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Use of air classification technology as green process to produce functional barley flours naturally enriched of alkylresorcinols, β-glucans and phenolic compounds

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ABSTRACT

In the last years, food researchers and food industries focused their attention on the content of bioactive compounds in food and in the re-use of food wastes. Sometimes, these goals can be obtained at the same time by the use of sustainable technologies. Cereal milling processes generate large amounts of cereal by-products that usually were used in zootechny or they represented the raw material for the extraction of bioactive compounds using solvents or expensive processes. The aim of this study is to propose air classification as a green technology for the production of barley flours using the whole grain and avoiding by-products production. Three non-waxy and one waxy barley cultivars were air-classified.

The results demonstrate that barley coarse fraction showed high amounts of β-glucans (until two-fold higher than whole meal). The same fraction showed concentration of free and bound phenolic compounds that were 1.2–1.3 times higher than whole meal. This improvement was confirmed by the antioxidant activity of barley fraction; in fact, both DPPH and ABTS tests reported the highest values when coarse fraction was analyzed. Moreover, as far as we are concerned, alkylresorcinols were determined in barley air classified fractions for the first time. As reported for phenolic compounds, their content increased 1.2–1.4 times in coarse fraction compared to whole meal.

In conclusion, air classification allows the production of two fractions from whole grain. Coarse fraction resulted naturally enriched in bioactive compounds.

1. Introduction

Cereals contribute to a balanced diet because they contain a proper mix of carbohydrates, fat, proteins, other micronutrients and numerous biologically active substances (Hill, 1998) such as dietary fiber (arabinoxylans, β-glucans, cellulose, lignin and lignans), sterols, tocopherols, tocotrienols, alkylresorcinols, phenolic acids, vitamins, etc. (Bartłomiej, Justyna, & Ewa, 2012). These compounds have attracted the attention of the researchers because it has been demonstrated that the intake of whole-grain cereal products is inversely related to the risk of developing illnesses such as cancer, obesity, cardiovascular diseases or diabetes (Fardet, 2010; Scalbert, Manach, Morand, Rémésy, & Jiménez, 2005).

Barley has usually been grown for feed uses because of the high consume of wheat and rice. However, nowadays, barley is becoming more interesting due to its high content in bioactive compounds (Baik & Ullrich, 2008). Among these biologically active components, β-glucans play an important role. They are soluble dietary fiber located in the cell wall of the endosperm of barley grains, and their content can reach up to 15%. They contribute to lower cholesterol levels, regulate blood glucose levels, control colon cancer and increase mineral and vitamin bioavailability (Khalon & Chow, 1997; Klopfenstein, 1988).

Barley also presents a high concentration of phenolic compounds belonging to different families as: derivatives of benzoic and cinnamic acids, flavonoids (particularly proanthocyanidins), tannins, and amino phenolic compounds (Bonoli, Marconi, & Caboni, 2004; Pihlava, 2014). Consumption of foods rich in polyphenols is becoming of great interest

Abbreviations: C, Catechin; CF, Coarse fraction; FF, Fine fraction; GC, Gallocatechin; PC, Procyanidin; PD, Prodelphinidin; WM, Whole meal.

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because these compounds are associated to the prevention of different diseases related to aging and also to the decrease of cardiovascular diseases and certain types of cancer (Tomás-Barberán & Andres-Lacueva, 2012).

Other biologically active compounds present in barley are alkylresorcinols. They are long chain phenolic lipids with side chains principally ranging from C17 to C25. There are evidences that alkylresorcinols have a low antioxidant activity; nevertheless these compounds have demonstrated a wide range of positive effects such as the inhibition of different enzymes, antibacterial and antifungal activities, anticancer activity, etc. (Ross, Kamal-Eldin, & Åman, 2004).

The occurrence of these three families of bioactive compounds is mainly in the outer layers of barley grains (Landberg, Kamal-Eldin, Salmenkallio-Marttila, Rouau, & Åman, 2008; Shirley, 1998; Vasanthan & Temelli, 2008). However, in the grain processing to obtain flour, the external part of the grains is discarded giving cause to by-products.

By-products were considered for many years as undervalued substrates due to their removal from food production line and the complicated problems arise from their treatment and disposal in the environment. Nowadays, the urgent demands for sustainability in the food and agricultural sectors led to their valorization as a source of nutraceuticals. To do so, five recovery stages are followed: maximizing the yield of the target compounds, suiting the demands of industrial processing, clarifying the high added-value ingredients from impurities and toxic compounds, avoiding deterioration and loss of functionality during processing and ensuring the food grade nature of the final product (Galanakis, 2013). However, utilization of conventional recovery methods are often restricted by several problems such as overheating of the food matrix, high energy consumption and general cost, loss of functionality and poor stability of the final product, accomplishment of increasingly stringent legal requirements on materials safety. Because of that, emerging and green technologies are encouraged to avoid these problems (Galanakis, 2012).

To make the most of these generated by-products and obtain flour fractions enriched in bioactive compounds, air classification represents an interesting separation technique. This separation is based on the density differences between particles. Through optimization of air-classification parameters such as feed rate, air flow rate, and classifier wheel speed it is possible to obtain flours with high content in bioactive compounds (Laudadio, Bastoni, Introna, & Tufarelli, 2013; Vasanthan & Temelli, 2008). Besides, this enrichment process is performed using a physical system (and not by chemical extraction of the bioactive compounds). Because of that, barley fractions obtained by air classification can be considered a safe ingredient for consumers (Verardo, Gómez-Caravaca, Marconi, & Caboni, 2011).

Thus, the aim of this work was to determine the content in bioactive compounds (phenolic compounds, alkylresorcinols and β-glucans) of naturally enriched barley flours by air classification. The use of this physical separation technique can suppose an important strategy to minimize barley by-products production.

2. Experimental

2.1. Chemicals

HPLC-grade acetonitrile and water, methanol, acetone, acetic acid, ethyl acetate, n-hexane, diethyl ether, NaOH, and HCl were purchased from Merck KGaA (Darmstadt, Germany). All chemical standards were from Sigma-Aldrich (St. Louis, MO).

2.2. Samples and sample preparation

The samples were harvested in an experimental field in Campobasso (Italy) in 2014. Hulled grain of four barley cultivars, three non-waxy (Gotic, Scarlett and Braemar) and one waxy (USA) were dehulled and pin-milled (whole meal). After that, the whole meal (WM) was micronized and air-classified into coarse fraction (CF) (40%) and fine fraction (FF) (60%) according to Verardo, Gómez-Caravaca, Marconi, and Caboni (2011). The most represented particle size of coarse and fine fraction was in the range of 120–477 and 45–120 μm, respectively.

The barley samples (WM, CF and FF) were stored at −18 °C until use.

2.3. Determination of β-glucans

As reported in AACC method 32–23.01 ("AACC International. Approved Methods of the Analysis, 11th Ed. Method 32-23.01 β-Glucan content of barley and oats—rapid enzymatic procedure"), (1-3)(1-4)-β-D-glucans were determined using lichenase to generate soluble mixed-linkage β-oligosaccharides, which were separated from insoluble polysaccharides by centrifugation. The oligosaccharides were hydrolyzed to glucose with β-glucosidase. Subsequent colorimetric measurement of the derived glucose was performed using glucose oxidase/peroxidase reagent.

2.4. Extraction of free and bound phenolic compounds

To isolate free and bound phenolic compounds from barley samples (WM, CF and FF) it was followed the methodology proposed by Verardo et al. (2011). Each extraction was replicated four times ($n = 4$). The extracts were stored at −18 °C until use.

2.5. Spectrophotometric determinations

The spectrophotometric analyses were performed using a UV-1601 spectrophotometer from Shimadzu (Duisburg, Germany) and they were replicated four times for each extract ($n = 4$) and three times for each calibration point ($n = 3$).

The free radical scavenging activity of extracts was determined using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay following the protocol proposed by Parejo, Codina, Petrakis, and Kefalas (2001). A Trolox calibration curve was arranged and the results were expressed as μmoles of Trolox equivalent/g of flour.

Moreover, the radical-scavenging capability of phenolic extracts was evaluated using the ABTS• + radical cation assay (2,2′-azinobis(3-ethylbenzothiazoline)-6-sulfonic acid, diammonium salt according to the method of Re et al. (1999) with detection at 734 nm. Results were expressed in Trolox equivalents using its calibration curve.

2.6. Reverse phase-high performance liquid chromatography (RP-HPLC) analysis with UV-diode array absorption and mass spectrometry detections (UV-DAD/MSD)

RP-HPLC analysis was performed by a HP 1100 Series (Agilent Technologies, Palo Alto, CA, USA), equipped with a binary pump delivery system, a degasser, an autosampler, a UV-Vis Diode Array Detector (DAD) and a Mass-Spectrometer Detector (MSD). A fused core type column Kinetex™ C18 (100 mm × 4.6 mm, 2.6 μm) (Phenomenex, Torrance, CA, USA) was used. The method was carried out using the conditions optimized by Gómez-Caravaca et al. (2014).

Calibration curves of catechin, ferulic acid and procyanidin B2 were arranged from LOQ-500 μg/ml, respectively, at six concentration levels for each compound, plotting peak area vs. analyte concentration. The HPLC analyses were replicated three times for extracts and calibration points ($n = 3$).

2.7. Determination of alkylresorcinols

The extraction of alkylresorcinols from barley flours and the methodology used for the analyses were the previously described by Ross (2012). Briefly, 0.5 g of sample was extracted using 20 ml of ethyl acetate for 24 h and then centrifuged at 2000*g* to obtain a