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Physicochemical interactions of maize starch with ferulic acid

Rusiru Karunaratne, Fan Zhu *

School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

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ABSTRACT

Ferulic acid is widely present in diverse foods and has great health benefits. Starch is a major food component and can be flexibly employed to formulate various products. In this study, the effect of ferulic acid addition on various physicochemical properties of normal maize starch was explored. The properties including swelling, pasting, steady shear and dynamic oscillation rheology, gelatinization, retrogradation, and gel texture were affected by ferulic acid to various extents, depending on the addition level. Enzyme susceptibility of granular starch to α-amylase was not affected. These influences may be explained by the functions of solubilized as well as insoluble ferulic acid which was in the form of crystals in starch matrix. On the molecular level, V-type amylose–ferulic acid inclusion complex formation was not observed by both co-precipitation and acidification methods. The results of this study may inspire further studies on the interactions of phenolics with other food ingredients and their role in food quality.

1. Introduction

Ferulic acid [(E)-3-(4-hydroxy-3-methoxyphenyl)-prop-2-enoic acid] (Supplementary Fig. 1) is a type of hydroxycinnamic acid found in many fruits and vegetables. It is sometimes called "chain breaking" antioxidant due to the radical scavenging properties (Packer, Sies, Eggersdorfer, & Cadenas, 2010). Ferulic acid has demonstrated diverse beneficial effects on human health such as anti-inflammation and free radical scavenging (Mancuso & Santangelo, 2014; Packer et al., 2010). It has been suggested that ferulic acid can treat diverse disorders including Alzheimer's disease, cancer, cardiovascular diseases, diabetes mellitus, and skin disease (Mancuso & Santangelo, 2014). It is, thus, natural to develop functional foods and nutraceuticals using ferulic acid as the bioactive ingredient. Another scenario is that during food processing and formulation such as tissue disruption, mixing, and cooking, diverse endogenous and exogenous ingredients come into contact and interact with each other. These interactions may impact physicochemical and nutritional properties of food. Ferulic acid in bound and free forms can be found in various types of food items such as cereals (Boz, 2015; Singh, Rehal, Kaur, & Jyot, 2015). Processing of these foods may release ferulic acid from cellular compartments and bound form (Singh et al., 2015), and the released compound may interact with other components such as protein and starch, affecting food quality.

Starch is one of the most common food components in human diets. It consists of two major types of macromolecules: the linear amylose and the branched amylopectin. In nature, starch chains are assembled in the form of semi-crystalline granules. Gelatinization, retrogradation, and interactions of starch can be critical for the quality of many food items rich in starch (e.g., cereal products). The interactions between starch and phenolic compound are gaining research focus during the last few years due to the possible impacts on food properties and nutrition (Zhu, 2015). On the molecular level, the non-covalent interactions between various phenolics and starches can be categorized into V-type amylose inclusion complex formation and non-inclusion complex formation (Zhu, 2015). Amylose undergoes structural changes in the presence of a guest molecule and forms V-type complexes (Ryno, Levine, & Iovine, 2014). Hydrophobic cavities are present within the helices of V-type amylose, entrapping the guest molecules (Lesmes, Cohen, Shener, & Shimoni, 2009). Both amylose and amylopectin interact with starch, but starches with high amylopectin contents (e.g., waxy starch) tend to form fewer or no complexes (Obiro, Ray, & Emmambux, 2012). Non-inclusion complex formation involves the interactions through hydrogen bonds, hydrophobic interaction, and electrostatic and ionic interactions (Bordenave, Hamaker, & Ferruzzi, 2014). On the macroscopic level, phenolics impact various physicochemical properties of starch such as rheology, gelatinization, and retrogradation (Sun-Waterhouse, Zhou, & Wadhwa, 2012; Xiao, Lin, Liu, & Yu, 2012; Zhu, 2010; Zhu & Wang, 2012). For example, with regard to the pasting properties, contradicting results were reported. In one study, tea polyphenols reduced peak viscosity, holding strength, final viscosity and setback viscosity, while increasing the breakdown viscosity (Guo, Tu, Pan, Zhang, & Zhang, 2012). Another study concluded that pasting properties were not influenced by the grain polyphenol content

* Corresponding author.
E-mail address: fzhu5@yahoo.com (F. Zhu).

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(Beta, Corke, Rooney, & Taylor, 2001). This contradiction may be due to the differences in the types of phenolics and starch, and reflects the needs to better understand factors affecting starch–phenolics interactions. Apart from physical properties, several studies have demonstrated the ability of polyphenols in the inhibition of starch enzymatic hydrolysis (Barros, Awika, & Rooney, 2012; Chiang, Li Chen, Jeng, Lin, & Sung, 2014). This suggests the positive role of the interactions on glucose metabolism management for human health.

Factors affecting the impact on starch properties include the type of starch and phenolic compound, composition and concentration of the system, and processing conditions (Zhu, 2015; Zhu, Cai, Sun, & Corke, 2009). Another much neglected but important point is that solubility of phenolics tends to play a major role in phenolics–starch interactions. Phenolics tend to have an increasing solubility with the increase of temperature (Cuevas-Valenzuela, González-Rojas, Wisniak, Apelblat, & Pérez-Correa, 2014). Ferulic acid, caffeic acid, and *p*-coumaric acid have melting points of 170, 196, and 215 °C, respectively (Murga, Sanz, Beltrán, & Cabezas, 2003). Most foods are not processed at such high temperatures, which may cause certain polyphenols to be unevenly dispersed in water. Solubilized phenolics may have different interactions with starch and other molecules present in the system due to the much increased mobility in a liquid medium. This was observed in two studies where one study demonstrated that tea polyphenols, which has a good water solubility, increased the peak temperature (T_p) of starch gelatinization from 71.0 to 74.9 °C (at 15% polyphenol concentration), while another study demonstrated that rutin, which has a rather low solubility, decreased the T_p of rice starch from 67 to 66.5 °C (at 50% concentration) (Xiao et al., 2012; Zhu & Wang, 2012). Phenylpropenoic acids (*trans*-cinnamic, caffeic, and ferulic acids) tend to have lower water solubility than hydroxybenzoic acids (gallic and salicylic acids) (Mota, Queimada, Pinho, & Macedo, 2008). The diversity in the solubility of different phenolics contributes to the difficulty in understanding the interactions of starches with various phenolic compounds.

This study mainly focused on observing the effect of ferulic acid addition on the swelling, rheological properties, gelatinization, retrogradation, and enzymatic hydrolysis of normal maize starch. Weather V-type amylose inclusion complexes could be formed with ferulic acid was also tested, employing a high amylose maize starch and two preparation methods.

2. Materials and methods

2.1. Materials

Normal maize starch (Amioca™) (moisture content: 13.32%, apparent amylose content: 24.5%) and high amylose maize starch Gelose 80 (moisture content: 12%, apparent amylose content: 80.4%) were from Ingredion Singapore Pte. Ltd. (Singapore). Gelose 80 was specifically used for the test of amylose inclusion complex formation due to the high amylose content. Normal maize starch was used for the other tests. Apparent amylose contents of starch were measured by iodine-binding based spectrophotometry. *Trans*-ferulic acid (purity 99%) and α-amylase of *Bacillus subtilis* were from Sigma–Aldrich (St. Louis, MO, USA). The chemical structure of ferulic acid is illustrated in Supplementary Fig. 1.

2.2. Methods

2.2.1. Particle size determination

Mastersizer 2000 (Malvern Instruments, Worcestershire, United Kingdom) was used to measure the particle sizes of normal maize starch and ferulic acid which was dispersed in water (1%, w/w). Particles size was measured with the refractive index of 1.5 and absorption index of 0. Sample was dispersed in the dispersion unit using water as dispersant (stirring speed at 2040 rpm), and the obscuration percentage was kept between 10 and 20%. Ultrasound was used for a better dispersion of particles. D[4,3] value and size distribution were monitored.

2.2.2. Swelling power and solubility

Starch (150 mg, db, W0) were measured directly into screw capped tubes and 10 mL of water was added and vortexed for 5 s. Ferulic acid was added in proportion (5–20%, w/w). The tubes were incubated in a water bath at 85 °C for 30 min with vortex mixing at 2 min intervals. The tubes were then immediately transferred to an iced water bath for cooling down. The tubes were centrifuged at 2000×*g* for 35 min. The supernatant was then transferred to aluminum pans. The material that adhered to the tube was considered as the sediment and the weight of the sediment was measured (Ws). The pans containing supernatant were placed in a forced air oven at 100 °C till a constant weight (W1). Water solubility index (WSI) and swelling power were calculated as:

$$\text{Water solubility index} = W1/W0 \times 100\% \quad (1)$$

$$\text{Swelling power} = Ws/[W0 \times (1 - WSI/100)] \ (g/g) \quad (2)$$

2.2.3. Differential scanning calorimetry (DSC)

Starch or mixtures (2 mg, db) (ferulic acid was at 5–20%, w/w) was weighed into DSC pans and 4 mL of water was injected through a micropipette. Samples were analyzed by a DSC (Q1000, TA instruments, New Castle, USA) by equilibrating at 30 °C for 2 min before ramping to 135 °C and cooling to 25 °C at a rate of 10 °C/min. After the gelatinisation, the pans were kept in the refrigerator at 4 °C for 21 days. The pans were then re-scanned with the same settings. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and enthalpy change (ΔH) of gelatinisation were noted. ΔH was calculated on the basis of starch weight.

2.2.4. Pasting

Starch or mixtures (1.75 g, db) (ferulic acid was at 5–20%, w/w) was blended with water to achieve a total weight of 17 g in the canister of a rheometer (Physica MCR 301, Anton Paar, Graz, Austria). Samples were held at 50 °C for 1 min, heated to 95 °C in 7.5 min, held at 95 °C for 5 min before cooling down to 50 °C in 7.5 min and holding at 50 °C for 2 min. The peak time, peak viscosity (PV), hot paste viscosity (HPV), final viscosity (FV), pasting temperature, and peak temperature were measured. Breakdown (BD = PV − HPV) and setback (SB = CPV − HPV) were calculated.

2.2.5. Steady shear analysis

Starch suspensions were prepared by mixing total solid weights (19.92 mg, db) with 0.4 mL of water (ferulic acid was at 5–40%, w/w). The suspensions were then transferred onto the plate of rheometer (Physica MCR 301, Anton Paar, Graz, Austria) using a parallel plate with a diameter of 40 mm and a gap of 1 mm. The edge of the gap was covered with a thin layer of soybean oil to minimize water evaporation. The suspensions were conditioned at 25 °C for 1 min. At a constant shear stress of 5 Pa, temperature was ramped from 25 °C to 95 °C before cooling to 25 °C with a rate of 10 °C/min. Then the samples were sheared from 0.1 s^{-1} to 800 s^{-1} and from 800 s^{-1} to 0.1 s^{-1} at 25 °C. The data was modeled by the power law (3) and Herschel–Bulkley (4) equations.

$$\delta = k \times \gamma^n \quad (3)$$

$$\delta = \delta_o + k \times \gamma^n \quad (4)$$