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Resistant starch III from culled banana and its functional properties in fish oil emulsion

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ABSTRACT

Resistant starch from culled banana was produced by lintnerization (acid hydrolysis) and lintnerization prior to autoclaving of obtained starch. The functional properties and bioactivity were evaluated. Oxidative stability and sensory properties of fish oil emulsions produced with soy protein isolate (SPI) and mixtures of SPI with culled banana resistant starch (CBRS) or Hylon VII were evaluated. There was no significant difference ($p < 0.05$) in resistant and non resistant starch contents among native and different concentration of Lintnerized culled banana starch (CBS). Amylose content was decreased after lintnerization but increased in lintnerized-autoclaved CBS. Fourier transform infrared analysis revealed the modified structures and bonding of the starch materials with the shifting of C=O stretch. Rapid visco-analyser (RVA) viscosity values had reduced significantly with increasing the concentration of acid level. Maximum peak viscosity, trough, final viscosity, setback viscosity and peak time were found in native- autoclaved CBS. Swelling power had reduced by lintnerization and further reduced during lintnerization followed by autoclaving. Solubility had augmented drastically in lintnerized CBS ranging from 46.62 to 72.05% but only slight reduction in lintnerized-autoclaved starch than their only lintnerized counterparts. Emulsion made by the mixture of SPI, CBRS and 5% fish oil was the most stable among all emulsions as it produced lowest amount of peroxide value and anisidine value and scored minimum fishy odour intensity initially and throughout the storage period.

1. Introduction

Resistant starch (RS) is the amount of starch and starch degradation product that is resistant to break down by α-amylase. RS escapes digestion in the small intestine and passes to the large intestine where it is fermented by bacteria in healthy individuals. Prospective physiological benefits and high quality of the final food products make RS much important to the food formulators and nutritionists. Importance of RS is disease prevention including modulation of glycaemic index, diabetes, cholesterol lowering capability and weight management (Sajilata, Singhal, & Kulkarni, 2006). Physicochemical properties, particularly the low water holding capacity, stability in high processing temperatures (type RSIII), bland flavour, white colour provides better appearance, texture and mouth feel than do conventional fibre sources and improves expansion and the crispness in certain food applications. Native starches are modified with chemical, physical, and enzymatic methods (Betanchur & Chel, 1997) for the formation of RS, indigestible residues. Resistant starch is generally categorized in four forms based on the nature of starch and type of sources (Englyst, Kingman, & Cummings, 1992). RSI includes physically inaccessible starch, such as in grains, seeds or legumes; RSII is granular starch, non-gelatinized sources, such as green banana or native potato; RSIII is indigestible retrograded starch that is formed upon retrogradation after gelatinization; RSIV is chemically modified starch, such as hydroxypropyl starch and cross linking starch. Among four types, RSIII seems to be attractive because of its polymorphic crystallinity and survives most food-processing conditions as well as preserving its nutritional characteristics (Sievert, Czuchajowska, & Pomeranz, 1991). RSIII is produced by gelatinization after disruption of the granular structure by heating starch with excess water and retrogradation, a slow recrystallization of amylose and amylopectin during cooling or drying. On the other hand, partial acid hydrolysis (lintnerization) and debranching of amylopectin are very effective in generating RS from various starches (Brumovsky & Thompson, 2001). The advantages of debranching over mild acid hydrolysis include a shorter processing time, better processing control and higher RS yields.

Fish oil, a rich source of nutritionally important omega-3 polyunsaturated fatty acids (PUFA) is very susceptible to lipid oxidation

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(Anal, Jaisanti & Noomhorm, 2012). The incorporation of PUFA-enrich oils into food is the major confront as it should be oxidatively stable with minimum fishy flavour during production and storage. Protein-reducing sugars heated mixture can form the Maillard reaction products (MRP) with enhanced emulsifying properties (Kato, 2002; Morris, Sims, Robertson, & Furneaux, 2004; Shepherd, Robertson, & Ofman, 2000) and the oxidative stability of fish oil emulsions and microcapsules (Augustin, Sanguansri, & Bode, 2006; Drusch et al., 2009). Increasing severity of the heat treatment (60 °C–100 °C for 30–90 min) of protein (sodium caseinate, whey protein isolate, soy protein isolate, or skim milk powder) and carbohydrate (glucose, glucose/dried glucose syrup, or oligosaccharide/dried glucose syrup) mixtures reduced the susceptibility of the fish oil powder to oxidation (Augustin et al., 2006). RS has been used in combination with milk protein for preparation of fish oil capsules for *in vitro* lipolysis and their oxidative stability (Chung, Sanguansri, & Augustin, 2010).

Physical instability of an emulsion directed by four different droplet loss mechanisms: 1) Brownian flocculation, 2) creaming, 3) sedimentation flocculation and 4) disproportionation that may occur simultaneously and in any order (Becher, 1993). On the other hand, chemical instability occurred due to primary and secondary oxidation of fatty acids. During primary oxidation, odourless compounds are produced, measured with PV test. In second phase of complex oxidation reactions, the peroxide degrades into many substances as volatile aldehydes, responsible for rancid odour and flavour. The anisidine value represents the level of non-volatile aldehydes, primarily 2-alkenals present in the oil. According to Natural Health Products Directorate (NHPD) (2012), PV should not exceed 5meq/kg and AV should not be more than 20 in marine oils or omega-3 fatty acids derived from marine oils to ensure their oxidative stability.

Banana that is undersized or partially injured called “cull”. Approximately 20% (w/w) of all harvested bananas become culls (Zhang, Whistler, BeMiller, & Hamaker, 2005). These culled bananas are the good source of starch. About 82% of the total banana production in Thailand is Kluai Namwa (*Musa* ABB group) (Boonyanuphap, Wattanachaiyingcharoen, & Sakurai, 2004) contains high amount of amylose and resistant starch (RSII) that makes it suitable raw materials to produce resistant starch (RSIII). Therefore, the purpose of this study is to produce RSIII from culled banana starch of Kluai Namwa variety by lintnerization and autoclaving treatments and its utilization to produce fish oil emulsion with SPI comparing that produce with Hylon VII and SPI.

2. Materials and methods

2.1. Materials

Fish oil from Menhaden, SPI, pancreatic α-amylase and amyloglucosidase were purchased from Sigma Aldrich. High amylose-resistant starch (Hylon VII) was obtained from National starch, Thailand. All other chemicals used in the experiments were chemical grade.

2.2. Preparation of CBS

Kluai Namwa banana of aged 100–110 days (full green stage of maturity) after anthesis was collected from a local market (Pathumthani, Thailand). The last two hands (under sized, called cull) having green peel and sharp edges were selected. Injured portion (if any) of culled banana was removed and peeled. The peeled pulp were cut into 1.25 ± 0.25 cm thickness and rinsed into 1% (w/v) citric acid solution to avoid colour development. Slices were disintegrated by laboratory blender (Philips, HR-2001) with 0.05% NaOH solution (1:2 ratios, w/v). Water was added to slurry (5:1 ratio by volume) and passed through 60 and 200 mesh screens to remove fibrous materials and washed with water until it was white and clean. Starch was dried at 40 °C in a hot air oven for overnight then cooled, ground and passed through 100 mesh sieve. CBS was packed into high density polyethylene (HDP) bag by vacuum sealing and stored into desiccators for further use.

2.3. Lintnerized starch

Lintnerization (acid hydrolysis) was followed as described by Koksel, Basman, Kahraman, & Ozturk (2007) with modifications. At first, CBS was suspended into 1 N, 1.5 N and 2 N HCl solutions at 1:1.5 (w/v) ratios. Mixtures were heated at 40 °C for 3 h and then pH was adjusted to 6.5 with 10% NaOH. Samples were washed properly with distilled water and centrifuged at 1000 rpm for 5 min. The washed samples were dried at 40 °C and ground to pass through 100 mesh sieves. Dried lintnerized starch were packed into HDP pouch by vacuum sealing and stored into desiccators for further use.

2.4. Autoclaving of native & lintnerized CBS

Native CBS and three different concentrations of lintnerized CBS samples were suspended into water (1:10) and gelatinized at 85 °C for 30 min. The sample were further autoclaved at 135 °C for 30 min followed cooling and storing at 4 °C for 24 h. This autoclaving and storing process was repeated three times at same temperature and time (total 72 h storing time) for each sample. It was then dried at 50 °C in hot air oven, ground by grinder (Princess, Model No-2194, China) and sieved through 100 mesh. Dried starch products were packed into HDP pouch by vacuum sealing and stored into desiccators for further use.

2.5. Chemical analysis

Amylose content of native, lintnerized and autoclaved CBS samples was determined according to Juliano (1971). Starch (hundred mg) was kept into 100 mL volumetric flask. One mL 95% ethanol and 9 mL 1 N NaOH was added into the flask. Suspension was heated for 10 min in boiling water bath, cooled and made up the volume to 100 mL. Aliquot (5 mL) was pipetted out from the 100 mL into another 100 mL volumetric flask. 1 N acetic acid (1 mL) and then 2 mL iodide solution was added and made up the volume to 100 ml and shaken properly. After 20 min, absorbance was measured using a spectrophotometer (model UV2, Unicam, England) at 620 nm. A series of standard starch solution containing 0, 20, 40, 60, 80 and 100% amylose was prepared like sample preparations. Absorbance of the standards was read at 620 nm and a standard graph was plotted. Amylose content of the sample was determined in reference to the standard curve and expressed on percent basis.

Percent RS and non-resistant starch (NRS) of the samples were analysed according to the method described by McCleary & Monaghan (2002) with some modifications. Samples were incubated in a shaking water bath with 1 M sodium malate buffer (pH 6.0) containing pancreatic α-amylase (10 mg/mL) and amyloglucosidase (3 U/mL) for 16 h at 37 °C to solubilise and hydrolyse the NRS. The reaction was stopped by adding ethanol and followed by centrifugation at 3000 rpm for 10 min to obtain the RS. This lump of RS was washed with ethanol (50% v/v) and further centrifuged at 3000 rpm for 10 min. RS was suspended in 2 M KOH, followed by mixing 8 mL of 1.2 M sodium acetate buffer (pH 3.8) and 0.1 mL of amyloglucosidase (3300 U/mL). The mixture was then incubated at

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