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Volatile profile, fatty acids composition and total phenolics content of brewers' spent grain by-product with potential use in the development of new functional foods

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ABSTRACT

Brewers' spent grain (BSG) is the insoluble residue generated from the production of wort in the brewing industry. This plant-derived by-product is known to contain significant amounts of valuable components, which remain unexploited in the brewing processes. Therefore, it is essential to develop a more detailed characterization of BSG in order to highlight its potential in developing new value-added products and simultaneously solve the environmental problems related to its discharge. The content of BSG in several biologically active compounds (fatty acids, polyphenols, flavonoids, antioxidant capacity) as well as its volatile fingerprint were assessed and compared with the composition of barley, malt and wheat flour samples. The obtained results emphasized the importance and the opportunities of the re-use of this agro-industrial by-product.

1. Introduction

Nowadays, increasing efforts are being directed towards the exploitation of agro-industrial by-products, from both economic and environmental standpoints. Brewers' spent grain (BSG) is an important by-product from the brewing process, representing up to 30% (w/w) of the starting malted grain. BSG is therefore a readily available, high volume and low cost by-product within the brewing industry. It is estimated that worldwide the annual output is around 30 million tons, about 200 tons of wet spent grain (70–80% water content) being produced per 10000 hl of produced beer (Kunze, 1996; Niemi et al., 2012).

The great interest shown in the last years in this by-product is due to its chemical composition that permits its re-use in different areas (food ingredient, feed, raw material for microbiological or chemical conversion, pharmaceutical, cosmetic or other industries) (Mussatto, 2013; Niemi et al., 2012; del Rio et al., 2013). Basically, BSG is composed of the barley malt residual constituents and includes the barley grain husk, in the greatest proportion, but also minor fractions of pericarp and fragments of endosperm (Mussatto et al., 2006). Malt is one of the key ingredients in brewing, providing the starch and the enzymes necessary to produce the fermentable sugars that are turned by yeasts into alcohol in the fermentation process. Malt also provides the colour and the flavour compounds, generated during the kilning step, which contribute to the final character of the beer.

As described in the literature (Santos et al., 2003) the composition of BSG is variable according to the barley variety and harvest time, malting and mashing conditions, type and quality of secondary raw materials added in the brewing process. Nevertheless, this plant-derived by-product is known to contain significant amounts of valuable components, which remain unexploited in the brewing process.

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List of abbreviations

BSG	brewers' spent grain
BSGd	dried brewers' spent grain
BSGl	lyophilized brewers' spent grain
DPPH	2,2-diphenyl-1-picrylhydrazyl
dw	dry weight
EI	electron ionisation
FAMEs	fatty acid methyl esters
fw	fresh weight
GAE	gallic acid equivalents
GC	gas chromatography
GC–MS	gas chromatography – mass spectrometry
ITEX	in-tube extraction
MCf	Carafa malt
MCm	Caramunich malt
MP	Pilsner malt
MUFAs	monounsaturated fatty acids
PCA	principal component analysis
PUFAs	polyunsaturated fatty acids
QE	quercetin equivalents
SB	spring barley
sd	standard deviation
SFAs	saturated fatty acids
TIC	total ion chromatogram
TLs	total lipids
TPC	total phenolic content
tr	trace
VLCSFAs	very long chain saturated fatty acids
WF	wheat flour
WWF	wholemeal wheat flour

BSG has high levels of dietary fibre, protein and particularly essential amino acids, as well as appreciable levels of lipids, minerals, polyphenols and vitamins (Mussatto et al., 2006). These compounds, when incorporated into human diets, may provide a number of benefits by lowering the risk of certain diseases including cancer, gastrointestinal disorders, diabetes, obesity and coronary heart disease (Fastnaught, 2001).

BSG is still traditionally supplied to local farmers or, alternatively, it is composted, dried and incinerated, dumped or anaerobically fermented (Fillaudeau et al., 2006). Therefore the development of economically viable technologies for the exploitation of this agro-industrial by-product has been encouraged. Although the by-products from the brewing and also from other fruit and vegetable processing industries are considered agricultural wastes and an environmental problem, they are suitable to be used in the human diet and efforts have been made to utilise them as functional ingredients (Rodriguez et al., 2006). Consequently, it is essential to develop a detailed and comprehensive characterization of BSG in order to highlight its potential as a valuable source of biologically active compounds in the development of new added-value food products.

Previous studies have been focused on determining the carbohydrate, protein and polyphenol composition of BSG (Waters et al., 2012) and more recently on its lipid and lignan profile (Niemi et al., 2012; del Rio et al., 2013). Besides the aforementioned classes of compounds, an important role in the acceptance of a food product by the consumers is played by its aroma. For the exploitation of BSG as a food ingredient, its volatile profile must also be taken into consideration. However there is limited information regarding the volatile constituents of BSG (Ktenioudaki et al., 2013), the recent research on this area being directed to the malt volatile profile characterization (Coghe et al., 2004; Dong et al., 2013). Thus, in order to complete the existing information on BSG, the present study's principal objective was to determine the BSG volatile profile together with its composition in fatty acids, antioxidant activity, total polyphenolics and flavonoid content.

2. Materials and methods

2.1. Materials

All the materials (malt, brewers' spent grain) were supplied by the Microbrewery of the Faculty of Food Science and Technology of University of Agricultural Sciences and Veterinary Medicine from Cluj-Napoca. The BSG used in this work was obtained as a by-product from the mashing process of dark lager beer with 100% all grain malted barley (Weyermann Specialty Malting Company, Bamberg–Germany). Besides Pilsner malt (MP) which imparts a malty-sweet and gentle note of honey to the beer, Caramunich (MCm) and Carafa (MCf) malts were added in small amount (5–10%) to obtain a dark colour and to enhance the flavour characteristics with notes of caramel, biscuit, coffee, cacao, dark chocolate and roastiness.

The high initial moisture content of fresh BSG (75–80%) and the presence of considerable levels of polysaccharide and protein make it particularly susceptible to microbial degradation within a few days. Therefore, the fresh BSG samples were preserved in two ways: by lyophilisation using laboratory freeze dryer Alpha 1-2 Lyo Display Plus and by oven-drying at 78 °C for 12 h to reach a moisture content of 6%. Then, the dried samples were packed in sealed polyethylene bags and stored at room temperature while the lyophilized samples were kept at −20 °C until further analyses.

A commercial wheat flour (WF) used for traditional bread making (type 650 according to ash content by Romanian classification) with 14.5% moisture, 10.6% protein, 0.9% fat, 0.65% ash, 73.2% total starch and 0.6% fibre was purchased locally, Pambac, Bacău – Romania. The wholemeal wheat flour (WWF) was also purchased from a local producer (Panemar, Cluj-Napoca – Romania).

2.2. Chemicals

All reagents used for the lipid extraction and fatty acid methyl ester (FAMEs) preparation were of chromatographic grade (Sigma–Aldrich, St. Louis, MO, USA). The FAMEs standard (37 component FAME Mix, SUPELCO, catalog No: 47885-U) were purchased from Supelco (Bellefonte, PA, USA). The standard compounds (gallic acid, quercetin) and reagents: 2,2-diphenyl-1-picrylhydrazyl (DPPH), Folin-Ciocâlteu, methanol, aluminium chloride, sodium carbonate, sodium nitrite and sodium hydroxide were purchased from Sigma–Aldrich or Merck (Darmstadt, Germany).

2.3. Extraction and analysis of volatile compounds

The extraction of volatile compounds was performed using the in-tube extraction technique (ITEX) as described in our previous work (Socaci et al., 2014) using 3 g of sample. The analysis of volatile compounds was carried out on a GCMS QP-2010 (Shimadzu Scientific Instruments, Kyoto, Japan) model gas chromatograph – mass spectrometer. The volatile compounds were separated on a Zebron ZB-5ms capillary column of 50 m × 0.32 mm i.d and