Food Chemistry xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Resistant starch improvement of rice starches under a combination of acid and heat-moisture treatments

Pham Van Hung [a,*], Ngo Lam Vien [a], Nguyen Thi Lan Phi [b]

[a] School of Biotechnology, International University, Vietnam National University in HoChiMinh City, Quarter 6, Linh trung Ward, Thu Duc District, HoChiMinh City, Viet Nam
[b] Faculty of Chemical Engineering, University of Technology, Vietnam National University in HoChiMinh City, 268 Ly Thuong Kiet Street, District 10, HoChiMinh City, Viet Nam

ARTICLE INFO

Article history:
Received 10 September 2014
Received in revised form 10 January 2015
Accepted 1 February 2015
Available online xxxx

Keywords:
Rice starch
Resistant starch
Heat-moisture treatment
Acid hydrolysis
Physicochemical properties

ABSTRACT

The effects of a combination of acid and heat-moisture treatment on formation of resistant starch (RS) and characteristics of high-amylose, normal and waxy rice starches were investigated in this study. The degrees of polymerization of the rice starches treated with citric acid, lactic acid or acetic acid were significantly reduced as compared to the native starches. The RS contents of acid and heat-moisture treated rice starches were in a range of 30.1–39.0%, significantly higher than those of native rice starches (6.3–10.2%) and those of heat-moisture treated rice starches (18.5–23.9%). The acid and heat-moisture treatments reduced swelling power and viscosity, but increased solubility of the starches, while the crystalline structure did not change. Among the organic acids used, citric acid had the most impact on starch characteristics and RS formation, followed by lactic acid and acetic acid. The results are useful in production of RS for functional food application.

1. Introduction

Starch is the most important carbohydrate in the human diet and serves as a major energy source. Based on *in vivo* digestion, starch is classified into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) according to the rate of glucose release and its absorption in the gastrointestinal tract (Englyst, Kingman, & Cummings, 1992). RDS and SDS represent the starch fractions that are completely digested, while RS is the portion which resists digestion and absorption in the small intestines of healthy individuals and is available for fermentation in the large bowel by human colonic microflora to short-chain fatty acids (SCFA), mainly acetate, propionate, and butyrate (Englyst, Kingman, Hudson, & Cummings, 1996; Topping & Clifton, 2001). The products of RS fermentation help to prevent colorectal cancer, to lower the risk of heart disease, and to influence metabolic and inflammatory bowel diseases such as diabetes and diverticulitis (Craig, Holden, Troup, Auerbach, & Frier, 1998; Topping & Clifton, 2001). The SDS fraction has also been reported to possess potential health benefits such as stable glucose metabolism, diabetes management, mental performance, and satiety (Lehmann & Robin, 2007).

Recently, a number of studies on improvement of SDS and RS in granular starches from various starch sources have been reported. The heat-moisture treatments (HMT), those performed at temperatures above the gelatinization temperatures with insufficient moisture to gelatinize (below 35%), have been investigated to improve both SDS and RS levels of the starch (Zavareze & Dias, 2011). Chung, Liu, and Hoover (2009) reported that when corn, pea, and lentil starches were heat-moisture treated at 120 °C and 30% moisture, the RDS decreased by 10.2%, 14.0%, and 15.1%, the SDS content increased by 2.5%, 2.8% and 4.7%, and the RS content increased by 7.7%, 11.2% and 10.4%, respectively, as compared to gelatinised unmodified starches. The SDS contents of maize, yam, rice, potato, plantain, and cocoyam flours were also increased after heat-moisture treatments by autoclaving and parboiling (Niba, 2003). Beside the effects of heating temperature, moisture content and time on the digestibility of starch, the amounts of SDS and RS in the heat-moisture treated starches were also affected by amylose contents of starches. Starches, which contained higher amylose contents, showed higher levels of resistant starch than normal starches both with and without modification (Chung et al., 2009). The resistant starch contents of native and heat-moisture treated corn starch were only 4.6% and 10.5%, respectively, whereas those of native and heat-moisture treated high-amylose corn starch contained 18.4% and 43.9%, respectively (Brumovsky & Thompson, 2001; Chung et al., 2009). The different chain-length distribution and crystallinity of starch were key factors for

* Corresponding author. Tel.: +84 8 37244270.
E-mail address: pvhung@hcmiu.edu.vn (P.V. Hung).

http://dx.doi.org/10.1016/j.foodchem.2015.02.002
0308-8146/

improvement of SDS and RS of heat-moisture treated starch. Partial acid hydrolysis of starches before heating at a high temperature improved resistant starch yield over the heat treatments without acid hydrolysis (Brumovsky & Thompson, 2001; Shin, Byun, Park, & Moon, 2004). Several studies reported that treatments of starches with citric acid solution at high temperature increased the SDS and RS contents (Liu et al., 2014; Shin, Lee, Kim, Lee, et al., 2007; Xie & Liu, 2004). In these studies, starches were heated in an excess amount of citric acid solution, the starch chains that swell from the starch granule during heat treatment are easily attacked by the citric acid and then the citric anhydride may substitute the hydroxyl on the starch chains (Liu et al., 2014). In contrast, Klaushofer, Berghofer, and Steyrer (1978) developed a dry reaction method for the esterification of root and cereal starches with organic poly-carbonic acids, in which the citric acid solution was used in concentrations of 5–40% of the dry weight of starch to react with starch at high temperature (between 110 and 140 °C) resulting in reduction of the *in vitro* digestibility of the starch citrates. The formation of the cross-linking structure by an esterification reaction between the citric anhydride and the starch chains led to the high content of RS. However, a concurrent reaction to esterification of starch by citric acid is hydrolysis. The starch can easily be hydrolyzed by citric acid at high temperature, in which amylopectin was more susceptible to hydrolysis than amylose during citric acid-heat treatment (Liu et al., 2014; Shin, Lee, Kim, Lee, et al., 2007). Thus, the citric acid and heat treatments were reported to change the internal structure and physicochemical properties of starch such as producing more various short chains, forming different crystallites that have different melting temperatures, increasing in apparent amylose content and cold-water solubility, and deceasing in viscosity and gel-forming ability (Liu et al., 2014; Shin, Lee, Kim, Lee, et al., 2007; Shin, Lee, Kim, Choi, et al., 2009). Although there have been several studies on improvement of SDS and RS of starch by citric acid and heat treatments, the starches were heated in excess water at high temperature, during which the granules were gelatinized into a dispersion of polymers to be easily esterified and hydrolyzed. In addition, the study on the impact of different organic acids on the formation of SDS and RS of starches are still limited. Therefore, the objective of this study is to investigate the formation of SDS and RS of rice starches with different amylose contents by treatment with various food-grade organic acids including acetic, lactic and citric acids under heat-moisture treatment condition, which used insufficient amount of water/acid solution and heated at high temperature without destroying starch granule structure. The physicochemical properties of the treated starches are also investigated in this study.

2. Materials and methods

2.1. Materials

Mature grains of three rice cultivars (*Oryza sativa* L.) with different amylose contents were purchased from local provinces in Vietnam. The nonsticky, short-grained varieties, Ham Trau rice (OM 576) and 504 rice (IR 50404) was grown in Can Tho Province, Vietnam. The sticky, short-grained variety, Nep Cai Hoa Vang rice (glutinous rice) was obtained in Hai Duong province, Vietnam. The cultivars, "Ham Trau" and "504", contained high and intermediate amylose contents, respectively, and the "Nep Cai Hoa Vang" cultivar was a waxy rice.

α-amylase from *Aspergillus oryzae* (~30 U/mg) and amyloglucosidase from *Aspergillus niger* (⩾300 U/ml) used in this study were purchased from Sigma–Aldrich Co. (St. Louis, MO, US). Other chemicals were purchased from Merck Co. (Darmstadt, Germany).

2.2. Rice starch isolation and composition analysis

Rice starch was isolated with 0.2% sodium hydroxide according to the method of Shodhi and Singh (2003) with a slight modification. Rice flour (50 g) was soaked in 0.2% sodium hydroxide solution (400 ml) at 4 °C overnight to remove proteins. The starch slurry was then centrifuged at 1500×*g* for 20 min. After discarding the supernatant, the alkaline extraction was repeated twice. Then the resultant starches were washed thoroughly in clean water to remove all contaminant substances and passed through the sieves (0.232 and 0.105 mm in aperture size). The starch sediment was recovered by centrifugation and dried in an oven at 40 °C to 10–11% moisture.

After isolation, rice starches were analyzed for their composition and purity. Amylose content of starch was determined according to the method previously descried by Hung and Morita (2005). Protein content was determined using a Kjeldahl digestion system (KI 26, Gerhardt, Germany) based on the standard AACC Approved Method 46–10 (American Association of Cereal Chemists, 2000). Lipid contents were determined by extraction with hexane for 6 h using a Soxhlet apparatus (AACC Approved Method 30–10). Ash content was determined by burning in a muffle furnace at 550 °C for 3 h (AACC Approved Methods 08-01). Total starch was calculated as follows: total starch (%, db) = 100% − protein content (%, db) − lipid content (%, db) − ash (%, db).

2.3. Acid and heat-moisture treatments

The isolated rice starch (100 g) was dispersed in measured volumes of different acid solutions (0.2 M lactic acid, 0.2 M acetic acid and 0.2 M citric acid) with moisture levels adjusted to 30% in screw capped bottles. Then the bottles were equilibrated at room temperature for 24 h before heating at 110 °C for 8 h. After heat-moisture treatment, the starch samples were neutralized with 1 M sodium hydroxide and then washed thoroughly with distilled water. The treated starches were recovered by centrifuging at 10,000×*g* for 30 min and then dried at 40 °C for 24 h.

2.4. Determination of degree of polymerization of starch

The number-average degrees of polymerization ($\overline{DP_n}$) of native and treated starches were determined by the method of Hizukuri, Takeda, Yasuda, and Suzuki (1981). $\overline{DP_n}$ was calculated as the difference between reducing residues and total glucose concentration of the starches (Hung, Maeda, Miskelly, Tsumori, & Morita, 2008).

2.5. Determination of starch fractions (RDS, SDS and RS)

Percentages of the starch fractions including rapid digestible starch (%RDS), slowly digestible starch (%SDS) and resistant starch (%RS) of the native and treated rice starches were measured based on the method of Englyst et al. (1992) with a moderate modification as follows. Starch (0.3 g, db) was mixed with 20 ml of sodium acetate buffer (pH 6.0) and then boiled for 30 min in a water bath. After equilibrating at 37 °C for 15 min, an enzyme solution (5 ml) of α-amylase (1400 U/ml) and amyloglucosidase (13 AGU/ml) was added and the slurry was incubated with shaking at 37 °C. After 20 min and 120 min, the hydrolysate (0.5 ml) was removed and determined for total glucose concentrations (G_{20} and G_{120}, respectively) using the phenol–sulfuric acid method. The remain residue was intensively hydrolyzed with 7 M KOH and then with amyloglucosidase (50 AGU/ml). The final hydrolysate was then determined for total glucose concentration (TG). The values

Please cite this article in press as: Hung, P. V., et al. Resistant starch improvement of rice starches under a combination of acid and heat-moisture treatments. *Food Chemistry* (2015), http://dx.doi.org/10.1016/j.foodchem.2015.02.002