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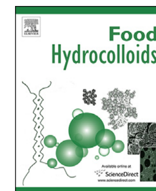
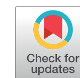


Complexation with phenolic acids affect rheological properties and digestibility of potato starch and maize amylopectin



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As well-documented inhibitors of starch digestive enzymes, dietary phenolics are less known for the ability to modify starch structures and functionality. This study aimed to characterize changes in starch structures by complexing individual phenolic acids with maize amylopectin and potato starch respectively, and to determine pasting properties and digestibility of the resulting complexes. FTIR-ATR results confirmed (995/1022 and 1047/1022 cm^{-1}/cm^{-1}) reduced crystallinity in short-range order of both starches, which were likely caused by a decrease in moisture content and/or by attenuation of molecular interactions in both crystalline and amorphous lamellas. Measurements of apparent amylose content and amylose leaching discovered formation of amylose-like structures in amylopectin and V-type amylose in potato starch. These structural changes were negatively associated with pasting temperature, peak viscosity, hot paste viscosity and cold paste viscosity. Digestibility was modestly lower for starch-phenolic acid complexes than for native starch and starch-phenolic acids mixtures. More interestingly, a small fraction of phenolic acids remained bound to starch molecules after pasting of starch-phenolic acid complexes, suggesting bound phenolic acids as a potential factor inhibiting starch hydrolysis.
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1. Introduction

The growing sentiment regarding negative associations between carbohydrate intake and risks of degenerative diseases, including diabetes and cardiovascular diseases (Eckel et al., 2014; World-Health-Organization, 2016), has placed a focus on modulating glycemic features of starchy foods as a potential strategy to meet the needs of select consumer products for sustained energy and reduced glycemic excursion (Singh, Dartois, & Kaur, 2010). Various techniques have been applied to optimize digestibility of starchy foods including processing (Aldughpassi, Abdel-Aal, & Wolever, 2012), formulation (Chai, Wang, & Zhang, 2013) and chemical modification (Chung, Liu, & Hoover, 2009). However, these approaches generally do not lend themselves to the consumer desire for a clean label product.

Phenolic compounds are a group of natural antioxidants present in plant extracts, fruits, vegetables and grains. Interestingly, dietary phenolics have been reported to attenuate starch digestion and intestinal glucose transport as well as systemic glycemic factors including regulation of pancreatic β-cell and liver functions (Kim, Keogh, & Clifton, 2016). Recent clinical research suggests that dietary phenolics can modulate the glycemic index of starchy foods (Coe, Clegg, Armengol, & Ryan, 2013; Somaratne et al., 2017). While biological activities of phenolics are often associated with their ability to modulate oxidative and inflammatory stress (Korkina, Kostyuk, De Luca, & Pastore, 2011), in regards to starch digestion and glucose transport, benefits most likely originate from both covalent and non-covalent interaction with protein and starch (Bordenave, Hamaker, & Ferruzzi, 2014; Li & Hagerman, 2013), suggesting that phenolics could serve as ideal modifiers in the generation of "better for you" starchy foods and snacks.

Modulation of starch digestion may be achieved through phenolic interactions with either digestive enzymes and/or the starch molecule itself. On the one hand, phenolics may compete with starch molecules for active sites of α-amylase and α-glucosidase resulting in suppression of the catalytic efficiency of starch hydrolysis (Adisakwattana, Chantarasinlapin, Thammarat, & Yibchok-Anun, 2009; Li, Koecher, Hansen, & Ferruzzi, 2017). On the other hand, semi-crystalline structures of starch could be altered by phenolic extracts with formations of inclusive V-type

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amylose (Cohen, Schwartz, Peri, & Shimoni, 2011) and non-inclusive starch-amylopectin complex (Chai et al., 2013). In both cases these interactions would lead to a reduction in starch digestion and an extension of glycemic response to a given dietary challenge.

While promising, further application of dietary phenolics is limited by insufficient knowledge on the inhibitory activity of structurally different phenolic compounds and by inconclusive evidence on glycemic feature of starch-phenolics complexes. Barros and colleagues reported that cooking with sorghum extract (polymeric flavonoids) can reduce digestibility of high amylose starch (Barros, Awika, & Rooney, 2012). However, a stimulating effect was reported by Chai et al. (2013) using similar experimental conditions and tea extract (monomeric flavonoids). These results suggest that there may be distinct differences in effects based on conditions or phenolic profiles. Contribution of individual phenolic compound to the overall anti-glycemic activity is still relatively unknown for most food matrices. More importantly, digestibility of starch-phenolics complexes in most studies has been determined with excessive quantities of phenolics, which are not practical for food applications, and may exceed the binding capacity of the starch molecules (Barros et al., 2012; Chai et al., 2013; Li et al., 2017). Presence of high free phenolics levels in the matrix can undermine the ability to evaluate the contribution of structural alterations to starch digestibility. The resulting digestibility may thus be a result of phenolic-enzyme interactions rather than alterations to starch structure or function.

To expand our understanding of the impact of phenolics on starch structure and function, including digestibility, the present study focused on the determination of structural and functional impacts of phenolic interactions on starch pasting properties and digestibility of starch-phenolics complexes. Caffeic acid, ferulic acid and gallic acid were selected to evaluate influence of different functional groups on interactions between simple phenolic acids and starch granules (potato starch and amylopectin). Changes in structure and physicochemical properties of starch granules were characterized by Fourier transform infrared spectroscopy (FTIR) and iodine binding technique. Contribution of bound phenolics to digestibility of starch-phenolics was also evaluated.

2. Materials and methods

2.1. Materials and chemicals

Caffeic acid, gallic acid, ferulic acid, ethyl gallate, iodine, all LC-MS solvents and other reagents were purchased from Fisher Scientific (NH, USA). Potato starch (0210295402) and maize amylopectin (0219504883) was purchased from MP Biomedicals LLC (OH, USA). Amylose (potato, A0512), α-amylase (porcine, A3176), amyloglucosidase (*Aspergillus niger*, 10115), and invertase (baker's yeast, I4504) were purchased from Sigma-Aldrich (MO, USA).

2.2. Preparation of starch-phenolics complexes and processed starch

Amylopectin or potato starch were dispersed with caffeic acid, gallic acid or ferulic acid at a 20:1 ratio in HCl-acidified water (pH 2.0), respectively. The mixture was oscillated at 210 stroke/min and 5 °C overnight, followed by 5 min of 1500 × g centrifugation. While supernatant was stored for analysis of amylose leaching, the resulting precipitates were washed with distilled water at a 1:50 (w/v) ratio five times and then lyophilized to obtain starch-phenolics complexes. Processed starch was prepared in a way similar to starch-phenolics complexes by dispersing native starch with HCl-acidified water (pH 2.0) instead of with acidified phenolics solutions. In addition, starch-phenolics mixtures in this study were prepared by simply mixing native starch with phenolic acids just prior to experiments. Total phenolic contents of these mixtures were matched to those of starch-phenolics complexes.

2.3. Extraction of phenolic acids

Extractable phenolic content: starch granules (100 mg dry weight, DW) were first spiked with 100 μL of 0.05 mg/mL ethyl gallate (internal standard), and then extracted three times with 3 mL of 80% methanol containing 0.2% formic acid. Pooled extracts were dried under nitrogen to evaporate methanol fraction, purified by Waters Oasis HLB extraction cartridge (WAT094225) according to a method previously described by Blount et al. (Blount et al., 2015), and reconstituted in 2 mL of 20% methanol containing 0.2% formic acid. *Free and bound phenolic contents*: 20 mg of dry starch was gelatinized at 83 °C in 10 mL of water followed by 10 min of centrifugation at 3500 × g. The supernatant was spiked with 100 μL of 0.05 mg/mL ethyl gallate, purified by Waters Oasis HLB cartridge, and then reconstituted in 1 mL of 20% methanol. The precipitate was extracted against 3 mL of 80% methanol solution for 3 times, and then purified by Waters Oasis HLB cartridge for LC-MS/MS analysis. Average extraction recovery was 85.8 ± 5.5% across all samples.

2.4. Measurement of phenolic content by LC-MS/MS

Phenolic contents of native starches, starches treated by phenolics, and gelatinized starch were determined by a Waters UPLC Acquity H Class system equipped with a TUV and TQD detector. Prior to analysis, all samples were filtered by 0.45 μm cellulose acetate membranes. Separation was performed on a BEH C18 column (2.1 μm, 1.7 mm id x 50 mm) at a flow rate of 0.5 mL/min. Samples were eluted with a gradient of 0.2% formic acid in acetonitrile (solvent A) and 0.2% formic acid in water (solvent B) as follows: 0 min, 100% B; 0.5 min, 94% B; 2.0 min, 91% B; 3.0 min, 87% B; 4.5 min, 65% B; 5.3 min, 100% B; 6 min, 100% B. The elution profile was recorded at 280 and 320 nm upon injection (10 μL), since gallic acid has maximum absorbance at 280 nm, while caffeic acid and ferulic acid have maximum absorbance around 320 nm. Phenolic acids were identified by comparing retention time and molecular mass of peaks with those of authentic standards. Content of phenolic acids were determined according to calibration curves for caffeic acid, ferulic acid, and gallic acid covering 0.1–20 μg/mL. MS conditions were as follows: ionization mode: ESI^-; Selective ion responses used were 169, 179, and 193 m/z for above-mentioned phenolics respectively; capillary voltage: 0.5 kV; probe temp: 150 °C; source temp: 600 °C; desolvation gas flow: 1000 L/hr; cone gas flow: 5 L/hr.

2.5. FTIR spectroscopy

Infrared spectra of starches and starches treated with phenolic acids were recorded on an IRPrestige-21 spectrometer (Shimadzu Corporation, Japan) equipped with a deuterated L-alanine doped tri-glycine sulfate detector using a MIRacle attenuated total reflectance (ATR) (PIKE Technologies, USA) accessory at a resolution of 4 cm^{-1} by 20 scans. Spectra were baseline-corrected, and then deconvoluted by drawing a straight line between 1200 and 800 cm^{-1} using 0.1 cm^{-1} width (Shimadzu IRsolution 1.30 software). No resolution enhancement (or apodization) was applied during the deconvolution. Intensity was recorded by the height of the absorbance bands from the baseline.

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