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Molecular order and functional properties of starches from three waxy wheat varieties grown in China

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ABSTRACT

Molecular order and functional properties of starch from three waxy wheat varieties grown in China were investigated by a combination of various technical analyses. The total starch content of the waxy wheat ranged between 54.1% and 55.0%, and the amylose content of the starch was between 0.71% and 1.63%. Average particle diameter of the three starches varied between 16.5 and 17.4 μm. Three waxy wheat starches presented the typical A-type X-ray diffraction pattern, with relative crystallinity between 38.7% and 40.0%. No significant differences were observed in relative crystallinity, IR ratios of 1047/1022 cm^{-1} and 1022/995 cm^{-1}, and FWHH of the band at 480 cm^{-1}, indicating the similarity in long-range order of crystallites and short-range order of double helices of three starch granules. Small differences were observed in swelling power, gelatinization parameters, pasting viscosities, and *in vitro* enzymatic digestibility of three waxy wheat starches. Under the stored condition, no retrogradation occurred for three waxy wheat starches.

1. Introduction

Wheat, one of the oldest crops, is widely cultivated in many countries around the world. As a major staple food, wheat is consumed in various forms such as breads, noodles and other baked or steamed products by over one-third of the global population. Wheat is one of the top three most produced crops in the world, along with maize and rice (Kumar & Prabhasankar, 2014). According to the report of Food and Agricultural Organization (FAO), the world total production of wheat has reached 660 million tons in 2012, of which one-fifth (126 million tons) is produced in China. China is not only the largest wheat producer, but also the biggest wheat consumer in the world. Common or wild-type wheat has been cultivated for over 10,000 years, and in China, it has been 4000–5000 years for wheat cultivation (Dodson et al., 2013). In contrast to common wheat, completely waxy wheat was first developed by traditional hybridizations in 1995 (Nakamura, Yamamori, Hirano, Hidaka, & Nagamine, 1995). Since then, waxy wheat has been successively produced in Australia, USA and Canada (Zhang, Zhang, Xu, & Zhou, 2013). In 2005, the Chinese famous wheat breeding expert Shunhe Cheng developed a completely waxy wheat variety. In last 5 years, several new waxy wheat varieties have been produced in China and their application in foods has been explored (Ma et al., 2013).

Wheat grains are mainly composed of starch and protein, which account for about 50–60% and 8–20% of the dry weight grain, respectively. Protein, especially gluten, plays an important role in the rheological properties of the mixed dough and the textural properties of the finished food products (Goesaert et al., 2005). In contrast, starch makes diverse contributions to control of moisture, viscosity, texture, consistency, mouth-feel, shelf life and nutrition of the starch-based foods (Wang & Copeland, 2013). The extent of starch contribution to food quality and nutrition mainly rely on the functionality of starch in the presence of water, which refers to swelling power, solubility, gelatinization, pasting, retrogradation and susceptibility to enzymatic digestion. The high variability in native starch functionality derives from variability of structure, which is due to diversity in the genes that encode the starch biosynthetic enzymes and environmental factors that act on the genes and enzymes concerned during plant growth (Wang & Copeland, 2015). Waxy wheat starch, which is biosynthesized when the three granule-bound starch synthesis (GBSS) genes are absent or nonfunctional, has distinct structural characteristics such as very low amylose content and high crystallinity. These structural characteristics endow waxy wheat starch the desirable functional properties such as high swelling power and peak viscosity, low retrogradation, setback viscosity and pasting temperature

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(Hung, Maeda, & Morita, 2006). These desirable functional properties make waxy wheat starch highly potential in replacing the normal wheat starch in food products (Hung et al., 2006; Ma et al., 2013).

With the increasing development of new waxy wheat varieties, the comprehensive understanding of starch structure and functionality in waxy wheat grains is extremely important for their appropriate application in foods. There have been some studies regarding the characterization of waxy wheat starch (Chakraboty et al., 2004; Fujita, Yamamoto, Sugimoto, Morita, & Yamamori, 1998; Kim & Huber, 2010; Yoo & Jane, 2002; Zhang et al., 2013). However, little information is available for starches from waxy wheat grown in China. Moreover, the short-range molecular order of waxy wheat starches as measured by FTIR and Raman spectroscopy, and their relationship with the long-range order (crystallinity) were not well understood. In the present study, three waxy wheat varieties (Ning Waxy1-NW1, Tian Waxy1-TW1, and Yang Waxy1-YW1) developed in China were obtained for the comprehensive characterization of starch molecular order and functionality. For the first time, the short-range molecular order of three waxy wheat starches is fully characterized by Fourier transform infrared (FTIR) and laser confocal micro-Raman (LCM-Raman) spectroscopy. The relationship between molecular order and starch crystallinity is also investigated.

2. Materials and methods

2.1. Materials

Three waxy wheat grains were kindly provided by Lixiahe Agricultural Research Institute, Jiangsu Province, China. Wheat grains were harvested in the 2012–2013 season. Total starch assay kit, glucose oxidase/peroxidase (GOPOD) kit and amyloglucosidase (3260 U/ml) were purchased from Megazyme International Ireland Ltd. (Bray Co., Vicklow, Ireland). Amylose (A0512) and amylopectin (A8515) from potato starch, and α-amylase (Sigma, EC 3.2.1.1, type VI-B from porcine pancreas, 28 U/mg) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Other chemical reagents were of all analytical grade.

2.2. Isolation of starch

Starch was isolated from waxy wheat grains according to the method of Wang, Hassani, Crossett, and Copeland (2013) with minor modifications as follows. Wheat grains (250 g) were soaked in 1 L of ammonia solution (0.2 M) for 24 h at room temperature. The supernatant was decanted and the softened grains were blended in a kitchen blender with ammonia solution (wheat/ammonium: 1/6 (w/v)) for 1–2 min. The resulting slurry was filtered through a 250 μm nylon mesh (filtrate 1). The residue was mixed with ammonia solution, blended and filtered through a 250 μm nylon mesh (filtrate 2). The combined filtrate 1 and filtrate 2 was centrifuged at 3500*g* for 15 min and the supernatant was decanted. The top layer of sedimented starch (SS1) was resuspended in ammonia solution and centrifuged at 5000*g* for 10 min. The top layer of the sedimented starch (SS2) was scrapped off. The combined SS1 and SS2 was resuspended in ammonia solution and centrifuged at 5000*g* for 10 min. This process was repeated for three times. After centrifugation, the sedimented starch was suspended in water and centrifuged at 5000*g* for 10 min. The starch precipitate was blended in 0.2 M acetic acid solution and filtered through a 120 μm nylon mesh. The filtrate was centrifuged at 5000*g* for 10 min and the crude starch was obtained. The crude starch was washed with distilled water for three times and then washed with ethanol twice. The resulting starch was dried in air condition and then stored in a container at 4 °C.

2.3. Chemical composition of wheat grains and isolated starches

Dry wheat grains were milled into flour and passed through a 250 μm sieve. The resulting flour was used for the determination of total starch and protein content of wheat. Total starch content of wheat was determined by Megazyme total starch assay kit. The nitrogen content of wheat grains and starch granules were determined by standard Kjeldahl methodology. Protein content was estimated by multiplying the nitrogen content by a conversion factor of 6.25. Apparent amylose content of the wheat starches was determined by the iodine binding method of Chrastil (1987) using a standard curve of 0%, 5%, 10%, 20%, 25% and 30% potato amylose mixed with potato amylopectin. The lipid content of starch granules was determined gravimetrically after extraction with ether at 60–70 °C for 12 h. Moisture content was determined by oven drying of the starch at 105 °C until constant weight.

2.4. Granule morphology

The morphology of starch granules was imaged using a SU1510 scanning electron microscope (Hitachi High-technologies Corporation, Japan). Starch samples were mounted on the aluminum stub using double-sided carbon adhesive tape and sputter-coated with gold. An accelerating voltage of 5 kV was used during imaging.

2.5. Granule size distribution

Size distribution of starch granules was determined using a BT-9300S laser particle size analyzer (Dandong Bettersize Instruments Ltd., Dandong, China). The starch was dispersed in distilled water with magnetic agitation to attain an obscuration of about 12%. All measurements were performed in triplicate and the median volume-based diameter was used to represent the average granule size.

2.6. X-ray diffraction (XRD)

X-ray diffraction analysis was performed using a D/max-2500vk/pc X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) operating at 40 kV and 30 mA. Starches were equilibrated over a saturated sodium chloride (NaCl) solution at room temperature for one week before analysis (Wang, Yu, Zhu, Yu, & Jin, 2009). The intensity was measured from 5° to 35° as a function of 2θ and at a scanning speed of 1°/min and a step size of 0.02°. The relative crystallinity was quantitatively estimated as a ratio of the crystalline area to the total area between 5° and 35° (2θ) using the Origin software (Version 7.5, Microcal Inc., Northampton, MA, USA).

2.7. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of three waxy wheat starches were obtained using a Tensor 27 FTIR spectrometer (Bruker, Germany) equipped with a DLATGS detector. The sample preparation and operation conditions were described elsewhere (Wang, Luo et al., 2014). The ratios of absorbance at 1045/1022 cm^{-1} and 1022/995 cm^{-1} were used to estimate the short-range ordered structure of starch.

2.8. Laser confocal micro-raman (LCM-Raman) spectroscopy

A Renishaw Invia Raman microscope system (Renishaw, Gloucestershire, United Kingdom) equipped with a Leica microscope (Leica Biosystems, Wetzlar, Germany) and a 785 nm green diode laser source was used in this study. Spectra were taken from the same spot size of each sample in the range of 3200–100 cm^{-1},