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Original Article

Gluten-free cakes with walnut flour: a technological, sensory, and microstructural approach

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Summary Walnut flour (WF), a by-product of walnut oil production, is characterised by high polyunsaturated fatty acids, proteins, and fibre contents and presents suitability for bakery products. However, when using non-traditional ingredients, it is essential to evaluate the effect on the quality properties of the final product. So, this work aimed to assess the impact of WF on the technological, physicochemical, and sensory properties of gluten-free (GF) cakes. WF was added at a flour blend (cassava (CS) and maize (MS) starches and rice flour) at 0, 10%, 15%, and 20%. The results showed that WF modified starch gelatinisation, increased amylose–lipid complex (ALC) content, and made crumbs easier to chew. Besides, the total dietary fibre (TDF) and protein content significantly increased. Cakes with 15% WF presented the highest specific volume (SV) and no differences in overall acceptability with respect to control. Hence, WF is a suitable ingredient for gluten-free bakery products.

Keywords Acceptability, Amylose–lipid complex, fractal dimension, SEM, TPA.

Introduction

When celiac people consume gluten, their immune system attacks the small intestine, causing inflammation, which leads to poor absorption of several nutrients (Barbara *et al*., 2021; Cardo *et al*., 2021). A gluten-free (GF) diet is achieved by excluding wheat, barley, oats, and rye (CIR-EU No828, 2014). This diet is restrictive but is the only option for celiac people nowadays. Luckily the market for GF products is steadily growing, but GF-baked ones keep on being one of the most challenging products to develop (Roman *et al*., 2019). Notably, in gluten-free bread and muffins, fibre-rich by-products reduce specific volume (SV) and change crumb texture (Rocha Parra *et al*., 2015; Singh *et al*., 2016). Concerning the use of oil cakes in gluten-free products, to our knowledge, few works have focused on their use. However, the valorisation of these sub-products is vital to contribute to the circular economy (Petraru & Amariei, 2020). For instance, the addition of coconut oil cake decreased the hardness, springiness, resilience, and chewiness in muffins (Beegum *et al*., 2017), while the use of chia cake led to bread with higher sensory quality (Zdybel *et al*., 2019).

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Walnuts (*Juglans regia* L.) are extensively consumed, and their industrialisation is growing every year. A partially defatted cake is obtained from the production of walnut oil. From the milling of this press cake, walnut flour (WF) is obtained. WF presents a high level of polyunsaturated lipids, and it is a source of proteins, fibre, minerals, and other minor bioactive compounds (Burbano & Correa, 2021). However, for certain individuals, the ingestion of nuts can present a health risk due to hypersensitivity (Costa *et al*., 2014). The Codex Alimentarius Commission stated the mandatory labelling of foods susceptible to potentially allergenic ingredients (CXS 1-(1985) revised in 2018). When introducing a non-traditional ingredient in a formulation, it is vital to know how they would affect the properties of the final product to obtain proper use. Therefore, this research aimed to evaluate the effect of WF on the technological, physicochemical, and sensory properties of gluten-free cakes.

Materials and methods

Materials

The ingredients employed were rice flour (RF); cassava (CS) and maize (MS) starches, sugar, sodium chloride,

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baking powder (corn starch, sodium bicarbonate, monocalcium phosphate, and calcium carbonate), sunflower oil, vanilla essence, and whole milk, all acquired from nationally recognised brands in Argentina. Also, walnut flour (WF) (*Juglans regia* L.) provided by Grupo Aceites del Desierto SRL (Córdoba, Argentina), dehydrated egg from Ovobrand (Brandsen, Argentina), hydroxypropyl methylcellulose (HPMC) F4 M (Dow Chemical, Midland, MI, USA), and distilled water were used. The WF composition (dry basis) was: 55.7% lipids, 24.6% proteins, 9.4% dietary fibre content, and 2.7% ash.

Formulation of gluten-free cakes

The following flour blend was employed: 70 g RF, 15 g CS, and 15 g MS. Additionally, each 100 g of flour blend were added 66.4 g water, 50 g sugar, 40 g milk, 11.1 g dehydrated egg, 11 g sunflower oil, 5 g baking powder, 2.2 g HPMC, 1.1 g salt, and 0.25 g vanilla essence. The WF was added on three levels (w/w) 10, 15, and 20 g·100 g^{-1} flour blend (WF10, WF15, and WF20, respectively). As lipid matter is WF main constituent, the amount of sunflower oil used was proportionately reduced to keep the fat content close to 11 g·100 g^{-1} in all samples.

Cakes' preparation

The batter preparation is described in detail in previous work (Burbano *et al.*, 2022). Briefly, batters were prepared in a Kenwood Major-1200W planetary mixer (Kenwood Ltd., Havant, UK). First, the reconstituted egg, milk, oil, and water were mixed. Subsequently, the solid ingredients were added (mixing time: 7:30 min). Then, the batter (100 g) was poured into moulds (6 cm × 9.5 cm) and baked at 180°C for 15 min in Lanin II-Panier oven (Argental, Gdro. Baigorria, Argentina). At least two independent batches per formulation were made.

Thermal transitions

Thermal transitions of batters were determined with a differential scanning calorimeter calibrated with indium (DSC Q100 TA Instruments-Waters LLC, New Castle, DE, USA). Approximately 10.00 mg of each batter (without baking powder) was weighed in aluminium pans hermetically sealed. Batters were heated from 10°C up to 160°C at 10°C·min^{-1} and as reference was used an empty aluminium pan. Thermograms were analysed using the Universal Analysis 2000 software (TA Instruments-Waters LLC). The onset (To), peak (Tp), and final (Tf) temperatures and enthalpies (ΔH) of starch gelatinisation and dissociation of the amylose–lipid complex (ALC) were determined. All the measurements were performed in triplicate.

Thermorheological characterisation

The test was performed at least in duplicate using an AR-G2 rheometer (TA Instruments-Waters LLC, New Castle, DE, USA) with parallel-plate geometry (gap: 1 mm, diameter: 40 mm). The temperature sweep experiments were carried out from 25 to 90°C at 5°C·min^{-1} at 1 Hz and constant stress (0.2 Pa) within the linear viscoelastic region (Burbano *et al.*, 2022). The bottom plate temperature was controlled with a Peltier system, and sample evaporation was prevented using a solvent trap cover.

Bakery quality of cakes

Physicochemical parameters

Crumb water activity (Aw): It was carried out at 25°C in an AquaLab (Decagon Devices-Inc., Pullman, WA, USA) (n = 6).

Crumb pH: Values were determined at room temperature using a pH-meter SevenMulti (Mettler-Toledo GmbH, Greifensee, Switzerland) with an electrode for solid samples (n = 6).

Specific volume: Cakes were weighed and then the volume was determined by the rapeseed displacement method (n = 12). The specific volume (cm^3·g^{-1}) was calculated by dividing the volume by the respective weight.

Crumb and crust colour: Colour was measured employing a colorimeter (Chroma Meter CR-400, Konica-Minolta, Tokyo, Japan). Browning index (BI) was calculated from CIE-XYZ space (Buera *et al.*, 1985) (n = 20).

Crumb structural porosity: Images of fresh cake slices were obtained (n = 12) with an HP-Scanjet-4070 scanner (Hewlett-Packard, Palo Alto, USA). Then, the centre of each slice was analysed using ImageJ v1.53e (Wayne Rasband and NIH, Bethesda, USA) (Correa *et al.*, 2021). The parameters determined were the following: air fraction (%), cell density (CD) (number of cells·cm^{-2}), circularity (0 to 1), and fractal dimension. Also, from the centres, the surface intensity plot of crumbs was plotted, where the x- and y axes are the sides (2.5 cm × 2.5 cm), and the z-axis is the colour intensity from 0 to 150.

Textural analysis of crumb and crust

The textural parameters of the crumb were measured using a CT3 Texture Analyzer (AMETEK-Brookfield, Chandler, AZ, USA). Two slices (thickness: 2 cm) were cut from the centre of each cake, and a cylindrical portion was obtained from each one (diameter: 3 cm). A plane cylinder probe (diameter: 5.08 cm) was used to compress the crumb on two consecutive cycles up to 40% of their original height (n = 8). The TexturePro CT software (AMETEK-Brookfield, Chandler, AZ, USA) was used to obtain hardness, springiness, resilience, cohesiveness, and chewiness.

Stress relaxation assay of crumb cylinders (diameter: 3 cm, height: 1.5 cm) was determined according to Correa *et al.* (2021), with the difference that the total test time was 2 min (n = 6).

Crust hardness was measured using a knife-edge acrylic probe (width: 3 mm, length: 60 mm) and a test speed of 0.5 mm·s^{-1}. Maximum peak force (N) from the penetration curve was taken as crust hardness (n = 8).

Microstructure of crumb

The crumb was fixed with glutaraldehyde (2.5% v/v), dehydrated, and coated with gold. A scanning electron microscope (SEM) (Quanta 200, FEI Company, Hillsboro, OR, USA) was used to obtain at least three micrographs at 500x. Micrographs were acquired at 'Servicio de Microscopía Electrónica y Microanálisis (SeMFi-LIMF)— Facultad de Ingeniería, UNLP, Argentina'.

Proximal composition

Protein (factor = 6.25), fat, ash, and dietary fibre contents of GF cakes were determined in accordance with AACC (American Association of Cereal Chemists) methods 46-12.01, 30-10.01, 08-01, and 32-05.01, respectively (AACC, 2000). The moisture content was determined at 105°C until constant weight. The carbohydrate content was calculated by difference. The energy was calculated according to Atwater factors (FAO, 2003). All the assays were done at least in duplicate.

Sensory analysis of cakes

An acceptance test was performed to compare Control and WF15 samples. Forty-eight untrained consumers aged between 19 and 51 years old (50% female, 38% male, and 13% preferred not to be categorised) were recruited. Samples were placed in plastic plates and coded with random three-digit numbers. Samples were randomly assigned to each evaluator, and they were asked to rinse their mouth with water between samples. Also, consumers were asked to evaluate first all the attributes of one sample and then the attributes of the second one. Almost 67% of the evaluators stated that they occasionally consume gluten-free products. They evaluated the appearance, texture, flavour, colour, and overall acceptability of samples on a hedonic scale ranging from 1 (dislike very much) to 7 (like very much).

Statistical analysis

The one-way analysis of variance (ANOVA), Least Significant Difference (LSD) test for the determination of statistically different means (α: 0.05), and multivariate analysis-Pearson's correlations ($P \leq 0.05$) were performed with Statgraphics Centurion XVII Version-17.2.00 (Statpoint Technologies Inc., Warrenton, VA, USA).

Results and discussion

Thermal behaviour

During heating, the differential scanning calorimetry (DSC) assay gives information about the thermal transitions occurring in the system when the batter turns into the crumb. Table 1 shows the onset, peak, and final gelatinisation temperatures. Only the final temperature was statistically different among the control and samples with walnut flour (WF). However, the range of temperatures was consistent with those previously reported by Goranova *et al.* (2019). Although several processes occur during heating, that is, protein denaturation, Maillard reaction, and starch gelatinisation, the latter is the primary factor in these systems. The gelatinisation enthalpy decreased as WF addition increased because of the reduction of starch content of the batters and the lower water availability (Table 1). These results agree with the findings of Sabanis *et al.* (2009) on GF bread with cereal fibre.

On the other hand, starch and lipids are important components in baked goods. It is well known that amylose has helical structure and forms inclusion complexes with other substances, such as iodine, alcohols, fatty acids, and other fat-soluble bioactive substances. The amylose–lipid complexes (ALC) can be found in native starch granules and processed starch. These complexes restrict the swelling of starch granules and enzyme hydrolysis (Morrison *et al.*, 1984; Hasjim *et al.*, 2010). The formation of ALC depends on various factors, including the type of starch, degree of amylose polymerisation, the ratio of starch–ligand, and the structure of the included molecule (Huang *et al.*, 2020). On baked foods, these complexes could be formed during mixing and baking.

The parameters related to the dissociation of the amylose–lipid complex are shown in Table 1. All the formulations presented approximately the same lipid content but different lipid compositions. The control had only sunflower oil, while WF cakes had sunflower and walnut lipids. Besides, sunflower oil was proportionately reduced as the WF level increased. In control and WF10, T_o and T_p were higher while increasing WF, the peak shifted to lower temperatures. It showed the different compositions of the ALC and that the complexes with WF lipids were more easily dissociated. The addition of WF showed a significant effect on the enthalpy of dissociation of ALC. The higher the WF content, the higher the energy required to

Table 1 Thermal transitions of gluten-free batters during heating

	Starch gelatinisation				
	Temperatures (°C)				
	T_o	Tp	Tf	ΔT	ΔHgel*
Control	79.5 ± 0.5^a	85.0 ± 0.8^a	111.0 ± 0.9^b	31 ± 1^b	6.1 ± 0.3^c
WF10	80.4 ± 0.9^a	85.7 ± 0.9^a	105 ± 2^a	24 ± 2^a	5.3 ± 0.1^b
WF15	79.9 ± 0.7^a	85.9 ± 0.6^a	105 ± 1^a	25 ± 2^a	3.6 ± 0.2^a
WF20	79.1 ± 0.6^a	86 ± 1^a	103.7 ± 0.5^a	25 ± 1^a	3.4 ± 0.1^a
	Dissociation of amylose–lipid complex				
	Temperatures (°C)				
	T_o	T_p	T_f	ΔT	ΔH_{AL}*
Control	122.7 ± 0.2^c	126.1 ± 0.3^c	132 ± 1^c	9 ± 1^{ab}	0.076 ± 0.002^a
WF10	117 ± 1^b	119.67 ± 0.05^b	124 ± 1^a	7 ± 2^a	0.219 ± 0.006^b
WF15	112 ± 2^a	118.2 ± 0.8^a	126 ± 1^{ab}	14 ± 2^{bc}	0.58 ± 0.02^c
WF20	110 ± 2^a	118.2 ± 0.6^a	126.7 ± 0.4^b	17 ± 2^c	0.636 ± 0.008^d

T_o: Onset temperature, T_p: Peak temperature, T_f: Final temperature, Δ*H:* phase transition enthalpy * (J·g^{-1} solids). Addition levels: 0.1, 0.15, and 0.20 g walnut flour g^{-1} flours' blend, Mean± standard deviation. Different letters in the same column indicate significant differences ($P < 0.05$, $n = 3$).

dissociate the complex, for example, 0.076 ± 0.002 for control and 0.636 ± 0.008 (J·g^{-1} solids) for WF20. This effect exhibited a higher degree of complexed amylose, despite having all batters, a similar lipid content, on flour blend basis. This agrees with Moreira *et al*. (2015), who found that the microstructural characteristics and accessibility of lipids and starches are more important than their concentration. Besides, the higher range of this transition as the WF level increased showed that, as expected, the nature of the formed complexes was different. Thus, probably part of the amylose was complexed with walnut lipids.

Finally, it is noteworthy that the higher degree of amylose complexation is related to beneficial health effects, since these complexes are classified as type V resistant starch (Arp *et al*., 2021).

Rheological characterisation during heating

Temperature sweep assays were conducted to understand the structural changes in the batters during heating. The experimental conditions applied in the rheometer are not equal to the real baking process, but it is considered a valuable tool to understand the structural events during baking (Herranz *et al*., 2016; Bozdogan *et al*., 2019).

The complex modulus (G*) values as a function of temperature for the batter formulations studied are shown in Fig. 1a. The storage modulus (G') contribution to G* was higher than that of loss modulus (G'') throughout the range of temperatures tested (Fig. 1b). All formulations exhibited an increase in G* around 35°C. The control batter was more sensitive to the temperature change, and at about 45°C, it reached a plateau. In the case of batters with WF, the increase of G* ranged from ~35°C up to ~60°C. Schober *et al.* (2007), in a GF batter with sorghum flour (with 8.5% of protein), observed the same behaviour, the increase in G* shift to higher temperatures with respect to samples with higher available starch. The curves of G* for control and WF batters cross over at around 51°C, but below this value, control batter exhibited higher G* values. The lower values of WF batters could be related to the lower starch content and the higher content of polyunsaturated lipids. This first part of the curve could be associated with changes in the protein conformations induced by heating. Also, the formation of HPMC pre-gel involving a reduction of G' occurs at about 30°C (Pérez *et al*., 2006). However, this phenomenon would be overlapped, and it was not noticed in this case. Then, around 60°C, HPMC forms a gel network due to dehydration and formation of hydrophobic clusters leading to an increase of G' (Rosell & Foegeding, 2007). The control sample exhibited an inflection point while it was not observed in WF batters. As the temperature increases, the cake structure is set, leading to the rise of G*. In the control formulation, this event occurred earlier (~65°C), whereas, in WF samples, the setting occurred around ~80°C. The WF batters had lower starch content and higher content of proteins and fibre than the control. Thus, these components could compete for water with starches during the formation of the crumb delaying it.

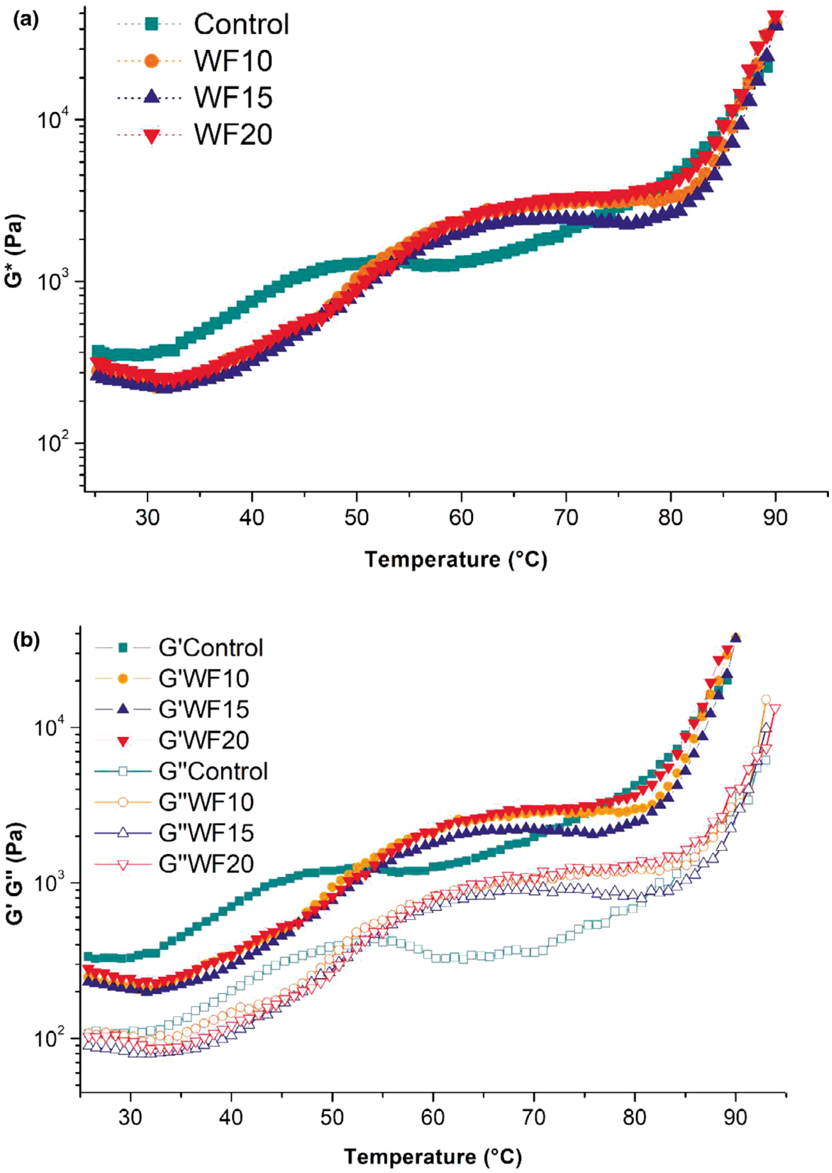

Figure 1 (a) Complex modulus (G*) as a function of temperature in the gluten-free batters, (b) Storage (G') and loss moduli (G") as a function of temperature.

Bakery quality of cakes

A good indicator of the sponginess of cakes is the specific volume. The increase of WF concentration in cakes increased their specific volume (Table 2). WF15 formulation showed the maximum volume; the specific volume was slightly lower by increasing the WF content to WF20. This trend was previously reported in chestnut and rice flour gluten-free cakes (Demirkesen *et al.*, 2010). The results obtained here are attributed to the increase of batter consistency with WF concentration (Burbano *et al.*, 2022), since batter consistency is essential to the final volume of cakes. Figure S1 shows the slices of all formulations of GF cakes with WF.

Water distribution is important in bakery's technological quality because it modifies texture perception. All formulations showed relatively high Aw values (around 0.96). The only formulation that presented a statistically significant difference was WF15, but this difference lacks practical impact (Table 2). Accordingly, the addition of WF slightly decreased the moisture in those formulations (Table 2).

Likewise, the increase of WF concentration decreased the pH values. They ranged from 7.94 (control) to 6.15 (WF20). Aguilar *et al.* (2016) also reported a reduction of pH in gluten-free cakes as the addition of chestnut flour increased, which is attributed to the presence of organic acids in chestnut flour.

Table 2 Physicochemical parameters of gluten-free cakes

		Crumb structural porosity			
	SV ($cm^3 \cdot g^{-1}$)	Air fraction (%)	CD ($number \cdot cm^{-2}$)	Circularity	Fractal dimension
Control	1.2 ± 0.1^{a}	31 ± 1^{a}	68 ± 5^{d}	0.26 ± 0.02^{b}	1.72 ± 0.01^{a}
WF10	1.3 ± 0.1^{ab}	32 ± 1^{b}	52 ± 2^{c}	0.16 ± 0.01^{a}	1.76 ± 0.01^{b}
WF15	1.4 ± 0.2^{c}	34.2 ± 0.9^{c}	45 ± 3^{a}	0.15 ± 0.02^{a}	1.78 ± 0.01^{c}
WF20	1.3 ± 0.1^{bc}	32.8 ± 0.7^{b}	49 ± 3^{b}	0.16 ± 0.01^{a}	1.77 ± 0.01^{bc}

	Crumb				Crust	
	Aw	Moisture (%)	pH	BI	BI	CV of BI(%)
Control	0.962 ± 0.002^{b}	38.9 ± 0.3^{b}	7.94 ± 0.09^{d}	26.4 ± 0.7^{a}	62 ± 10^{c}	15.5
WF10	0.962 ± 0.003^{b}	38.8 ± 0.3^{b}	6.46 ± 0.09^{c}	29 ± 2^{b}	60 ± 9^{bc}	15.1
WF15	0.959 ± 0.003^{a}	38.0 ± 0.4^{a}	6.36 ± 0.06^{b}	31 ± 1^{c}	58 ± 8^{ab}	14.5
WF20	0.962 ± 0.002^{b}	38.3 ± 0.4^{a}	6.15 ± 0.06^{a}	32 ± 1^{d}	56 ± 7^{a}	12.6

BI, browning index; CD, cell density; CV, coefficient of variation; SV, specific volume.
Mean ± standard deviation, For addition levels, see Table 1. Different letters in the same column indicate significant differences ($P < 0.05$).

Colour is an essential characteristic in food and contributes to consumer preference. The crust shows a great colour variability due to the nature of the baking process (Maillard reactions and caramelisation of sugars) (Purlis, 2010). Contrary to expectations, the addition of WF decreased the intensity of brown colour on the crust of cakes. Besides, a tendency to obtain more uniform crusts was observed, as shown by the coefficient of variation (CV) (Table 2).

On the other hand, the brown intensity of the crumb increased progressively with the addition of WF. This change is due to the characteristic colour of the walnut integuments.

Crumb structural porosity and microstructure

The crumb porosity parameters are shown in Table 2. The air fraction increased with the addition of WF, following the same tendency as the specific volume. Turabi *et al*. (2010) obtained similar area values in rice flour cakes using hydrocolloids. At the same time, the particles of WF affected the alveoli form, which was reflected in the values of circularity. Significant differences among control and WF formulations were found, but not among the WF cakes.

For irregular objects like cake crumbs, the conventional measures such as length and area, sometimes, are not totally representative, and fractal dimension (FD) is helpful to characterise them (Theiler, 1990). FD serves as an index of morphological roughness and summarises the complexity of the irregular alveoli in cake crumbs. The use of WF led to a slight but significant increase in FD with respect to the control (Table 2).

Figure 2 shows the surface intensity plots of samples. In these plots, the valleys represent the crumb alveoli (alv.), and the darker particles (walnut flour particles (WFP)) correspond to the remaining structures of WF. The plots of WF formulations (Fig. 2 a2-a4) presented a more irregular appearance, which was related to a higher air fraction and a more complex matrix as was reflected by FD.

Micrographs of control crumb (Fig. 2 b1) and WF formulations (Fig. 2b2-b4) showed a matrix formed by smooth films of leached amylose and rough protein arrangements with partially gelatinised starch granules embedded. As expected, micrographs of the control crumb presented a larger content of starch granules than WF crumbs. The more prominent starch granules from cassava and maize were more swollen than the smaller ones from rice in all samples. Besides, rice granules were agglomerated, while corn and cassava granules were more dispersed. Crumbs presented a heterogeneous and discontinuous matrix and a more compact one in WF20.

Textural analysis of crumb and crust

Hardness, resilience, cohesiveness, springiness, and chewiness are important to consumer acceptability. These textural parameters of crumbs of WF cakes are compared in Table 3. The hardness of cakes only showed a considerable increase in WF20; the same effect was observed in GF bread with chestnut flour (Aguilar *et al*., 2016). Likewise, cohesiveness, springiness, and resilience are related to crumb recovery after compression. These parameters showed a slight decrease as WF increased. Finally, chewiness also decreased by WF, showing that WF cakes could be easier to chew.

Stress relaxation assays have been used to evaluate the viscoelastic behaviour of solid systems, such as

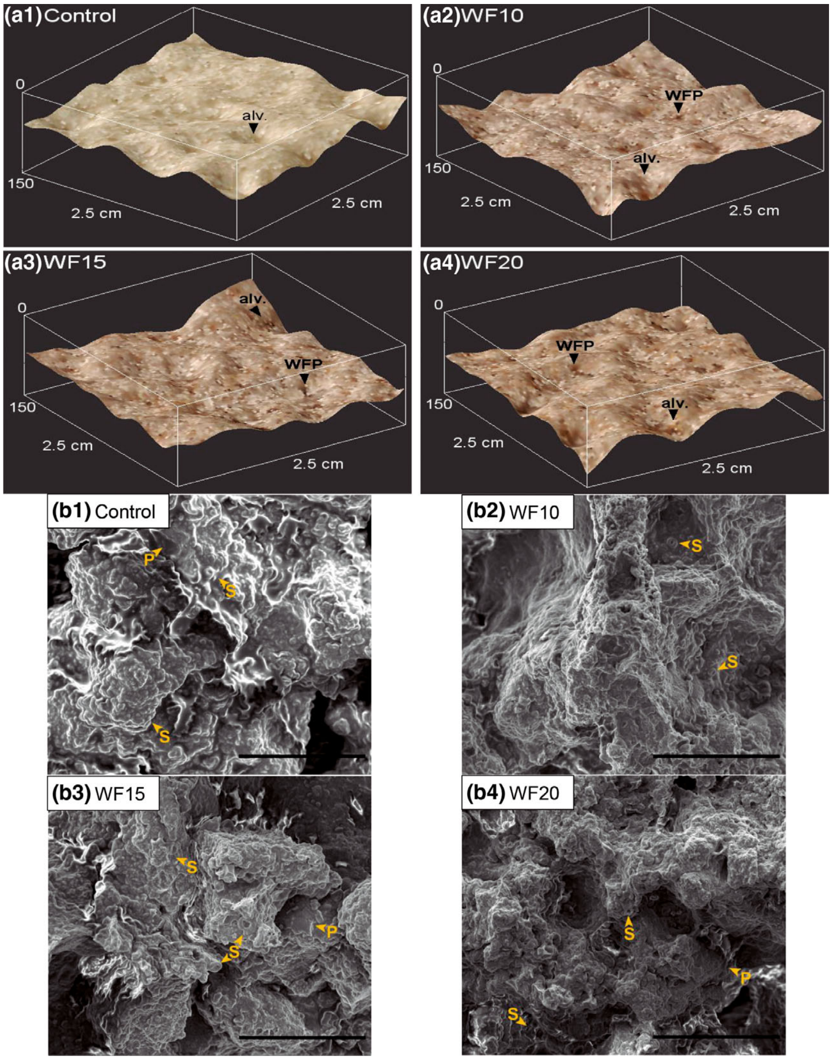

Figure 2 (a) Surface intensity plot of control and walnut flour crumbs (alv.: alveoli and WFP: walnut flour particles), (b) Scanning electron microscopy (SEM) micrographs of crumbs at 500x. The black bar corresponds to 200 μm. s=starch; p=protein.

crumbs (Correa *et al.*, 2021). The sample is compressed, and the stress needed to maintain the deformation over time is registered. The curves were adjusted to the generalised Maxwell model with a second-order exponential decay, showing that two molecular mechanisms were involved in crumb relaxation. The first zone of decay is related to small molecules that rapidly relax, which is reflected in the low relaxation times (λ_1), and it is related to a more viscous behaviour. On the other hand, the higher values of λ_2 are associated with slower movements of polymers of higher molecular weight, indicating a more solid-like behaviour (intermediate zone of the curve). The addition of WF did not affect the relaxation of polymers of high molecular weight since there were no significant differences among samples.

The crust hardness (N) was 10.4 ± 0.9, 10.2 ± 0.9, 10 ± 1, and 10.1 ± 0.8 for control, WF10, WF15, and WF20, respectively. No significant differences were observed among samples, showing that WF did not affect crust formation.

Proximal composition of cakes

The proximal composition of cakes (dry basis) is shown in Table 4. All formulations with WF were significantly different from the control. The content of proteins, total dietary fibre (TDF), and ash increased as the WF content increased. Otherwise, the content of carbohydrates and lipids decreased with the addition of WF. In the case of lipids, it was related to the reduction of sunflower oil content as the WF level increased to maintain a relatively constant lipid level (with respect to flour blend). However, the intrinsic heterogeneity of WF could contribute to obtaining a reduction of lipid content. According to Food and

Table 3 Textural and relaxation parameters of crumb of gluten-free cakes

	Texture profile analysis					Relaxation assay*		
	Hardness (N)	Resilience	Cohesiveness	Springiness	Chewiness(N)	λ_1 (s)	λ_2 (s)	R^2 adj.
Control	26 ± 4[a]	0.35 ± 0.01[b]	0.55 ± 0.02[b]	0.86 ± 0.02[b]	12.9 ± 0.9[c]	2.1 ± 0.1[b]	32.6 ± 0.8[a]	0.9950
WF10	25 ± 2[a]	0.24 ± 0.01[a]	0.44 ± 0.03[a]	0.80 ± 0.02[a]	9.2 ± 0.9[a]	2.0 ± 0.2[a]	31 ± 1[a]	0.9945
WF15	26 ± 2[a]	0.25 ± 0.02[a]	0.45 ± 0.04[a]	0.80 ± 0.03[a]	9 ± 1[a]	2.0 ± 0.1[a]	32.3 ± 0.9[a]	0.9945
WF20	29 ± 4[b]	0.25 ± 0.02[a]	0.46 ± 0.03[a]	0.81 ± 0.02[a]	11 ± 2[b]	1.9 ± 0.2[a]	32 ± 1[a]	0.9944

Mean ± standard deviation. For addition levels, see Table 1. Different letters in the same column indicate significant differences ($P < 0.05$), *adjustment of generalised Maxwell model with the experimental values, λ_1 and λ_2 relaxation times.

Table 4 Proximal composition of gluten-free cakes

	Proximate composition (%)					
	Proteins	Lipids	TDF	Ash	Carbs	CC
Control	6.30 ± 0.05[a]	9.0 ± 0.4[c]	2.1 ± 0.1[a]	2.45 ± 0.01[a]	80.2 ± 0.4[b]	431[c]
WF10	7.40 ± 0.08[b]	8.2 ± 0.3[b]	5.56 ± 0.04[b]	2.50 ± 0.02[b]	76.3 ± 0.3[a]	420[b]
WF15	8.8 ± 0.1[c]	7.1 ± 0.4[a]	5.5 ± 0.4[b]	2.50 ± 0.01[b]	76.1 ± 0.6[a]	415[ab]
WF20	8.79 ± 0.09[c]	6.9 ± 0.6[a]	6.1 ± 0.3[b]	2.55 ± 0.03[c]	75.7 ± 0.7[a]	412[a]

Mean ± standard deviation. For addition levels, see Table 1, Different letters in the same column indicate significant differences ($P < 0.05$) Carbs: carbohydrates calculated by difference, CC: caloric content (kcal·100 g^{-1} solids), TDF: total dietary fibre.

Drug Administration, the reference amounts customarily consumed (RACC) for heavyweight cakes is 125 g, and the reference daily intake (RDI) of fibre is 28 g. When a product covers 20% or more of RDI per RACC it is considered a 'high source' and between 10 and 19% of RDI per RACC it is considered a 'good source' (Food & Drug Administration, 2020). The amount of fibre RDI per RACC (wet weight) covered by WF10 and WF15 was 17% and for WF20 was 19%. Hence, all WF formulations could be labelled as a good source of fibre, and in the case of WF20, almost a high source of fibre.

Thus, cakes made with the by-product presented a higher protein and dietary fibre content and lower lipid content than control, providing a slightly lower caloric content (CC) (kcal per 100 grams of dry cake). The CC was reduced from 431 for the control to 412 for WF20.

Sensory analysis of cakes

Sensory evaluation of control and WF15 formulations was done. The WF15 formulation was selected from among the other samples with WF due to its bakery quality. Unlike WF20, the WF15 cakes presented a good baking quality, such as higher specific volume, more complex crumb structure (porosity), and suitable texture parameters. The mean score of each attribute is shown in Fig. 3. The evaluators did not find difference between samples' scores for appearance (Control: 5.8 ± 1.0 and WF15: 5.5 ± 1.2), texture (Control: 5.0 ± 1.6 and WF15: 5.1 ± 1.4), and overall acceptability (Control: 5.5 ± 1.3 and WF15: 5.2 ± 1.4), while in terms of colour and flavour, the difference was slight but significant. The yellowish colour of control was slightly more attractive than the brownish colour of WF15 (Control: 5.9 ± 1.1 and WF15: 5.3 ± 1.4). This result was consistent when wheat flour was replaced by WF in wheat bread (Almoraie, 2019). On the other hand, the flavour score of control was higher than that of WF15 (5.4 ± 1.3 and 4.8 ± 1.6, respectively). Likewise, some evaluators stated that they noticed a nutty aftertaste when tasting WF15 and also that WF15 was less sweet. That is because the relative content of sugar was diluted for the addition of WF. Finally, all the mean scores for both samples were relatively high, considering that the highest possible score was 7.

Multivariate analysis: Pearson's correlations

A multivariate analysis was performed, taking into account the following parameters of batters and cakes: crumb cohesiveness, crust BI, protein content, TDF, specific volume, chewiness, and the enthalpies of gelatinisation and amylose–lipid complex dissociation (Table S1). Crumb cohesiveness showed a negative and significant correlation ($P < 0.05$) with TDF. A higher level of TDF provided by WF could interfere with the formation of the crumb matrix. The crust BI

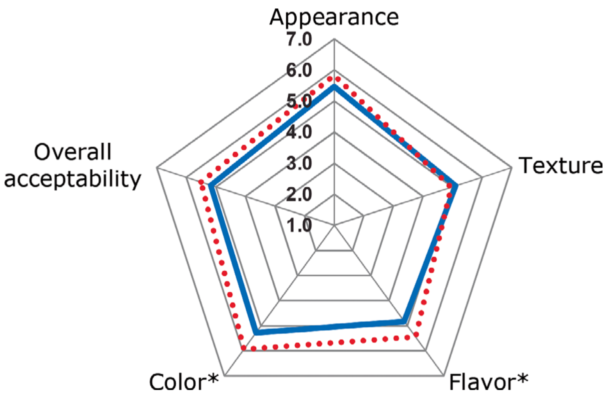

Figure 3 Sensory analysis of cakes (Control: dotted line and WF15: solid line) *attributes with significant differences (P < 0.05, n = 48).

presented a positive correlation with ΔH_{gel} and a negative correlation with ΔH_{AL}. The addition of WF, and the consequent dilution of starch, led to a higher formation of the amylose–lipid complex and a lower browning of the crust. Both facts could be related to the dilution of starches. Thus, the lipid/starch relation increased at higher WF levels, favouring the amylose–lipid complex formation. The browning could be reduced due to a lower amount of reducing sugars present together with starches. Similarly, protein content correlated with these thermal parameters for the same reasons, the dilution of starches as the WF level increased. As expected, the specific volume positively correlated with the air fraction. Finally, ΔH_{gel} and ΔH_{AL} presented a negative correlation (P < 0.01). This is related to the fact that with higher WF, a reduction of starch gelatinisation was observed due to lower starch content and lower water availability. At the same time, the formation of amylose–lipid content could be favoured due to the higher lipid/starch ratio and the chemical characteristics of WF lipids.

Conclusion

The use of walnut flour (WF) in gluten-free cakes increased fibre and protein contents, specific volume, air fraction, and alveoli complexity. The higher specific volume could be related to the fact that WF batters were set at higher temperatures than control. Also, an increase in crumb hardness was observed by WF addition, but at the same time, these crumbs were easier to chew. The sensory evaluation of cakes with 15% WF presented similar acceptance as the control sample. Hence, these results showed that WF is a suitable ingredient for incorporating into a gluten-free cake. However, products must be labelled appropriately due to the allergenic potential of walnuts. Besides, a study about the impact of WF on shelf-life would be convenient.

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Author contribution

Juan José Burbano: Data curation (lead); Formal analysis (lead); Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Dario Marcelino Cabezas:** Conceptualization (equal); Investigation (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (supporting). **María Jimena Correa:** Conceptualization (equal); Data curation (supporting); Formal analysis (supporting); Funding acquisition (lead); Investigation (equal); Methodology (equal); Project administration (lead); Resources (lead); Supervision (lead); Validation (equal); Writing – original draft (equal); Writing – review & editing (lead).

Conflicts of interest

There are no conflicts of interest to declare.

Ethical approval

Ethics approval was not required for this research.

Peer Review

The peer review history for this article is available at https://publons.com/publon/10.1111/ijfs.15591.

Data availability statement

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

References

Aguilar et al., 2016. This work evaluated the use of chestnut flour in a gluten-free (GF) bakery product.
Burbano et al., 2022. This work evaluated the properties (rheological behaviour, thermal transitions, and microstructure) of the batters from which are obtained the cakes presented here.

Burbano & Correa, 2021. This work presents a detailed description of the walnut flour (WF) used in the present work.

Schober et al., 2007.This work was valuable for discussing the rheological characterisation of batters during heating.

AACC (2000). *Approved Methods of the American Association of Cereal Chemists*. St. Paul, MN: AACC Approved Methods Committee.

Aguilar, N., Albanell, E., Miñarro, B. & Capellas, M. (2016). Chestnut flour sourdough for gluten-free bread making. *European Food Research and Technology*, **242**, 1795–1802.

Almoraie, N.M. (2019). The effect of walnut flour on the physical and sensory characteristics of wheat bread. *International Journal of Food Science*, **2019**, 1–7.

Arp, C.G., Correa, M.J. & Ferrero, C. (2021). Resistant starches: a smart alternative for the development of functional breads and other starch-based foods. *Food Hydrocolloids*, **106949**. https://doi.org/10.1016/j.foodhyd.2021.106949

Barbara, G., Barbaro, M.R., Fuschi, D. *et al*. (2021). Inflammatory and microbiota-related regulation of the intestinal epithelial barrier. *Frontiers in Nutrition*, **8**, 623.

Beegum, S., Sharma, M., Manikantan, M.R. & Gupta, R.K. (2017). Effect of virgin coconut oil cake on physical, textural, microbial and sensory attributes of muffins. *International Journal of Food Science & Technology*, **52**, 540–549.

Bozdogan, N., Kumcuoglu, S. & Tavman, S. (2019). Investigation of the effects of using quinoa flour on gluten-free cake batters and cake properties. *Journal of Food Science and Technology*, **56**, 683–694.

Buera, M.P., Lozano, R.D. & Petriella, C. (1985). Definition of colour in the non-enzymatic browning process. *In: Die Farbe*, **32**, 316–326.

Burbano, J.J., Cabezas, D.M. & Correa, M.J. (2022). Effect of walnut flour addition on rheological, thermal and microstructural properties of a gluten free-batter. *LWT*, **154**, 112819. https://doi.org/10.1016/j.lwt.2021.112819

Burbano, J.J. & Correa, M.J. (2021). Composition and physicochemical characterization of walnut flour, a by-product of oil extraction. *Plant Foods for Human Nutrition*, **76**, 233–239.

Cardo, A., Churruca, I., Lasa, A. *et al*. (2021). Nutritional imbalances in adult celiac patients following a gluten-free diet. *Nutrients*, **13**, 2877.

CIR-EU No 828, R (2014). Commission Implementing Regulation (EU) No 828/2014 on the requirements for the provision of information to consumers on the absence or reduced presence of gluten in food. No 828/2014.

Codex Alimentarius (1985). *CXS 1-1985. General Standard for the Labelling of Prepackaged Foods*. Rome, Italy: Codex Alimentarius. FAO. WHO.

Correa, M.J., Moreano, J.J.B., Guardianelli, L.M., Weisstaub, A.R., Zuleta, A. & Salinas, M.V. (2021). Garlic: A natural bread improver for wheat bread with a high level of resistant starch. *Journal of Food Processing and Preservation*, **45**, e15519. https://doi.org/10.1111/jfpp.15519

Costa, J., Carrapatoso, I., Oliveira, M.B.P.P. & Mafra, I. (2014). Walnut allergens: molecular characterization, detection and clinical relevance. *Clinical & Experimental Allergy*, **44**, 319–341.

Demirkesen, I., Mert, B., Sumnu, G. & Sahin, S. (2010). Utilization of chestnut flour in gluten-free bread formulations. *Journal of Food Engineering*, **101**, 329–336.

FAO, F.A.O. of the U.N. (2003). *Food Energy–Methods of Analysis and Conversion Factors*. Rome, Italy: Food and Nutrition Paper.

Food and Drug Administration. (2020). *Food Labeling - FDA, 21CFR101.54*. Silver Spring, MD: Food and Drug Administration.

Goranova, Z., Marudova, M. & Baeva, M. (2019). Influence of functional ingredients on starch gelatinization in sponge cake batter. *Food Chemistry*, **297**, 124997.

Hasjim, J., Lee, S., Hendrich, S., Setiawan, S., Ai, Y. & Jane, J. (2010). Characterization of a novel resistant-starch and its effects on postprandial plasma-glucose and insulin responses. *Cereal Chemistry*, **87**, 257–262.

Herranz, B., Canet, W., Jiménez, M.J., Fuentes, R. & Alvarez, M.D. (2016). Characterisation of chickpea flour-based gluten-free batters and muffins with added biopolymers: rheological, physical and sensory properties. *International Journal of Food Science & Technology*, **51**, 1087–1098.

Huang, Q., Chen, X., Wang, S. & Zhu, J.(2020). Amylose–lipid complex. In: *Starch Structure, Functionality and Application in Foods* (edited by S. Wang). Pp. 57–76 Singapore: Springer Singapore.

Moreira, R., Chenlo, F. & Arufe, S. (2015). Starch transitions of different gluten free flour doughs determined by dynamic thermal mechanical analysis and differential scanning calorimetry. *Carbohydrate Polymers*, **127**, 160–167.

Morrison, W.R., Milligan, T.P. & Azudin, M.N. (1984). A relationship between the amylose and lipid contents of starches from diploid cereals. *Journal of Cereal Science*, **2**, 257–271.

Pérez, O.E., Wargon, V., & Pilosof, M.R.A. (2006). Gelation and structural characteristics of incompatible whey proteins/hydroxypropylmethylcellulose mixtures. *Food Hydrocolloids*, **20**, 966–974.

Petraru, A. & Amariei, S. (2020). Oil press-cakes and meals valorization through circular economy approaches: A Review. *Applied Sciences*, **10**, 7432.

Purlis, E. (2010). Browning development in bakery products – A review. *Journal of Food Engineering*, **99**, 239–249.

Rocha Parra, A.F., Ribotta, P.D. & Ferrero, C. (2015). Apple pomace in gluten-free formulations: effect on rheology and product quality. *International Journal of Food Science & Technology*, **50**, 682–690.

Roman, L., Belorio, M. & Gomez, M. (2019). Gluten-Free Breads: The gap between research and commercial reality. *Comprehensive Reviews in Food Science and Food Safety*, **18**, 690–702.

Rosell, C.M. & Foegeding, A. (2007). Interaction of hydroxypropylmethylcellulose with gluten proteins: Small deformation properties during thermal treatment. *Food Hydrocolloids*, **21**, 1092–1100.

Sabanis, D., Lebesi, D. & Tzia, C. (2009). Effect of dietary fibre enrichment on selected properties of gluten-free bread. *LWT - Food Science and Technology*, **42**, 1380–1389.

Schober, T.J., Bean, S.R. & Boyle, D.L. (2007). Gluten-Free sorghum bread improved by sourdough fermentation: Biochemical, rheological, and microstructural background. *Journal of Agricultural and Food Chemistry*, **55**, 5137–5146.

Singh, J.P., Kaur, A. & Singh, N. (2016). Development of eggless gluten-free rice muffins utilizing black carrot dietary fibre concentrate and xanthan gum. *Journal of Food Science and Technology*, **53**, 1269–1278.

Theiler, J. (1990). Estimating fractal dimension. *Journal of the Optical Society of America A*, **7**, 1055.

Turabi, E., Sumnu, G. & Sahin, S. (2010). Quantitative analysis of macro and micro-structure of gluten-free rice cakes containing different types of gums baked in different ovens. *Food Hydrocolloids*, **24**, 755–762.

Zdybel, B., Różyło, R. & Sagan, A. (2019). Use of a waste product from the pressing of chia seed oil in wheat and gluten-free bread processing. *Journal of Food Processing and Preservation*, **43**, e14002.

Supporting Information

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

Figure S1. Slices of gluten-free cakes with addition of walnut flour.

Table S1. Pearson's correlation coefficients of gluten-free batters and cakes with walnut flour.