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Brewer's spent grain from different types of malt: Evaluation of the antioxidant activity and identification of the major phenolic compounds

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ABSTRACT

The antioxidant activity and phenolic composition of brewer's spent grain (BSG) extracts obtained by microwave-assisted extraction from two malt types (light and dark malts) were investigated. The total phenolic content (TPC) and antioxidant activity among the light BSG extracts (*pilsen*, *melano*, *melano 80* and *carared*) were significantly different ($p < 0.05$) compared to dark extracts (*chocolate* and *black* types), with the pilsen BSG showing higher TPC (20 ± 1 mg_{GAE}/g dry BSG). In addition, the antioxidant activity assessed by 2,2-diphenyl-1-picrylhydrazyl, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) and deoxyribose assays decreased as a result of increasing kilning temperatures in the following order: pilsen > melano > melano 80 > carared > chocolate > black. HPLC-DAD/ESI-MS/MS analysis indicated the presence of phenolic acids, such as ferulic, *p*-coumaric and syringic acids, as well as several isomeric ferulate dehydrodimers and one dehydrotrimer. Chocolate and black extracts, obtained from malts submitted to the highest kilning temperatures, showed the lowest levels of ferulic and *p*-coumaric acids. These results suggested that BSG extracts from pilsen malt might be used as an inexpensive and good natural source of antioxidants with potential interest for the food, pharmaceutical and/or cosmetic industries after purification.

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1. Introduction

Brewer's spent grain (BSG), the barley malt residue obtained after wort manufacture, is the main by-product from breweries, representing approximately 20 kg per 100 L of beer produced (Aliyu & Bala, 2011). BSG is available at low or no cost all through the year, but its main application has been limited to animal feed. Nevertheless, it is a ligno-cellulosic material that can be better used, since it is rich in oligo- and polysaccharides as well as in polyphenols (Mussatto, 2009). Several attempts have been made to reuse this material for industrial applications such as the production of alpha-amylase (Hashemi, Razavi, Shojaosadati, & Mousavi, 2011), activated carbon (Mussatto et al., 2010), ethanol (White, Yohannan, & Walker, 2008), lactic acid (Mussatto, Fernandes, Dragone, Mancilha, & Roberto, 2007) and xylitol (Mussatto & Roberto, 2005).

In the last few years, numerous research studies have associated the consumption of foods rich in bioactive compounds with the ability to promote a number of benefits for human health. The most common bioactive compounds include secondary metabolites such as antibiotics, mycotoxins, alkaloids, food grade pigments, plant growth factors, and phenolic compounds (Martins et al., 2011; Meneses, Martins, Teixeira, & Mussatto, 2013; Routray & Orsat, 2012). Particularly, phenolic compounds are of considerable interest to scientists, manufacturers and consumers due to their importance in food quality, with protective and preventive roles in certain types of cancer and several other chronic diseases (Barbosa-Pereira, Angulo, Paseiro-Losada, & Cruz, 2013; Krishnaswamy, Orsat, Gariépy, & Thangavel, 2013; Naczk & Shahidi, 2004). Hydroxycinnamic acids, which are the predominant phenols in BSG (Bartolomé & Gómez-Cordovés, 1999; Bartolomé, Santos, Jiménez, del Nozal, & Gómez-Cordovés, 2002; Mussatto, Dragone, & Roberto, 2007), have shown antioxidant properties and the *in vitro* antioxidant effect of these compounds was reported to be similar to that exhibited by the well-known antioxidants α-tocopherol and ascorbic acid (McCarthy et al., 2012). Moreover, the low-cost and large availability of BSG, associated with the current interest in the health benefits of

Abbreviations: ABTS, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid); DPPH, 2,2-diphenyl-1-picrylhydrazyl; TPC, Total phenolic content; BSG, Brewer's spent grain; MAE, Microwave-assisted extraction; FA, Ferulic acid; *p*-CA, *p*-Coumaric acid; DiFA, Dehydrodiferulic acid; TriFA, Triferulic acid; GA, Gallic acid; ARP, Antiradical power; KT, Kilning temperature; GAE, Gallic acid equivalents; TE, Trolox equivalents; DW, Dry weight.

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phenolic acids, opens up new possibilities for the use of this brewery by-product.

Although there is a large amount of information available relating to the health effects of polyphenol-rich foods, such as tea (catechins), coffee (chlorogenic acid), wine (resveratrol) and fruits, the information regarding the antioxidant potential of BSG is scarce. To the best of our knowledge, there are no published reports relating the phenolic composition and antioxidant activity of BSG obtained from different malt types. Recently, McCarthy et al. (2012) have investigated the ability of phenolic rich BSG extracts to protect against DNA damage in human lymphocytic U937 cells measured by the Comet assay. Their results showed that black BSG extracts, which had the highest phenol content, provided the greatest protection against H_2O_2-induced DNA damage.

The present study aims at evaluating the phenolic composition and antioxidant activity of BSG extracts obtained by microwave-assisted extraction (MAE). Light (pilsen, melano, melano 80 and carared) and dark (chocolate and black) malts were assessed for the total phenolic content (TPC) by the Folin–Ciocalteu assay, and for the antioxidant activity by the 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and 2-deoxyribose degradation assays. The phenolic compounds present in the BSG extracts were identified by HPLC-DAD/ESI-MS/MS.

2. Materials and methods

2.1. Chemicals and reagents

Folin-Ciocalteu's reagent (Merck, Darmstadt, Germany) and sodium carbonate (Sigma-Aldrich) were employed for the measurement of the total phenolic content (TPC). The calibration curve was constructed with gallic acid (GA, Sigma-Aldrich).

For the antiradical activity assessment, DPPH (Sigma-Aldrich) was used. The ABTS methodology employed ABTS and potassium persulfate ($K_2S_2O_8$) purchased from Sigma-Aldrich. 2-deoxyribose assay was performed using L(+)ascorbic acid (Sigma-Aldrich), trichloroacetic acid (Riedel-de-Haën), 2-thiobarbituric acid, 2-deoxy-D-ribose, hydrogen peroxide 35% and $FeCl_3$ (Fluka).

Ferulic acid (FA, 99%) and *p*-coumaric acid (*p*-CA, 98%) standards were purchased from Sigma-Aldrich. Stock standard solutions (500 mg/L) of these compounds were prepared by rigorous dissolution of the analyte in methanol. Standard solutions were stored at −20 °C and used for further dilutions. High-purity water from a Millipore Simplicity 185 water purification system (Millipore Iberian S.A.) was used for all chemical analyses and glassware washing. The solvents employed for HPLC analyses were filtered through a nylon filter of 0.45 μm pore size (Whatman) and degassed for 10 min in an ultrasound bath.

2.2. Samples

BSG samples used throughout this work were kindly supplied by *Unicer* — Bebidas de Portugal, S.A. (S. Mamede de Infesta, Portugal) and *Os Três Cervejeiros*, Lda (Porto, Portugal), and were obtained from six malt types. Different malt types result from special malting procedures applied to a range of raw materials. These are usually grouped into three types based on the material used, namely, raw cereals, pale malt, or green malt (germinating cereal) (Guido & Moreira, 2013). For a matter of facilitation, the different BSG extracts from the six malt types were divided into two main families, named here light malts (pilsen, melano, melano 80 and carared) and dark malts (chocolate and black). Pilsen malt is an exceptionally light colored 2-row base malt that produces a very light colored, clean, crisp wort and is used as a base malt for all beer styles. Caramel malt is made from green malt that is produced by drying the wet germinated barley at controlled temperatures, causing the starches to convert to sugars and caramelize. Melano malts are specialty malts slowly dried as the temperature is raised, allowing melanoidins to form as part of the kilning process. Chocolate malt shares many of the characteristics of black malt but, because it is roasted for a slightly shorter period and end temperatures are not so high, some of the harsher flavors of black malt are not so pronounced and EBC (European Brewing Convention) color is 200 units lighter. The specifications of each malt type, in particular color range and kilning temperature (KT) are listed in Table 1.

The BSG samples used for phenolic extraction correspond to the remaining solid fraction obtained following the removal of wort during the pilot scale production of beer in the brewing process. For wort production 25 g of pilsen malt was mixed with the same quantity of the colored malt and milled in a Bühler Miag disk mill. 200 mL of distilled water, at 45 °C, was added. After 30 min, temperature was increased at 1 °C/min for 25 min until it reached 70 °C. The temperature was maintained at 70 °C for 1 h. The mash was cooled, made up to 450 g with water and filtered. The obtained solid residue was frozen, lyophilized and then finely ground in a laboratory mill (Casella, London, UK) and sieved through a 35-mesh (≤0.5 mm) sieve. The dried BSG samples were stored at −20 °C until further use. Pilsen wort production was obtained using 50 g of pilsen malt, and following the same procedure.

2.3. Microwave-assisted extraction

BSG's phenolics were extracted according to the method previously optimized and reported by Moreira, Morais, Barros, Delerue-Matos, and Guido (2012). MAE was performed with a MARS-X 1500 W (Microwave Accelerated Reaction System for Extraction and Digestion, CEM, Mathews, NC, USA) configured with a 14 position carousel. Dried BSG sample (1 g) was transferred to the PTFE extraction vessels with 20 mL of 0.75% NaOH concentration; then the vessels were closed. Extraction was performed during 15 min at 100 °C at maximum stirring speed. During operation, both temperature and pressure were monitored in a single vessel (control vessel). Magnetic stirring in each extraction vessel and a sensor registering the solvent leaks in the interior of the microwave oven were also used.

After extraction, vessels were allowed to cool at room temperature before opening and the extracts were then centrifuged for 15 min at 4000 rpm. The pH of the supernatant was adjusted to pH 6.5 with HCl 6 M, and after filtration through a cellulose filter (0.45 μm), the extracts were preserved at −20 °C until further analysis.

2.4. Determination of total phenolic content

The TPC of the BSG extracts was determined by the Folin–Ciocalteu method as described by Dvorakova et al. (2008). In a test tube, 1 mL of diluted sample or standard solution and 5 mL of 10-fold diluted Folin-Ciocalteu's phenol reagent were mixed. After 5 min of incubation, 4 mL of sodium carbonate solution (7.5%, w/v) was added and mixed well. After 2 h of incubation at room temperature in the dark, the absorbance was measured at 740 nm in a Shimadzu UV-3101 spectrophotometer (Kyoto, Japan). The total polyphenol concentration was calculated from a calibration curve, using GA as standard (5–150 mg/L). The results were expressed as mg GA equivalents

Table 1
Color and kilning temperatures for the six malt types used in the wort production.

	Malt type	Color range/EBC units	Kilning temperatures/°C
Light malts	Pilsen	3.5–5.7	80–85
	Melano	37–43	130
	Melano 80	75–85	130
	Carared	90–360	120–160
Dark malts	Chocolate	800–1000	220
	Black	1350–1500	230

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