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PRODUCTION AND QUALITY ANALYSIS OF MALT PRODUCED FROM HULLESS BARLEY

Marina Tišma[1*], Gordana Šimić[2], Alojzije Lalić[2], Mirela Planinić[1], Gordana Šelo[1], Ana Bucić-Kojić[1]

[1]*Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 20, 31000 Osijek, Croatia*
[2]*Agricultural Institute Osijek, Južno predgrađe 17, 31000 Osijek, Croatia*
[*]corresponding author: mtisma@ptfos.hr

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SUMMARY
In this work, micromalting of two hulless barley samples (lines GZ-186 and GZ-189) was performed. Barley and malt quality control parameters, as well as the concentration of total phenolic compounds, total flavonoids and proteins in barley and malt extracts were analysed. The both lines of hulless barley comprise high protein content (12.3 - 12.9%). Values of extract content from produced malt samples were from 83.92% to 84.46%, fine/coarse extract difference from 7.64% to 8.05%, Kolbach index from 34.1% to 35.2%, viscosity from 1.95 mPas to 2.04 mPas, friability from 33.1% to 41.56%.
It was shown that tested hulless barley samples present rich source of phenolic compounds (364.19 mg_{GAE}/cm^3 and 316.99 mg_{GAE}/cm^3 GZ-186 and GZ-189, respectively), and poor source of total flavonoids (GZ-186: 1.69 mg_{CE}/cm^3 and GZ-189: 1.25 mg_{CE}/cm^3). Consequently, malt samples are characterized with higher phenolic concentration (GZ-186: 408.95 mg_{GAE}/cm^3 and GZ-189: 375.540 mg_{GAE}/cm^3) and lower flavonoids concentration (GZ-186: 1.22 mg_{GAE}/cm^3 and GZ-189: 1.24 mg_{GAE}/cm^3).

Keywords: hulles barley, malt, quality analysis, phenolic compounds

INTRODUCTION

Barley (*Hordeum vulgare* L.) is a highly adaptable cereal grain that is produced from subarctic to subtropical climates. It is the primary cereal used in the production of malt in the world. Malting is defined as the controlled germination of cereals, to ensure specific physical and biochemical changes within the grain, which is then stabilized in the phase of kilning. Three main phases occur during malting: (a) steeping, to ensure good absorption of water by the grain, (b) germination, to maintain embryo growth, enzyme synthesis and a limited endosperm breakdown, and (c) kilning, to ensure malt stability (Gupta et al., 2010).

Hulless barley is the barley without husk. In the Republic of Croatia, it is not traditionally cultivated. However, in China, hulless barley, known as qingke, presents an economical crop widely grown in the highlands with the multiple applications in food industry, such as in the production of low alcohol liquor and noodle, as well as in bakery (Chang and Lv, 2016). It is one of the staple foods for Tibetans and an important livestock feed in the Tibetan Plateau. Cultivated history of hulless barley in Tibetan Plateau dates as far back as 3500 years ago (Zeng et al., 2015).

In the last few years, an interest for the hulless barley production and its application in human nutrition and industrial alteration, *e.g.* in brewing, has been growing worldwide. Some of the recently developed hulless barley cultivars are Roseland (Badea et al., 2017), Ozen (Ergun et al., 2017), and Sawtooth (Bregitzer et al., 2017).

The main advantage of the hulless barley for application in food industry is its use without need to remove the husk after the harvest. The absence of hulls means that the grain has more nutrients and higher energy per unit weight in comparison with hulled barley and therefore it requires less space for storage and transport. In the terms of nutrient composition, hulless barley is comparable with commonly consumed cereals due to high content of proteins, dietary fibres, and various trace elements. Among dietary fibres, *β*-glucans are known in the production of functional food (Šimić et al., 2017). Additionally, hulless barley starch has great potential to be an alternative starch due to its cheap price and wide resource (Chang and Lv, 2016).

In this work, two-rowed winter type hulless barley samples lines GZ-186 and GZ-189, developed at the Agricultural Institute Osijek, were micro-malted. They have good lodging resistance, higher test weight and threshability and are tolerant to most prevalent barley diseases.

Basic analyses on barley and malt samples, regarding brewing quality parameters, are done in this work. Additionally, special attention was given to the analyses of total phenolic compounds, total flavonoids and proteins in both, barley and malt extracts.

The aim of this study was to examine the main brewery characteristics of hulless barley varieties of two diverse genetic origins, while malting was performed to compare the barley grain and its corresponding malt samples for the differences in total phenolic and flavonoid content and to analyse if the two lines of barley could be used in brewing.

MATERIALS AND METHODS

Barley samples

Barley samples (lines GZ-186 and GZ-189) were obtained from the Agricultural Institute Osijek. Samples from the line trials of Agricultural Institute Osijek were collected and analysed during the 2013/2014 season. Barley varieties were grown

under field conditions on location Osijek. The experiments were conducted in randomized block designs (RCBD) with six replications; plot size was 7.56 m^2. Sampling (5 kg per sample) was performed on cleaned and processed barley grains (EBC 3.3.1.) and samples were kept refrigerated in dry containers.

Barley quality analysis

Moisture, hectolitre weight, protein and starch content were determined using Infratec 1241 Grain Analyzer (Foss Tecator AB, Sweden).

Micro-malting

Barley samples were screened over a 2.5 mm sieve prior to malting. 500 g of the sample was malted in an Automated Joe White Malting Systems Micro-malting Unit (Perth, Australia). The malting program consisted of a 37 h interrupted steep program (16 °C, 5 h submerged, 17 °C, 12 h air rest with 100% airflow, 17 °C, 6 h submerged, 18 °C, 12 h air rest with 100% airflow, 17 °C, 2 h submerged), a 96 h germination program (17 °C, 75% airflow, 1.5 turn every 2 h) and a 18 h kilning program (60 °C, 6 h; 65 °C, 3 h; 68 °C, 2 h; 70 °C, 2 h; 80 °C, 2 h; 83 °C, 2 h; 85 °C, 1 h). Rootlets were removed and the finished malt was then stored in plastic containers with caps until analysis.

Malt quality analysis

Malts were ground (particle size 0.2 mm) using a Bühler Universal Laboratory Disc Mill (DLFU type). The malt moisture content (EBC method 4.2) and corresponding extract (EBC method 4.5.1), Kolbach Index (EBC methods 4.3.1 and 4.9.1), viscosity (EBC method 4.8), extract difference between finely and coarsely ground malt (EBC method 4.5.2) and friability (EBC method 4.15) were determined according to European Brewery Convention methods (EBC Analysis Committee, 1998).

Analysis of total phenolic compounds (TP), total flavonoids (TF), and proteins (TP) concentration

Samples were milled to 1 mm particle size (Retsch ZM200). Circa 1.0 g of milled sample was extracted by solvent (50:50, water/ethanol, v/v) with solid/liquid ratio 1:40. Extraction was performed in a water bath at 80 °C (Julabo, SW23, Germany) by shaking (200 rpm) during 120 min. After the extraction, samples were centrifuged at 10,000×g (Multifuge 3 L-R Centrifuge, Heraus, Germany) for 10 min in order to obtain liquid extracts for further analysis.

TP content was estimated by a colorimetric assay using Folin-Ciocalteu methods (Bucić-Kojić et al., 2011) with gallic acid as standard. The absorbance was read at 765 nm (UV-1700 Shimadzu, Japan) and the results were expressed as gallic acid equivalent (GAE). TF content was measured using colorimetric method with aluminium chloride proposed by Marinova et al. (2005). The absorbance was read at 510 nm and the result were expressed as (+)-catechin equivalent (CE). TF content was estimated according to Bucić-Kojić (2009).

Extractable protein concentration was determined by the Bradford method with bovine serum albumin (BSA) as standard, and the absorbance was read at 595 nm.

RESULTS AND DISCUSSION

Barley breeders use malting tests to select malt of good qualities. Basic brewery quality parameters of hulless barley and malt, and total content of phenolics, flavonoids and proteins were analysed.

The results of the content of proteins, moisture, starch, hectolitre mass, as well as mass concentration (γ) of total polyphenols (TP), total flavonoids (TF) and proteins (PC) in hulless barley samples are presented in **Table 1**.

Table 1 The content of proteins, moisture, starch, hectolitre mass in barley grains. Mass concentration (γ) of total polyphenols (TP), total flavonoids (TF) and proteins (PC) in barley extracts.

Sample	Parameter	Unit	GZ-186	GZ-189
Barley grain	Proteins	[%]	12.90	12.30
	Moisture	[%]	9.80	10.10
	Starch	[%]	58.40	60.10
	Hectolitre mass	kg	72.50	75.20
Barley extracts	Total polyphenols	[mg_{GAE}/cm^3]	364.20	316.99
	Total flavonids	[mg_{CE}/cm^3]	1.69	1.25
	Total extractible proteins	[mg_{BSA}/cm^3]	2.30	2.23

Based on the obtained results it can be concluded that the both hulless barley lines comprise high protein content (12.3 - 12.9%) which is not typical for the brewing barley. The results are compared with the results of the same barley lines produced in different years (2012/2013) using the same cultivation procedure and were as follows: 13.45% and 13.70%, for GZ-186 and GZ-189, respectively (Šimić et al., 2017). It can be concluded that the samples used in this study contained lower protein concentration (12.90% for GZ-186, and 12.30% for GZ-189) in comparison with the barley samples produced in 2012/2013 (Šimić et al., 2017), which can probably be the consequence of the environmental conditions during growing season and harvest time. Starch, the most abundant carbohydrate in barley grain, is an important quality indicator to maltsters and brewers of malt extract content. In the current study the content of starch ranged from 58.4% to 60.1% (**Table 1**). Test weight is a measure of density and is expressed as kilograms per hectolitre (kg/hL). Hulless barley usually has hectolitre weight higher than standard hulled barley, and in this study it ranged from 72.5 kg to 75.2 kg for GZ-186 and GZ-189, respectively.

It was shown that hulless barley samples present rich source of phenolic compounds (364.19 mg_{GAE}/mL and 316.99 mg_{GAE}/mL, for GZ-186 and GZ-189, respectively), and poor source of total flavonoids (1.69 mg_{CE}/mL and 1.25 mg_{CE}/mL

for GZ-186 and GZ-189, respectively). Among cereal grains, barley is known to be naturally high in phenolic compounds, which was proved also here.
Malting is a complex process of barley modifications. The structural changes occur due to the broad enzymatic activities, including enzymatic catalysed release of phenolic compounds bound to the cellular structures of barley, and glycosylation, which lead to the easier extraction of free phenolic acids due to the changes in the matrix in the early phases of kilning (Šimić et al., 2017).
A large number of parameters have been proposed to define malting quality. The general malt quality parameters of the malt produced from hulless barley line GZ-186 and GZ-189 are presented in **Table 2**.

Table 2 Malt quality control parameters

Parameters	Samples	
	GZ-186	**GZ-189**
PC [$\%_{db}$]	13.20	12.80
M [%]	6.59	6.67
E [%]	84.46	83.92
F/C [%]	8.05	7.64
SP [$\%_{db}$]	4.50	4.50
F [%]	41.56	33.10
V [mPa s]	1.95	2.04
IK [%]	34.10	35.20
MC [EBC units]	2.40	2.80

Abbreviations: PC [% db]– protein content per gram of dry basis; M – moisture content; E – extract content; F/C – fine/coarse extract difference; SP – soluble protein content per gram of dry basis; F – friability; V – viscosity; IK – Kolbach's index; MC – malt colour

The most important feature of malt is its behaviour in the mashing process and its potential for producing a wort soluble extract. Hulless barley malts produce significantly higher levels of malt extract than covered barley varieties. Values of extract content from malt samples in this study were from 83.92% to 84.46% while fine/coarse extract difference was from 7.64% to 8.05%, respectively. As it was shown in the previous study (Šimić et al. 2017), results of hulless barley micro-malting showed higher malt extract contents when compared with malting varieties. Edney and Langrell (2004) reported in their study extract values approaching 87% for the hulless variety CDC Dawn in comparison to values less than 81% obtained for the covered variety Harrington. According to the results of Li et al. (2006), who investigated three Canadian hulless barley varieties with micro and pilot malting equipment, all three varieties could be micro malted successfully to produce malt with impressively high malt extract levels, 3 - 5% higher than a covered malting barley control. Their results also indicated that the quality traits of hulless malt, especially malt friability and *β*-glucan and *α*-amylase levels, were

sensitive to acrospire damage during turning and handling and also to harsh kilning conditions.

Friability was lower for both lines analysed in this work, in comparison to the samples from 2012/2013 and consequently, higher F/C difference in both lines were detected in this work. The obtained values are also lower than friability values observed in the Canadian hulless barley (CDC Dawn) that were form 60% to 70% (Edney and Langrell, 2004).

The higher levels of extracts resulted in higher values of wort viscosity. The results of the viscosity were from 1.95 mPas to 2.04 mPas, while friability was from 33.1% to 41.56%, for GZ-186 and GZ-189, respectively.

Kolbach index of the barley sample line GZ-186 was lower in this work in comparison with the previous one, while the IK value for the line GZ-189 did not differ much. Kolbach index represents the degree of protein degradation in malt grain and its values were 34.1% to 35.2%, for GZ-186 and GZ-189, respectively. These results are in accordance with results from quality analysis of malt produced from the three hulless barley varieties in Canada (Li et al., 2006). Edney and Langrell (2004) have noticed in their work Kolbach index values higher than 40%, and even approaching 48% for the hulless variety CDC Dawn when longer germination period was applied.

The results of the mass concentration (γ) of total polyphenols (TP), total flavonoids (TF) and proteins (PC) in hulless malt samples are presented in **Table 3**.

Table 3 The mass concentration (γ) of total polyphenols (TP), total flavonoids (TF) and proteins (PC) in malt samples

Sample	γ_{TP} [mg_{GAE}/cm^3]	γ_{TF} [mg_{CE}/cm^3]	γ_{PC} [mg_{BSA}/cm^3]
GZ-186	408.95	1.22	1.93
GZ-189	375.54	1.24	1.89

According to the results of the mass concentration of total polyphenols (TP), total flavonoids (TF) and proteins (PC) in malt samples (**Table 3**) it can be perceived that malt samples are characterized with high phenolic concentration (408.95 mg_{GAE}/cm^3 and 375.540 mg_{GAE}/cm^3, for GZ-186 and GZ-189, respectively) and low flavonoids concentration (1.22 mg_{GAE}/cm^3 and 1.24 mg_{GAE}/cm^3, for GZ-186 and GZ-189, respectively).

CONCLUSIONS

Hulless barley lines GZ-186 and GZ-189 are characterized with high protein contents. Tested barley samples present rich source of phenolic compounds and poor source of total flavonoids. Malt samples were characterized by higher phenolic concentration and lower flavonoids concentration than barley samples. Generally, malt samples produced from GZ-186 and GZ-189 satisfy the malt quality

in terms of extract content and Kolbach's index and have bright yellow colour, but possess low friability, high viscosity, and high value of F/C difference.

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