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## Technological Quality of New Croatian Barley Varieties Intended for Whisky Malt Production

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## Abstract

The aim of this paper was to assess the technological quality of three novel Croatian spring barley varieties and lines intended for brewing and distilling. Two tested lines Osk.5.45/2-15 and Osk.5.33/23-15 and one variety Pivarac were developed at the Agricultural Institute Osijek, while the used control sample was the recognised whisky barley variety Grace. The quality of starting barley and final malts were assessed. The results indicate that the tested varieties/lines of spring barley have the potential to become recognised as whisky malt varieties. In order to confirm the obtained results, further monitoring should be employed during the statistically relevant period. The tested quality values the OSK.5.33/23-15 has shown were the closest to the recommended values for whisky malts. In all tested varieties  $\beta$ -glucans content should be reduced which would consequently improve the F/C extract difference and friability values and increase the fermentability and extract yield during fermentation.



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**Keywords** 

Spring Barley Varieties; Technological Quality; Whisky Malt.

## Introduction

Barley is one of the earliest cultivated cereals and besides the use as human and animal feed it was utilised as a source of fermentable extract for the production of beer and spirits. There are over 300.000 barley varieties that are generally categorized as two-row and six-row.<sup>1</sup> Today's barley selection has been significantly advanced and there are distinct varieties strictly intended for brewing and distilling, in general intended for malting. The selection of barley varieties for malting depends on several factors: availability, cost and final use of the produced malt (feed, brewing, distilling, etc.). However, Croatian commercial barley varieties can be dually declared as brewing/feed (B/F) varieties. Even though this kind of labelling is avoided in the European Union (EU), the reason it still applies in Croatia is that there were no strictly intended

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varieties (brewing or feed) upon the entry of Croatia in the EU. This would restrict the domestic barley production to introduce the different varieties to brewing or distilling industries even though they have shown good malting characteristics.<sup>2</sup> Based on the quality requests set up by brewing and distilling industries, that are in many ways opposite to the requests of the food and feed industries, the Institute of Agriculture Osijek has developed new varieties of spring barley intended for brewing and whisky malt (WM) production.<sup>3</sup> The brewing industry inclines to two-row spring varieties, leaving winter varieties with no current approval for use in distilling.4,5 Whisky malt quality depends on the appropriate barley variety and thus it is obvious that distinct varieties have profiled from the total assortment as the ones with the most satisfactory WM qualities. These varieties are referred to as standards and serve both for observing the impact of various agro-environmental and environmental conditions on the crop (climate specifics of the season, different cultivation methods, location changes, etc.) as well as for orientation when introducing new varieties in the assortment. It is well known that the European brewing industry uses only several barley varieties as standards (Vanessa, Tiffany, Casanova, etc.) because of the fact that they are grown in varietal experiments across the continent, so there are a handful of available data for selectors. Although in a smaller count, there are standard varieties for distilling industry too, and one such variety, Grace, has been used in this research. Plant breeding takes up 10-15 years from selection to the point where the variety can be placed on the market with increased yield and resistance to disease, better overall quality or some other economic advantage.6,7 In the case of brewing and WM barleys, after the variety has been recognized, it is subjected to the examination regarding the stability of its technological indicators during a statistically relevant period (3-5 years). After that, the influence of agro-technical and environmental conditions on these properties is also to be verified. However, this is no longer a question of determining purely agronomic quality indicators,

as the micromalting process and the determination of technologically relevant indicators are carried out in the relevant institutes dealing with brewing technology. In countries that have a developed industry of beer and spirits, these data appear as regular annual reports for all the standard and other most abundant cultivars in the breeding. The aim of this paper is to follow the quality indicators over a minimally statistically relevant period and to present them as an annual report. Since these are the first domestic varieties and lines intended for WM, the data from this research could be of interest to the selectors as well as for the malting and distilling industry.

#### **Material and Methods**

The tested variety, Pivarac, and lines Osk.5.45/2-15 and Osk.5.33/23-15 were compared with the WM control variety Grace. Grace is accepted in variety testing in many countries, mainly in Northern Europe and Northern America<sup>8,9,10,11</sup> and the results can be well related with other research. Pivarac, the new variety of spring two row barley, just emerged on the market and selectors consider it as a potential WM variety. Lines Osk.5.45/2-15 and Osk.5.33/23-15 are also purposely developed as WM varieties.

All barley varieties were grown under field conditions on location Osijek. The experiment was conducted in randomized block designs (RCBD) with six replications; plot size was 7.56 m2. Sampling (5 kg per sample) was performed on cleaned and processed barley grains (according to the EBC 3.3.1. method) and the samples were kept refrigerated in sterile dry containers. Grain samples (5 kg per sample) were collected as untreated and conditioned grain, scaled and packed into in double-walled paper bags (1 kg). Until micromalting, the material was stored in sterile dry containers for two months in a dry and cool place (18-20 °C) to overcome post-harvest grain dormancy. Laboratory micro-malting of barley was carried out, as shown in Table 1, in the micromalting plant Joe White Malting Systems (Pty. Limited East Melbourne, Victoria, Australia; Automatic Micro Malt Unit, 10 kg capacity). Four samples of 2×1 kg of each barley variety were malted. Degermination of dry malt was performed manually. After micromalting, 500 g of each sample was weighed and stored in paper bags for one month in order for moisture content to stabilize.

Barley and malt quality indicators were determined according to European Brewing Convention<sup>12</sup> (methods: 3.2., 3.3.1., 3.10.1., 4.2., 4.3.1., 4.9.1., 4.10., 4.4., 4.5.1., 4.10., 4.5.2., 4.11., 4.7.1.) and MEBAK, 199713 (methods: 2.2.7.,

2.3.3., 2.3.4., 2.4.1.1., 4.1.4.6., 1.4.7.1., 4.1.4.5., 4.1.4.11., 4.4.2.4., 4.1.4.2.9., 4.1.4.2.7., 4.8., 4.15., 4.16.1., 4.12., 4.13.). Mass fraction of starch in barley was determined according to ICC (2003) 14 standard method No. 122/1. The results shown in (Table 2) and (Table 3) are the average results obtained from consecutive micro-malting procedures in two repetitions.

	micromalting stage	air flow (%)	Т. (°С)	t (h)	
STEEPING	immersion steeping	-	16	5	
	dry steeping	100	17	12	
	immersion steeping	-	17	6	
	dry steeping	100	18	12	
	immersion steeping	-	17	2	
		-	-	-	
	dry steeping				
		moisture c	moisture correction to 44.5% by		
		spraying w	spraying with water		
GERMINATION	germination parameters	75	17	96	
	turning over time: 2 number of rotation during turn over: 3				
KILNING	first phase	100	60	6	
	second phase	100	65	3	
	third phase	90	68	2	
	fourth phase	90	70	2	
	fifth phase	50	80	2	
	sixth phase	50	83	2	
	seventh phase	40	85	1	

#### Table 1: Micromalting scheme of barley samples

## **Results and Disscussion**

The selection of barley varieties for malting depends on availability, cost and end use of the malt. Since variety has a decisive influence on finished malt quality, standard (desirable) values defining barley and malt quality were determined. Values of malt quality indicators are given in Table 3 as "recommended value". Starting quality indicators are given in Table 2.

General quality demands for WM barley are similar as for the spring malting barley and it is expected to contain low N share (11.2-1.65%), high starch share (60-65%), great 1000 kernel weight and high diastatic power of malt.<sup>5</sup> The results in Table 2 show that all tested varieties have the demanded percentage of first class grain (88.5%),<sup>13</sup> except the control variety Grace that showed a significantly lower share of the first class grain. Although this should be considered in the light of the fact that all tested material was taken as processed and clean grain (no field testing were conducted), the reason for the results deviation of the control sample could be that Grace is a variety from Northern Europe. Namely, forced maturation is a common phenomenon related with the climatic conditions of our region and domestic varieties have well adapted to it, whereas Grace had no time to adapt. It is well known that forced maturation significantly deteriorates agro-economic and technological grain quality.<sup>15</sup> Thousand kernel weight for all varieties was >45 g. This classifies all varieties as heavy barley, which is an excellent score from the malting point of view. Line OSK.5.45/2-15 showed excellent results even though this was previously processed grain. The average values of vitreosity indicate that all tested varieties have the recommended number of starchy kernels, >80%. Average vitreosity is an indicator of possible problems during malting, such as weak endosperm degradation.<sup>16,17</sup> Germinative capacity represents the percentage of grains that germinate under normal malting conditions, is determined after 5 days and should be >98%. Again, according to this parameter, all tested varieties showed satisfactory results. Total protein content was within the recommended values (10.5-11.5%) for all varieties, Pivarac showed excellent value. Starch share in the endosperm should be as high as possible since it contributes to the fermentable extract and directly influences the produced ethanol during fermentation. Starch and proteins formally correlate, meaning they complement each other

up to 100. This is obvious from Table 2 where it is visible that the variety with higher 1000 kernel weight contains a higher starch share, while this is not the case for protein content. Pivarac variety had a lower share of proteins and less starch content than OSK.5.33/23-15. The share of  $\beta$ -glucans in the grain can have a huge impact on the technological quality of a certain variety.<sup>18</sup>. Although the final value for  $\beta$ -glucan content in wort is one of the most important parameters in brewing, it is, nevertheless, recommended that the initial values do not exceed 4g/100g dm.<sup>13</sup>Regarding this demand for malting barley, varieties OSK.5.45/2-15, Pivarac and Grace showed borderline values, while OSK.5.33/23-15 oversteps the aimed values.

#### Table 2: Quality characteristics of the tested barley varieties

			Samp	le of culti	var				
- Physical analysis:		OSK.5.45/ 2-15		OSK.5.33/PIVARAC 23-15		GRACE (control)			
1 Grading	above 2.8	86.9		90.8		82.6		63.7	
	mm (%) above 2.5 mm (%)	9.8	96.7	7.8	98.6	14.0	96.6	29.0	92.7
	above 2.2 mm (%)		1.3		0.5		2.4		6.5
2	Tailings (%)	2.0		0.9		1.0		0.8	
3	Breakage (%) Thousand kernel	0.2		0.3		0.5		0.2	
7	weight (g/dm)	49.86		50.72		45.66		47.58	
5	Test weight (kg/hL)	72.07		70.09		69.25		68.45	
6	Average vitreosity (%)	2		0		3		1	
Physiologi	cal analysis:								
7	Germinative capacity								
	(%)	98		98		98		98	
Chemical a	analysis:								
8	Moisture content of								
-	grain (%)	11.9		12.2		12.0		11.9	
9	Total proteins								
	(g/dm)	9.6		11.5		10.5		9.7	
10	Starch (%)	61.8		61.8		60.4		58.8	
11	β-glucan (g/100 g dm)	4.1		4.4		4.8		4.2	

Considering the quality of finished malts (Table 3), quality indicators can be categorized into several groups: the ones that indicate the successful cytolytic degradation; indicators of starch degradation and indicators of protein degradation. Some of the quality indicators intertwine and they have to be considered separately. The tested samples had excellent 1000 kernel weight, but, again, it should be taken into consideration that previously processed grain was used, which is not the case in malt factories. Furthermore, a uniform decrease of 1000 kernel weight can be noticed in malt samples, in comparison with barley samples. This represents an equal grain modification in all tested varieties. Total protein content in all tested samples was satisfactory, except for line OSK.5.33/23-15 which held its value below the recommended limit. It is often more useful to use the N share as a better indicator, which is obvious from Table 3 where OSK.5.33/23-15 and Pivarac go over the aimed values. Soluble N is the N that ends up in wort and the results of this research put the tested varieties among the recommended values. However, the control variety Grace showed lower values for soluble N.

Kolbach index is defined as the ratio of total and soluble proteins and gives the information on how successful the proteolysis was during malting. Pivarac had somewhat lower values than recommended. Free a-amino N is the low-molecular N. important for fermentation as N source for the yeast metabolism and is also a part of the fermentable extract. In this research, free α-amino N was lower than recommended values in all varieties. However, recent research consider lower values (than currently recommended) as safe for yeast.<sup>19</sup> Hartong number (VZ°45) is a good indirect indicator of cytolytic and proteolytic enzyme activity and represents the share of extract obtained at 45°C, which is the optimal temperature for the activity of cytolitic enzymes. Experienced maltsters can estimate the malting quality of a certain barley variety by looking just at several indicators: fine extract, Kolbach index and Hartong number. The most significant malt characteristic is the amount of extract. The, so-called, laboratory utilization of extract is the indirect criteria for fermentation guantification.<sup>20</sup> Malting variety Pivarac had a higher share of fine extract than the tested WM lines. The extract difference is connected with the grain's ability to be degraded and correlates with the grain's friability. Varieties with high F/C (fine/ coarse) difference have significantly lower friability than the aimed values. Fermentability, or the final attenuation limit, of the congress wort points out to the actual extract utilization, respectively, the amount of produced ethanol by a certain amount of attenuated wort (i.e. 410-430L of alcohol/1ton of malt).<sup>21</sup> Fermentability, because it can be can be influenced by many factors, should be observed separately.22 The tested line OSK.5.45/2-15, has showed excellent values for fermentability, while Pivarac and Grace fall under category acceptable. This is surprising since the indicators that indirectly point out to the grain's modification degree ( $\beta$ -glucan, F/C difference, friability, viscosity of wort) showed off significantly better for OSK.5.45/2-15 in comparison to the rest of the varieties that had significantly lower or higher values than the recommended ones. This could have a negative or positive cumulative effect on the attenuation limit.23 Hence, the friability and viscosity of OSK.5.33/23-15 line and Pivarac variety are not within the recommended limitations, and if we consider the  $\beta$ -glucan values (Table 3), it can be seen that these values are not within the borderlines, too. The activity of enzymatic complexes are expressed as total diastatic power and  $\beta$ -amylase activity. Diastatic power is the common term for the activity of all malt enzymes that partake in the starch degradation process. This indicator can give the information on the activity of  $\beta$ -amylase, while  $\alpha$ -amylase forms in the course of malting and is mostly phenotypically determined. In general, the enzymatic activity of Northern European varieties has a tendency to be higher because of the forced maturation, a very often occurring effect in warmer climate areas. Forced maturation is extremely unfavourable for barley and malt guality indicators.<sup>24</sup> The aimed values are set according to the Northern European climatic conditions, a factor that cannot be influenced. This directs the conclusions of this research that the obtained values can be considered as acceptable and in accordance with the recommended values for all tested varieties. The rest of the determined indicators are within the recommended limits. Further investigations can be conducted on correlation of wort colour with total share and distribution of protein fractions and FAN in malt.

		cultivar				
		OSK.5.45/ 2-15	OSK.5.33/ 23-15	PIVARAC	GRACE (control)	Recommended value
1	Moisture (%)	4.3	4.5	1.9	4.9	4.5-5*
2	Thousand corn weight (g dm.)	46.9	47.7	43.1	42.8	25-35+
3	Total proteins (%)	8.9	11.1	9.8	8.2	≤ <b>12.8</b> ***
4	Soluble proteins (%)	4.00	3.75	3.31	2.94	4.4-5.6***
5	Total N (g dm.)	1.42	1.78	1.57	1.31	1.5** < 11.5⁺
6	Soluble N (g dm)	0.64	0.60	0.53	0.47	0.55-0.75+
7	Kolbach index	45	34	34	36	40-47***
8	FAN (mg/100 g dm.)	134	122	102	92	
9	FAN (mg/L)	150	136	113	102	>190***
10	Hartong number VZ°45 (%)	37.3	33.9	32.0	29.4	36-41+
11	Coarse extract content (% dm)	82.2	77.7	81.0	80.5	/
12	Fine extract content (% dm)	82.9	80.9	83.7	83.7	> 77.5** >81***
13	Extract difference (%)	0.7	3.2	2.7	3.2	< 1.0* < 1.2*** < 2.5*
14	Saccharification rate (min)	10-15	15	10-15	15	< 2.5 10 – 15⁺
15	Odour of wort	Ν	Ν	Ν	Ν	Ν
16	Attenuation limit (%)	86	80	76	79	> 88* 87** > 80*
17	Clarity (EBC)	3	2	3	4	
18	Wort colour (EBC)	3.2	2.9	2.8	2.6	3-5⁺
19	Colour congress wort after boiling (EBC)	5.3	4.9	4.3	4.0	2-2,5+
20	Filtration rate (min)	Ν	Ν	Ν	Ν	
21	pH of wort	6.02	6.04	6.05	6.1	5,9 - 6,1+
22	Viscosity of wort)	1.49	1.68	1.72	1.8	<1,5*** < 1.80⁺
23	Friability (%)	97.0	70.0	74.0	75.0	> 80+
	Glassy corns (%)	0.1	0.8	0.4	1.0	< 2,5+
		1.0	15.0	11.0	11.4	
	Partly glassy corns (%)	1.0	15.0	11.0	11.4	/
24	$\beta$ -glucan (mg/L)	135	>500	485	>500	<100***
25	Diastatic power (°WK dm )	110	124	108	125	150-300+
26	α-amylase (DU dm.)	49	38	42	39	65 °DU** >50*** 30-50⁺

 Table 3: Quality indicators of finished malts

\* according to Russel (2003); \*\*according to Ann. (2017); \*\*\*Ann. (2008); \*MEBAK (1997)

## Conclusion

This research has shown that the tested varieties of spring barley have the potential to become good or excellent WM varieties and should be monitored for statistically significant period of time (3-5 years). The tested quality values of the OSK.5.33/23-15 has shown they were the closest to the recommended values for whisky malts. In all tested varieties  $\beta$ -glucans content should be reduced in order to improve the F/C extract difference and friability and to increase the fermentability and extract yield during fermentation.

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#### **Conflict of Interest**

The authors do not have any conflict of interest.

#### Reference

- 1. Trimindis A. Single malt whisky is produced from three main ingredients, barley, water and yeast. Why Barley?, www.singlemaltlodge. com. Accessed March 1, 2019.
- Krstanović V, Lalić A, Kosović I, Velić N, Mastanjević K, Mastanjević K. A survey of total β-glucan content in Croatian barley varieties. *Cereal Res Commun.* 2016; 44(4):650-657. doi:10.1556/0806.44.2016.032.
- Wood J., and Kelliel D. Evaluating the feed vs. malt barley production choice. Economics & Competitiveness-AgriProfit Technical Bulletin, Agriculture and Rural

Developmment Gov. of Alberta. https://www1. agric.gov.ab.ca/\$Department/deptdocs.nsf/ all/econ10236/ \$FILE/TB\_ Evaluating%20 Feed%20vs%20Malt%20Barley\_April%2016, %202013.pdf. Accessed January 15, 2019.

- 4. DeClerck J. Textbook of brewing. London UK: Chapman and Hall; 1957.
- Dillon G. How Scotch Whisky is Made #1: Barley. https://flaviar.com/blog/barley-in-thewhisky-making-process. Published Oct.13<sup>th</sup> 2016. Accessed January 06, 2019.
- Patterson HD, Silvey V. Statutory and Recommended List Trials of Crop Varieties in the United Kingdom. J R Stat Soc Ser A. 1980;143(3):219. doi:10.2307/2982128.
- Thomason WE, Phillips SB. Methods to evaluate wheat cultivar testing environments and improve cultivar selection protocols. *F Crop Res.* 2006;99(2-3):87-95. doi:10.1016/J.FCR.2006.03.007.
- 8. Ann. List of preferred varieties of malteurs de france and brasseurs de France malting

barley crop 2017.

http://www.secobra.fr/downloads/en/files/ List%20of%20preferred%20varieties %20 -malting%20barley%20-%202017%20crop. pdf. Accessed January 12, 2019.

- Ann. Crop Report #1 for German 2016 Spring Barley BESTMALZ (2016). https://bestmalz. de /en/crop-report-1-german-2016-springbarley/. Accessed December 04, 2018.
- 10. Ann. Malting Barley Report September 2015 - Viking Malt.

https://www.vikingmalt.com /wp-content/ uploads/2015/09/Malting-Barley-Report-September-2015.pdf. Accessed December 12, 2018.

- 11. Hertrich. Topics in Brewing: Malting Barley. *Tech Q.* 2013. doi:10.1094/TQ-50-1-0331-01.
- 12. EBC (European Brewery Convention), Analytica 5. ed. (1998), Getränke-Fachverlag Hans Carl, D - Nürnberg
- MEBAK Middle European Brewing Analysis Commission), Brautechnische Analysenmethoden 3.ed. Band I (1997), Selbstverlag der MEBAK, Freising-Weihenstephan
- 14. ICC International Association for Cereal Science and Technology – Standard method (2003). Vienna, Austria
- Singh S., El Maayar M., André P., Bryant C.R., Thouez J.P. (1998). Impacts of a Ghginduced climate change on crop yields: effects of acceleration in maturation, moisture stress and optimal temperature. *Clim Chang.* 1998;38(1), 51-86.

doi.org/10.1023/A:1005392517715

- Allison MJ, Borzucki R, Cowe IA. Variation in a Barley Collection for Endosperm Attributes that Relate to Malting Quality. J Inst Brew. 1979;85(2):86-88. doi:10.1002/j.2050-0416.1979.tb06831.x.
- Nair S, Knoblauch M, Ullrich S, Baik B-K. Microstructure of hard and soft kernels of barley. *J Cereal Sci.* 2011;54(3):354-362. doi:10.1016/J.JCS.2011.06.014.
- Gupta M., Nissren A.G., Gallaghar E. Barley for brewing (2010): Characteristic changes during malting, brewing and applications of its products. Food Science and Food Safety, 9, 318-328. https://doi.org/10.1111/j.1541-4337.2010.00112.x
- Lekkas C, Hill AE, Taidi B, Hodgson J, Stewart GG. The Role of Small Wort Peptides in Brewing Fermentations. *J Inst Brew.* 2009;115(2):134-139. doi:10.1002/j.2050-0416.2009.tb00358.x.
- 20. Marić V.Tehnologija piva. Karlovac, Croatia:

Veleučilište u Karlovcu; 2009.

- Bathgate G.N. A review of malting and malt processing for whisky distillation. *J Inst Brew.* 2016;122(2), 197-211. doi.org/10.1002/ jib.332
- Koljonen T, Hämäläinen JJ, Sjöholm K, Pietilä K. A model for the prediction of fermentable sugar concentrations during mashing. *J Food Eng.* 1995;26(3):329-350. doi:10.1016/0260-8774(94)00061-D.
- Edney MJ, LaBerge DE, Langrell DE. Relationships Among the β-Glucan Contents of Barley, Malt, Malt Congress Extract, and Beer. *J Am Soc Brew Chem.* 1998;56(4): 164-168. doi:10.1094/ASBCJ-56-0164.
- Tabatabaei SA. The effect of aging on germination of barley seeds the changes of germination characteristics and enzyme activity of barley seeds under accelerated aging. *Cercetări Agronomice în Moldova*. 2015;48(2):61-67.