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Phenolic compounds, antioxidant capacity and gelling properties of glucoarabinoxylans from three types of sorghum brans

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ABSTRACT

Arabinose to xylose ratio (A/X), phenolics, antioxidant capacity and gelling properties were evaluated in glucoarabinoxylans (GAX) extracted from white (W-GAX), red (R-GAX) and high tannin (T-GAX) sorghum brans (SB). The characterization of arabinoxylans from corn fiber (CFAX) was used as benchmark. Sorghum GAX had higher branched structure (A/X 1.08–1.41) than CFAX (0.59). Nine 3-deoxyanthocyanins (3-DAs) were identified in SB and two glycosylated forms remained associated to the R-GAX and T-GAX extracts. T-GAX was the only that contained tannins (0.41 mg catechin equivalents (CE)/g dry basis (db)) and exerted the highest antioxidant capacity (81.75 mM Trolox equivalents (TE)/g db) followed by R-GAX (48.49 mM TE/g db), which contained the highest amount of 3-DAs (0.11 mg Luteolinidin equivalents (Lut eq)/g db), and W-GAX (35.45 mM TE/g db) that was not significantly different from the CFAX (25.83 mM TE/g db). Among sorghums, only the W-GAX gelled but it formed a weaker gel compared to CFAX likely due to its lower hydroxycinnamic acids (HCA) concentration. The presence of 3-DAs in the structure of R-GAX and T-GAX affected negatively their solubility and gelling properties. The different SB showed potential as sources of GAX with antioxidant capacity.

1. Introduction

Sorghum (*Sorghum bicolor* L.) is the fifth leading crop in the world after wheat, maize, rice, and barley. In 2013, 61.4 million tons were produced worldwide (FAO, 2015). Sorghum contains about 5–6% (w/w) of cell wall material, which mainly consists of non-starch polysaccharides associated to phenolic compounds (Verbruggen et al., 1995). According to their genetics and chemical composition, sorghums are classed into three groups: type I or white sorghums that do not have a pigmented seed coat without tannins; type II (usually red colored) which possesses testa without tannins; and type III or bird resistant that have a pigmented testa with condensed tannins (Dykes and Rooney, 2006). Sorghum bran might contains significant quantities of anthocyanins and phenolic acids (hydroxybenzoic and HCA). Sorghum anthocyanidins are unique since they do not have a hydroxyl group in the C-ring and thus are called 3-DAs. Luteolinidin and apigeninidin are the most common 3-DAs in sorghum (Carbonneau et al., 2014).

Cereal cell wall polysaccharides are composed mainly of arabinoxylans (AX), (1–3), (1–4)-β-D-glucans and cellulose. AX from cereals have generated research interest thanks to their nutraceutical properties for the control of diabetes mellitus, cardiovascular disorders, the improvement of calcium and magnesium absorption and prevention of colon cancer (Saeed et al., 2011). The presence of HCA such as *p*-coumaric (*p*-CA), ferulic acid (FA) and their oligomers impart antioxidant capacity to AX (Ayala-Soto et al., 2014a). Unfortunately, the structure of hemicelluloses from sorghum has received little attention; only a limited number of studies have

Abbrevations: AP, apigeninidin; AP-5-GLC, apigeninidin-5-glucoside; A/X, Arabinose/xylose ratio; AX, arabinoxylans; AAPH, 2,2′ azobis(2-amidinopropane) dihydrochloride; T-GAX, high tannin glucoarabinoxylans; TSB, high taninn sorghum bran; CA-Ara-5-OAP, Caffeic acid ester of arabinosyl-5-O-apigeninidin; CE, catechin equivalents; CFAX, corn fiber arabinoxylans; CF, corn fiber; CYN, cyanidin; CYN-3-GLC, cyanidin-3-glucoside; *p*-CA, *p*-coumaric; 3-DAs, 3-deoxyanthocyanins; di-FA, dehydrodiferulic acids; dXyl, di-substituted xylosyl residues; EF, extraction efficiency; FA, ferulic acid; G′, elastic modulus; G″, viscous modulus; GA, gallic acid; GAX, glucoarabinoxylans; HPLC, high performance liquid chromatography; HCA, hydroxycinnamic acids; LUT, luteolinidin; LUT-5-GLC, luteolinidin-5-glucoside; 7-MeO-AP, 7-methoxyapigeninidin; 5-MeO-LUT, 5-methoxyluteolinidin; mXyl, mono-substituted xylosyl residues; ORAC, oxygen radical absorbance capacity; R-GAX, red-glucoarabinoxylans; RSB, red sorghum bran; SB, sorghum brans; tri-FA, dehydrotriferulic acids; TE, trolox equivalents; uXyl, un-substituted xylosyl residues; WUS, water-unextractable cell wall material; W-GAX, white glucorabinoxylans; WSB, white sorghum bran.

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reported the isolation and sugar characterization of AX from its water-unextractable cell wall material (WUS) (Nandini and Salimath, 2001; Verbruggen et al., 1995). These researchers described a backbone of (1–4)-b-linked D-xylopyranose residues, with single arabinofuranose units attached at O-3 or at both O-2 and O-3 of certain xylose units. Other structures such as glucoronic acid and 4-O-methylgucoronic acid are attached through O-2 of xyloses and arabinose residues, single or as chains at O-3. Verbruggen et al. (1995) reported that glucose was co-extracted and linked to AX after neutral sugar and methylation analyses. Due to the high glucose concentration in their structure, sorghums extracts are named GAX. On the other hand, several studies concluded that sorghums rich in phenolics exert cholesterol-lowering, anti-inflammatory and anti-carcinogenic properties, but these benefits have been not studied with isolated GAX (Carbonneau et al., 2014; Suganya Devi et al., 2012).

In the last years, the conversion of cereal by-products such as brans into value added components or additives have raised attention. The different types of sorghum brans are potential rich sources of GAX with high antioxidant potential. Therefore, the aim of this research was to establish a relationship between the composition (A/X ratio and phenolics), antioxidant capacity and gelling properties of GAX extracted from white, red and high tannin sorghum brans. Functionality, structure and potential uses of corn fiber have been previously characterized (Ayala-Soto et al., 2014a, 2014b; Carvajal-Millán et al., 2007; Lapierre et al., 2001). In the present study, the corn fiber extract represents an ideal benchmark to analyze whether sorghum extracts could have more or less potential as antioxidant or gelling agents.

2. Materials and methods

2.1. Samples

A white (TX631 RTx431) from a tan colored plant (WSB) and a high tannin sorghum (Pioneer 81G67) (TSB) were kindly donated by the Texas A&M breeding program whereas the red sorghum (RSB) was purchased in a local store. All sorghums were decorticated to remove 11.5% of the outer layers rich in pericarp, aleurone, testa and germ tissues using a horizontal millstone pilot plant PRL mill (Nutana Machine, Saskatoon, SK, Canada), Resulting brans were ground into a fine meal in a mill equipped with a 1 mm mesh sieve. A commercial corn fiber (CF) provided by Mexstarch Industry Sapi de C.V. (Sinaloa, México) was obtained from a wet-milling process, which removes the corn germ by density. Therefore, the CF was mainly composed of pericarp and outer endosperm tissue. All the experimental brans were used as raw materials for the extraction of GAX.

2.2. Chemical composition of brans

Standard methods were used for the determination of moisture (Method 44–15, AACC, 2000), protein and lipids (Methods 978.02 and 945.16, AOAC, 1992). Fiber was assayed according to the National Renewable Energy Laboratory (Sluiter et al., 2008). The analysis for neutral and acid detergent fibers (NDF and ADF), acid detergent lignin and ash (ADL and ADA) were performed in extractives-free samples. The difference between NDF and ADF was considered as hemicellulose. The cellulose was estimated by subtracting the values for ADL and ADA from ADF.

2.3. Glucoarabinoxylans extraction

The alkaline treatment protocol of Ayala-Soto et al. (2014a) was used to extract GAX from the three SB and AX from the CF. Briefly 3 g of SB samples and CF were suspended in 45 mL of sodium hydroxide (NaOH) 0.5 N at 25 °C in darkness and agitated on a rotary shaker (100 rpm) during 8 h. The alkaline treated solutions were centrifuged (IEC Central MP4R Needham Heights, Ma) at 17,000 g and 20 °C during 15 min. The supernatants were acidified to pH 4 with 3N hydrochloric acid, and centrifuged (17,000 g, 15 min at 20 °C) again. The acidified supernatants were precipitated by adding absolute ethanol (representing 65% of final volume) overnight at 4 °C. The precipitate was recovered by centrifugation (17,000 g at 4 °C, 15 min) and air-dried (50 °C) for 1 h to eliminate the ethanol. All the extracts were re-suspended in water and freeze-dried (Virtis FM 25 EL 85, Gardiner, NY). The amount of GAX and CFAX were determined as g of dry extract per 100 g of dry extraction source (g/100 g db).

2.4. Sample preparation

For sugars (glucose, xylose and arabinose) the GAX sample were hydrolyzed under acidic conditions as described by Ayala-Soto et al. (20014a). A volume of 500 μL of trifluoroacetic acid was added to 10 mg of freeze dried GAX extract. The samples were hydrolyzed during 2 h at 120 °C as reported previously Ayala-Soto et al. (2014a). The reaction was stopped on ice and the extracts were dried under nitrogen to evaporate the solvent. Two washes were performed by rising with 200 mL of water and then subjected to drying under vacuum at 35 °C (GeneVac EZ-2plus). Each sample extract was solubilized in 500 μL of water HPLC grade and filtered through a 0.22 μm syringe filter.

Phenolics were extracted as reported by Awika et al. (2004). Briefly, 10 mL of 1% MeOH–HCl was added to 0.5 g of bran or 5 mL to 0.1 g of GAX extracts. The extraction was performed during 2 h on a rotatory shaker (200 rpm) at 25 °C, and the resulting extracts obtained after centrifugation (IEC Central–MP4R, Needham Heights, MA) at 10,000 g for 10 min at 20 °C. The residues from bran samples were washed twice with 5 mL of 1% MeOH–HCl or 3 mL for GAX. Supernatants were pooled, mixed and evaporated to near dryness under vacuum at 35 °C (GeneVac EZ-2plus). The phenolic bran and GAX extracts were re-dissolved in 5 mL or 2 mL of 1% MeOH–HCl. All samples were filtered through a 0.45 μm syringe filter and stored at −20 °C before analysis.

For tannin determinations, 0.2 g of bran samples or 0.1 g of GAX were extracted with 10 mL or 5 mL of 1% MeOH–HCl. Extractions were performed during 20 min in a water bath set at 30 °C. Then, samples were centrifuged at 5000 rpm for 10 min at 20 °C. The supernatants were pooled, mixed and evaporated to dryness under vacuum conditions at 35 °C. Resulting extracts were re-dissolved in 5 mL or 2 mL of 1% MeOH–HCl for bran extracts and GAX extracts respectively and filtered through a 0.45 μm filter.

Sample preparation to quantify hydroxycinnamic acids (HCA) was performed under the same conditions described previously by Ayala-Soto et al. (2014a).

2.5. Determination of glucose content and A/X ratio

Sugars (glucose, xylose and arabinose) were quantified by high performance liquid chromatography (HPLC) using a 8 × 300 mm, Shodex SUGAR 7u SP810 column (Phenomenex, Torrence, CA) eluted with HPLC water at 0.6 mL/min at 85 °C. A refractive index detector (Waters 2414) was used to quantify sugars and the arabinose/xylose ratio (A/X) was calculated.

2.6. Total phenolics

Total phenolics were determined using the modified Folin–Ciocalteau colorimetric method described by Sánchez-