

Effect of Ferulic Acid and Catechin on Sorghum and Maize Starch Pasting Properties

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ABSTRACT

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The effects of ferulic acid and catechin on starch pasting properties were studied as part of an investigation into the structure and functionality of phenolics in starch-based products. Commercial maize starch, starches from sorghum cultivars (SV2, Chirimaugute, and DC-75), and the phenolic compounds ferulic acid and catechin were used in the investigation. Pasting properties were measured using rapid viscosity analysis. Ferulic acid and catechin (up to 100 mg each) were added to maize or sorghum starch (3 g, 14% mb) in suspensions containing 10.32% dry solid content. Addition of catechin resulted in pink-colored pastes, whereas ferulic acid had no effect on paste color. Ferulic acid and catechin decreased hot paste viscosity (HPV), final viscosity, and setback viscosity of maize and sorghum starch pastes, but had no influence on the

peak viscosity (PV) of the former. Both phenolics increased breakdown viscosity. Ferulic acid had greater influence on HPV, final viscosity, breakdown, and setback than catechin. Addition of catechin under acidic conditions (pH 3) decreased HPV, final viscosity, and setback of maize starch, but alkaline conditions (pH 11) slightly increased setback. Both acidic and alkaline conditions resulted in increased breakdown. Investigations on model-system interactions between ferulic acid or catechin and starch demonstrated that phenolic type and pH level both significantly influence starch pasting properties, with ferulic acid producing a more pronounced effect than catechin. The significance of these interactions is important, especially in food matrices where phenolics are to be added as functional food ingredients.

Phenolic compounds, including phenolic acids and flavonoids, are secondary plant metabolites naturally present in cereals and other plants as minor nonnutritive components (Harborne 1980). There is growing recognition that phenolics present in foods may possibly exert beneficial effects on human health through their antioxidant action (Parr and Bolwell 2000), however the amounts of phenolic compounds relevant in food products are yet to be established. Total phenolic content assayed by the vanillin method had ranges from not detectable (nd) to 3,900 mg/100 g in sorghum; 316–1,040 mg/100 g in lentil; nd–740 mg/100 g in faba beans; and 4–414 mg/100 g in wine vinegar (Art et al 2000). Cereal grains are rich sources of phenolic compounds with total amounts approaching 5,000 mg/100 g (Senter et al 1983). Consumption of whole-grain cereals containing free phenolic acids and phenolics esterified to polysaccharides seems to have the greatest potential to benefit health (Baublis et al 2000). Phenolics that pose challenges during processing of cereal grains (Beta et al 1999) are concentrated in the bran layers (Gao et al 2002). However, because the bran is removed during milling, grain products such as bread, pasta, and noodles derived from the starchy endosperm may be devoid of measurable phenolic content.

Grain phenolics have been implicated as causative agents of a pinkish or off-color of some starches (Freeman and Watson 1971; Davis and Hosney 1979; Beta et al 2000). Our previous work indicated the possible influence of grain phenolics on functional properties of isolated starch (Beta et al 2000). Ferulic acid is one of the major phenolic acids found in cereals (Nishizawa et al 1998). The use of ferulic acid in starch ferulate production is also of interest as the latter has better water-holding capacity and lower retrogradation during cold storage than native starch (Ou and Yang 2001). Deshpande and Salunke (1982) reported that bound catechin (a flavonoid) decreased *in vitro* starch digestibility. Because starch-based foods are the basis of any staple diet, and food is generally cooked at high temperatures or exposed to different pH levels, specific studies are needed to examine the effect of phenolic compounds on starch properties. The present study investigates the effect of

addition of ferulic acid and catechin under different conditions on starch pasting properties. This preliminary investigation will form the basis for future work on structure-function relationships of phenolic compounds and their subsequent incorporation into starch-based products.

MATERIALS AND METHODS

Materials

Normal maize starch was obtained from Sigma Co. (St. Louis, MO). Based on our previous work indicating a possible influence of grain phenolics on starch functional properties (Beta et al 2000), the sorghums (SV2, Chirimaugute, and DC-75) were selected to represent cultivars containing low (not detectable [nd]), medium (3,780 mg/100 g), and high levels (6,290 mg/100 g) of phenolic compounds, respectively (Beta et al 1999). Starch was extracted from sorghum grains following a procedure described earlier (Beta et al 2000). The dry matter content of maize and sorghum starches was determined by drying for 16 hr at 105°C.

The phenolic compounds catechin and ferulic acid were obtained from Sigma Chemicals. Figure 1 shows the structure of these two phenolics. Ferulic acid is a hydroxycinnamate consisting of a double bond that is conjugated to the benzene ring. Catechin, a flavan-3-ol, consists of two separate aromatic ring systems; two benzene rings connected by a six-membered, nonaromatic, oxygen containing ring. The structure is therefore not planar, and the pi-electrons of the two benzene rings cannot interact with each other through conjugation.

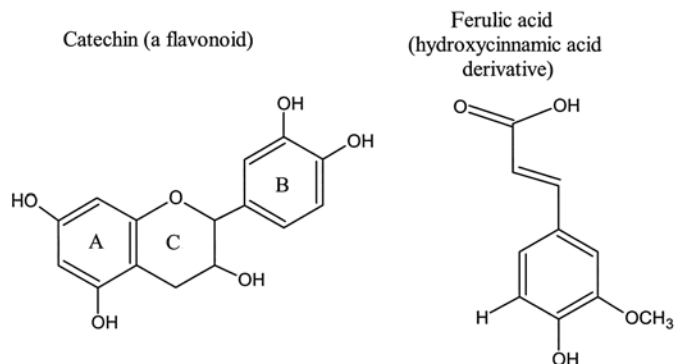


Fig. 1. Structures of catechin and ferulic acid.

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Pasting Profile Determination

Pasting properties of starches were determined using a Rapid Visco Analyser (RVA) (Newport Scientific, Warriewood, Australia). Starch (3 g, 14% moisture basis) was mixed with 25 g of water accurately weighed in the RVA aluminum canister to give 10.32% dry solid content. Ferulic acid or catechin (25, 50, 75, and 100 mg) was added to maize or sorghum starch to give levels of ≈0.8, 1.7, 2.5, and 3.3% of the starch weight. Initial experiments were conducted at pH 7 (neutral). Effect of addition of phenolic compounds (100 mg) under acidic and alkaline conditions on maize starch pasting properties was also investigated. Water was adjusted to pH 3 or 11 using HCl (1M) or NaOH (1M), respectively.

A programmed heating and cooling cycle was used in which the mixture was held at 50°C for 1 min, heated to 95°C in 7.5 min at the rate of 6°C/min, held at 95°C for 5 min before cooling to 50°C in 7.5 min, and holding at 50°C for 1 min. Peak viscosity (PV), time to reach PV (PV_{time}), hot paste viscosity (HPV), final (cool paste) viscosity, breakdown (PV – HPV), and setback (final viscosity – PV) were recorded. Color of cooled pastes was determined visually. Two replicates per sample were analyzed.

Statistical Analysis

The general linear model procedure (v. 8.2, SAS Institute, Cary, NC) was used for data analysis. Means were compared at the 5% significance level using Fisher's least significant difference (LSD).

RESULTS

Phenolics and Paste Color

The color of the cooled pastes was visually determined when ferulic acid and catechin (100 mg) were individually added to

aluminum canisters containing maize or sorghum starch. Ferulic acid gave a clean white paste, whereas catechin imparted a pale pink color to the paste. Thus visual observations indicated that unlike ferulic acid, catechin may impart pigmentation to starch products.

Effect of Ferulic Acid and Catechin on Pasting Properties of Maize Starch

Ferulic acid significantly affected starch pasting characteristics measured as PV_{time} , PV, HPV, breakdown, final viscosity, and setback (Table I, Fig. 2). PV_{time} of maize starch was slightly reduced in the presence of 25 mg of ferulic acid. Higher levels of ferulic acid resulted in further reduction of PV_{time} . Ferulic acid had very little influence on PV of starch pastes. The effects of phenolic compounds on starch pasting properties were better illustrated with HPV, breakdown, final viscosity, and setback than with PV. Breakdown increased while final viscosity and setback decreased with increase in levels of ferulic acid.

Catechin had minimal effects on pasting properties (Table I) compared with ferulic acid. Addition of catechin at different levels (25, 50, 75, and 100 mg) had no measurable influence on PV of maize starch pastes. HPV, breakdown, final viscosity, and setback followed trends similar to those observed with ferulic acid, although the changes in pasting properties were less pronounced. PV was unaffected when up to 100 mg of catechin was added to the starch paste. There was no measurable influence on HPV with addition of up to 50 mg of catechin. Breakdown increased slightly with increasing amounts of catechin. Setback and final viscosity decreased slightly as levels of catechin were increased in the starch paste. Increasing levels of catechin had less pronounced effect on starch pastes when compared with similar levels of ferulic acid.

TABLE I
Effect of Ferulic Acid and Catechin (0–100 mg) on Maize Starch Pasting Properties^{a,b}

| | PV_{time} (min) | PV (RVU) | HPV (RVU) | Breakdown (RVU) | Final Viscosity (RVU) | Setback (RVU) |
|-------------------|-------------------|----------|-----------|-----------------|-----------------------|---------------|
| Ferulic acid (mg) | | | | | | |
| 0 (control) | 8.13a | 335b | 167a | 169e | 326a | 159a |
| 25 | 8.00b | 337ab | 153b | 184d | 291b | 138b |
| 50 | 7.97b | 339a | 138c | 201c | 271c | 134c |
| 75 | 7.83c | 338a | 127d | 211b | 255d | 128d |
| 100 | 7.80c | 339a | 119e | 220a | 245e | 124e |
| LSD | 0.13 | 2.5 | 3.1 | 2.9 | 2.0 | 2.0 |
| Catechin (mg) | | | | | | |
| 0 (control) | 8.13a | 335a | 167a | 169b | 326a | 159a |
| 25 | 8.06b | 335a | 164ab | 171b | 318b | 154ab |
| 50 | 8.03bc | 334a | 163ab | 170b | 314c | 151bc |
| 75 | 8.00c | 337a | 159bc | 179a | 306d | 149cd |
| 100 | 8.00c | 336a | 158c | 177a | 303e | 144d |
| LSD | 0.05 | 2.9 | 5.5 | 4.4 | 2.7 | 5.4 |

^a Peak viscosity, PV; time (min) from initial to peak viscosity, PV_{time} ; hot paste viscosity, HPV; final viscosity, breakdown (PV – HPV), setback (final viscosity – HPV); measurements in rapid viscosity units (RVU); least significant difference, LSD.

^b Values within the same column with different letters are significantly different at $P < 0.05$.

TABLE II
Effect of pH and Ferulic Acid or Catechin (100 mg) on Maize Starch Pasting Properties^{a,b}

| | PV_{time} (min) | PV (RVU) | HPV (RVU) | Breakdown (RVU) | Final Viscosity (RVU) | Setback (RVU) |
|----------------|-------------------|----------|-----------|-----------------|-----------------------|---------------|
| Ferulic acid | | | | | | |
| pH 7 (control) | 7.80a | 339a | 119b | 220b | 242b | 124b |
| pH 11 | 7.73b | 340a | 127a | 213a | 259a | 132a |
| pH 3 | 7.73b | 334b | 93c | 241a | 199c | 106c |
| LSD | 0 | 0 | 7.0 | 7.0 | 1.3 | 5.5 |
| Catechin | | | | | | |
| pH 7 (control) | 8.00a | 336a | 160a | 177c | 303a | 144b |
| pH 11 | 7.60c | 333ab | 140b | 194b | 299a | 159a |
| pH 3 | 7.90b | 329b | 113c | 216a | 227b | 114c |
| LSD | 0.078 | 5.4 | 9.3 | 14.5 | 6.6 | 5.8 |

^a Peak viscosity, PV; time (min) from initial to peak viscosity, PV_{time} ; hot paste viscosity, HPV; final viscosity, breakdown (PV – HPV), setback (final viscosity – HPV); measurements in rapid viscosity units (RVU); least significant difference, LSD.

^b Values within the same column with different letters are significantly different at $P < 0.05$.

Effect of Ferulic Acid and Catechin (100 mg each) on Pasting Properties of Starches

Figure 2 shows the influence of ferulic and catechin on maize and sorghum starch pastes. The shape of the curves varied greatly for different starches. Ferulic acid significantly increased PV_{time} from 7.23, 7.00, and 5.97 min to 8.07, 8.07, and 8.27 min for SV2, Chirimaugute, and DC-75 sorghum starches, respectively ($P < 0.05$). Only a slight reduction of PV_{time} (0.34 min) was observed for maize starch. PV was markedly reduced by 27, 35, and 114 RVU for SV2, Chirimaugute, and DC-75 sorghum starches when ferulic acid was included. A reduction of 2 RVU was recorded for maize starch. Ferulic acid caused a significant reduction in final viscosity of sorghum and maize starch pastes (Fig. 2). However, catechin had minimal influence on sorghum and maize starch pasting characteristics.

Effect of Ferulic Acid and Catechin (100 mg each) on Pasting Properties of Maize Starch at Alkaline or Acidic pH Levels

The effects of pH (7, 3, and 11) on starch pasting properties in the presence of ferulic acid are summarized in Table II. PV_{time} was similar at acidic and alkaline pH but decreased slightly when compared with the control. Both neutral and acidic pH significantly lowered HPV in the presence of ferulic acid. Acidic pH caused the greatest paste breakdown. Final viscosity was reduced by acidic pH. Setback was highest and lowest at alkaline and acidic pH, respectively. Maize starch pastes containing ferulic acid were compared with starch pastes without added ferulic acid at similar pH levels. At pH 11, the presence of ferulic acid significantly increased PV (up by 25 RVU) and HPV (up by 10 RVU) at $P < 0.05$. Pastes containing ferulic acid at pH 3 had significantly higher PV (up by 52 RVU) and setback (up by 10 RVU). Acidic conditions in the presence of ferulic acid had greater influence on starch pasting characteristics than alkaline conditions.

The effects of pH (7, 3, and 11) on starch pasting properties in the presence of catechin are summarized in Table II. Alkaline pH gave the lowest PV_{time} . Both neutral and acidic pH lowered HPV significantly in the presence of catechin. As observed with ferulic acid, acidic pH caused the greatest paste breakdown. Final viscosity was not affected by alkaline pH. However, acidic pH lowered final viscosity significantly. Setback was highest and lowest at alkaline and acidic pH, respectively. Compared with maize starch pastes devoid of catechin at similar pH levels, pastes containing catechin at pH 11 had significantly higher PV (up by 18 RVU) and HPV (up by 23 RVU) at $P < 0.05$. Maize starch pastes containing catechin at pH 3 had significantly higher PV (up by 46 RVU) and setback (up by 19 RVU). With the exception of PV_{time} and setback, acidic conditions had more influence on starch pasting properties than alkaline pH.

DISCUSSION

Sorghum starch resembles maize starch; however, commercial production of the former has been pursued to a very limited extent. The great variability in sorghum kernel structure and level of phenolic compounds (Beta et al 1999) influence starch properties (Beta et al 2000). Davis and Hosney (1971) demonstrated that starch could adsorb and retain phenolic compounds from polyphenol-containing sorghum cultivars. We have shown in our previous work that sorghum starches have higher peak viscosities and breakdown viscosities than maize starch (Beta et al 2001). The extent to which addition of small amounts of phenolics could affect pasting properties is shown above.

Colored products have previously been obtained from starch extracted from grains containing polyphenols (David and Hosney 1979; Beta et al 2000; Beta and Corke 2001); however it appears that addition of ferulic acid would cause minimal pigmentation. The

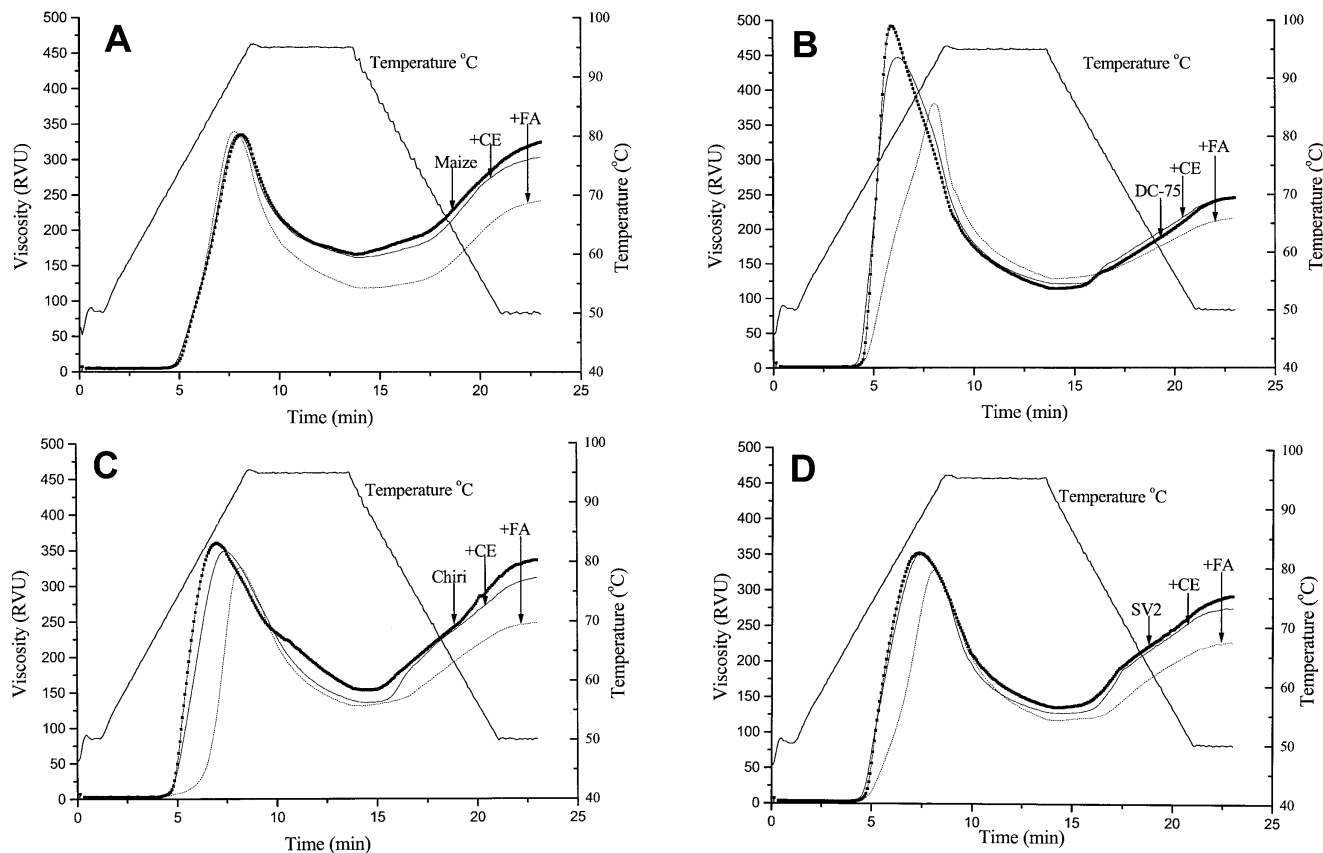


Fig. 2. Effect of ferulic (FA) and catechin (CE) (100 mg each) on RVA pasting profiles of maize (A) and sorghum DC-75 (B), Chirimaugute (Chiri) (C), and SV2 (D) starches.

above data confirms our previous findings on the negative correlation between grain phenolics and starch PV_{time} (Beta et al 2000). The latter was rationalized in terms of grain phenolics appearing as minor starch components that enhanced granule swelling. HPV, breakdown, final viscosity, and setback properties were markedly altered when ferulic acid was added to the maize starch. HPV was significantly reduced in the presence of 100 mg of ferulic acid.

The effect of phenolic compounds on starch pasting properties can be explained in terms of inclusion complexes. In the presence of small molecules, starch forms inclusion complexes (clathrates) (Belitz and Grosch 1999). Among the molecules that are bound by phenolics, only starch has this embedding characteristic. Phenols are capable of forming clathrate compounds with amylose molecules. The amylose molecule has six glucose residues per helical turn, the helix becoming more extended in the presence of alkali. Because the helix is internally hydrophobic, the enclosed ferulic acid or catechin also has lipophilic properties. These complexes presumably resemble those formed between amylose and lipids and serve to stabilize the V-conformation of cereal starches (Belitz and Grosch 1999). The presence of phenolics generally lowered the swelling power (measured as PV_{time}) of maize and sorghum starches as ferulic acid and catechin were included as guest molecules in the helices.

The interactions of starch with phenolics include associations that are hydrophobic in nature and formation of hydrogen bridges through the hydroxyl groups. Such interactions are governed by the molecular weight, low solubility, and conformational flexibility of the different starches (Belitz and Grosch 1999). Differences in pasting characteristics in the presence of phenolics displayed by maize and sorghum starches are evidence of the variations in the fine structures and molecular weights of the amylose and amylopectin fractions (Takeda et al 1988; Jane et al 1992). While both starch chains interact with organic compounds, the amylose fraction appears to be mainly responsible for the existence of distinct binding zones (Rutschmann et al 1990) with the longest amylose chains forming the most stable complexes (Rutschmann et al 1989). This was evident in DC-75 starch which has slightly higher apparent amylose content compared with the other starches.

The significant reduction in HPV and final viscosity when phenolics were added to starch pastes was probably due to formation of starch-phenol complexes that interfered with the alignment of polymer chains. Ferulic acid strongly interfered with the reassociation of starch molecules resulting in reduced final viscosity. Addition of phenolics resulted in lower setback values, an indication that inclusion complexes stabilized the starch pastes.

The results confirmed our previous data indicating that starch extracted from a polyphenol-rich cultivar had the lowest setback (Beta et al 2000). Although catechin binds to starch (Deshpande and Salunke 1982), the interference with starch pasting characteristics was limited.

Neutral conditions favor retrogradation of glucan chains (Belitz and Grosch 1999). However, the tendency toward retrogradation in the presence of ferulic acid and catechin in maize starch pastes seemed to interfere with reassociation of polymer chains as shown by a significant decrease in final viscosity and setback. In the presence of alkali, the helical conformation becomes more extended (Belitz and Grosch 1999). Granular swelling is enhanced and peak viscosity is increased (Mistry and Eckhoff 1992; Beta et al 2001).

Indeed, alkaline pH in the presence of ferulic acid and catechin further increased PV. Acids disrupt the glycosidic linkages, limiting swelling and lowering the final viscosity of starch products (Belitz and Grosch 1999). The observation that maize starch pastes containing ferulic acid and catechin at pH 3 had higher PV and setback compared with starch pastes devoid of these compounds at the same pH implied enhanced granular swelling and

breakdown in the former. PV could occur as a result of thermal breakdown of starch inclusion complexes for maize (Goering et al 1975).

CONCLUSIONS

Investigations on model system interactions between ferulic acid or catechin and starch demonstrated that both phenolic type and pH conditions significantly affected starch pasting properties. Starch possibly formed inclusion complexes with phenolics resembling amylose-lipid complexes. The extent of influence on starch pasting properties was explained in terms of structural differences among the various starch materials and the two phenolic compounds. It is assumed that catechin in comparison to ferulic acid possibly formed fewer inclusion complexes with starch. However, it appears feasible to include small amounts of ferulic acid or catechin in starch-based formulations where phenolics can play a role as functional food ingredients.

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