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Characteristics of the starch fine structure and pasting properties of waxy rice during storage

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ABSTRACT

Two waxy rice (TNW1 and TCSW1, exhibiting high and low amylase activity, respectively), were stored at 4 and 17 °C (polished rice) and at room temperature (paddy rice) for 15 months. The fine structure of starch isolated from the aged rice and the pasting properties of starch and rice flour were studied. After storage, the percentage of short amylopectin (AP) chains increased in TNW1, and no uniform changing pattern was observed in the chain-length (CL) distribution of TCSW1. The viscosity of starch isolated from the aged rice increased as the storage temperature and duration increased. We hypothesised that this increase was due to the hydrolysis of AP by endogenous amylase and the generation of small clusters during storage, which caused the simple dissociation of AP and a high swelling degree of starch granules during gelatinisation. Factor analysis of the first two factors associated with the characteristics of viscograms and the CL of AP explained 72% of the total variation.

1. Introduction

Waxy rice is a major rice variety used in producing Chinese snacks and festival foods. Similar to most varieties of rice used in rice products, waxy rice is generally aged from 2 months to few years before use to obtain desirable processing properties and a high-quality final product. During the ageing period, the physicochemical properties of rice flour exhibit changes, including decreases in hydration and solubility, inhibition of swelling, and altered viscosity of rice slurry during processing (Zhou, Robards, Helliwell, & Blanchard, 2002). Cooked aged rice exhibits a harder texture, lower cooking loss, and less stickiness compared with cooked fresh rice (Chrastil, 1992; Ohno & Ohisa, 2005; Zhou, Robards, Helliwell, & Blanchard, 2007; Zhou et al., 2002). The changes in the cooking and eating quality of aged rice depend on various conditions; the rice variety (waxy, low, intermediate, or high amylose rice), rice type (paddy, brown, or polished rice), and ageing conditions (temperature, relative humidity, and duration). Indudhara Swamy, Sowbhagya, and Bhattacharya (1978) indicated that the high amylose (AM = 28%) rice demonstrated a faster rate and greater degree of changes in its physicochemical properties than did the intermediate amylose (AM = 21%) rice during ageing. In general, the rice ageing process is accelerated at a high ageing temperature (Indudhara Swamy et al., 1978; Zhou et al., 2007).

Previous research has determined that the changes in the physicochemical properties of ageing rice were strongly associated with the endogenous enzymatic reactions on rice lipids, proteins, and starch (Dhaliwal, Sekhon, & Nagi, 1991; Yasumatsu & Moritaka, 1964). During rice ageing, the activities of α- and β-amylases decrease; however, the activities of protease, lipase, and lipoxygenase increase, causing an increased amount of free fatty acids (FAs) and free amino acids (Dhaliwal et al., 1991). Therefore, the pH level of the rice grain surface of polished aged rice generally decreases (Rehman, 2006).

Moritaka and Yasumatsu (1972) hypothesised that the hydroperoxides generated by lipoxygenase reacting on conjugated FAs and carbonyl compounds would accelerate the oxidation reaction of proteins so that certain intermolecular disulphide bonds (–S–S–) could be detected during rice ageing. The increase in the number of disulphide bonds and the average molecular weight (Mw) of oryzenin in aged rice were reported (Chrastil & Zarins, 1992; Qiu, Jin, & Zhou, 1998). The polymerisation of rice proteins caused by the disulphide bond formation resulted in the decrease of protein solubility, slurry viscosity, and cooked aged rice stickiness (Chrastil, 1990; Likitwattanasade & Hongsprabhas, 2010; Martin

Abbreviations: DP, degree of polymerisation; HPAEC–PAD, high-performance anion-exchange chromatography–pulsed-amperometric detector; HPSEC, high performance size exclusion chromatography; Mw, molecular weight; AP, amylopectin; CL, chain-length; RVA, Rapid Visco Analyzer; PT, pasting temperature; PV, peak viscosity; T, trough; BkD, breakdown; SB, setback; RT, room temperature; F-water, waxy rice flour in water; F-$AgNO_3$, waxy rice flour in $AgNO_3$ solution; S-water, waxy rice starch in water.

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& Fitzgerald, 2002; Zhou, Robards, Helliwell, Blanchard, & Baxterb, 2003).

Starch is generally considered an inert ingredient; thus, the changes of starch properties are believed to be insignificant over time during rice ageing. Rehman (2006) observed a slight increase of reducing sugar content in aged nonwaxy rice, and the enzymatic degradation of starch might occur during ageing, which could cause an increase in the percentage of short chains (DP 6–12) (Patindol, Wang, & Jane, 2005). Although the effects of ageing conditions on the pasting properties of waxy rice have been studied (Likitwattanasade & Hongsprabhas, 2010; Villareal, Resurreccion, Suzuki, & Juliano, 1976), the effects of endogenous amylase on the starch fine structure and its relationship to the pasting properties of aged waxy rice have not been sufficiently studied.

This study investigated the mechanism of waxy rice ageing by focusing on the starch fine structure and pasting properties of two domestically grown waxy rice varieties demonstrating distinct amylase activities during ageing. The proposed mechanism demonstrates the effects of endogenous amylase on the starch structure and its pasting property. In addition, the pasting properties of the rice flour slurry of aged waxy rice provide valuable information to rice processing industries for correlating the ageing conditions with the processing functionalities of waxy rice.

2. Materials and methods

2.1. Materials

Two domestic grown waxy rice, TNW1 (a *japonica* rice) and TCSW1 (an *indica* rice), were used for this study. The amylose contents of these two waxy rice varieties determined by using colorimetric method (AACC method 61-03) were 1.30% (TNW1) and 1.40% (TCSW1). The compositions of TNW1 were 13.5% moisture, 7.3% (on dry base, db) crude protein, 1.1% (db) crude fat, 85.6% (db) starch, and 0.6% (db) ash. Similarly, TCSW1 were 13.6% moisture, 8.1% (db) crude protein, 1.1% (db) crude fat, 84.4% (db) starch, and 0.6% (db) ash. Moisture content, crude protein, crude fat, and ash were determined according to AACC 44-31A, 46-12, 30-25, and 08-16 methods (AACC, 2001), respectively. The starch content was determined according to AACC method 76-13 using the total starch analysis kit (Megazyme Pty. Ltd., Warriewood, NSW, Australia).

The polished rice was stored at 4 and 17 °C, and the paddy rice was stored at room temperature (25 ± 4 °C) for up to 15 months. The rice samples were double packaged with polyethylene bags during storage. After storage, the paddy rice was dehulled and polished using a huller (TR-200, Kett, Tokyo, Japan) and a polisher (Pearlest, Kett, Tokyo, Japan). The polished rice was ground with a grinder (RT-02A, Yu Sheng Guang Food Machine, Taiwan) and then sieved through a 40 mesh sieve. Rice flour was collected and analysed immediately.

2.2. α-Amylase activity determination

α-Amylase activity of rice flour was determined according to AACC method 22-02 (AACC, 2001) by using an α-amylase analysis kit (Ceralpha method, Megazyme Pty. Ltd., Warriewood, NSW, Australia).

2.3. Rice starch isolation

Rice starch was isolated according to the method of Huang and Lai (2010). The rice flour (100 g) was steeped in 1 L of 0.05% NaOH solution containing 0.29 g of protease isolated from *Bacillus polymyxa* with the enzymatic activity of 1.2 U/mg (Sigma Co., MO, USA) for 2 h at 37 °C. The starch was then dried at 40 °C and ground into powder using a grinder (RT-02A, Yu Sheng Guang Food Machine, Taiwan), then sieved through a 100 mesh sieve.

2.4. Rice starch fine structure analyses

2.4.1. Chain-length distribution of debranched rice starch

The chain-length (CL) distribution of rice starch was determined using a high-performance anion-exchange chromatography equipped with a pulsed amperometric detector (HPAEC–PAD) (Dionex DS600, Sunnyvale, CA, USA). Sample preparation followed a published method of Huang and Lai (2010). Purified rice starch (2 mg) was first completely dissolved with 0.5 mL of 90% dimethylsulphoxide (DMSO) in a boiling water bath for 10 min. One millilitre of 10 mM acetate buffer (pH 3.8) and 20 μL of isoamylase from *Pseudomonas* sp. (enzymatic activity of 0.01 U/μL, Megazyme International Ireland Ltd., Wicklow, Ireland) were then added and incubation continued at 50 °C in a water bath for 2 h. After incubation, the debranched amylopectin solution was then filtered through a PVDF membrane filter (0.45 μm) before injected into the HPAEC–PAD system. The known DP standards including glucose (ChemService, PA, USA), maltotriose, maltotetraose, maltopentaose, and maltohexaose (Fluka, Buchs, Switzerland) were used to calibrate the elution time versus the DP of the sugars. The HPAEC–PAD determinations were repeated three times. The relative percentage (%) difference of each chain length was obtained by subtracting the percentage distribution of HPAEC intensity of each chain length in fresh waxy rice from that determined in aged rice.

2.4.2. Molecular weight of debranched rice starch

Debranched rice starch solution was prepared by the same way as described for the determination of the chain-length distribution. The solution was first filtered through a nylon filter (5 μm) before injecting into a high performance size exclusion chromatography (HPSEC) system. The HPSEC system (Hitachi Ltd., Tokyo, Japan) consisted of a L-6000 pump with an injector of 100 μL sample loop, an in-line degasser, a L3300 RI detector maintained at 40 °C, and a series TOSOH columns (G3000 PW and G5000 PW) maintained at 50 °C. The eluent was 0.1 M $NaNO_3$ and the flow rate was at 0.5 mL/min. The fractions of amylopectin were automatically calculated from the area of their corresponding peaks using an Omini-SEC software 2.0.3 (Viscoteck Corp., Houston, Texas, USA). A maltotriose (Mw 504 Da, DP 3) (Fluka, Buchs, Switzerland) and a serious of known Mw pullulans (Shodex standard P-82, Showa Denko Co., Ltd., Japan) which the Mw 5900 Da (DP 36), Mw 11,800 Da (DP 73), Mw 22,800 Da (DP 140), and Mw 47,300 Da (DP 292) were applied to plot the standard curve in the system.

2.5. Pasting properties and swelling power determination

The pasting property of rice flour and rice starch was determined by using a Rapid Visco Analyzer (RVA-4, Newport Scientific, Warriewood, Australia). According to the method of AACC 61-02, 3.00 g (based on 12% moisture) of rice flour (AACC, 2001) or rice starch (2.5 g, on dry basis) was added into an aluminium canister containing 25 g of distilled water or 2.5 mM $AgNO_3$ solution. The heating profile was set as following: heating from 50 to 95 °C in 15 min, holding at 95 °C for 10 min, then cooling down to 50 °C with the cooling rate at 3 °C/min. The measurements were performed twice. Swelling power of waxy rice starch was determined according to the method of Huang and Lai (2010).