting and fraying of edges and ends, and yield minimal leached solids into the broth (Bergman et al., 2004; Burns and Gerdes, 1985; Juliano and Hicks, 1996; Webb, 1979).

Past research on the interrelationships between stability during parboiling and canning and other parameters of rice quality showed that apparent amylose content was the best overall indicator for predicting parboiling and canning

Abbreviations: AAR, amylose–amylopectin ratio; CL, chain length; DMRT, Duncan's multiple range test; DP, degree of polymerization; HPAEC-PAD, high-performance anion-exchange chromatography with pulsed amperometry detector; HPSEC-MALLS-RI, high-performance size-exclusion chromatography with multi-angle laser light scattering and refractive index detectors; M_w , weight-average molar mass; R_z , z -average radius of gyration; SRC, specialty rice cultivars for canning

*Corresponding author. Tel.: +1 479 575 3871; fax: +1 479 575 6936.

E-mail address: yjwang@uark.edu (Y.-J. Wang).

stability (Alary et al., 1977; Webb, 1979). Rice cultivars that are ideal for use in parboiling and canning are those with intermediate to high amylose content and an intermediate gelatinization temperature (Alary et al., 1977; Juliano and Hicks, 1996; Webb, 1979). Consequently, apparent amylose content has been customarily used as a principal criterion in making selection and crossing decisions aimed at developing rice cultivars for parboil-canning application. Other important indicators are starch iodine-blue value, alkali spreading value (as index of gelatinization temperature), protein content, and grain width (Webb, 1979).

It has been recognized that apparent amylose content alone cannot explain all of the variations in rice functionality because varieties with similar apparent amylose content often show some differences in processing performance and final product organoleptic qualities. Parameters that can better differentiate rice varieties belonging to the same amylose class and grain type are needed. More recent studies have highlighted the importance of starch (amylose and amylopectin) molecular structure, size, weight, branching pattern, and other structural features on rice functionality (Bergman et al., 2004; Cameron and Wang, 2005; Han and Hamaker, 2001; Horibata et al., 2004; Inouchi et al., 2005; Mizukami et al., 1999; Ong and Blanshard, 1995; Patindol and Wang, 2002; Ramesh et al., 1999, 2000; Vandeputte et al., 2003). Studies that relate cultivar differences in canning stability with the structural features of starch are relatively scarce. Hence, this aspect of rice functionality was investigated in the present work. Four specialty long-grain rice cultivars, Bolivar, Cheniere, Dixiebelle, and L-205 were compared with a regular long-grain variety, Wells, for their starch fine structure, and canning, leaching, pasting, gelatinization, and other physicochemical properties. The findings of this study may be of value to rice breeders in their crossing and selection decisions and to rice growers and processors in choosing appropriate varieties and conditions for optimal canning application.

2. Materials and methods

2.1. Materials

Dried rough rice samples (MC~12.0%) from cultivars Bolivar, Cheniere, Dixiebelle, L-205 were obtained from the 2003 crop of the USDA-ARS Rice Research Unit at Beaumont, TX, USA. Wells, a regular long-grain cultivar, included as a control, was obtained from the 2004 crop of the Rice Research and Extension Center, Stuttgart, Arkansas, and provided by the Rice Processing Program at the University of Arkansas, Fayetteville, Arkansas. The samples were stored at 4°C until analyzed.

2.2. Milling

Samples of rough rice (150 g) were shelled with a rice dehuller (Satake THU-35, Satake Corporation, Hiroshima,

Japan), and the brown rice recovered milled for 30 s in a friction mill (McGill Miller #2, Rapsco, Brookshire, TX). The resulting milled rice was separated into head rice and broken kernels on a double-tray shaker table (GrainMan Machinery, Miami, FL) with 4.67-mm indentations on both trays. Only head rice kernels were used in the study.

2.3. Preparation of flour and starch samples

Head rice was ground into flour with a cyclone sample mill (Udy Corp., Ft. Collins, CO) fitted with a 0.50-mm sieve. Starch was isolated from head rice following the alkali-steeping method of Yang et al. (1984) with slight modifications (Patindol and Wang, 2002). A 10-g head rice sample was soaked in 40 ml of 0.1% NaOH overnight at room temperature. The soaked sample was then wet-milled in an Osterizer blender for 4 min at speed 6, filtered through a US standard sieve #230, and centrifuged at 1500g for 15 min. The supernatant and the top yellow layer (tailing starch) of the residue were discarded. The prime starch was then washed with 0.1% NaOH, centrifuged using the same speed as before, and the supernatant and top yellow layer were also discarded. The pH of the residue was then adjusted to 6.5 with 0.2 M HCl, and washed with 40 ml deionized water three times. After the final centrifugation, the starch residue was collected and dried in a convection oven at 40°C for 24 h, ground into powder with a mortar and pestle to pass through a standard 100-mesh sieve. A portion of the dried starch sample was defatted with water-saturated 1-butanol as described by Patindol and Wang (2002). Defatted starch samples were used for the preparation of amylopectin and for amylopectin and amylose structure characterization.

2.4. Chemical composition of rice flour and starch

Moisture content was determined by Approved Method 44-15A (AACC, 2000). Duplicate 2-g samples were placed in aluminum moisture dishes and dried at 130°C in a convection oven for 2 h. Crude protein content was measured by a micro-kjeldahl apparatus according to approved method 46-13 (AACC, 2000), using a 0.5 g sample and a factor of 5.95 for converting nitrogen content to protein. Total lipid was determined according to approved method 30-20 (AACC, 2000) with modifications (Matsler and Siebenmorgen, 2005). Rice flour (4–5 g) was extracted with 70 ml of petroleum ether by boiling at 135°C for 20 min and rinsing for 30 min in a soxtec system (Avanti 2055; Foss North America; Eden prairie; MN). Apparent amylose content was determined by iodine colorimetry (Juliano et al., 1981) for flour and leached solids, and iodine potentiometric titration for starch (Schoch, 1964). Total starch content in rice flour and leached solids was determined by amyloglucosidase/alpha-amylase enzymatic assay following approved method 79-13 (AACC, 2000) with an enzyme kit (Megazyme; Wicklow; Ireland). Sugars in the dried leached solids were extracted with 80% ethanol

at 75 °C (100 mg samples with 5 ml 80% ethanol) for 10 min with magnetic stirring; centrifuged at 1500g for 10 min, and repeating the extraction twice. The phenol-sulfuric acid method for the determination of total carbohydrates (Dubois et al., 1956) was used to estimate the amount of dissolved saccharides in the pooled supernatant.

2.5. Isolation of amylopectin from starch

Amylopectin was purified from starch by a modified procedure based on the method of Takeda et al. (1986). Defatted starch sample (~200 mg) was weighed into a 25-ml screw-cap test tube, dispersed with 12 ml of 0.2 M NaOH, and stirred in an oil bath at 65 °C for 18 h. The pH of the starch solution was neutralized with 1 M HCl, and then added with 2.4 ml of 1-butanol and stirred at 100 °C in an oil bath for 3 h under nitrogen. The capped test tube with its content was transferred into a tightly sealed 2-l Dewar thermo-flask (Lab-line Instruments Inc., Melrose Park, IL) filled with hot water and incubated for 24 h to allow the formation of amylose-1-butanol complexes. After incubation, the sample was removed from the Dewar flask and kept at 4 °C for 48 h in a refrigerator. The insoluble amylose-butanol complex was separated by centrifugation at 11,000g and 4 °C for 45 min. The supernatant containing mostly amylopectin was further purified by another recrystallization cycle with the addition of 1.0 ml of 1-butanol. At the end of the second recrystallization, the purified amylopectin was precipitated by adding 100 ml of methanol, and the mixture was kept at room temperature for 24 h. The precipitated amylopectin was then collected by centrifugation at 1500g for 15 min at room temperature, washed with 30 ml of methanol, and dried at 40 °C for 24 h.

2.6. Amylopectin chain length distribution

The chain length (CL) distribution of purified amylopectin was characterized by high-performance anion-exchange chromatography equipped with a pulsed amperometric detector (HPAEC-PAD) according to the method of Kasemsuwan et al. (1995) with modifications. The HPAEC-PAD system (DX500, Dionex Co., Sunnyvale, CA) consisted of the following components: GP50 gradient pump, LC20-1 chromatography organizer, ED40 electrochemical detector, 4 × 50-mm CarboPac PA1 guard column, 4 × 250-mm CarboPac PA1 analytical column, and AS40 automated sampler. Purified amylopectin (9.0 mg) was dissolved in 3.2 ml of deionized water by heating in a boiling water bath with stirring for 1 h. After cooling to room temperature, 0.4 ml of 0.1 M acetate buffer (pH 3.5) and 20 µl of isoamylase (EC 3.2.1.68) (1180U; Hayashibara Biochemical Laboratories, Okayama, Japan) were added, and the mixture was incubated at 40 °C for 48 h in a water bath shaker. Enzyme activity was arrested by heating the sample in a boiling water bath for 20 min, and an aliquot of the mixture was centrifuged at 5000g for

5 min. The supernatant was transferred into a sample vial for injection into the HPAEC-PAD system.

2.7. Amylopectin and amylose molecular structure

Amylopectin and amylose M_w , R_z , and polydispersity (ratio of weight-average and number-average molar mass, M_w/M_n) were measured by HPSEC-MALLS-RI (high-performance size-exclusion chromatography with multi-angle laser light scattering and refractive index detectors). The system consisted of a 515 HPLC pump with a 200 µl sample loop (Waters, Millford, MA), an inline degasser, a TSKgel PW_{XL} guard column (Tosoh Corp, Tokyo Japan), a series of two size exclusion columns (TSKgel G5000PW_{XL} and G4000PW_{XL}, Tosoh Corp.), a DAWN-EOS 18-angle light scattering detector (Wyatt Technology, Sta. Barbara, CA), and an Optilab rEX refractive index detector (Wyatt Technology). The mobile phase consisted of 0.15 M NaNO₃ and 0.02% NaN₃ (vacuum-filtered twice through a 0.1 µm membrane filter) at a flow rate of 0.7 ml/min. The output voltages for RI and LS detectors were collected with the temperature of the columns maintained at 55 °C and the RI detector at 35 °C, jumpers set at a 21× LS detector response, a dn/dc value of 0.146, and then processing the data with ASTRA 5.1.3 software (Wyatt Technology).

The sample for amylopectin structure characterization was prepared as follows: in a screw-cap test tube, 10 mg of defatted starch was mixed with 2 ml of 50 mM LiBr in 100% dimethyl sulfoxide, heated in a boiling water bath for 1 h and then stirred continuously for another 16 h at room temperature. A 0.5 ml aliquot was precipitated with 10 ml methanol, allowed to stand for 30 min, and centrifuged at 1500g for 10 min. The supernatant was discarded and the precipitate was redispersed in 5 ml deionized water and heated for 30 min in a boiling water bath with stirring. After cooling, a portion of the dispersed starch sample was centrifuged at 9000g for 10 min.

Molecular properties of amylose were determined from isoamylase-debranched starch. In a screw-cap test tube, 20 mg of defatted starch was added with 3.6 ml deionized water and heated in a boiling water bath for 1 h with magnetic stirring. The sample was allowed to cool, 0.4 ml of acetate buffer (0.1 M, pH 3.5), and 20 µl of isoamylase [EC 3.2.1.68]; 1180U; Hayashibara Biochemical Laboratories, Okayama, Japan) were added, and the mixture was incubated at 40 °C in a shaking water bath for 48 h. Enzyme activity was stopped by boiling the mixture for 30 min and the warm sample (about 70 °C) was filtered through a syringe with a 5.0 µm membrane filter prior to injection into the HPSEC-MALLS-RI system.

2.8. Canning properties

A 22.5 g head rice sample was weighed into a tared 211 × 304 enamel-coated can, and then deionized water was added to obtain a final weight of 150 g. The can was

sealed with its lid using an automatic can seamer (Dixie Canner Co., Athens, GA), allowed to stand for 15 min, and then cooked in a still retort (Standard Boiler and Tank Co., Riverdale, IL) at 115 °C and 90 kPa (~12 psi) for 15 min. The can was allowed to cool for 15 min under a stream of cold running water and then opened. The canning broth was allowed to drain into a pre-weighed 250-ml beaker for 10 min, and the weight of broth was taken.

A 5.0 ml aliquot of the canning broth was filtered through a syringe fitted with a 0.45 µm nylon membrane filter. The filtrate was injected into a high-performance size-exclusion chromatography (HPSEC) system for its soluble carbohydrate profile and molecular size distribution analysis based on the conditions used by Cameron and Wang (2005). The HPSEC system (Waters, Milford, MA) consisted of a 515 HPLC pump with a 100-µl sample loop injector, an in-line degasser, a Shodex OHpak SB-G guard column (Shoko Co., Kanagawa, Japan), a series of size exclusion columns (Shodex OHpak KB-804 and KB-802, Shoko Co.) maintained at 55 °C, and a 2410 refractive index detector maintained at 40 °C.

The amount of leached solids in the broth was measured by drying a 25-g broth sample to constant weight at 40 °C in a convection oven and calculations were based on the total amount of broth collected and raw rice sample weight. The height of the cooked rice in the can was measured at three points with a sliding steel tape. The average of the three measurements was used in calculating cooked rice volume. Volume expansion (cm³/g) was expressed as the quotient of cooked rice volume over raw rice sample weight.

2.9. Hot-water-soluble starch fractions

An aqueous flour or starch suspension (1.0% based on sample starch content) in a screw-cap test tube was heated in a boiling water bath for 30 min with magnetic stirring. The soluble fraction was collected by filtration through a syringe with a 0.45 µm nylon membrane filter and then a portion of the filtrate was injected into the HPSEC system for its carbohydrate molecular size distribution (Cameron and Wang, 2005).

2.10. Pasting properties

Pasting characteristics of rice flour and starch slurry (8%, w/w based on starch content) were determined with a Micro ViscoAmylograph (C.W. Brabender Instruments, Inc., South Hackensack, NJ) equipped with a 350-mg cartridge at a speed of 250 rpm. The slurry was heated from 50 to 95 °C at a rate of 3 °C/min, held at 95 °C for 5 min, and cooled down to 50 °C at a rate of 3 °C/min. Peak, hot paste (trough), and final viscosities were recorded. Paste breakdown was calculated by subtracting hot paste viscosity from peak viscosity; paste setback was taken as final viscosity minus peak viscosity; and paste consistency as final viscosity minus hot paste viscosity.

2.11. Gelatinization properties

Thermal properties were assessed by a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) (Perkin-Elmer Co., Norwalk, CT). The instrument was calibrated with indium and an empty pan was used as reference. Flour or starch (~4.0 mg) was weighed accurately into an aluminum DSC pan and then moistened with 8 µl of deionized water using a microsyringe. The pan was hermetically sealed and allowed to stand for at least 1 h prior to analysis. Samples were heated from 25 to 120 °C at a rate of 10 °C/min. Enthalpy, onset, peak, and conclusion temperatures were recorded.

2.12. Statistical analysis

Data from the completely randomized experiment consisting of five treatments (rice cultivars) and two replicates were analyzed with a SAS software version 9.1 (SAS Software Institute, Cary, NC). Analysis of variance (ANOVA) was used to detect significant differences among rice cultivars and Duncan's multiple range test (DMRT) was employed to identify significantly different means.

3. Results and discussion

3.1. Milled rice chemical composition

Table 1 presents the data on gross chemical composition of the flour and starch samples obtained from the head rice of the four specialty rice cultivars for canning (SRC), Bolivar, Cheniere, Dixiebelle and L-205, and the control (Wells). Total starch and apparent amylose content (measured by iodine colorimetry) of the flour samples were higher for the SRC compared with Wells. Based on the conventional classification of rice by milled rice apparent amylose content (Juliano, 1993), the SRC are all high-amylose type (amylose content >25.0%) while Wells is an intermediate-amylose type (between 20.0% and 25.0% amylose content). Crude protein content was lower for Cheniere; that of the other three SRC was comparable with Wells. Crude lipid content was lower for the SRC (0.2–0.3%) compared with Wells (0.5%).

Like the flour samples, the apparent amylose content (measured by iodine potentiometric titration) of starch purified by the alkaline steeping method was also higher for the SRC compared with Wells (Table 1). Starch residual protein content was also higher for the SRC, suggesting that the SRC may contain more of the granule-bound proteins (mostly starch synthase) that were quite difficult to remove by the alkali steeping method (Han and Hamaker, 2002). Granule-bound starch synthase catalyzes amylose elongation (Nakamura et al., 1993; Umemoto et al., 1995) and is logically higher for the SRC because of their higher amylose contents compared with Wells.

Table 1

Gross chemical composition of milled rice flour and starch samples from Bolivar, Cheniere, Dixiebelle, L-205, and Wells^a

	Bolivar	Cheniere	Dixiebelle	L205	Wells
Flour					
Total starch (% db)	91.2b	92.3a	92.6a	91.7ab	90.7b
Apparent amylose ^b (% db)	27.3b	29.8a	30.1a	28.5ab	22.1c
Crude protein (% db)	6.9a	5.8c	6.4ab	6.2bc	6.7ab
Crude lipid (% db)	0.3b	0.2c	0.3b	0.2c	0.5a
Starch					
Apparent amylose ^c (% db)	20.3ab	21.6a	20.6ab	20.1b	17.0c
Residual protein (% db)	0.6a	0.6a	0.5b	0.6a	0.3c
Swelling power at 85 °C (g/g)	10.6a	10.9a	11.2a	11.1a	10.8a
Soluble solids (%)	5.0c	10.2a	6.0b	5.3bc	5.7bc

^aIn a row, means of duplicate measurements followed by a common letter are not significantly different ($p < 0.05$) based on DMRT.^bDetermined by iodine colorimetry.^cDetermined by iodine potentiometric titration.

Table 2

Molecular properties of amylopectin and amylose from Bolivar, Cheniere, Dixiebelle, L205, and Wells

	Bolivar	Cheniere	Dixiebelle	L205	Wells
Amylopectin					
M_w^b ($\times 10^8$ g/mole)	2.3a	1.2c	1.9b	2.1ab	1.4c
M_w/M_n^c	1.8b	2.0ab	1.2c	1.6bc	2.2a
R_z^d (nm)	334.5a	262.5b	264.0b	338.0a	263.0b
Average chain length	21.2a	20.7bc	20.9ab	21.0a	20.6c
DP 6-12 (A Chain, %)	17.3c	17.8b	17.9b	17.6bc	19.4a
DP 13-24 (B1 chain, %)	57.8b	58.9a	58.1ab	58.2ab	57.4b
DP 25-36 (B2 chain, %)	14.0a	13.3ab	13.4ab	13.3ab	12.7b
DP 37-65 (B3+ chain, %)	10.9a	10.0b	10.7ab	10.9a	10.5ab
Amylose					
M_w ($\times 10^5$ g/mole)	5.2c	7.5a	6.3b	6.8ab	3.5d
M_w/M_n	2.0b	2.8ab	3.3a	2.6ab	2.6ab
R_z (nm)	37.2ab	40.4a	39.8a	31.0b	35.7ab

^aIn a row, means of duplicate measurements followed by a common letter are not significantly different ($p < 0.05$) based on DMRT.^bWeight-average molar mass.^cPolydispersity (ratio of weight-average and number-average molar mass).^d R_z -average radius of gyration.

3.2. Structural features of starches

The structural characteristics of amylopectin and amylose are listed in Table 2, and Fig. 1 shows in detail the differences in amylopectin CL distribution among the SRC in comparison with Wells. Amylopectin branch chains were classified into chain type and corresponding degree of polymerization (DP) according to Hanashiro et al. (1996) as follows: A chain (DP 6–12), B1 chain (DP 13–24), B2 chain (DP 25–36), and B3+ chain (DP 37–65). Except for Cheniere, the SRC had a larger amylopectin M_w and longer average CL than Wells. All the SRC had lower M_w/M_n , lower proportion of 6–12 branch chains but slightly higher DP 13–36 chains than Wells. Lower M_w/M_n implies a more homogeneous distribution of amylopectin molecules, particularly mass distribution, for the SRC. Cheniere and Dixiebelle were comparable to Wells in amylopectin R_z , whereas, that of Bolivar and L-205 were larger. Cheniere stood out among the SRC because of its smaller amylopectin M_w , shorter average CL, and a lower

proportion of B3+ chains. Overall, its amylopectin structural features were more similar to Wells. Bolivar and L-205 were very similar in terms of amylopectin fine structure because their M_w , M_w/M_n , R_z , average CL and CL distribution were statistically comparable.

The amylose structural characteristics of Cheniere differed distinctly from the rest because of their large M_w , M_w/M_n , and R_z . Considering that the SRC were comparable in milled rice apparent amylose content as measured by iodine colorimetry (Table 1), it can be deduced that for Cheniere, the blue color with iodine was primarily contributed by its amylose molecules per se; whereas, for the other SRC, the blue color may be contributed by both amylose molecules and amylopectin long chains that are also capable of forming blue complexes with iodine. These are consistent with recent findings (Horibata et al., 2004; Inouchi et al., 2005) that amylopectin long chains have a great influence on starch blue value. The amylose M_w and R_z of the control was smaller compared with the SRC, which is explicable

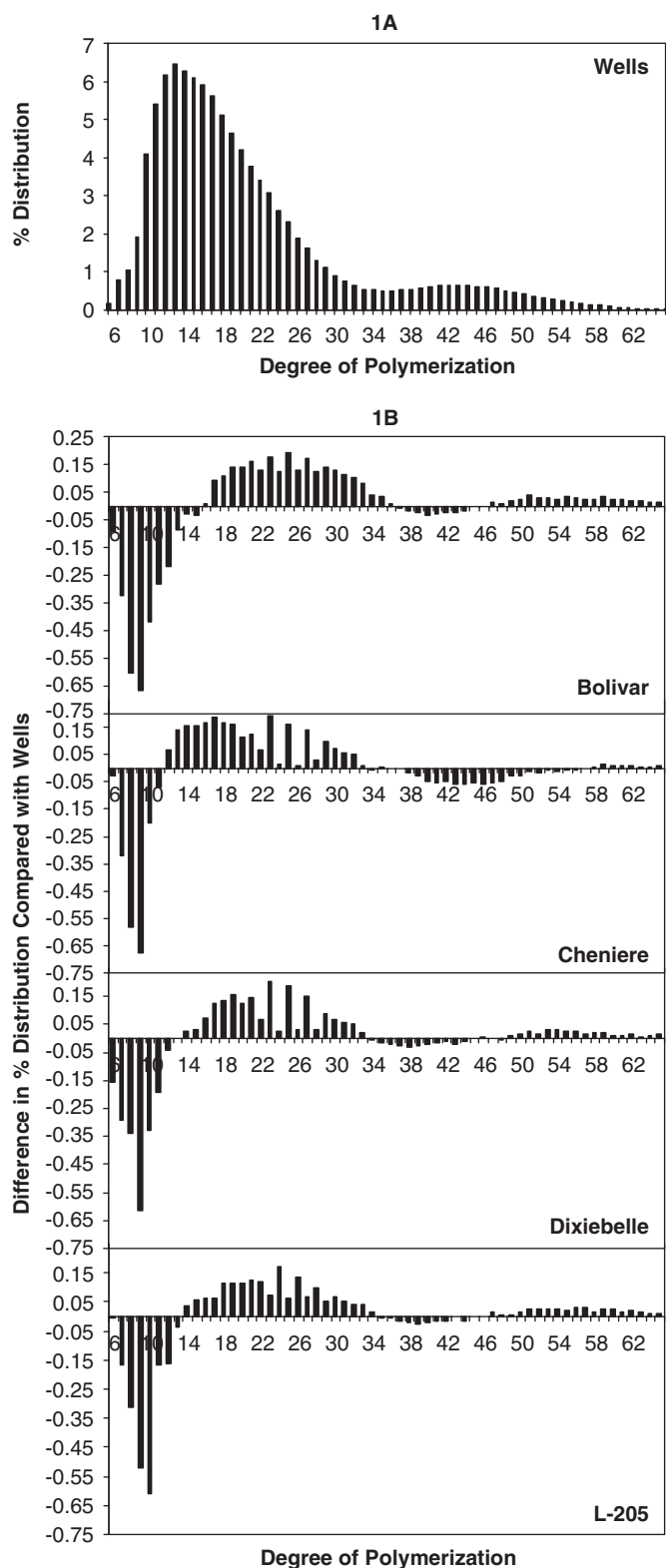


Fig. 1. Amylopectin chain-length distribution of the control cultivar, Wells (1A) and the difference in the percentage distribution of amylopectin branch chains from specialty rice cultivars in comparison with Wells (1B). Difference in % Distribution = % Distribution of SRC—% Distribution of Wells.

because Wells also had a lower apparent amylose content by iodine colorimetry or potentiometric titration.

3.3. Canning properties and starch structure

The canning and leaching properties of Cheniere were notably different from those of the other three SRC and the control (Table 3 and Fig. 2). It had a lower canned rice volume expansion and a higher amount of leached solids in the canning broth. Its leached solids essentially consisted of starch (~96.0%), a minimal amount of protein, and traces of soluble sugars and lipid. The other three SRC were comparable in volume expansion and in the amount of leached solids, although the composition of their leached solids also differed slightly, particularly in the amount of leached amylose, amylopectin, and protein. The amount of leached amylose was higher for Dixiebelle compared with Bolivar and L-205. Bolivar and L-205, which were the most similar in terms of amylopectin fine structure, were likewise similar in canning properties. The control had the lowest canned rice volume expansion; lowest amount of leached starch, but was the highest in leached protein and soluble sugars.

Amylose and amylopectin molecules were both leached into the canning broth in varying proportions (Table 3). In Fig. 2, the peaks corresponding to DP ~11,000 and DP ~2050 were designated as amylopectin and amylose, respectively, as reported in previous works (Cameron and Wang, 2005; Patindol and Wang, 2002). Shorter glucans (<DP 25) were leached into the canning broth as well. Indigenous simple sugars and oligosaccharides constitute 0.25–0.52% of milled rice on a dry weight basis (Pascual et al., 1978). The amount of sugars and oligosaccharides in rice tend to increase upon soaking and cooking due to the inactivation of starch-degrading enzymes (Tajima et al., 1994).

It appears that the excessive starch leaching of Cheniere compared with the other SRC may be attributed to its smaller amylopectin M_w , smaller R_z , shorter average CL, and lower proportion of amylopectin long chains (Table 2). Amylopectin molecules with these structural features may be less capable of interacting with each other, with amylose, and with other kernel constituents. Hence, they are possibly more prone to leaching and may less likely promote kernel stability during canning. Mizukami et al. (1999) reported that small amylopectin molecules dissolve more easily in hot water and amylopectin molecules with extended long chains resist solubilization, possibly by complexing with lipids or anchoring deeply inside the crystalline domains. Similarly, Ong and Blanshard (1995) inferred that long amylopectin chains, through their interaction with amylose, promote the formation of double helices in several crystallites, which in turn, may lower the degree of swelling and reduce the leaching of materials on cooking.

The present data also imply that protein and non-starch components may also take part in the leaching of solids

Table 3
Canning and leaching properties of Bolivar, Cheniere, Dixiebelle, L205, and Wells head rice samples

	Bolivar	Cheniere	Dixiebelle	L205	Wells
Volume expansion (cm ³ /g)	6.0a	5.2b	6.4a	6.3a	4.5c
Total leached solids (mg/g)	25.5bc	51.6a	28.3b	25.9bc	23.0c
Total starch (mg/g)	22.8b	49.5a	26.2b	23.7b	19.6c
Apparent amylose (mg/g)	12.1c	29.5a	18.3b	13.9c	8.7d
Amylopectin ^b (mg/g)	10.7b	20.0a	7.9c	9.8bc	10.8b
Crude protein (mg/g)	1.3b	0.6c	0.8c	1.0bc	1.7a
Soluble sugar (mg/g)	0.25b	0.09c	0.22b	0.22b	0.56a
Crude fat (mg/g)	0.16b	0.22a	0.21a	0.19ab	0.16b

^aIn a row, means of duplicate measurements followed by a common letter are not significantly different ($p < 0.05$) based on DMRT.

^bObtained by subtracting apparent amylose from total starch.

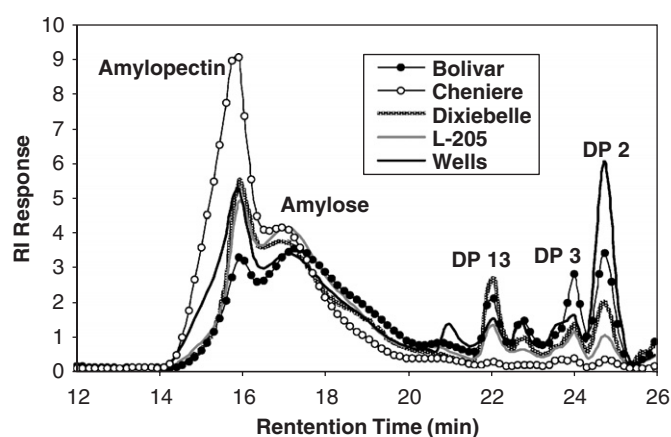


Fig. 2. Molecular weight distribution of the soluble carbohydrate moiety of the solids leached into the canning broth (with peaks corresponding to DP ~11,000 and DP ~2050 designated as amylopectin and amylose, respectively).

from the rice kernels during canning, considering that the hot-water-soluble components from flour and starch suspensions notably differed in their molecular size distribution (Fig. 3). The amylose:amylopectin ratio (AAR) of the hot-water soluble fraction ranged from 0.7 to 1.4 for flour, and 0.8 to 3.1 for starch suspension. For Cheniere, the AAR ratio did not differ appreciably (0.7 for flour and 0.8 for starch). For the other SRC, the difference was very evident, with ratios of 1.2–1.4 for flour and 2.2–3.1 for starch. Bolivar had the highest AAR (3.1) in the hot-water-soluble fraction of starch suspensions, which may be attributed to its large amylopectin M_w , higher proportion of amylopectin long chains, and longer average CL. These structural features suggest that the amylopectin molecules of Bolivar are bigger, are more capable of inter- and intra-molecular interactions, and may be more difficult to dissolve in hot water. Consequently, the hot-water-soluble fraction of Bolivar starch predominantly consisted of amylose, giving rise to a larger AAR. Cheniere displayed the opposite amylopectin structural features to Bolivar, implying that its amylopectin molecules are smaller and

may be easier to dissolve in hot water. This in turn may explain the lower AAR (0.81) of the hot-water-soluble starch fraction of Cheniere (Fig. 3).

3.4. Pasting and gelatinization in relation to starch structure

The pasting properties of the flour and starch pastes obtained with a Brabender Micro-ViscoAmylograph are shown in Table 4 and Fig. 4. A similar trend in viscosity profiles was observed for both flour and starch pastes despite the presence of non-starch constituents in flour. In the past, Brabender viscograms were often linked with rice apparent amylose content and cooked rice texture, and high amylose rice cultivars often show low peak viscosity and positive setback (Ramesh et al., 2000). Such generalizations do not hold true for the SRC used in this study as they were all high-amylose type, yet their pasting profiles differed, particularly that of Cheniere. Paste peak viscosity, which measures the extent by which starch granules swell in the presence of water and heat, followed the same order as the amylopectin M_w : Bolivar > L-205 > Dixiebelle > Wells > Cheniere. This suggests that peak viscosity may primarily be dictated by amylopectin, particularly its molecular size. Thus, the swelling of Cheniere starch was more constricted compared with the other cultivars because of its smaller amylopectin M_w and R_z , and shorter average CL (Table 2). The larger amylose M_w and R_z of Cheniere additionally explains its lower paste peak viscosity since amylose has been recognized to restrict starch granule swelling (Jane et al., 1999; Lii et al., 1996; Patindol and Wang, 2005; Tester and Morrison, 1990). These rationales may also explain the lower volume expansion of Cheniere kernels during canning (Table 3).

The data on gelatinization temperatures and enthalpies of flour and starch samples are presented in Table 5. Gelatinization is the melting of the crystalline region of starch granules, and lower gelatinization temperature and enthalpies are associated with a higher proportion of amylopectin short branch chains (Horibata et al., 2004; Inouchi et al., 2005; Jane et al., 1999; Ong and Blanshard, 1995; Patindol and Wang, 2003; Vandeputte et al., 2003).

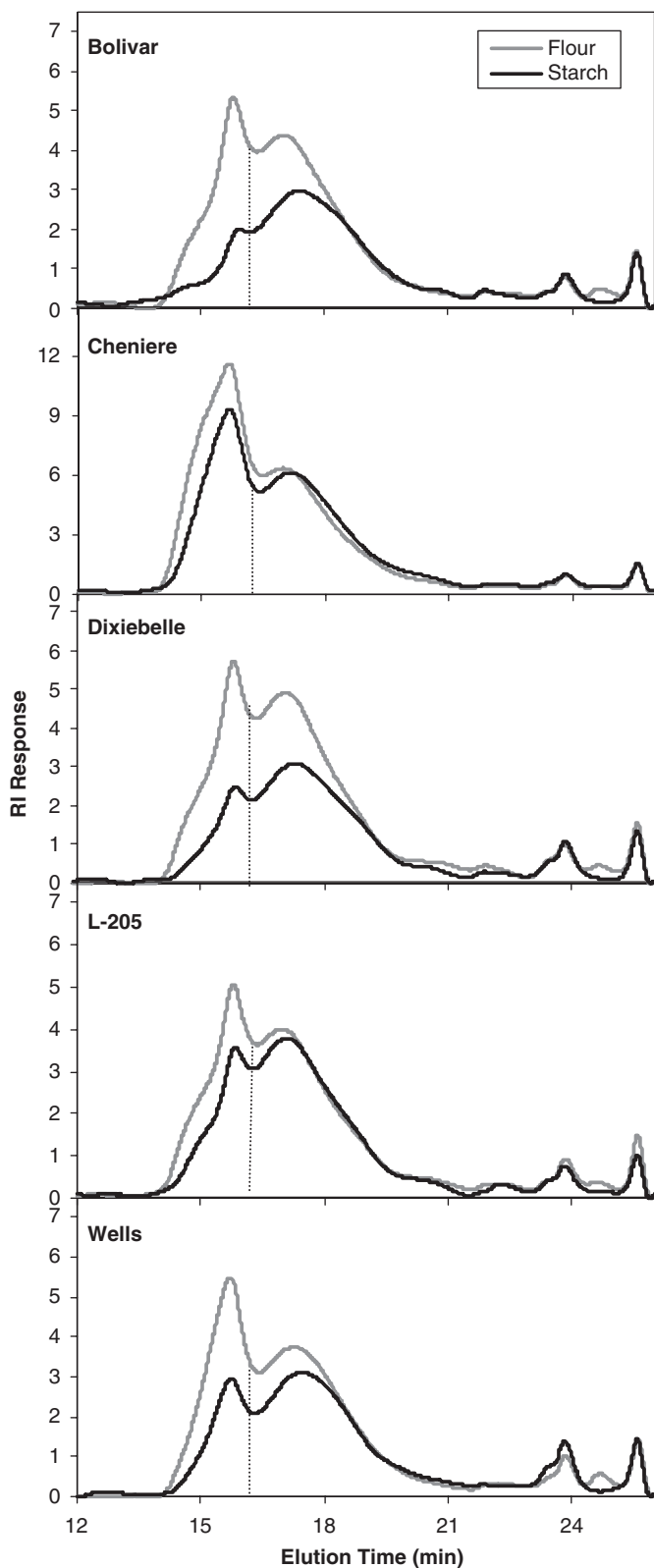


Fig. 3. Molecular size distribution of the hot-water-soluble components (two major peaks separated by a vertical line) of dilute flour and starch suspensions.

The short branch chains of amylopectin may reduce the packing order within the crystalline lamellae, whereas longer chains may form longer double helices within the

Table 4

Pasting properties of milled rice flour and starch samples from Bolivar, Cheniere, Dixiebelle, L205, and Wells^a

	Bolivar	Cheniere	Dixiebelle	L-205	Wells
Flour					
Peak viscosity (BU ^b)	541b	315d	608a	637a	422c
Final viscosity (BU)	855b	476d	875ab	911a	512c
Breakdown (BU)	90c	96c	150b	149b	174a
Setback (BU)	314a	161c	267 b	274 b	90d
Consistency (BU)	404a	257b	417a	423a	264b
Starch					
Peak viscosity (BU)	653a	330c	605b	647a	498b
Final viscosity (BU)	877a	548c	840a	886a	602b
Breakdown (BU)	201ab	120c	173b	178b	225a
Setback (BU)	224ab	218b	235a	239a	104c
Consistency (BU)	425a	338b	408a	417a	329b

^aIn a row, means of duplicate measurements followed by a common letter are not significantly different ($p < 0.05$) based on DMRT.

^bBU = Brabender units.

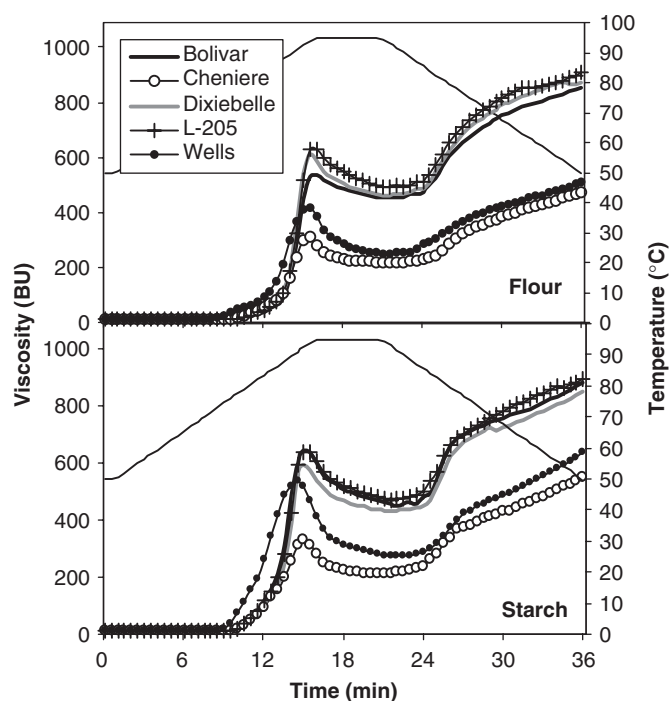


Fig. 4. Brabender Micro ViscoAmylograph profiles of flour and starch pastes from Bolivar, Cheniere, Dixiebelle, L205, and Wells.

crystalline lamellae of the rice starch granules and delay gelatinization (Vandeputte et al., 2003). Wells had a lower gelatinization temperature and enthalpy compared with the SRC because of its higher proportion of short branch chains (DP 6–12) and lower proportion of B chains (DP 13–65) (Table 2 and Fig. 1). Among the SRC, the gelatinization temperature and enthalpy of Cheniere were slightly lower, probably owing to its smaller proportion of B3+ chains (DP 37–65).

Table 5

Thermal properties of flour and starch samples from Bolivar, Cheniere, Dixiebelle, L205, and Wells^a

	Bolivar	Cheniere	Dixiebelle	L205	Wells
Flour					
Onset GT ^b (°C)	75.4ab	74.2c	76.0a	75.0b	72.2d
Peak GT (°C)	79.0ab	78.0c	79.6a	78.4b	76.7d
Conclusion GT (°C)	83.6b	83.0b	84.6a	83.4b	81.7c
Gelatinization enthalpy (J/g)	8.8a	8.3b	8.9a	8.6ab	8.2b
Starch					
Onset GT (°C)	76.1b	75.8b	77.0a	77.0a	73.4c
Peak GT (°C)	79.7b	79.4b	80.3ab	80.8a	78.0c
Conclusion GT (°C)	84.3b	84.2b	84.9b	86.1a	83.1c
Gelatinization enthalpy (J/g)	14.4a	14.1ab	14.2ab	13.9b	13.3c

^aIn a row, means of duplicate measurements followed by a common letter are not significantly different ($p < 0.05$) based on DMRT.^bGT = gelatinization temperature.

4. Conclusions

The data obtained from this study highlight the importance of starch fine structure in explaining cultivar differences in rice functional properties in relation to canning. The long-grain, high-amylose rice cultivars, Bolivar, Cheniere, Dixiebelle, and L-205 showed some distinct differences in pasting, gelatinization, leaching, and canning properties despite their similarities in gross kernel chemical composition. Lower levels of leached solids in the broth, higher canned rice volume expansion, and higher paste peak and final viscosity were associated with high amylopectin M_w , average CL and R_z , high percentage of long branch chains, and low percentage of short branch chains. These structural features may strengthen the interaction of amylopectin with other amylopectin molecules, with amylose, with protein, and with other kernel components, which in turn, may promote kernel integrity and minimize leaching of solids when rice is subjected to severe thermal process like wet-pack canning.

References

- Alary, R., Laignelet, B., Feillet, P., 1977. Effect of amylose content on some characteristics of parboiled rice. *Journal of Agricultural and Food Chemistry* 25, 261–264.
- American Association of Cereal Chemists, 2000. Approved Methods of the AACC, 10th ed. AACC-Method 44-15A, AACC-Method 46-13, and AACC-Method 61-02.
- Bergman, C., Bhattacharya, K., Ohtsubo, K., 2004. Rice end-use quality analysis. In: Champagne, E.T. (Ed.), *Rice Chemistry and Technology*, third ed. The American Association of Cereal Chemists, Inc., St. Paul, MN, pp. 415–472.
- Burns, E.E., Gerdes, D.L., 1985. Canned rice foods. In: Juliano, B.O. (Ed.), *Rice Chemistry and Technology*, second ed. The American Association of Cereal Chemists, Inc., St. Paul, MN, pp. 557–567.
- Cameron, D., Wang, Y.-J., 2005. A better understanding of factors that affect the hardness and stickiness of long-grain rice. *Cereal Chemistry* 82, 113–119.
- Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric method for the determination of sugars and related substances. *Analytical Chemistry* 28, 350–356.
- Han, X.Z., Hamaker, B.R., 2001. Amylopectin fine structure and rice starch paste breakdown. *Journal of Cereal Science* 34, 279–284.
- Han, X.Z., Hamaker, B.R., 2002. Partial leaching of granule-associated proteins from rice starch during alkaline extraction and subsequent gelatinization. *Starch/Stärke* 54, 454–460.
- Hanashiro, I., Abe, J.I., Hizukuri, S., 1996. A periodic distribution of chain length of amylopectin as revealed by high performance anion exchange chromatography. *Carbohydrate Research* 283, 342–347.
- Horibata, T., Nakamoto, M., Fuwa, H., Inouchi, N., 2004. Structural and physicochemical characteristics of endosperm starches of rice cultivars recently bred in Japan. *Journal of Applied Glycoscience* 51, 239–346.
- Inouchi, N., Hibi, H., Li, T., Horibata, T., Fuwa, H., Itani, T., 2005. Structure and properties of endosperm starches from cultivated rice of Asia and other countries. *Journal of Applied Glycoscience* 52, 303–313.
- Jane, J., Chen, Y.Y., Lee, L.F., McPherson, A.E., Wong, K.S., Radosavljevic, M., Kasemsuwan, T., 1999. Effects of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch. *Cereal Chemistry* 76, 629–637.
- Juliano, B.O., 1993. Rice in Human Nutrition. FAO, Rome, Italy, IRRI, Los Baños Laguna, Philippines, p. 162.
- Juliano, B.O., Hicks, P.A., 1996. Rice functional properties and rice food products. *Food Reviews International* 12, 71–103.
- Juliano, B., Perez, C., Blakeney, A., Castillo, D., Kongseree, N., Laignelet, B., Lapis, E., Murty, V., Paule, C., Webb, B., 1981. International cooperative testing on the amylose content of milled rice. *Starch/Stärke* 33, 157–162.
- Kasemsuwan, T., Jane, J.-L., Schnable, P., Stinard, P., Robertson, D., 1995. Characterization of the dominant mutant amylose-extender (ae1-5180) maize starch. *Cereal Chemistry* 72, 457–464.
- Lii, C.Y., Tsai, M.L., Tseng, K.H., 1996. Effect of amylose content on the rheological property of rice starch. *Cereal Chemistry* 73, 415–420.
- Matsler, A.D., Siebenmorgen, T.J., 2005. Evaluation of operating conditions for surface lipid extraction from rice using a Soxtec system. *Cereal Chemistry* 82, 282–286.
- Mizukami, H., Takeda, Y., Hizukuri, S., 1999. The structure of the hot water-soluble components in the starch granules of new Japanese rice cultivars. *Carbohydrate Polymers* 38, 329–335.
- Nakamura, T., Yamamori, M., Hirano, H., Hidaka, S., 1993. The waxy (Wx) proteins of maize, rice and barley. *Phytochemistry* 33, 749–753.
- Ong, M., Blanshard, J., 1995. Texture determinants of cooked, parboiled rice. II. Physicochemical properties and leaching behavior of rice. *Journal of Cereal Science* 21, 261–269.
- Pascual, C.G., Singh, R., Juliano, B.O., 1978. Free sugars of rice grain. *Carbohydrate Research* 62, 381–385.

- Patindol, J., Wang, Y.-J., 2002. Fine structures of starches from long-grain rice cultivars with different functionality. *Cereal Chemistry* 79, 465–469.
- Patindol, J., Wang, Y.-J., 2003. Fine structures and physicochemical properties of starches from chalky and translucent rice kernels. *Journal of Agricultural and Food Chemistry* 51, 2777–2784.
- Patindol, J., Wang, Y.-J., 2005. Structure-functionality changes in starch following rough rice storage. *Starch/Stärke* 57, 197–207.
- Ramesh, M., Ali, S., Bhattacharya, K., 1999. Structure of rice starch and its relation to cooked-rice texture. *Carbohydrate Polymers* 38, 337–347.
- Ramesh, M., Bhattacharya, K.R., Mitchell, J.R., 2000. Developments in understanding the basis of cooked rice texture. *Critical Reviews in Food Science and Nutrition* 40, 449–460.
- Schoch, T., 1964. Iodimetric determination of amylose, potentiometric titration: standard method. In: Whistler, R.L., Smith, R.J., BeMiller, J.N., Wolfrom, M.L. (Eds.), *Methods in Carbohydrate Chemistry*, vol. IV. Academic Press, London, pp. 157–160.
- Sharp, R.N., Sharp, C.Q., Kattan, A.A., 1981. A new method for thermally processed canned rice. *Food Technology* 35, 75–76.
- Takeda, Y., Hizukuri, S., Juliano, B., 1986. Purification and structure of amylose from rice starch. *Carbohydrate Research* 148, 299–308.
- Tajima, M., Kato, M., Iizuka, T., 1994. Maltooligosaccharides extracted from cooked rice. *Nippon Shokuhin Kogyo Gakkaishi* 41, 339–340.
- Tester, R.F., Morrison, W.R., 1990. Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose and lipids. *Cereal Chemistry* 67, 551–557.
- Umamoto, T., Nakamura, Y., Ishikura, N., 1995. Activity of starch synthase and the amylose content in rice endosperm. *Phytochemistry* 40, 1613–1616.
- Vandeputte, G.E., Derycke, J., Geeroms, J., Delcour, J.A., 2003. Rice starches, II: structural aspects provide insight into swelling and pasting properties. *Journal of Cereal Science* 38, 53–59.
- Webb, B.D., 1979. Assessing parboil-canning stability of rice in varietal improvement. In: *Proceedings of the Workshop on Chemical Aspects of Rice Grain Quality*. International Rice Research Institute, Los Baños, Laguna, Philippines, pp. 283–292.
- Yang, C., Lai, H., Lii, C.-Y., 1984. The modified alkaline steeping method for the isolation of rice starch. *Food Science* 11, 158–162.