Food Chemistry 167 (2015) 1–6

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

A comparative assessment of antioxidant properties, total phenolic content of einkorn, wheat, barley and their malts

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ARTICLE INFO

Article history:
Received 29 January 2014
Received in revised form 18 June 2014
Accepted 20 June 2014
Available online 1 July 2014

Keywords:
Einkorn wheat (*Triticum monococcum* L.)
Malt
Antioxidant activity
TPC
DPPH
TEAC
FRAP
ABTS

ABSTRACT

Two einkorn wheat, one barley, three optional winter cultivation wheat and five winter cultivation wheat samples harvested in Hungary in 2011, and their malts were evaluated for their DPPH radical and ABTS radical cation scavenging activity, ferric reduction capacity (FRAP) and total phenolic content (TPC).

All einkorn and barley samples exhibited significant antioxidant activities determined by DPPH and ABTS radical scavenging activities. The einkorn samples show higher polyphenol content than the other wheat samples. In all cases the barley sample had the highest antioxidant potential and polyphenol content. The einkorn malts had high DPPH and ABTS radical cation scavenging activities, but the phenolic content was lower against wheat samples. There was significant difference between the antioxidant potential of optional and winter cultivation wheat samples except on ABTS scavenging activities.

Einkorn wheat is potentially a new raw material to produce organic beer that might have beneficial effects with its increased antioxidant potential.

1. Introduction

The Einkorn (*Triticum monococcum ssp. monococcum* L.) is an ancient wheat and is suitable to be grown in environmentally friendly organic farming. Compared to common wheat, einkorn is generally more resistant to diseases, and has the ability to withstand drought. Einkorn is still cultivated on poor soils in Italy, where other wheat types would fail. The yield of einkorn, however, is considerably lower compared to common wheat varieties (Løje, Møller, Laustsen, & Hansen, 2003). In Hungary research has been started aiming the extensive utilisation of organic einkorn.

Einkorn (*T. monococcum ssp. monococcum* L.), a diploid hulled wheat (2n ¼ 2x ¼ 14) strictly related to durum (*Triticum turgidum durum*) and bread wheat (*Triticum aestivum*), is regarded as a high-nutritional-value cereal, especially considering its high protein and antioxidants content (Abdel-Aal, Young, Rabalski, Hucl, & Fregeau-Reid, 2007; Hidalgo, Brandolini, Pompei, & Piscozzi, 2006).

Different properties of einkorn wheat have been examined (Brandolini, Hidalgo, & Moscaritolo, 2008; Brandolini, Hidalgo, & Plizzari, 2010). The properties of einkorn wheat has been examined in bread (Hidalgo & Brandolini, 2011) and pasta (Brandolini et al., 2008). Hidalgo and Brandolini (2008) has examined the protein, ash, lutein and tocol distributions in einkorn seed fractions, and some specific antioxidant compounds, as well (Hidalgo et al., 2006).

Antioxidants are "any substance that, when present at low concentrations compared with those of an oxidizable substrate, significantly delays or prevents oxidation of that substrate" (Halliwell, 2007). Antioxidants act in various ways, which include complexation of redox-catalytic metal ions, scavenging of free radicals, and decomposition of peroxides. The intensity of these effects depends on the chemical structure and concentration of the AO present. Natural antioxidants may also protect DNA, protein, and membrane lipids from oxidative damage in biological systems, and provide additional health benefits for disease prevention and health promotion (Halliwell, 2007).

Free radical chain reaction is a common mechanism that may explain the direct attack of radicals on physiologically important components, including DNA, protein and membrane lipid, as well as other oxidative damage in the biological systems mediated by the radicals. Radical scavengers may react with and quench free

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http://dx.doi.org/10.1016/j.foodchem.2014.06.084
0308-8146/

radicals in the system and terminate their potentially hazardous effects. On the other hand, chelating agents reduce the availability of transition metals. This reduction may suppress the formation of free radicals and inhibit the initiation of the free radical chain reaction. Therefore, both radical scavenging and chelating activities are beneficial antioxidative effects against the radical-associated health problems, such as cancer and coronary heart disease. The most important antioxidant compounds are the polyphenols (Valko, Rhodes, Moncol, Izakovic, & Mazur, 2006). In the present study, einkorn and selected wheat samples and their malts were evaluated and compared for their free radical scavenging properties. In addition, total phenolic contents of the samples were determined since phenolic compounds, universal in plant materials, including wheat, have been shown to be a group of chemicals that may exhibit radical scavenging and chelating capacities.

Einkorn is mostly used for baking. All einkorns are suitable for bakery product preparation, some genotypes show very good bread making attitude, producing outstanding bread loaves with an appealing deep yellow crumb (Brandolini & Hidalgo, 2011). Einkorn could be a potentially new organic raw material for brewing. Antioxidants are generally thought to play a significant role in malting and brewing due to their ability to delay or prevent oxidation reactions and oxygen free radical reactions. Antioxidant activities and total phenolic contents of the most used malting barley had been evaluated (Zhao et al., 2008). However, no attempt has been undertaken to study the antioxidant activity of einkorn malt. Furthermore, antioxidant compounds present in einkorn extracts are complex, and their activities and mechanisms would largely depend on the composition and conditions of the test system (Frankel & Meyer, 2000).

Low temperature is an important stress factor which conclude that the sowing time could be important in formation of antioxidative compounds (Janda, Szalai, Rios-Gonzalez, Veisz, & Páldi, 2003). This statement was took into account in our experiment too.

Many authors emphasize for using more than one method for the examination of antioxidant capacity in plant foods, and we kept this in view in the course of planning experiments. First objective of this study was to determine the antioxidant capacity of organic hulled and de-hulled einkorn cropped in Hungary by measuring DPPH radical scavenging activity, ABTS radical cation scavenging activity, total phenolic contents, and by using the FRAP assay. The other objective was to monitor the changes of antioxidant capacity of einkorn and different bread wheat varieties during the malting process.

2. Materials and methods

2.1. Materials

2.1.1. Seed samples

Organic einkorn wheat (*Triticum monococcum* L.), organic barley (*Hordeum vulgare* L.), and eight bread wheat (*T. aestivum*) varieties were obtained from the agricultural plots of Kőrös-Maros Biofarm, Hungary. All seeds were cropped in 2011. All the samples were malted with the same malting procedure using a Schmidt-Seeger (Germany) micromalting plant. The malting was conducted with the next parameters: 12 h steeping in 22 °C water, 5 days germinating at 22 °C, kilning for 24 h at 45 °C, 12 h at 55 °C, 6 h at 70 °C, 6 h at 80 °C and finishing with aeration at room temperature. The malt was kept for 14 days to rest. All samples were sealed in polyethylene bag, and stored in a freezer at −20 °C until ready for extraction. The moisture content of the seed samples were between 8.46% and 10.3%, and that of the malt samples between 4.3% and 5.3%. The abbreviation and characteristics of the samples are summarised in Table 1.

2.1.2. Chemicals

2,2-Diphenyl-1-picrylhydrazyl (DPPH), 2,2′-azinobis (3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (TROLOX), Folin–Ciocalteu's phenol reagent, ascorbic acid and gallic acid, methanol, sulphuric acid, acetone, potassium persulfate, sodium acetate trihydrate, and hydrochloric acid were purchased from Sigma–Aldrich (Hungary). All reagents used were of analytical grade.

2.2. Sample preparation and extraction of antioxidants

Samples were milled to a particle size of less than 0.5 mm in a centrifuge mill. Analysis should be performed preferably immediately after extraction. Alternatively, samples may be stored at −20 °C until analysis.

The extraction of antioxidants was made according to the method of Pérez-Jiménez et al. (2008) with slight modifications. The extraction was carried out in two principal steps; both steps were repeated twice for better result. The first step has a shorter and lower temperature: 0.5 g of sample is placed in a capped centrifuge tube; 20 mL of acidic methanol/water (50:50, v/v; pH 2) is added and the tube is thoroughly shaken at room temperature for 1 h. The tube is centrifuged at 2500*g* for 10 min and the

Table 1
Used seed samples abbreviations and characterisation.

Sample	Type	Abbreviation	Characteristics
MV organic einkorn	Hulled	EH	Organic breeding, low-protein content (11–12%)
	De-hulled	EUH	
	De-hulled malt	EUM	
MV organic 4 row barley	Hulled	BRL	Organic breeding
	Hulled malt	BRLM	
MV 14-11 wheat	De-hulled, optional winter cultivar	WO 1	Experimental breeding
	De-hulled, malt	WOM 1	
MV 335-10 wheat	De-hulled, optional winter cultivar	WO 2	Experimental breeding
	De-hulled, malt	WOM 2	
MV 09-09 wheat	De-hulled, optional winter cultivar	WO 3	Soft wheat, low-protein content (10–13%)
	De-hulled, malt	WOM 3	
MV 05-08 wheat	De-hulled, winter cultivar	WW 4	Soft wheat, low protein content (10–12%)
	De-hulled, malt	WWM 4	
MV Regiment wheat	De-hulled, winter cultivar	WW 5	Soft wheat, normal protein content (12–15%),
	De-hulled, malt	WWM 5	high starch content (>70%)
MV 06-09 wheat	De-hulled, winter cultivar	WW 6	Experimental breeding
	De-hulled, malt	WWM 6	
MV 322-10 wheat	De-hulled, winter cultivar	WW 7	Experimental breeding
	De-hulled, malt	WWM 7	
MV Taller wheat	De-hulled, winter cultivar	WW 8	Hard wheat, normal protein content (12–14%)
	De-hulled, malt	WWM 8	