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Impact of ancient cereals, pseudocereals and legumes on starch hydrolysis and antiradical activity of technologically viable blended breads

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ABSTRACT

Wheat flour replacement from 22.5% up to 45% by incorporation of ternary blends of teff (T), green pea (GP) and buckwheat (BW) flours provided technologically viable and acceptable sensory rated multigrain breads with superior nutritional value compared to the 100% wheat flour (WT) counterparts. Blended breads exhibited superior nutritional composition, larger amounts of bioaccessible polyphenols, higher anti-radical activity, and lower and slower starch digestibility. Simultaneous lower rapidly digestible starch (57.1%) and higher slowly digestible starch (12.9%) and resistant starch (2.8%) contents (g per 100 g fresh bread), considered suitable nutritional trends for dietary starch fractions, were met by the blend formulated 7.5% T, 15% GP, 15% BK. The associated mixture that replaced 37.5% WT, showed a rather lower extent and slower rate of starch hydrolysis with medium-low values for C_∞, and H_{90}, and lowest k, and intermediate expected Glycaemic Index (86). All multigrain breads can be labelled as source of dietary fibre (≥3 g dietary fibre/100 g bread).

1. Introduction

Grains are basic, ubiquitous and healthy raw materials, good source of carbohydrates – mainly starch and dietary fibre – providing excellent vectors for diversity and innovation. It raises a great deal of recent interest that ancient crops (Angioloni & Collar, 2011a), pseudocereals (Collar & Angioloni, 2014a) and legumes (Angioloni & Collar, 2012), besides wheat, constitute nutrient-dense and healthy grains with explicited breadmaking applications.

A slow release and absorption of glucose may be generated in a food matrix according to the processing conditions and surrounding ingredients (Lehmann & Robin, 2007), encompassing beneficial effects in the management of diabetes and hyperlipidemia (Jenkins, 2007). Native cereal starches are ideal sources of slowly digestible starch (SDS) (>50%), and the slow progressive digestion property is realized by a layer-by-layer inside–outside (radial) digestion process (Zhang, Ao, & Hamaker, 2006a). Mechanical and thermal treatments change the structure and digestibility of starch. Thermal treatments such as the cooking process completely destroys the semicrystalline structure of native starch granules and causes the loss of SDS and resistant starch (RS) and increases rapid digestible starch (RDS) (Zhang, Venkatachalam, & Hamaker, 2006b). In cereal products, the starch gelatinization extent, which is mainly controlled by the moisture level and the cooking time and temperature influences the formation of SDS (Englyst, Vinory, Englyst, & Lang, 2003). In bread dough, although formation of resistant starch (RS3) may occur in the high water-containing parts during cooling, a large portion of starch is gelatinized during cooking and induces a rapid digestibility of starch (Bravo, Englyst, & Hudson, 1998). In extruded cooked cereal products such as breakfast cereals, in addition to the thermal treatment, the high pressure and shear forces destroy the starch granular structure and increase its gelatinization extent, making it more available to amylolytic enzymes (Le François, 1989). On the contrary, in pasta, a dense protein network is formed, which limits the accessibility of α-amylase to the starch and restricts the diffusion of water molecules to the starch granules. As a consequence, a reduction of the extent of starch gelatinization takes place (Englyst, Kingman, & Cummings, 1992). In some biscuits with very low moisture levels during the treatment, the extent of gelatinization is reduced and partially intact granules and gelatinized starch co-exist, resulting in a higher content of SDS compared to breakfast cereals and baked products (Englyst et al.,

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2003). In many plant sourced foods, such as legumes and minimally processed cereal grains, starch granules are trapped within the plant cell walls (*e.g.* whole grains), which retard their degradation (Würsch, Del Vedovo, & Koellreutter, 1986). Disruption of the granule structure as by milling can increase the susceptibility to enzymatic degradation.

Legumes that are low glycaemic index foods, which generate slow and moderate postprandial glucose and insulin response, have been shown to decrease blood glucose responses compared to other cereal based foods (Tovar, Granfeldt, & Bjorck, 1992) such as whole bread. The digestibility of legume starch is much lower than that of cereal starch (Madhusudhan & Tharanathan, 1996). Cooked legumes are prone to retrograde more quickly, thereby lowering the process of digestion. The higher content of amylose in legumes, which probably may lead to a higher RS content, may possibly account for their lower digestibility. Also, legumes contain more of proteins than cereals, and protein–starch interaction in legumes may equally contribute to their decreased glycaemic responses (Geervani & Theophilus, 1981). Additionally, the presence of high amounts of dietary fibre and antinutritional factors such as phytates and amylase inhibitors may greatly influence the rate and extent of legume starch digestibility.

The current proposal is aimed at exploring the competences and exploiting the suitability in mixed wheat matrices of non-breadmaking whole grains with unique nutritional components (teff, green pea and buckwheat flours), to obtain novel and healthy fermented baked goods meeting the functional and sensory restrictions of viscoelastic breadmaking systems. Bread functional and nutritional profiles were assessed in quaternary wheat blended matrices, and compared with the wheat flour counterparts. Special emphasis will be placed on starch hydrolysis kinetics and relevant starch nutritional fractions in mixed grain matrices.

2. Materials and methods

2.1. Materials

Commercial flours from refined common wheat *Triticum aestivum* (WT), and whole teff *Eragrostis tef* (T), green pea *Pisum sativum* (GP), and buckwheat *Fagopyrum esculentum* (BW) were purchased from the Spanish market. Refined WT (70% extraction rate) of 356×10^{-4} J energy of deformation *W*, 0.64 curve configuration ratio P/L, 95% Gluten Index, 62% water absorption in Brabender Farinograph, was used. Ireks Vollsauer sour dough was from Ireks (Spain); Novamyl 10,000 a maltogenic thermostable α-amylase from Novozymes (Denmark); and calcium propionate, from Sigma–Aldrich (USA).

2.2. Methods

2.2.1. Bread making of wheat and wheat-based blended flours

Doughs and breads were prepared for WT as control, and wheat-based blended flours (T, GP, BW) by WT replacement from 22.5% up to 45%, and incorporation of ternary blends of T, GP and BW flours according to a Multilevel Factorial Design with the following attributes: three experimental factors (T, GP and BW flours) at 2 levels, coded 0 (7.5% wheat flour replacement) and 1 (15% wheat flour replacement), and 5 error degrees of freedom. The model resulted in 8 randomized runs in 1 block. A 3 digit bread sample code was set referring to low (0) and high (1) wheat flour replacement by T (1st digit), GP (2nd digit), and BW (3rd digit) flours in sample formulation, as it follows: 010, 001, 011, 000, 111, 101, 100, 110. Blended flours (100 g), water (62%, flour basis), commercial compressed yeast (4%, flour basis), salt (1.5%, flour basis), vegetable fat–margarine-(4%, flour basis), sugar (2%, flour basis), commercial sour dough (4%, flour basis), milk powder (5%, flour basis), Novamyl 10,000 (7.5 mg, flour basis), and calcium propionate (0.5%, flour basis) were mixed in a 10 kg mixer at 60 revolutions min-1 for 10 min up to optimum dough development. Fermented doughs were obtained after bulk fermentation (10 min at 28 °C), dividing (500 g), rounding, moulding, panning and proofing up to maximum volume increment (30 min at 28 °C), and were baked at 200 °C for 30 min to make control and blended breads.

2.2.2. Chemical and nutritional composition of flours and breads

Moisture, protein, ash and fat contents of commercial flours, control and blended breads were determined following the ICC methods (ICC, 1976–1996). Total, soluble and insoluble dietary fibre contents were determined according to the AOAC method 991.43 (AOAC, 1991). Three replicates were made for each analysis. Digestible carbohydrates were calculated by indirect determination as 100 − [Moisture + Protein + Fat + Ash + Dietary Fibre] (FAO, 2003). Resistant starch determination was performed according to AOAC Official Method 2002.02 (AOAC, 2000) by using Megazyme kit K-RSTAR 08/11. Bioaccessible phenol determination was carried out by conducting an "in vitro" digestive enzymatic mild extraction that mimics the conditions in the gastrointestinal tract according to the procedure of Glahn, Lee, Yeung, Goldman, and Miller (1998) and adapted by Angioloni and Collar (2011b) for breads.

The stable 2,2-diphenyl-1-picrylhydrazyl ($DPPH^{\bullet}$) radical was used to measure the radical scavenging capacity of flour and bread samples according to the $DPPH^{\bullet}$ method (Brand-Williams, Cuvelier, & Berset, 1995), modified by Sánchez-Moreno, Larrauri, and Saura-Calixto (1998) and adapted. 2 g of flour, and 3 g of French bread (freeze-dried and milled <0.5 mm) were placed in a centrifuge tube (50 mL) and 20 mL of acidic methanol/water (50:50 v/v, pH 2) was added (10 mL for French bread). The tube was thoroughly shaken at room temperature for 1 h. The tube was centrifuged at 2500*g* for 10 min, and the supernatant was recovered. 20 mL of acetone/water (70:30, v/v) was added to the residue (10 mL for bread), and shaking and centrifugation were repeated. Both methanolic and acetonic extracts were combined and adjusted to 25 for bread or 50 mL with methanol. After gentle shaking, aliquots of 0.1 mL were taken, and 3.9 ml of a solution of DPPH 0.050 g/L (equivalent to 0.1268 μmol/mL) was added. Tubes were gently shaken, and 4 mL of each tube were added to a 4 mL cuvettes, and A515 nm was read at 1 min and every 5–10 min until the plateau was reached. A cuvette containing 4 mL of DPPH 0.494 μmol in methanol was read at the same periods. A blank of methanol was used. Lectures were taken in duplicated samples. Plots of μmol DPPH *vs* time (min) were drawn, and calculations were made to know the antiradical activity (AR). $AR = [([DPPH]_{INITIAL} - [DPPH]_{PLATEAU}) \times 100]/[DPPH]_{INITIAL}$.

2.2.3. Bread measurements

2.2.3.1. Enzymatic/biochemical determinations. In vitro starch hydrolysis kinetics and relevant starch fractions in blended breads was determined following the AACC (2005) method 32–40, adapted as previously described (Angioloni & Collar, 2011c). Rapidly digestible starch (RDS) and slowly digestible starch (SDS) were measured after incubation for 20 min and 120 min, respectively, as stated by Englyst et al. (2003). Total digestible starch (DS) was determined in the supernatant after 16 h of incubation while resistant starch (RS) was determined in the pellet as the starch remaining after 16 h incubation. The digestion kinetics and expected glycaemic index (eGI) of bread were calculated in accordance with the procedure followed by Chung, Liu, Pauls, Fan, and Yada (2008) based on the method established by Goñi, Garcia-Alonso, and Saura-Calixto (1997). A first order kinetic equation $[C = C_{\infty}(1 - e^{-kt})]$ was applied to describe the kinetics of starch hydrolysis, where *C*, C_{∞} and *k* were the hydrolysis degree at each time, the maximum hydrolysis extent and the kinetic