



β-Glucan Degradation During Malting of Different Purpose Barley Varieties

Kristina Habschied ^{1,*}, Alojzije Lalić ², Daniela Horvat ², Krešimir Mastanjević ^{1,*}, Jasmina Lukinac ¹, Marko Jukić ¹ and Vinko Krstanović ¹

- ¹ Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, F. Kuhača 20, 31000 Osijek, Croatia; ptfosptfos2@gmail.com (J.L.); ptfosptfos@gmail.com (M.J.); vkrstano@ptfos.hr (V.K.)
- ² Agricultural Institute Osijek, Južno predgrađe 17, 31000 Osijek, Croatia; alojzije.lalic@poljinos.hr (A.L.); daniela.horvat@poljinos.hr (D.H.)
- * Correspondence: kristinahabschied@gmail.com (K.H.); kmastanj@ptfos.hr (K.M.); Tel.: +385-31-224-300

Received: 27 December 2019; Accepted: 4 February 2020; Published: 6 February 2020



MDP

Abstract: The aim of this study was to investigate the possibility of predicting the concentration of β -glucan from starting barley and malt, as well as malt and wort for different types and purpose of barley groups. The strength of the correlation between types and purpose of barley groups was determined between the values of β -glucans and other indicators of cytolytic degradation. Statistically significant correlations were obtained for β -glucans in barley-malt (r = 0.9717) and barley-wort (r = 0.9998) for brewing (B *w*-*tr*) and brewing/feed winter two-row (B/Fe *w*-*tr*) varieties, and for brewing/brewing feed/feed spring varieties (B/B-Fe/Fe *w*-*tr*) between barley and Δm ($\Delta m = \beta$ -glucan difference between barley and malt) (r = 0.8779). For the dual-purpose varieties (B/Fe *w*-*tr*), a strong correlation for β -glucan in malt in regard to the starting β -glucan in barley) (r = -0.9099), as well as Δm and Δm^* (r = 0.9951). The results indicate that the starting concentration of β -glucan in barley and malt can be used as predictors of their concentration in wort only in brewing and dual-purpose (brewing-feed) varieties.

Keywords: barley; β-glucan degradation; different purpose varieties

1. Introduction

Malting is a process of forced germination, conducted in order to degrade starch molecules and to obtain certain levels of amylolytic and proteolytic enzymes which are important in brewing. In short, the grains are soaked in water, left to germinate, and the germination is then halted by drying with hot air. During malting, it is important to ensure the degradation of the polysaccharide components of the endosperm cell walls in order to obtain the sufficiently deep modification of the grain for satisfactory brewing performance. Better malting performance is associated with lower levels of β -glucan content in grains and higher levels of β -glucanase in malted barley [1–5]. The high starting content of β -glucan in barley can lead to insufficient degradation of cell walls, which in turn hinders the diffusion of enzymes produced during the mobilization of kernel reserves and disrupts many quality parameters of finished malt. The levels of β -glucan in wort are influenced by their initial concentration in malt and β -glucanase activity during germination but can also be affected by the malting process itself [1]. In order to avoid the process problems associated with the elevated content of β -glucan (poor lautering performance and colloidal (in) stability of the finished beer), the main objective of optimizing the malting process, with respect to β -glucans, is to obtain their low concentration in the wort and, consequently, in the beer [6,7]. However, it is very difficult to optimize the malting process for multiple quality indicators because some are mutually exclusive (i.e., deep β -glucan degradation is

regularly accompanied by enhanced proteolysis, etc.). For this reason, brewers rely on barley varieties proven for malting and brewing properties. They are relatively reliable for the prediction of the final concentration of β -glucan in malt and wort, based on the knowledge of their starting concentration in barley. Recently, the emergence of new winter dual-purpose barley varieties (brewery, livestock, and B/Fe) have resulted in several acceptable varieties in brewing practice [8]. Dual-purpose two-row barley varieties show higher yields (tons per hectar) as compared with malting barley varieties, which makes these varieties attractive to barley growers. According to Broderick et al. [9], two-row barley results with malt exhibit higher extract, are lighter in color, and have lower enzyme content than the six-row type. Upon Croatia's entry into the European Union (EU), the Croatian market has been opened to malting barley varieties. For varieties that have shown good quality indicators for brewing and were so-far labeled as feed varieties, the Croatian Varietal Commission has allowed dual-purpose labeling.

The aim of this paper is to determine the confidence level for predicting the degradation of β -glucan in chosen varieties during malting.

2. Materials and Methods

2.1. Barley Samples

All available barley (*Hordeum vulgare* L.) varieties of the Agricultural Institute Osijek were selected for this investigation. A total of 25 varieties were included as follows: feed winter two-row (Fe *w*-*tr*) as Group 1; dual-purpose varieties brewing-feed winter two-row (B/Fe *w*-*tr*) as Group 2; brewing (B *w*-*tr*) as Group 3; feed winter six-row (Fe *w*-*sr*) as Group 4; brewing, feed-brewing and feed spring two-row (B *s*-*tr*, B/Fe *s*-*tr*, Fe *s*-*tr*) as Group 5; and naked barley (H) as Group 6. All varieties tested were obtained from variety trials conducted under the same conditions and at the same location (Osijek) in order to maximize the equal impact of environmental and agrotechnical factors on them. Sampling was performed on cleaned and processed barley grains according to the EBC (European Brewery Convention) 3.3.1. method [10] and the samples were kept refrigerated in sterile dry containers. Grain samples (10 kg per sample) were collected as untreated and conditioned grain (according to the EBC 3.3.1. method) and packed in double-walled paper bags. Until micro malting, the material was stored for two months in a dry and cool place (20 °C) to overcome post-harvest grain dormancy.

2.2. Micro Malting

Micro malting was conducted in a micro malting plant (Joe White Malting Systems Pty Limited in East Melbourne, Victoria, Australia) using an Automatic Micro Malt Unit, 10 kg capacity, according to the procedure shown in Table 1. After micro malting, the degermination was performed manually. Malt was stored for one month in order to stabilize the moisture content. Malting was done in duplicate for each variety.

	Micro Malting Stage	Air Flow (%)	T (°C)	t (h)
	immersion steeping	-	16	5
	dry steeping	100	17	12
Steeping	immersion steeping	-	17	6
	dry steeping	100	18	12
	immersion steeping	-	17	2
	dry steeping	moisture correcti	on to 44.5% by spra	ying with water
	germination parameters	75	17	96
Germination	turning over time: 2 number of rotations during	turn over: 3		

Table 1. The applied micro malting scheme of barley samples.

	first phase	100	60	6	
	second phase	100	65	3	
	third phase	90	68	2	
Kilning	fourth phase	90	70	2	
	fifth phase	50	80	2	
	sixth phase	50	83	2	
	seventh phase	40	85	1	

Table 1. Cont.

2.3. β-Glucan Analysis

The determination of total β -glucan content in barley was conducted in accordance with EBC Method 3.11.1, in accordance with EBC Method 4.16.1 for malt, and EBC Method 8.11.1. for wort [10]. First, the barley samples were milled using a standard laboratory mill with a 1 mm sieve (MF10.2 basic, IKA Labortechnik, Freiburg, Germany) and after that, using a DLFU Mill Buhler 0.2 mm. The ground samples were kept in sealed plastic bags until the enzymatic determination of total β -glucan content. Mixed linkage β -glucan assay kit purchased from Megazyme Int., Bray, Ireland was used for β -glucan quantification. Congress worts were prepared according to EBC Method 4.5.1. Friability, extract, extract difference, and wort viscosity (indicators of cytolitic degradation) were also determined in the samples. The analyses of malt quality indicators were performed accordingly to EBC [10] and MEBAK (Middle European Brewing Analysis Commission) [11] methods. The analysis, for each sample, was done in triplicate.

2.4. Statistical Analysis

Statistical analysis was carried out using Statistica Ver. 8.0 (StatSoft Inc., Tulsa, OK, USA). Data analysis of the raw materials, micro malting, and finished malt quality indicators were done in triplicates. The same parameters were subjected to correlation analysis (Pearson's correlation test) in order to determine possible statistically meaningful relationships.

3. Results and Discussion

From the data presented in Tables 2 and 3, it can be seen that the range of β -glucan concentrations in the tested varieties (3.18% to 5.49%) differed significantly by individual tested varieties and by the tested cultivar groups. Brewing (B w-tr) and about 50% of the dual-purpose (brewing/feed) varieties (B/Fe w-tr) resulted with recommended concentrations of β -glucan in barley (4%) [2,12]. The average value for the tested varieties (B/Fe *w*-*tr*) was 3.90%, which was significantly lower than the concentration in the control varieties (Casanova and Sandra), but slightly higher than in the strictly brewing varieties (B *w*-tr) (Table 3). The obtained results are in agreement with the average values obtained in previous research by Krstanović et al. [12], in 2016. This confirms that the β -glucan content is a relatively stable and predominantly genotypically determined variety trait, although other factors (i.e., climatic conditions, agrotechnical measures, and soil type) can also contribute to the total β -glucan content in barley [13]. The determined shares of β -glucan by type and end-use group of varieties showed expected values. It is evident from Tables 2 and 3 that the feed varieties (Fe *w*-*tr*) showed higher concentrations of β -glucan, but some B/Fe *w*-tr varieties had shares similar to that of the Fe *w*-tr varieties (Table 2). The β -glucan molecules are subjected to degradation during the germination phase when the cytolytic degradation takes place. The β -glucan degradation has to be conducted in such a way to provide the satisfactory extract content. However, it is important to ensure that soluble β -glucan (as well as other undesirable constituents such as soluble and high molecular weight N) stays within the recommended limits. Therefore, it is important to keep the β -glucan degree of degradation (in its absolute amount of β -glucan in malt and Δm) and the percentage of β -glucan reduction in the grain (Δm^*) as high as possible. From the results obtained for β -glucan content in malt, Δm and respectively Δm^* (Table 3) it can be seen that brewing (B w-tr) and two-row spring varieties exhibited the best degradation results

existing literature, the expected and desirable β -glucan degradation can reach approximately 50% to 60% [1,14,15], but maximally 80% [16].

Although these results are not conditioned only by genotype, but rather by a number of factors related to the process conditions during malting [1,2], it can be stated that the degradation degree for the tested dual-purpose varieties should be at least 70%.

The main goal of malting process optimization with respect to β -glucan content is to obtain the lowest possible concentrations in wort and, consequently, in beer. Depending on the recommendations, the results shown in Tables 2 and 3 are considered good, acceptable, or unacceptable because the recommendations significantly differ from one another. Edney et al. [17] reported wort β -glucan content ranging from 60 to 140 mg/L for Canadian barley varieties. Although, for brewers, there are no recommendations regarding the total β -glucan content in malt, the recommendation for wort is <200 mg/L [18].

The American Malting Barley Association is even more stringent and recommends that β -glucan concentrations in the wort should not exceeded 100 mg/L for two-row barleys, whereas the limit for six-row barley is <120 mg/L [19]. However, in everyday practice, higher values are tolerated, i.e., the IGB (Institute & Guild of Brewing) has reported a limit of <200 mg/L [20], whereas the EBC [10] tolerates <250 mg/L. According to this, the expected good results were obtained for the B *w*-*tr* (Vanessa and Tiffany) and the two-row spring varieties (*s*-*tr* B/B-Fe/Fe). Pivarac, a spring variety, showed an extremely low value for β -glucan content in wort. Some of the tested dual-purpose B/Fe *w*-*tr* varieties showed acceptable values. All other varietal groups resulted with high content of β -glucan in wort. Although the tested B/Fe *w*-*tr* varieties had a starting concentration of β -glucan similar to the control varieties, a significantly lower β -glucan degradation occurred which resulted in higher concentrations in malt and, consequently, in wort (Table 2). In this case, the tested B/Fe *w*-*tr* varieties exhibited a significantly lower degree of degradation as compared with the B/Fe *w*-*tr* control varieties and brewing varieties (Tables 2 and 3), with Maestro showing the best value.

				Moisture (%)						
Group	Type/End use	nd use	Variety	Worst	lre (%)		(g/100 g d.m.)		(%)	(mg/L)
				Barley	Malt	Barley	Malt	Δm	Δm^*	Wort
		1	Bravo	10.56 ± 0.00	7.44 ± 0.01	4.22 ± 0.10	1.69 ± 0.06	2.53 ± 0.04	60.0 ± 1.31	268.40 ± 0.70
		2	Bingo	10.70 ± 0.00	7.54 ± 0.04	4.07 ± 0.05	2.72 ± 0.02	1.35 ± 0.03	33.2 ± 0.47	303.23 ± 1.41
1	Fe / <i>w</i> - <i>tr</i>	3	Maxim	11.14 ± 0.06	7.69 ± 0.02	4.05 ± 0.03	2.54 ± 0.03	1.51 ± 0.06	37.3 ± 1.23	288.86 ± 0.50
		4	Rex	10.86 ± 0.01	7.03 ± 0.02	5.49 ± 0.14	2.90 ± 0.07	2.59 ± 0.07	47.2 ± 0.10	323.18 ± 0.25
		5	Tuna	10.79 ± 0.01	7.77 ± 0.07	4.14 ± 0.07	2.16 ± 0.04	1.98 ± 0.03	47.8 ± 0.14	295.09 ± 0.20
		6	Barun	10.71 ± 0.07	7.64 ± 0.01	3.52 ± 0.02	1.63 ± 0.04	1.89 ± 0.02	53.7 ± 0.82	205.34 ± 0.71
		7	Lukas	11.47 ± 0.04	7.48 ± 0.08	4.13 ± 0.07	1.87 ± 0.14	2.26 ± 0.07	54.7 ± 0.95	317.33 ± 0.24
		8	Gazda	10.84 ± 0.11	7.49 ± 0.02	3.86 ± 0.09	2.61 ± 0.07	1.25 ± 0.05	32.4 ± 0.61	334.95 ± 0.64
2	B-Fe / <i>w</i> - <i>tr</i>	9	Maestro	10.91 ± 0.02	7.25 ± 0.01	4.17 ± 0.21	1.53 ± 0.02	2.64 ± 0.20	63.3 ± 1.12	247.23 ± 0.75
		10	Osk. 6.61-4-13	11.14 ± 0.05	7.75 ± 0.01	3.18 ± 0.08	1.91 ± 0.02	1.27 ± 0.05	40.0 ± 0.69	210.01 ± 0.83
		11	Casanova ⁺	11.77 ± 0.00	7.44 ± 0.05	3.92 ± 0.03	1.05 ± 0.03	2.87 ± 0.02	73.2 ± 0.81	153.39 ± 0.91
		12	Sandra ⁺	11.43 ± 0.04	7.62 ± 0.02	4.55 ± 0.04	1.85 ± 0.04	2.7 ± 0.02	59.3 ± 0.47	237.59 ± 0.67
3	B/w-tr	13	Vanessa	11.85 ± 0.03	7.54 ± 0.01	3.63 ± 0.42	1.02 ± 0.03	2.61 ± 0.39	72.0 ± 0.88	110.71 ± 0.70
3	\mathbf{D}/ω - $\iota \mathbf{r}$	14	Tiffany	11.70 ± 0.06	7.54 ± 0.02	3.55 ± 0.35	0.83 ± 0.03	2.72 ± 0.33	76.6 ± 0.98	100.15 ± 0.80
		15	Titan	11.28 ± 0.09	7.46 ± 0.00	4.09 ± 0.07	1.96 ± 0.10	2.13 ± 0.14	52.0 ± 1.01	287.60 ± 1.15
4	Fe/w-sr	16	Lord	11.15 ± 0.05	7.58 ± 0.04	4.07 ± 0.14	2.05 ± 0.07	2.02 ± 0.15	49.6 ± 0.89	268.85 ± 0.74
		17	Oliver	11.38 ± 0.08	7.94 ± 0.00	4.22 ± 0.15	1.87 ± 0.14	2.35 ± 0.04	55.7 ± 0.94	264.72 ± 0.81
		18	Matej	11.33 ± 0.03	7.66 ± 0.06	4.06 ± 0.14	1.27 ± 0.07	2.79 ± 0.09	68.7 ± 0.62	235.27 ± 1.02
		19	Stribor	11.02 ± 0.06	5.53 ± 0.06	4.18 ± 0.07	0.83 ± 0.03	3.35 ± 0.04	80.0 ± 0.35	179.46 ± 0.75
5	B/Fe/B-Fe/s-tr	20	Jaran	11.37 ± 0.03	7.64 ± 0.12	4.15 ± 0.10	1.40 ± 0.07	2.75 ± 0.03	52.8 ± 0.93	192.41 ± 0.72
5	D /1 C/D-1 C/3-11	21	Ikar	11.11 ± 0.00	7.29 ± 0.05	4.50 ± 0.21	1.35 ± 0.05	3.15 ± 0.17	70.0 ± 0.51	149.65 ± 0.76
		22	Dado	10.73 ± 0.01	7.37 ± 0.13	5.11 ± 0.08	1.22 ± 0.11	3.89 ± 0.04	76.0 ± 1.06	155.22 ± 0.80
		23	Pivarac	11.53 ± 0.08	7.29 ± 0.04	4.80 ± 0.21	0.83 ± 0.07	3.97 ± 0.19	82.7 ± 0.35	80.70 ± 0.49
6	Н	24	Osvit	11.51 ± 0.08	7.21 ± 0.02	4.83 ± 0.09	2.78 ± 0.06	2.12 ± 0.04	42.5 ± 0.15	312.86 ± 0.75
0	11	25	Osk. 5.119-10-12	11.33 ± 0.11	7.29 ± 0.06	4.51 ± 0.20	2.93 ± 0.14	1.58 ± 0.07	35.0 ± 0.19	280.47 ± 0.33

Table 2. Shares and mass difference for β -glucan content in barley, malt, and wort.

1, **2**, **3**, **4**, **5**, **6** = group of varieties; **B**, **Fe**, **Fe**-**B**, **H** = end use of varieties; *w*-*tr*, *w*-*sr*, *s*-*tr*, *H* = tip of varieties; ⁺ = dual-purpose B/Fe control varieties; $\Delta \mathbf{m} = \Delta \mathbf{m} \beta$ -glucan (barley-malt); $\Delta \mathbf{m}^* = \%$ of degraded β -glucan in malt in regards to the starting β -glucan in barley; all values are shown as average \pm SD.

	β-glucan					
Group/Type/End Use	(g/100 g d.m.)			(%)	(mg/L)	
	Barley	Malt	Δm	Δm^*	Wort	
1 Fe <i>w</i> - <i>tr</i>	4.39 ± 0.55	2.40 ± 0.46	1.99 ± 0.53	45.3 ± 10.12	295.75 ± 18.97	
2 B/Fe <i>w-tr</i> B/Fe <i>w-tr</i> CONTROL	3.90 ± 0.43 4.24 ± 0.23	1.78 ± 0.44 1.45 ± 0.43	2.12 ± 0.65 2.79 ± 0.48	54.4 ± 13.14 65.8 ± 12.15	243.69 ± 61.45 195.49 ± 22.13	
3 B w-tr B w-tr + B/Fe <i>w-tr</i> CONTROL	3.59 ± 0.32 3.91 ± 0.45	0.93 ± 0.11 1.19 ± 0.21	2.66 ± 0.32 2.72 ± 0.29	74.1 ± 3.75 69.6 ± 2.65	$105.43 \pm 6,12$ 150.46 ± 7.11	
4 Fe w-sr	4.13 ± 0.36	2.0 ± 0.38	2.13 ± 0.58	51.6 ± 11.79	273.72 ± 56.76	
5 (B/B-Fe/Fe) s-tr	4.47 ± 0.38	1.15 ± 0.25	3.32 ± 0.39	74.3 ± 6.44	165.45 ± 49.07	
6 (H)	4.67 ± 0.26	2.86 ± 0.11	1.81 ± 0.29	38.8 ± 4.23	296.67 ± 18.55	

Table 3. The average share and mass difference in β -glucan content in barley, malt, and wort by tested purpose groups.

1, **2**, **3**, **4**, **5**, **6** = group of varieties; **B**, **Fe**, **Fe**-**B**, **H** = end use of varieties; *w*-*t*,*w*-*sr*, *s*-*tr*, *H* = type of varieties; $\Delta \mathbf{m} = \Delta \mathbf{m} \beta$ -glucan (barley-malt); $\Delta \mathbf{m}^* = \%$ of degraded β -glucan in malt in regards to the starting β -glucan in barley; all values are shown as average \pm SD.

In order to obtain the results for a reliable prediction of β -glucan concentration in wort, based on its concentration in barley and malt, it is necessary to establish a strong correlation between these parameters. In Table 4, a statistically significant correlation between the β -glucan share in barley, malt, and wort and its degradation degree during malting (Δm and Δm^*) for different purpose varieties is presented. A strong positive correlation between malt/wort in Group 1 (Fe w-tr) was found. For the B/Fe w-tr and B w-tr varieties, strong positive correlations were determined for concentrations of β -glucan between barley and malt, as well as barley and wort. As expected, a negative correlation between β -glucan concentrations in malt and the degree of degradation Δm^* was also established. For B/Fe *w*-tr (control) and B *w*-tr varieties, strong positive correlations were obtained between the starting barley and malt, and between malt and wort. For these varieties, a strong correlation between malt/wort was expected [17,21], but a very high correlation between barley/malt and barley/wort was a bit surprising. These varieties serve as longstanding standards in the brewing barley selection and are used strictly for brewing purposes, thus, a reliable prediction of β -glucan degradation and its final concentration in wort can be obtained. In the case of B/B-Fe/Fe s-tr spring varieties, a strong positive correlation was found only between the concentration of β -glucan in barley and its degradation in the absolute amount (Δm). Indicators of the cytolytic degradation and the percentage loss of β -glucan from barley to malt (Δm^*) were determined for the tested assortment, the values of which are shown in Table 5. With respect to the individual values, it can be observed that the tested B/Fe *w*-*tr* varieties have a significantly lower friability than recommended (>80%). The B/Fe *w*-tr control varieties and B *w*-tr varieties were borderline acceptable, whereas most B/Fe *w*-tr varieties did not show satisfactory values. The other tested varieties also showed a similar trend. When used in conjunction with other analyses that indicated malt modification, friability was a great tool that indicated lautering performance because slow lautering was often a consequence of under-modification of malts which lead to increased viscosity. A strong negative correlation between friability and extract difference for B/Fe w-tr, Fe *w*-*tr*, and B/B-Fe/Fe *s*-*tr* varieties was established, however, this was not found for other groups of varieties (Table 6). Extract difference is an indicator of endosperm cell walls degradation efficiency. High quality malt has an extract difference <1.80%, whereas extract difference >1.80% defines malt as a moderate quality [8]. A satisfactory value for this indicator was obtained only for the Pivarac variety. A strong negative correlation between Δm^* /friability was expected but was also not reported for the other groups. The expected strong negative correlation of friability/extract difference was only determined for B/Fe *w*-tr and B/B-Fe/Fe *s*-tr varieties. Correlations obtained between coarse extract, extract fine, and extract difference were also expected. Although the authors are aware of the fact that the current literature deviates from the use of standard congress mashing procedure applied in

this research for β -glucan determination and that the performance indicator extract difference (extract fine/coarse) according to EBC and MEBAK is nowadays eliminated from the assessment of brewing malt, some brewers or malsters still use the old performance parameters. Therefore, the values of the extract difference are still presented in this paper. A viscosity value <1.53 mPas represents a very good level of degradation, while >1.68 mPas indicates a weaker degradation level [22]. Satisfactory results were obtained only for the B *w*-*tr* varieties, Cassanova from the B/Fe *w*-*tr* group, and Pivarac and Ikar from the B/B-Fe/Fe *s*-*tr* group. There was no variety from the B/Fe *w*-*tr* and B/Fe *w*-*tr* controls that showed satisfactory results for this indicator. The Casanova variety was closest to the above recommended value. Correlation analysis did not determine the dependence of the degradation rate of β -glucan and the viscosity of the obtained wort for any of the examined group of varieties.

Group of Varieties	Type/End Use	Parameters	r
1	Fe <i>w</i> -tr	malt:wort	0.8971
		malt:wort	0.8188
2	B/Fe w-tr	malt:∆m*	-0.9099
		$\Delta m: \Delta m^*$	0.9523
2	D/E	barley:malt	0.9717
2	B/Fe <i>w</i> -tr _{control}	barley:wort	0.9998
+	+	malt:wort	0.9668
3	B w-tr	malt:∆m*	-0.9951
5	B/B-Fe/Fe s-tr	barley:∆m	0.8779

Table 4. Statistically significant correlation between the β -glucan share in barley, malt, and wort and its degradation degree during malting (Δm and Δm^*) for different purpose varieties (Pearson correlation matrix).

r = correlation coefficient; **1**, **2**, **3**, **4**, **5**, **6** = group of varieties; **B**, **Fe**, **Fe**-**B**, **H** = end use of varieties; *w*-*tr*,*w*-*sr*, *s*-*tr*, *H* = tip of varieties; $\Delta m = \Delta m \beta$ -glucan (barley-malt); $\Delta m^* = \%$ of degraded β -glucan in malt in regards to the starting β -glucan in barley.

	End Use/Type	No	Varieties	Friability (%)	Extract Coarse (%)	Extract Fine (%)	Extract Difference (%)	Viscosity (mPas)
		1	Bravo	52.42 ± 0.11	74.93 ± 0.29	79.17 ± 0.14	4.24 ± 0.02	2.290 ± 0.04
		2	Bingo	36.70 ± 0.09	72.86 ± 0.14	78.84 ± 0.21	5.98 ± 0.03	2.257 ± 0.06
1	Fe w-tr	3	Maxim	22.78 ± 0.17	72.78 ± 0.21	79.09 ± 0.16	6.30 ± 0.05	2.369 ± 0.09
		4	Rex	13.94 ± 0.10	68.86 ± 0.15	77.64 ± 0.23	8.78 ± 0.03	2.338 ± 0.10
		5	Tuna	32.18 ± 0.14	69.78 ± 0.12	76.98 ± 0.25	7.20 ± 0.01	1.870 ± 0.05
		6	Barun	45.68 ± 0.14	73.26 ± 0.13	77.69 ± 0.19	4.44 ± 0.09	1.713 ± 0.11
		7	Lukas	44.54 ± 0.08	74.57 ± 0.08	80.35 ± 0.24	5.79 ± 0.02	2.157 ± 0.05
		8	Gazda	37.70 ± 0.21	71.59 ± 0.28	77.76 ± 0.33	6.17 ± 0.03	2.080 ± 0.12
2	B-Fe w-tr	9	Maestro	59.80 ± 0.28	75.58 ± 0.19	80.02 ± 0.20	4.44 ± 0.03	1.983 ± 0.09
		10	Osk.6.61-4	50.40 ± 0.11	75.00 ± 0.16	79.77 ± 0.26	4.77 ± 0.01	1.784 ± 0.04
		11	Casanova	64.90 ± 0.32	71.65 ± 0.31	79.48 ± 0.11	2.07 ± 0.01	1.6536 ± 0.10
		12	Sandra	60.60 ± 0.20	71.09 ± 0.24	80.27 ± 0.22	3.32 ± 0.05	1.9759 ± 0.09
3	D (13	Vanessa	66.94 ± 0.23	70.98 ± 0.20	79.57 ± 0.17	2.80 ± 0.04	1.5191 ± 0.04
3	B w-tr	14	Tiffany	69.30 ± 0.19	70.89 ± 0.31	79.26 ± 0.31	2.59 ± 0.01	1.5162 ± 0.07
		15	Titan	41.02 ± 0.13	72.17 ± 0.27	78.14 ± 0.25	5.97 ± 0.03	2.107 ± 0.10
4	Fe wsr	16	Lord	40.82 ± 0.19	75.47 ± 0.14	79.72 ± 0.18	4.25 ± 0.02	1.987 ± 0.05
		17	Oliver	36.28 ± 0.10	72.08 ± 0.26	78.71 ± 0.12	6.62 ± 0.05	1.911 ± 0.08
		18	Matej	55.36 ± 0.22	77.51 ± 0.11	81.46 ± 0.36	3.96 ± 0.03	1.818 ± 0.12
		19	Stribor	57.92 ± 0.14	71.84 ± 0.32	81.44 ± 0.30	3.74 ± 0.01	1.8415 ± 0.09
5	B/ Fe/	20	Jaran	56.36 ± 0.17	66.43 ± 0.21	78.21 ± 0.26	6.29 ± 0.01	1.6873 ± 0.10
5	B-Fe/s-tr	21	Ikar	68.80 ± 0.29	79.02 ± 0.12	81.93 ± 0.39	2.91 ± 0.04	1.714 ± 0.10
		22	Dado	66.44 ± 0.17	71.83 ± 0.34	81.18 ± 0.25	3.63 ± 0.07	1.6989 ± 0.08
		23	Pivarac	78.14 ± 0.13	74.61 ± 0.29	82.14 ± 0.30	1.67 ± 0.08	1.5567 ± 0.10
	11	24	Osvit	14.88 ± 0.33	73.80 ± 0.18	83.31 ± 0.29	9.51 ± 0.06	3.220 ± 0.11
6	Н	25	Osk.5.119	34.80 ± 0.21	76.10 ± 0.25	82.96 ± 0.19	6.87 ± 0.09	2.669 ± 0.12

Table 5. Malt quality indicators.

1, **2**, **3**, **4**, **5**, **6** = group of varieties; **B**, **Fe**, **Fe**-**B**, **H** = end use of varieties; *w*-*tr*, *w*-*sr*, *s*-*tr*, *H* = tip of varieties; ⁺ = dual-purpose B/Fe control varieties; all values are shown as average ± SD.

Group of Varieties	Type/End Use	Indicator	r
1	Fe <i>w-tr</i>	friability:extract diff. extract fine:extract coarse	-0.9039 0.8917
		extract fine:extr. diff.	-0.9643
2	B/Fe <i>w-tr</i>	Δm*:friability Δm*:extract diff. friability:extract diff.	0.8614 -0.7956 -0.9247
5	B/B-Fe/Fe <i>s-tr</i>	Δm*:extract fine Δm*:extr. diff. friability:extr. diff. ext. fine:extract coarse ext. fine:extract diff.	$\begin{array}{r} 0.8626 \\ -0.8664 \\ -0.9595 \\ 0.8228 \\ -0.9286 \end{array}$

Table 6. Statistically significant correlation between the established quality indicators of malt and β -glucan loss from barley to malt (Δm^*) for different end use varieties (Pearson correlation matrix).

r = correlation coefficient; **1**, **2**, **5**, **6** = group of varieties; **B**, **Fe**, **Fe**-**B**, **H** = end use of varieties; *w*-*tr*, *w*-*sr*, *s*-*tr* = tip of varieties; $\Delta \mathbf{m} = \Delta \mathbf{m} \beta$ -glucan (barley-malt); $\Delta \mathbf{m}^* = \%$ of degraded β -glucan in malt in regards to the starting β -glucan in barley.

Considering the results obtained for β -glucan and other indicators, we conclude from the correlation analyses results that the tested dual-purpose varieties range shows the expected values for the area of the Pannonian Plain where the phenomenon of the so-called "forced maturation" (accelerated aging) is common and has an adverse effect on numerous grain quality indicators of almost all grains [23].

The results obtained in this study indicate that the depth of β -glucan degradation under the same process conditions during malting is predominantly a variety trait. For each dual-purpose variety, tests should be conducted in a statistically relevant time period on a representative number of samples and only, then, based on the starting data for their concentration in the starting barley, the depth of β -glucan degradation during malting and their expected concentration in the wort could be predicted with sufficient certainty.

The results obtained in this study indicate that the depth of β -glucan degradation under the same process conditions during malting is predominantly a variety trait. For each dual-purpose variety, tests should be conducted in a statistically relevant time period on a representative number of samples and only, then, based on the starting data for their concentration in the starting barley, the depth of β -glucan degradation during malting and their expected concentration in the wort could be predicted with sufficient certainty.

4. Conclusions

A high positive correlation for β -glucan concentrations between barley-malt and barley-wort was determined, but only for the B *w*-*tr* and B/Fe *w*-*tr* control group of cultivars, whereas for the malt-wort it was found in the above groups and in Fe *w*-*tr* and dual-purpose B/Fe *w*-*tr* varieties. A high negative correlation for the degree of degradation of β -glucan Δm^* and their concentration in malt was established for the dual-purpose B/Fe *w*-*tr* and B *w*-*tr* and B/Fe *w*-*tr* control groups studied. On the basis of the results obtained, we conclude that the starting concentration of β -glucan in barley and malt can be the basis for the prediction of their concentration in finished wort only in breweries and already proven dual-purpose varieties, whereas for the other examined groups it is missing. In newly selected dual-purpose cultivars, this prediction cannot be made based on baseline data for β -glucan concentration in barley.

Author Contributions: Conceptualization, V.K.; methodology, A.L. and D.H.; software, K.M. and M.J.; writing—original draft preparation, V.K.; writing—review and editing, K.H. and J.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Narziss, L. *Die Bierbrauerei: Band I: Die Technologie Der Malzbereitung*, 8th ed.; F. Enke Verlag: Stuttgart, Germany, 2012.
- 2. Jamar, C.; Jardin, P.; Fauconnier, M.L. Cell wall polysacchraydes hydrolysis of malting barley (*Hordeum vulgare* L.)—A review. *Biotechnol. Agron. Soc. Environ.* **2011**, *15*, 301–3013.
- 3. Jin, Y.L.; Speers, R.A.; Paulson, A.T.; Stewart, R.J. Barley β-glucan and their degradation during malting and brewing. *Tech. Q. Master Brew. Assoc. Am.* **2004**, *41*, 231–240.
- 4. Izydorczyk, M.S.; Storsley, J.; Labossiere, D.; MacGregor, A.W.; Rossnagel, B.G. Evidence of intermolecular interactions of β-glucans and arabinoxylans. *Carbohydr. Polym.* **2000**, *41*, 417–420. [CrossRef]
- 5. Izydorczyk, M.S.; Dexter, J.E. Barley β-glucans and arabinoxylans: Molecular structure, physicochemical properties, and uses in food products: A review. *Food Res. Int.* **2008**, *41*, 850–868. [CrossRef]
- 6. Bamfort, C.W. Barley β-glucans: Their role in malting and brewing. *Brew. Dig.* **1982**, *3*, 22–35.
- 7. Mc Cleary, B.V. Problems caused by beta-glucans in the brewing industry. *Chem. Aust.* 1986, 53, 306–309.
- 8. Kunze, W. Technology Brewing and Malting, 6th revised ed.; VLB: Berlin, Germany, 2019.
- 9. Broderick, H. *El Cervecero en la Practica: Un Manual Para la Industria Cervecera*, 3rd ed.; Assn. de Maestros Cerveceros de las Americas: Wisconsin, WI, USA, 2002.
- 10. Fachverlag Hans Carl. *European Brewery Convention (EBC), Analytica,* 5th ed.; Fachverlag Hans Car: D-Nürnberg, Germany, 1998.
- 11. Middle European Brewing Analysis Commission (MEBAK), Band I and Band II. *nBrautechnische Analysenmethoden*, 3th ed.; Selbstverlag der MEBAK: Freising-Weihenstephan, Germany, 1997.
- 12. Krstanović, V.; Lalić, A.; Kosović, I.; Velic, N.; Mastanjević, K.; Mastanjević, K. A survey of total β-glucan content in Croatian barley varieties. *Cereal Res. Commun.* **2016**, *44*, 650–657. [CrossRef]
- 13. Zhang, G.; Chen, J.; Wang, J.; Ding, S. Cultivar and environmental effects on $(1 \rightarrow 3, 1 \rightarrow 4)$ - β -D-glucan and protein content in malting barley. *J. Cereal Sci.* **2001**, *34*, 295–301. [CrossRef]
- Kuusela, P.; Hämäläinen, J.; Reinikainen, P.; Olkku, J. A simulation model for the control of β-D-glucanase activity and β-D-glucan degradation during germination in malting. *J. Inst. Brew.* 2004, *110*, 309–319. [CrossRef]
- 15. Chandra, G.S.; Proudlove, M.; Baxter, E.D. The structure of barley endosperm—An important determinant of malt modification. *J. Sci. Food Agric.* **1999**, *79*, 37–46. [CrossRef]
- 16. Wang, J.; Zhang, G.; Chen, J.; Wu, F. The changes of β-glucan content and β-glucanase activity in barley before and after malting and their relationships to malt qualities. *Food Chem.* **2004**, *86*, 223–228. [CrossRef]
- 17. Edney, M.J.; LaBerge, D.E.; Langrell, D.E. Relationships among the β-glucan contents of barley, malt, malt congress extract, and beer. *J. Am. Soc. Brew. Chem.* **1998**, *56*, 164–168. [CrossRef]
- 18. Davis, N. Malt and malt products. In *Brewing—New Technologies*, 1st ed.; Bamforth, C.W., Ed.; Woodhead Publishing Ltd.: Cambridge, UK, 2006; pp. 68–101.
- 19. Davis, D. Influence of Roasted Barley on Quality of Beer. Master's Thesis, Colorado State University, Fort Collins, Colorado, CO, USA, 2013.
- 20. O'Rourke, T. Malt specifications and brewing performance. *Brew. Int.* **2002**, *2*, 27–30. Available online: http://www.ibdlearningzone.org.uk/article/show/pdf/500/ (accessed on 3 December 2019).
- 21. Sungurtas, J.A.; Swanston, J.S.; Davies, H.V.; McDougall, G.J. Xylan-degrading enzymes and arabinoxylan solubilization in barley cultivars of different malting quality. *J. Cereal Sci.* **2004**, *39*, 273–281. [CrossRef]
- 22. Vis, R.B.; Lorenz, K. β-Glucans: Importance in brewing and methods of analysis. *LWT Food Sci. Technol.* **1997**, *30*, 331–336. [CrossRef]
- 23. Tabatabaei, S.A. The changes of germination characteristics and enzyme activity of barley seeds under accelerated aging. *Cercet. Agron. Mold.* **2015**, *48*, 62–67. [CrossRef]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).