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Antioxidant capacity, arabinoxylans content and *in vitro* glycaemic index of cereal-based snacks incorporated with brewer's spent grain

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ABSTRACT

Extruded snacks and breadsticks were formulated with increasing levels of brewer's spent grain (BSG). The phenolic content increased by 4 and 7 fold with BSG addition in extrudates (40 g/100 g) and in breadsticks (35 g/100 g), respectively. Consequently, antioxidant capacity (DPPH, FRAP) also increased despite a recorded loss of phenolic compounds in extruded snacks. Arabinoxylans content increased up to 20 and 25 g of BSG addition/100 g of formulated extruded snacks and breadsticks, respectively. Further addition of BSG did not improve the content of arabinoxylans due to the possible formation of polysaccharide–protein complexes. Medium GI breadsticks were obtained with 35 g of BSG incorporation/100 g formulation. Phenolic content, arabinoxylans content and antioxidant capacity increased in the final products with BSG addition while the glycaemic response decreased. BSG can be incorporated as an ingredient in the formulation of extruded snacks and breadsticks generating products richer in antioxidants and fibre and with low GI.

1. Introduction

Busy lifestyles and the increasing demand from consumers for meals and snacks that are quick sources of good nutrition have prompted the food industry to develop foods like ready-to-eat snacks that combine convenience and nutrition. Consumers demand nutritious, convenient, tasty snacks that satisfy their hunger momentarily until the next meal. Four in ten consumers are looking for snacks that provide a health benefit beyond basic nutrition and similarly, due to the increase in the incidence of multi-tasking while eating, there has been upsurge in demand for "on-the-go" handheld snack (Sloan, 2011). Efforts are being made to improve snack food nutritional value via the modification of their nutritive composition (Ainsworth, Ibanoglu, Plunkett, Ibanoglu, & Stojceska, 2007; Ajila, Leelavathi, & Prasada Rao, 2008; Stojceska, Ainsworth, Plunkett, & Ibanoglu, 2008; Sun-Waterhouse, Teoh, Massarotto, Wibisono, & Wadhwa, 2010).

Brewer's spent grain (BSG) is the most abundant brewing by-product amounting to around 85% of total by-products generated by the brewing industry (Mussatto, Dragone, & Roberto, 2006). BSG is the residue left after separation of the wort (fermentation medium to produce beer) during the brewing process (Santos, Jiménez, Bartolomé, Gómez-Cordovés, & del Nozal, 2003). The Environmental Protection Agency estimates 3.4 million tonnes of BSG are produced annually across Europe. The common applications are the direct disposal to soil, in a landfill or use as an animal feed which are not sufficient to drain the several tones produced per year (Mussatto et al., 2006).

In general BSG is considered as a lignocellulosic material rich in protein and fibre, which account for 20 and 70 g of its proximate composition (as per 100 g), respectively (Mussatto et al., 2006).

The fibre is constituted of cellulose (17 g/100 g), non-cellulosic polysaccharides namely arabinoxylans (28 g/100 g) and lignin (28 g/100 g). The monosaccharide analysis of the non-cellulosic polysaccharide fraction is composed of xylose, glucose, arabinose, galactose and mannose (Mussatto et al., 2006). The pentose sugar residues, arabinose and xylose are the main components due to the presence of the arabinoxylans (Santos et al., 2003). Arabinoxylans posses a β-(1→4)-linked xylopyranosyl backbone substituted with α-L-arabinofuranosyl residues. The degree of arabinoxylan substitution is usually evaluated by the arabinose/xylose ratio, which is typically in the range of 0.4–0.7. The arabinose molecules may be esterified with hydroxycinnamic acids, monomeric or dimeric ferulic acid and *p*-coumaric acid (Bartolomé, Santos, Jiménez, del Nozal, & Gómez-Cordovés, 2002; Jay et al., 2008; Mussatto et al., 2006; Vanbeneden, Gils, Delvaux, & Delvaux, 2007). Ferulic and *p*-coumaric acids bound to the cellular walls of the germinated barley grains were pointed as very interesting potential antioxidants (Maillard & Berset, 1995). Arabinoxylans isolated from cereals

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have been related to the prevention and treatment of obesity, cholesterol, gastrointestinal cancer and diabetes (Broekaert et al., 2011; Neyrinck et al., 2011).

Due to its relatively low cost and potential nutritional value, BSG has been considered as an attractive adjunct for human food as an alternative application to animal feed or deposition in landfills. Its dietary fibre and protein-rich flours have been used as ingredients in baking and extrusion processes (Ainsworth et al., 2007; Ajanaku, Dawodu, Ajanaku, & Nwinyi, 2011; Ktenioudaki, Chaurin, Reis, & Gallagher, 2012; Öztürk, Özboy, Cavidoglu, & Köksel, 2002; Prentice & D'Appolonia, 1977; Prentice, Kissell, Lindsay, & Yamazaki, 1978; Steinmacher, Honna, Gasparetto, Anibal, & Grossmann, 2012; Stojceska et al., 2008).

The glycaemic index (GI) is the concept used to classify foods on the basis of their postprandial blood glucose response (Goñi, Garcia-Alonso, & Saura-Calixto, 1997). Foods with high GI are those rapidly digested and absorbed resulting in marked fluctuations in blood glucose levels and greater insulin demand. Low GI foods are the ones slowly digested and absorbed, resulting in gradual rise in blood glucose and insulin levels (Augustin, Franceschi, Jenkins, Kendall, & La Vecchia, 2002). There is increasing evidence that a low GI diet provides potential beneficial health effects by improving glucose and lipid levels in people with diabetes (Type 1 and 2), also reducing insulin levels and insulin resistance (Foster-Powell, Holt, & Brand-Miller, 2002). A reduction in the GI of starch-based foods can be obtained with the use of fibres (Chillo, Ranawana, & Henry, 2011; Foster-Powell et al., 2002; Shirani & Ganesharanee, 2009; Zabidi & Aziz, 2009), which can be beneficial to diabetic patients and also to healthy subjects.

The incorporation of enriched fibre and protein flours with significant values of antioxidants is an approach to improve the nutritional value and health benefits of extruded and baked snacks since they are predominantly made from cereal flour or starches and tend to be low in protein, therefore with low biological value (Ainsworth et al., 2007). The use of BSG as enriched protein and fibre flour is also a potential approach to solve a serious environmental problem. The aim of this work is the determination of the phenolic content, antioxidant capacity, arabinoxylans content and glycaemic index in extruded snacks and breadsticks with increasing levels of BSG incorporation. These determinations will allow the evaluation of BSG as a functional ingredient for the improvement of cereal-based snacks.

2. Material and methods

2.1. Chemicals

All chemicals were purchased from Sigma–Aldrich (Wicklow, Ireland) except for hydrochloric acid, sulphuric acid, ethyl acetate, methanol, acetone and dichloromethane, which were purchased from Fisher scientific (Ballycoolin, Ireland).

2.2. Brewer's spent grain (BSG)

BSG was obtained from the micro distillery plant located in University College Cork, Cork (Ireland). The dried BSG was coarsely ground and passed through 250 μm sieve and stored in polyethylene bags at −20 °C for further analysis. The proximate composition (as per 100 g) of the dried and ground BSG was as follows: moisture (5.6 g), protein (20.8 g), fat (4.5 g), ash (3.2 g), total starch (3.3 g) and total dietary fibre (60.5 g).

2.3. Incorporation of BSG in extruded products

Extruded products were prepared from blends of rice flour and wheat semolina in a ratio of (2:1) with different proportions (0, 10, 20, 30 and 40 g) of BSG/100 g of formulation on a dry weight basis. The samples were then conditioned to 15–20% (g/100 g) of moisture by spraying with a calculated amount of water and mixing continuously at medium speed in a mixer (Hobart Mixer, Model F-50, USA), followed by storing at 4 °C overnight. Extrusion was performed in a single-screw, laboratory model extruder (Brabender, Duisburg, Germany) with a DCE 330 attachment consisting of three independent zones of controlled temperature in the barrel. The screw speed used was 50 rpm and the length to diameter (L/D) ratio for the extruder was 20:1. The temperature profiles in the feed and compression metering zones were kept constant at 110 and 150 °C, respectively, and the die head temperature was 175 °C. After stable conditions were established, extrudates were collected and dried in air oven at 60 °C for 1 h. The extruded material was coarsely ground and passed through 250 μm sieve stored at 4 °C in polyethylene bags for further analysis.

2.4. Incorporation of BSG in baked products

The baked products were formulated as breadsticks with wheat flour blends containing 0, 15, 25 and 35 g of BSG/100 g formulation according to Ktenioudaki et al. (2012).

2.5. Extraction of phenolic compounds

The extraction of phenolic compounds was performed with an adaptation of the methods described by other research groups (Bartolomé et al., 2002; Jay et al., 2008). In brief, the dried and ground samples (10 mg) were hydrolyzed under nitrogen with NaOH (4 mol/dm^3) solution for 17 h in the dark at 25 °C and 100 rpm (incubator Innova 42, Mason technology, Dublin, Ireland). Samples were adjusted to pH 2 with HCl (6 mol/dm^3) and centrifuged (14,400 rpm, 15 min). The supernatants were extracted five times with (650 μL) ethyl acetate and the combined extracts were evaporated till dryness (Genevac, EZ-2 Plus). The dried extracts were resuspended with methanol (50 mL/100 mL) for further analysis.

2.6. Determination of phenolic compounds

Total phenolics were determined in the methanol resuspended extracts using the Folin–Ciocalteu assay accordingly to the method described by the same authors (Reis, Rai, & Abu-Ghannam, 2012).

2.7. Antioxidant capacity evaluation

The antioxidant capacity was evaluated in the methanol resuspended extracts by the DPPH radical scavenging activity and ferric reducing antioxidant power (FRAP) according to the methods described by Reis et al. (2012).

2.8. Total dietary fibre (TDF) and protein determination

Extruded snacks protein was determined as total nitrogen content (N*6.25) using the Kjeldahl method following the method 920.87 of AOAC International (2000). TDF of extruded snacks was determined using Sigma analysis kit (Sigma–Aldrich, Inc., USA) based on AOAC method 991.43. TDF and protein content of breadsticks was determined according to Ktenioudaki et al. (2012).

2.9. Sugar analysis

Neutral sugars were released by Saeman hydrolysis and analysed as their alditol acetates by gas chromatography (Coimbra, Delgadillo, Waldron, & Selvendran, 1996; Selvendran, March, &