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Original article

Impact of moisture and grinding on yield, physical, chemical and thermal properties of wholegrain flour obtained from hydrothermally treated sorghum grains

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Summary The present work evaluates the potential of sorghum with high content of tannins for wholegrain flour production. Two types of mills were used: a roller mill (RM) and a blade (BM) mill. The impact of moisture and grinding on yield, physical, chemical and thermal properties were evaluated. Maximum yield was obtained using a BM with 25% moisture in the grain, resulting in 60.9% versus 28% (g flour g^{-1} of wholegrain sorghum) for the RM. Grain moisture and milling type affected flour colour and ashes. For both mills, the pasting and thermal properties of flour with grain moisture variation were significantly different from the untreated control sample. By studying the procedures for flour production and quality characteristics, it is possible to produce flour with good physical attributes, which can contribute to the development of gluten-free foods based on sorghum for the coeliac population.

Keywords Chemical composition, food processing aspects, gluten free, polyphenols.

Introduction

Sorghum contains several polyphenol compounds that offer health benefits. The antioxidant action of polyphenols is their most important contribution. Tannins, which belong to the polyphenol family, reduce pre and postharvest losses, thus reaching high yields (Queiroz *et al*., 2018). The antioxidant capacity of sorghum is of scientific interest, even though some of its components such as proteins and starch are less available because of their interaction with polyphenols (Taylor *et al*., 2014; Girard & Awika, 2018). Tannin reduction in grains is necessary to improve flour nutritional quality and to reduce astringency and unpleasant bitter taste caused by the interaction of the polyphenols with proteins (Belhadi *et al*., 2013; Links *et al*., 2015).

While conventional methods for polyphenol extraction are based on the utilisation of organic solvents such as methanol and acetone among others (Barros *et al*., 2013), this study was conducted with water, as it allows the direct use of the flour without the need to separate the residual solvent. Water solvent was used in several cereals in comparison with others, and results showed that the extract obtained had the highest antioxidant capacity (Tufan et al., 2013).Therefore, tannin extraction with water was performed in this work, not only to promote the cleaning of grains but also for their steeping, thus achieving certain softening that allows better grinding and better flour properties (Acquisgrana *et al*., 2016).

The production of wholegrain flour consists of grinding wholegrain to take advantage of the nutrients found in the pericarp and the fibres that contribute to the improvement of the gastrointestinal tract function, reducing the incidence of chronic diseases (Van der Kamp & Lupton, 2013). There are many milling techniques applied by the food industry, including the use of ball and roller milling which employ mechanical force such as impact, compression, shear and friction to break grains into smaller fragments or fine particles (Leewatchararongjaroen & Anuntagool, 2016). During the grinding process, the granular, crystalline and molecular structures of starch in grains could be damaged or degraded by mechanical and friction forces.

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Starch is the main component in most cereals; it normally represents more than 50% of the grain weight and, therefore, the changes in their structure. For example, the changes caused by grinding can greatly affect the functional properties of flour, such as sticking, swelling, solubility and digestibility (Hasjim *et al.*, 2012). Numerous studies have investigated the effects of milling on the structures of starch and the effects of structural changes induced on the functional properties (Hasjim *et al.*, 2012).

The objectives of this work are the production of wholegrain red sorghum flour, reduced in tannins by hydrothermal treatment (Acquisgrana *et al.*, 2016), from two types of mills: roller and blade mills; the evaluation of moisture effect on yield and the evaluation of the physical, chemical and thermal properties of flours.

Materials and methods

Cleaning, steeping and annealing of grains

Sorghum bicolour (L.) Moench, variety TOB 60T, harvested in 2017, from the Experimental Agricultural Station–National Institute of Agricultural Technology (INTA) Argentina, with high content of tannin (Table 1), was selected for this study. Sorghum grains (1 kg) of each sample were steeped in 2 L of 0.5% (v/v) sodium hypochlorite (NaOCl) solution. The procedure was done at 25 °C during 18 h. The preparation was incorporated to a heat bath at 75 °C for 240 min. At this stage tannins are extracted and grains are prepared for milling (Singh *et al.*, 2011; Acquisgrana *et al.*, 2016). Sorghum samples were dried in a forced convection oven at 50 °C and humidity was evaluated at different drying times to obtain samples of 30%, 25% and 20% moisture (samples M1, M2 and M3, respectively). At the same time, samples were ground to evaluate flour yield. To evaluate water retention capacity (WRC), pasta properties and the thermal properties of the flours, the untreated sample or control sample (CS) of dry milled wholegrain sorghum was used as target. The CS moisture was 12.1 ± 0.2%. The CS was ground with both mills. Determinations were made in duplicate.

Grinding and sieving

After drying, samples were milled using a roller mill (RM) with a separation of 0.5 mm (CIBART, Argentina), or a blade mill (BM) (IRALOF, Argentina).The ground samples were dried in an oven at T: 50 °C for 24 h. They were subsequently screened with a standard mesh screen N° 35 (A.S.T.M), of 500 μm aperture size. Samples of wholegrain sorghum (WGS) were weighed for yield calculation and finally packaged and stored in a dry place.

Colour

Colour determination was performed using a HunterLabUltraScan XE tristimulus colorimeter (Hunter Associates Laboratory, Inc., Reston, VA) under the following conditions: D65 illuminant, 10° observer angle and reflected colour with component speculate excluded. Results were expressed by parameters of the Hunter Lab scale (L^*, a^* and b^*). The Codex (Codex Alimentarius Commission, 2019) establishes the standard code 173-1989 for sorghum flours and sets a range from 18 to 30 Kent-Jones units for colour. The Kent-Jones parameter was calculated from Eq. (1) according to Oliver *et al.* (1992). Determinations were made in duplicate.

$$\mathrm{KJ} = 65.2 - 0.7\,L^* + 0.1\,a^* - 0.3\,b^* \tag{1}$$

The L^* parameter measures the degree of brightness ($L^* = 100$ white, $L^* = 0$ black), a^* measures the degree of the red or green component ($a^* > 0$ red, $a^* < 0$ green) and b^* the degree of yellow or blue component ($b^* > 0$ yellow, $b^* < 0$ blue). To compare the colour of samples, the whiteness index (WI) was used (Eq. 2) according to Caivano & Buera (2016). WI: indicates the closeness of the sample colour to a white ideal target (WI = 100).

$$\mathrm{WI} = 100 - \left[(100 - L^*)^2 + a^{*2} + b^{*2}\right]^{1/2} \tag{2}$$

Water retention capacity (WRC)

Samples of sorghum wholegrain flour (WGF) (0.5 ± 0.05 g on a dry basis) were weighed in 15 mL centrifuge tubes; 6 mL of distilled water were added and maintained in incubation at 30 °C, shaking for 30 min. Then, samples were centrifuged at 4000 × g for 20 min (Tyfon II, Zelian centrifuge). Supernatant liquid was carefully separated. Finally, the hydrated solid (HS) was weighed and water retention capacity (WRC) was calculated according to Eq. (3) (Palavecino *et al.*, 2016). Determinations were made in duplicate and expressed as grams of water retained per gram of wholegrain flour.

$$\mathrm{WRC} = \mathrm{HS}\,/\,\mathrm{WGH} \tag{3}$$

Proximal analysis

To evaluate these parameters, standardised chemical methods were used: ash (AACC, 2000) moisture, protein (N × 6.25) and crude fibre (AOAC, 2005). Fat content was determined following the IUPAC Standard Method 1.122. Tannins (T) were estimated using

Table 1 Proximal analysis, yield, Kent-Jones parameter (kJ) and whiteness index (WI) of control sample (CS) and treated flours at different moisture (M1: 30%; M2:25% and M3: 20%), grinded with a Blade Mill (BM) and Roller Mill (RM), expressed in % w/w

Sample	Ash	Crude fibre	Fat	TC	Protein	Tannin	Yield	kJ	WI
BM									
CS	1.38^{a}	14.83^{a}	1.74^{a}	75.60^{a}	5.08^{a}	1.37^{a}	38.9^{a}	18.29^{a}	58.2^{a}
M1	1.36^{a}	15.71^{b}	1.81^{b}	75.61^{a}	5.16^{b}	0.35^{b}	40.1^{b}	15.02^{b}	65.53^{b}
M2	1.34^{a}	15.64^{b}	1.92^{b}	75.32^{b}	5.51^{c}	0.27^{c}	60.9^{c}	15.68^{b}	66.26^{c}
M3	1.37^{a}	17.12^{c}	1.74^{a}	73.97^{b}	5.54^{c}	0.26^{c}	36.7^{d}	13.29^{c}	68.75^{d}
RM									
CS	1.02^{b}	10.65^{d}	1.62^{c}	81.00^{c}	4.97^{a}	0.74^{d}	18.8^{a}	12.10^{a}	67.3^{a}
M1	0.97^{b}	11.68^{d}	1.72^{c}	80.52^{c}	4.84^{a}	0.27^{c}	25.1^{b}	10.37^{b}	73.15^{b}
M2	1.16^{c}	11.20^{d}	1.60^{c}	80.85^{c}	5.01^{a}	0.18^{e}	28.0^{c}	10.23^{b}	73.29^{b}
M3	1.15^{c}	14.80^{a}	1.71^{c}	77.02^{a}	5.14^{b}	0.18^{e}	21.4^{d}	8.36^{c}	76.17^{c}

Means with different superscript letters within a column are significantly different ($P < 0.05$).

the HCl-vainillin midific method (Price *et al.*, 1978). Tannin extraction from the whole sorghum flour samples was performed with HCl in methanol (1% V/V) for 20 min at 30 °C, in a centrifuge. A volume of 0.8 mL of the extract (supernatant) was then mixed with 4 mL of vanillin reagent, and absorbance was read at a wavelength of λ: 500 nm. It was used as a standard reagent catechin (Sigma-Aldrich Inc., St Louis, MO). Tannin content was determined in triplicate and expressed as mg catechin per kg of solid matter.

Total carbohydrates (TC) were estimated by difference applying Eq. (4):

$$TC = 100 - (\text{Fat} + \text{protein} + \text{fibre} + \text{ash} + T) \quad (4)$$

Pasting properties

To obtain the viscosity profiles of the WGF pastas, a rapid viscosity analyser RVA 4500 was used (Perten Instruments, Australia). Flour suspensions were prepared by weighing 3.5 g of flour samples (14% moisture) into 25 g of distilled water and placed in an aluminium canister.

Pasting properties were analysed using the RVA standard profile with some modifications. Dispersions were stirred at 960 r.p.m. for 10 s followed by constant stirring at 160 r.p.m. until the end of the assay, with temperature maintained at 50 °C for 1 min, increased to 95 °C at minute 5 and maintained for 2.5 min, cooled to 50 °C in 3 min, and finally held at 50 °C for 2 min. Thermocline for Windows© software (V 3.15, Perten Instruments, Australia) was used to obtain pasting parameters, which included pasting temperature (PT, onset temperature at the moment of viscosity increase), peak viscosity (PV, maximum hot-paste viscosity), peak time (Pt), trough viscosity (TV, lowest viscosity when maintained at 95 °C) and final viscosity (FV, viscosity at the end of the assay). Other parameters calculated were breakdown (BD = PV−TV) and setback (SB = FV–TV) (Palavecino, *et al.*, 2016). Samples were prepared in duplicate.

Thermal properties

The thermal analysis of samples was carried out using a differential scanning calorimeter (DSC 823e, Mettler Toledo, Switzerland), with thermograms being evaluated by STARe software (V 9.00, Mettler Toledo, Switzerland). Flour samples (10 mg db) were weighed and placed on 100 μL aluminium pans with 20 μL of deionised water. Pans were then hermetically sealed and allowed to stand for 24 h at room temperature before heating in the DSC, beginning at 20 °C and reaching 120 °C at a heating rate of 10 °C min^{-1}. An empty and sealed pan was used as a reference for all measurements. Thermal transitions were characterised from onset temperature (To), through peak temperature (Tp), to final temperature (Tf), gelatinisation temperature range (Tf-To), peak width (PW) and gelatinisation enthalpy (ΔH), with the latter expressed in J g^{-1} of flour.

Scanning electronic microscopy

SEM images of flour with RM and BM with and without hydrothermal treatment at 25% of moisture were presented in Fig. 1. The samples of flours were analysed through scanning electronic microscopy (SEM) with a SEM microscope (LEO, EVO 40, Carl Zeiss Microscopy Ltd., Cambridge, United Kingdom). Flour samples were treated with 2.5 % glutaraldehyde in phosphate buffer pH = 7.2. Then, the samples were put on glass coverslips within polylysine film (ε-poly-L-lysine, EPL) for an hour. Afterwards, the coverslips were washed with a buffer solution of dehydrated phosphate with 25%, 50%, 75% and 80% and three times with 100% solution of acetone and finally desiccated at critical point (Polaron E3000 CPD, U.S.A.) with acetone and CO_2 as intermediate fluids. The samples were gold sputtered with an ion bombardment coat (Sputter Coater, Pelco 91000) and analysed at acceleration voltage of 10 KeV (Benítez *et al.*, 2013; Lataza Rovaletti *et al.*, 2014; Martínez Amezaga *et al.*, 2018).

Statistical analysis

All assays were performed at least in duplicate. The analysis of variance (ANOVA, multiple comparison test by Tukey, $\alpha = 5$ %) was performed with Infostat software (Di Rienzo *et al.*, 2008).

Results and discussion

Moisture and mills yield

Table 1 shows the influence of grain moisture on the yield of wholegrain flours obtained with RM and BM.The complete profile of moisture vs. yield is presented in Fig. S1. In both mills, an increasing tendency of the yield was observed, going through a maximum with 25% of moisture, and a later decrease. The moisture values applied were lower than those reported by other authors on processing wet flour with 30% to 40% of moisture by pounding wooden pestles in a mortar (Ratnavathi, 2016). However, in this new study with higher moisture, grinding was difficult since the pasting of the mills occured, and the yield decreased. Better yield was obtained with BM compared with RM, a maximum of 60.9% (g g^{-1} WGF/WGS) was reached, 33% higher than the RM, which only yielded 28.0% (g g^{-1} WGF/WGS) at 25% grain moisture. It should be noted that no retention problems were observed in the operation of both mills with the semi-wet grain, which allowed working with moisture as already explained. A great advantage of grinding dry

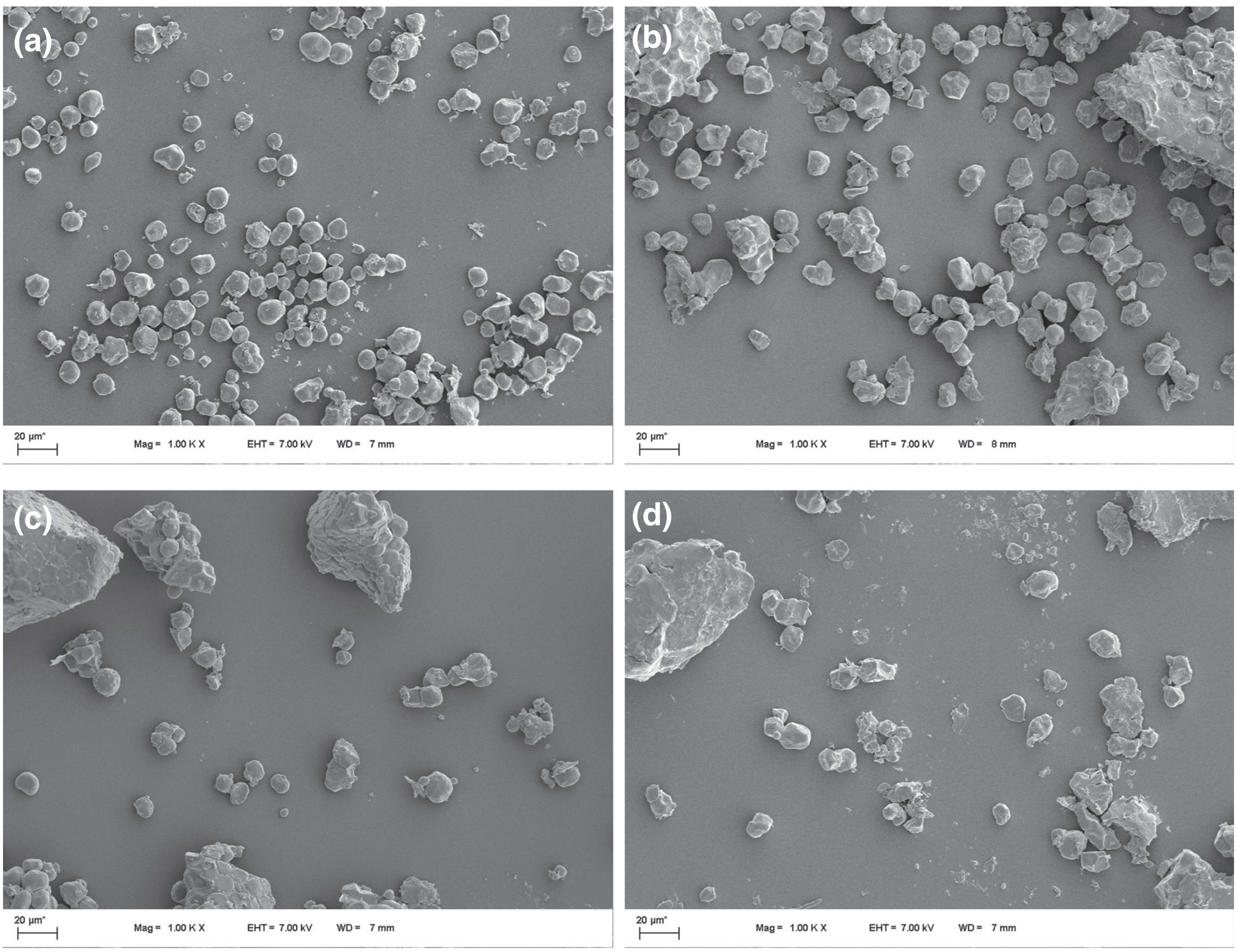

Figure 1 SEM images of flour with (a) roller mill (RM) without hydrothermal treatment, (b) RM with hydrothermal treatment at 25% of Moisture, (c) blade mill (BM) without hydrothermal treatment (d) BM with hydrothermal treatment at 25% of Moisture. Magnification of 1.00 KX. Scale bar: 20 µm = 63 pixels

grain is that the external part of the grain is dry while its interior is more humid, which allows grinding at higher moisture than other cereals such as wheat, where 18% grinding moisture is used (Warechowska *et al*., 2016).

Proximal analysis

Table 1 shows the chemical composition of sorghum flour on a dry basis, where significant differences among mills and moisture can be observed. Maximum ash values were reached with the BM, varying between 1.34 and 1.38% (g ash g^{-1} WGF). As to RM, values between 0.97% and 1.16% (g ash g^{-1} WGF) were obtained. The results with both types of mills were within the limits set by the Codex, which establishes a minimum of 0.9% and a maximum of 1.5% on a dry basis (Codex Alimentarius Commission 1989).

It is observed that values are similar to those found by Palavecino *et al*. (2016), but in this case, flours were obtained with decorticated grains. The percentage of ashes was higher with BM, indicating greater quantity of nutrients due to the higher percentage of bran and germ.

It has been reported that phenolic compounds and antioxidant activities are concentrated in sorghum bran (Girard & Awika, 2018). This fact could be very attractive to produce flour with more phytonutrients. It is known from previous studies that the hydrothermal treatment of the wholegrain reduces polyphenol content in the grain, and its concentration in the final flour is still significant (Acquisgrana *et al*., 2016). In this new study, tannin concentrations are listed in Table 1. It could be observed that tannin concentrations for the CS for both mills were higher than for treated samples. All treated samples showed values below the limit set by the Codex Alimentarius.

Regarding the values of fat and proteins, no significant differences were found between samples for both mills and moisture. The values found were lower than those found by other authors, probably due to the higher fibre content in the samples. The bran components are rich in dietary fibre, essential lipids, B vitamins, minerals and phytochemicals, so it would be beneficial especially for people with type II diabetes, since they improve the gastrointestinal tract function and reduce the incidence of chronic diseases according to Van der Kamp & Lupton (2013).

TC showed significant differences between mills, being higher for the RM. It was observed that TC values decreased slightly as moisture increased. However, the values found were similar to those reported by other authors (Palavecino *et al*., 2016).

Colour analysis

Flours obtained with RM were whiter than those obtained with BM. RM works with shear force and compression, which facilitates grain breakage and thus size decrease, resulting in a continuous 'rolling of the bran', significantly improving the subsequent endosperm separation. On the other hand, BM, which uses shear and cutting force, caused more colouration and bran in the flour. Regarding colour attributes, whiter flours were obtained with the RM than with the BM (Colour parameters: L, a, b see Table S1), being their predominance in the low values of Kent-Jones and in their greater WI. It was observed that the WI values were lower than those found by Palavecino *et al.* (2016) (Table 1). Although colour is important for the visual appearance of flour finished products like bread or pasta, the decrease of nutrients with respect to the degree of refinement can modify nutritional advantages, according to Subramanian, Honesey & Bramel-Cox(1994), who reported sorghum starches isolates, where WI exhibited a negative correlation with protein content and total polyphenol content.

The Codex establishes a minimum of 18 and a maximum of 30 kJ units for the colour of sorghum flours. Results indicated that the use of the flours obtained by both types of mills would be feasible, since they are in the range, and even below 18 kJ in some cases.

Analysis of water retention capacity

Table 2 shows the water retention capacity (WRC) of native and treated flours. WRC was used to characterise flour behaviour in aqueous systems. The results obtained were in agreement with those reported by Palavecino *et al*. (2016). The treated samples (M1, M2 and M3) for both mills had a higher water retention capacity with respect to the CS, which could be due to the damage in the starch caused by milling (Dendy & Dobraszczyk, 2004).

Samples M1, M2 and M3 milled with RM showed an increase in the WRC of 5.5 and 12%, with respect to the CS, while with the BM presented an increase of 9, 10 and 13%, regarding CS. The variation between the results of WRC is related to the hydrophilic constituents of carbohydrates, proteins, polyphenols, fibres, etc. Those components can interact with water and contribute to the WRC (Acevedo *et al*., 2017). Differences may be due to the type of cut of each mill, resulting in the greatest exposure of the hydrophilic domains for grain moisture of 30%, with the RM with a 7% increase, with respect to the BM. Good WRC can be useful in products for which good viscosity is required, such as soups and sauces (Acevedo *et al*., 2017).

Table 2 Water retention capacity (WRC) and Pasting properties of control sample (CS) and treated flours at different moisture (M1: 30%; M2:25% and M3: 20%), grinded with a Blade Mill (BM) and Roller Mill (RM)

Sample	WRC	PV	TV	BD	FV	SB	Pt	PT
BM								
CS	2.28[a]	4216[a]	1905[a]	2311[a]	3399[a]	1494[a]	5[a]	73.0[a]
M1	2.49[b]	3086[b]	2016[b]	1070[b]	3467[b]	1451[a]	5[a]	77.8[b]
M2	2.51[c]	2124[c]	1651[c]	473[c]	2549[c]	898[b]	6[b]	80.5[c]
M3	2.58[d]	2635[d]	1971[ac]	664[d]	3164[d]	1193[c]	6[b]	79.1[bc]
RM								
CS	2.43[a]	4668[a]	2098[a]	2570[a]	3759[a]	1661[a]	5[a]	73.0[a]
M1	2.54[b]	2781[b]	2027[ac]	755[b]	3366[ab]	1339[b]	6[b]	79.1[b]
M2	2.56[b]	2853[c]	2298[b]	556[c]	3666[ab]	1368[b]	6[b]	79.0[b]
M3	2.73[c]	2155[d]	1926[c]	229[d]	3076[c]	1150[b]	7[c]	80.5[b]

Means with different superscript letters within a column are significantly different ($P < 0.05$).

WRC, water retention capacity (g H_2O g^{-1} flour); PV, maximum viscosity (mPa·s); TV, minimum viscosity (mPa·s); BD, breakdown (mPa·s); FV, final viscosity (mPa·s); SB, setback (mPa·s); Pt, peak time (s); PT, pasting temperature (°C); TS, total setback (mPa·s).

The CS ground with both mills presented significant differences ($P < 0.05$), with a 6% increase of the WRC for the RM with respect to the BM. The CS of the BM showed more compact structures than the CS of the RM (Fig1a and c), a greater exposed surface of the CS of the RM could explain the increase in the WRC. In addition, it is also known that the smaller the particle size, the higher the rate of nutrient digestion due to an increase in the relative surface area for the enzymes reaction (Al-Rabadi *et al*., 2012).

From previous studies (Acquisgrana *et al*., 2016), it is known that hydrothermal treatment does not break starch granules. However, drying and grinding the grains at different moisture levels through the RM and BM produced compact and partially gelatinised starches that could be observed in Fig1 and could be postulated from the thermal properties analysed. In the CS from the RM, packed granules were not observed as in the BM (Fig1a), probably due to the type of cut that could allow a better separation of granules from the endosperm. Treatment at a humidity of 25% increased the yield and the WRC (Fig1b) owing to the possible softening of the corneal endosperm and better crushing, with an increase in available surface area as a result of starch damage. In the CS of the BM (Fig1c), the packed structures are observed, which could belong to the corneous endosperm, according to Wong *et al.,* (2009) by reason of the shear force caused by the type of mill. The existence of a protein matrix maintained the internal structure of the starch granules and no gelatinised starch was observed. For both mills, there was an increase in the WRC with the increase in moisture (Fig1d). With this increase in the WRC the damaged appearance became evident: squashing of the packaging and the loss of the internal structure of the starch granules.

Pasting properties

Table 2 summarises the RVA parameters of samples (see Fig. S2 for the pasting profiles of representative samples), which achieve a wide range of variation of the different parameters.

Pasting temperature (PT) indicates the minimum temperature required to cook the flour. The highest value of PT was observed for the treated flour. PT was higher with the increase of sample moistures. PT for M1, M2 and M3 processed with the RM increased by 7.5 °C; 6.0 °C and 6.1 °C, respectively, regarding CS while for the BM it was 6.1 °C; 7.0 °C and 4.8 °C, respectively. Similar values were obtained by Sun *et al.* (2014), who performed a hydrothermal treatment on sorghum flours at 20% and 25% humidity and reported an increase in treated flours compared with untreated flours.

Changes in the functionality of the suspensions were observed due to moisture content in grains. The magnitude of peak viscosity in relation to the CS was affected. A rearrangement in molecule structure might have been caused by the treatment. In addition, the presence of other chemical compounds, such as proteins and lipids, could restrict the swelling of the starch granules responsible for the decrease in viscosity (Li*et al*, 2014).

Maximum viscosity was reached for CS, with RM (4668 mPa s), versus BM (4216 mPa s).

Final viscosity (FV) is the parameter most commonly used to define the properties of the pasta of a given sample and the particular quality of a product. FV indicates the ability of the material to form a viscous paste or gel after cooking and cooling (Cozzolino *et al*., 2012). No significant tendency was observed in the values obtained by the treatments and types of mills; values were similar to those obtained by Sun *et al*. (2014).

The reassociation of the starch molecules during cooling is commonly known as setback (SB). The M1, M2 and M3 samples showed lower SB than the CS for both mills, which is indicative of slower rates of starch retrogradation according to Varavinit *et al.* (2003). It implies less retrogradation, or rearrangement of the starch molecules. It has been correlated with the texture of several products and allows projecting if it is easier or more difficult to retrograde. The breakdown (BD) of the treated flours showed a decrease with respect to the CS, indicating an improvement in the shear stability of the modified dough according to Sun *et al*. (2014).

However, the use of BM gives a maximum viscosity, TV, BD and TS significantly different from RM,

Table 3 DSC parameters of control sample (CS) and treated flours at different moisture (M1: 30%; M2:25% and M3: 20%), grinded with a Blade Mill (BM) and Roller Mill (RM)

Sample	To	Tp	Tf	Tf - To	PW	ΔH
BM						
CS	68.71 ± 0.73^{a}	74.48 ± 0.87^{a}	82.81 ± 1.45^{a}	14.11 ± 0.73^{a}	8.10 ± 0.41^{a}	9.71 ± 0.55^{a}
M1	72.53 ± 0.19^{b}	79.11 ± 0.27^{b}	87.09 ± 0.71^{ab}	14.56 ± 0.51^{a}	8.64 ± 0.24^{a}	7.33 ± 0.12^{b}
M2	76.28 ± 0.33^{c}	81.25 ± 0.78^{b}	88.52 ± 1.78^{b}	12.25 ± 1.45^{a}	6.97 ± 0.89^{a}	3.46 ± 0.13^{c}
M3	73.67 ± 0.54^{b}	80.18 ± 0.49^{b}	88.23 ± 0.74^{b}	14.55 ± 0.21^{a}	8.44 ± 0.51^{a}	7.45 ± 0.45^{b}
RM						
CS	69.65 ± 1.40^{a}	76.04 ± 1.29^{a}	85.19 ± 1.16^{a}	15.54 ± 0.24^{a}	8.86 ± 0.14^{b}	8.99 ± 0.75^{a}
M1	71.81 ± 0.11^{ab}	79.31 ± 0.11^{ab}	86.96 ± 0.14^{b}	15.15 ± 0.04^{a}	8.56 ± 0.11^{b}	5.80 ± 0.12^{b}
M2	73.84 ± 0.03^{b}	80.13 ± 0.23^{b}	87.26 ± 0.04^{b}	13.42 ± 0.01^{b}	7.63 ± 0.07^{a}	5.49 ± 0.49^{b}
M3	75.1 ± 1.33^{b}	80.55 ± 1.04^{b}	87.40 ± 0.75^{b}	12.30 ± 0.58^{b}	6.97 ± 0.33^{a}	5.41 ± 0.83^{b}

Data are expressed as means values ± standard deviation. Means with different superscript letters within a column are significantly different ($P < 0.05$).

To, temperature of onset (°C); Tp, peak temperature (°C); Tf: final temperature (°C); (Tf-To): gelatinisation temperature range (°C); PW: peak width (°C) and ΔH: enthalpy of gelatinisation (J g^{-1}).

therefore, many of the changes were due to the type of mill used.

Thermal properties

Table 3 shows the thermal behaviour of the CS and treated flours. The enthalpy values of the treated flours decreased significantly compared to those of the CS, from 8.99 ± 0.75 to 5.41 ± 0.83 J g^{-1} for the RM and from 9.71 ± 0.55 to 7.33 ± 0.12 J g^{-1} for the BM decreasing by 40% and 23%, respectively, for M3 (30% moisture in the grain). The results agreed with those published previously by Loubes et al. (2012), who reported the decrease of ΔH for rice starch processed in a ball mill and, likewise, were consistent with the results found by Palavecino *et al*. (2016) and Sun *et al*. (2014) for sorghum flour. Partial gelatinisation during treatment may have disrupted starch crystallites and/or changed crystallite orientation. Higher values of ΔH may also be attributed to stronger interactions between adjacent amylopectin double helices within the crystalline domains (Singh *et al*., 2011). The onset (To), peak (Tp) and final temperatures (Tf) of the treated flours increased with respect to the CS for both mills. The gelatinisation temperature range for CS with RM (69.65-85.19 °C) and BM (68.71-82.81 °C) was within the range according to Sun *et al*. (2014). According to Singh *et al*. (2011) the To, Tp and Tf increase after the hydrothermal treatment could be attributed to changes in the fine structure of starches. In hydrothermally treated starches, the amylose molecules interact more freely with the amylopectin chains present in the branched crystalline regions, consequently reducing the mobility of the amylopectin chains, which results in an increase in gelatinisation temperatures. Likewise, the formation of amylose–amylose and amylose-lipid complexes also contributes to higher gelatinisation temperatures. This could explain the increase in To, Tp and Tf in the samples of treated flours (Table 3). On the other hand, the increase in temperatures is consistent with the results obtained from the pasting properties.

Conclusions

The present study showed that the methodology of extraction of tannins with the variation of wholegrain moisture for subsequent milling with different mills, affected the physical, chemical, bonding and thermal properties of the wholegrain flour of sorghum, causing significant changes in the consistency of starch suspensions, as well as in temperature and enthalpy of gelatinisation.

It might be possible to use wholegrain flour, without the need of previous decorticating. It was possible to obtain flour reduced in tannins with good yield, within the limits established in the Codex Alimentarius. Therefore, with the proposed treatment, manipulating grain drying times and moistures before grinding, flours with different yields, different indexes of whiteness, ash content, pasta and thermal properties could be obtained. Results indicated that it could be possible to use the flour obtained in food systems for production of new foods for the coeliac, people with allergy to gluten or those who choose a gluten-free diet.

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Conflict of interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article: María del Rosario Acquisgrana: rosarioacquisgrana@gmail.com; Laura Cecilia Gomez Pamies: lauragomezpamies@hotmail.com; Nancy María Jimena Martinez Amezaga: ji.m.amezaga@gmail.com; Fernanda Micaela Quiroga: fquiroga@agro.unc.edu.ar; Pablo Daniel Ribotta: pribotta@agro.unc.edu.ar; Elisa Inés Benítez: eibenitez@hotmail.com.

Ethical guidelines

Ethics approval was not required for this research.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Yields of the roller mill (RM) and blade mill (BM) at different levels of moisture.

Figure S2. Pasting curves for flour obtained with roller mill without hydrothermal treatment (control sample) (CS-RM), with hydrothermal treatment at 25% of Moisture(M2-RM), with blade mill without hydrothermal treatment (CS-BM) and with hydrothermal treatment at 25% of Moisture (M2-BM).

Table S1. Color parameters: L, a, b of Control Sample (CS) and treated flours at different moisture (M1: 30%; M2:25% and M3: 20%), grinded with a Blade Mill (BM) and Roller Mill (RM)