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Comprehensive Comparative Study of the Malting Qualities of Winter Hull-Less and Hulled Barley (2016–2019)

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Abstract: This paper aimed to compare the quality indicators of hull-less (naked) barley malt with malt obtained from hulled barley, according to the recommended values for standard pale malt. Five domestic hull-less barley varieties (Osvit, Mandatar, GZ-184, Osk.8.26/1–14 and Osk.6.24/4–12) and five hulled (Barun, OsLukas, Vanessa, Casanova, and Maestro) barley varieties were malted according to the standard procedure. The results of starting barley quality indicators (hectolitre weight, protein, starch, 1000 kernel weight, first class grain) and of finished malts (malt moisture, extract, extract difference, friability, wort viscosity, soluble protein, Kolbach index, wort color, and wort pH) were then compared. The results indicate that the main problem of hull-less barley is the resistance to deeper modification of grain. This is expressed as lower water absorption during steeping, and lower friability. The intensification of the process of malting could be boosted with the extension of steeping time and decreased temperatures during germination. This should result with higher friability but other indicators of malt quality should also show better values.

Keywords: malt; malting quality; Croatian hull-less barley; hulled barley

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1. Introduction

Most barley varieties have an outer husk called a hull. If the hull does not adhere to the kernel, the barley is considered to be hull-less. The hull-less grain trait is controlled by a single recessive gene *nud*, located on the long arm of chromosome 7H [1]. Barley variety, particularly *Hordeum vulgare* L. var. *nudum* Hook. f. has a loosely attached hull and during harvest, the hull falls off by itself which makes the cleaning processing much easier and economical. This also aids in reducing the germ damage and flour loss during milling.

The development of new hull-less barley varieties started in the 1970s in Canada. This kind of barley was designated and used as cattle feed, but the growing interest lead for it to be repurposed for human nutrition. Subsequently, this expanded its designation to raw material for malt in brewing and distilled products (Scotch, Whisky). The utilization of hull-less barley in the industry of strong alcoholic drinks such as Whisk or Scotch is mainly propelled by the fact that it showed higher alcohol yields, and resolved filtration issues that have been previously associated with hull-less barley [2]. Currently, hull-less barley cultivars, even though they are suitable for quality malt production, are not the top wanted varieties for brewing. Big malting and brewing companies are still suspicious of its brewing properties [3]. Nevertheless, its application in the brewing industry is still a novelty. The most important advantage of hull-less barley utilization in the brewing industry is the economical aspect. Namely, because the hull is absent (the hull makes 10% of dry matter loss in barley grains) [4], hull-less barley significantly boosts malt extracts by 5–7% (minimally > 2) in comparison with hulled barley [5–9]. According to Edney and Langrell [6], the lack of hull during mashing helps in eliminating the extraction of specific polysaccharides from hulls, which have been identified to cause premature yeast flocculation during fermentation. Some hull compounds (tannins and other polyphenols) are considered to be undesirable. The use of hull-less barley malt has some restrictions due to the fact that the intact hulls affect the efficiency of the lautering operation. However, with new technologies, such as mash filters and centrifuges, an increased interest in the advantages of hull-less barley malt emerged [8].

Malting of hull-less barley, however, does have certain disadvantages and puts many challenges before maltsters and brewers. The most obvious differences can be noticed in chemical and physical characteristics. The missing hull makes the barley embryo susceptible to damage during handling and malting which can result in inadequate endosperm modification [8] or incomplete germination [10]. According to several authors, poorly modified or incompletely degraded grains can be related to many undesirable quality characteristics of dry malt [6,8]. For instance, poor modifications of hull-less barley malt could cause a reduced level of extract. This is presumably related to unmodified cell walls that are known to restrict starch hydrolysis and, consequently the solubilization of starch during the stage of mashing [11].

Friability values for malt from hull-less barley appear to be much lower than the recommended values for hulled barley malt [6,7]. Water uptake during steeping is much easier and quicker in hull-less barley than in hulled barley [12], but Bhatty [13] reported that hull-less barley is harder than hulled malting barley. To adequately process hard, steely barley, prolonged steeping and germination times may be required. This requires alterations and adjustments of standard malting conditions. The Kilning step may also cause problems because the absence of a hull allows high kilning temperatures to cause hull-less malt to become extra hard.

To keep up with the world′s trends, several Croatian hull-less barley varieties have been created. Currently, there are several Croatian varieties of hull-less barley being developed at the Agronomic Institute in Osijek. Hull-less barley is also well known for its positive physiological effects on human health and is recognized as a functional food. It is rich in dietary fiber and minerals (calcium, phosphorus, iron, copper, zinc, and selenium).

The effects of the malting procedure applied to five domestic hull-less barley varieties (Osvit, Mandatar, GZ-184, Osk.8.26/1–14 and Osk.6.24/4–12) and five hulled (Barun, OsLukas, Vanessa, Casanova, and Maestro) varieties were investigated in this paper. The aim was to assess the malting quality of available varieties of hull-less barley from the brewing point of view and to determine their brewing potential in comparison to hulled varieties that are well established as brewing.

2. Materials and Methods

2.1. Materials

Ten genotypes of hull-less and hulled barley (*Hordeum vulgare* L.), obtained from the Agricultural Institute Osijek, Osijek, Croatia, were used for the comparative study of the grain quality and malting performance. The study was conducted on the two varieties (Osvit, Mandatar) and three advanced breeding lines (GZ-184, Osk.8.26/1–14 and Osk.6.24/4–12) of hull-less barley and five varieties of hulled barley (Barun, Lukas, Vanessa, Casanova, and Maestro) during four (2015/2016, 2016/2017, 2017/2018 and 2018/2019) consecutive seasons. Lines and varieties of hull-less and hulled barley were grown in experimental fields of Agricultural Institute Osijek located in the eastern part of Croatia. The exploratory experiments were set on an area of 7.56 m^2 field plots arranged in a complete randomized block design. All barley samples included are two-rowed winter type barleys. Vanessa and Casanova were included in this research as commonly used standard malting barley varieties.

2.2. Barley Samples Analysis

After the harvest, barley grain samples were cleaned and protein, starch, and hectoliter weight were determined by Infratec 1241 Grain Analyzer (FOSS, Hillerød, Denmark), with a calibration supplied by the manufacturer. Measurement of the thousand kernel weight was done by an electronic counting machine and includes counting and weighing the seeds. Sieve analysis of barley samples was done according to MEBAK [14] (Mitteleuropäischen Brautechnischen Analysenkommission). In sieve analysis, three sieves were used with oblong (slotted) holes 2.8, 2.5, and 2.2 mm in width. The amount of grain remaining on 2.8 + 2.5 mm sieves is reported as sieve analysis over 2.5 mm, i.e., 1st class grain, and the grain passing through 2.2 mm sieve is reported as sieve analysis under 2.2 mm. Grains of size higher than 2.5 mm were used for the micro-malting procedure.

2.3. Micro-Malting Procedure

Micro-malting of barley grain samples was done according to standard laboratory procedure at the Agricultural Institute Osijek, Croatia. Before micro-malting, the grain samples were screened over a 2.5 mm sieve and five hundred grams of each variety was placed into boxes of the micro-malting unit (Automated Joe White Malting Systems Micro-malting unit, Perth, Australia) in a randomized order. Barley samples were steeped to reach approximately 44–46% of the grain moisture following 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). After 96 h of germination (17 °C, 75% airflow, 1.5 turn every 2 h) green malts were subjected to 18 h integrated 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) to produce approximately 5–7% moisture malt. Dried rootlets were easily removed and malt samples were stored in plastic wide mouth jars with matching insert plug and screw lid at room temperature until analysis.

2.4. Malt Analysis

Malts quality attributes were determined according to European Brewery Convention methods [15]. The following parameters were determined: friability, malt extract content, extract difference between fine and coarse ground malt, malt soluble protein content, Kolbach index, wort color and pH, and viscosity.

2.5. Statistical Analysis

Statistical analysis (shown in Tables 3 and 4) was carried out using the analysis of variance (ANOVA) and Fisher's least significant difference test (LSD), with a statistical significance set at $p < 0.05$. Statistical analysis was carried out using Statistica 13.1. (TIBCO Software Inc., Palo Alto, CA, USA).

The statistical calculation that was carried out as a principal component analysis (PCA) aims to best represent the variation in the data based on a multitude of original variables. Calculation of each principal component can be seen as statistical model building based on the data, scores (distance from the PC origin for every data point), loadings (variable contributions for each PC), and residuals [16]. Components are created in a way that the first component explains the most variation, the second component explains the second most variation while reducing the correlation with the first component, etc. PCA efficiently solves collinearity between variables [17] and was hence used to analyze the quality and agronomic data sets of explored cultivars. The presence of some collinearity in parameters derived from given data points towards this multivariate approach, therefore, PC analysis presented itself as the optimal statistical method in that regard. All the variables were log-transformed and components explaining at least 10% of variation present in the dataset were analyzed. The analysis was performed with PAST software (v. 3.26, 2001).

3. Results and Discussion

In Table 1 the results of basic barley quality indicators are presented. Since the share of proteins is immensely important for maltsters and brewers, this can be observed from their point of view. It can be seen that hull-less barley contains significantly more proteins (13–15% in 2016, 2017, and 2019) than the hulled varieties. In 2018, the protein content dropped for both hull-less and hulled varieties and amounted to 10–12% for hull-less (the lowest was for Osvit, while Osk.6.24/4–12 showed the highest value for 2018). Hulled barley also showed low values for protein content in 2018. Namely, all values were below 10% (OsLukas and Maestro with 8.83%) and Casanova having 9.08%. It seems that the year had some influence on the protein content and Casanova showed the best adoptive properties; this should be considered in future research plans. Grains that underwent thermal or water stress during the grain-filling period exhibited higher protein content than grain samples from barley crops that have not suffered stress [18–20]. Often, fertilization during a drought period will result in higher protein content in smaller/thinner grains. According to Magliano et al. [21], protein content in grains corresponds to the environmental settings, such as nitrogen availability, thus making the crop's protein content closely related to the amount of available nitrogen per unit of actual yield. Namely, higher precipitation during the growing period cause a higher yield but as a consequence brings a dilution effect of the nitrogen content in the grain [22].

First class grains were more pronounced in hulled barley varieties and hull-less barley showed certain discrepancies and lower values throughout the observed years. This is also an important factor for maltsters and affects the suitability of barley for malting.

In Table 2, basic malt quality indicators are presented. Malt extract is usually a basic indicator of the malting procedure success and grain quality. Extract represents water-soluble components (fermentable and non-fermentable) that end up in wort. The obtained results indicate that hull-less barley, in general, has somewhat higher values of extract than the hulled varieties used in this research. In research published in 2016 by Krstanović et al. [7], malting procedures A and D for the GZ-184 variety resulted in higher extract values, which are in accordance with the obtained results.

Extract difference (fine and coarse grind) is an indirect measure of malt modification [23]. A significant difference between hulled and hull-less malt extracts can be noted in this research. Namely, hull-less varieties showed significantly higher values for this quality indicator, for all years. Values for hulled varieties amounted to max 5.89% while hull-less varieties values were constantly and significantly higher than 5%. Interestingly, both min and max values can be designated to the same line (Osk.8.26/1–14), but in different years with the max being 13.75% in 2016 and min was 5.93% in 2019. In general, lower extract difference values indicate the existence of parts of non-degraded endosperm with lower enzyme activity (giving lower wort quality). Extract difference also correlates with friability values. Namely, the increase in friability results in decreased extract difference and, consequently, lower values of congress wort viscosity.

When comparing hulled and hull-less varieties, a relatively high soluble protein content in hull-less barley and malt (Tables 1 and 2) is noted. However, this is followed by a low soluble protein content which can be caused by weak grain degradation (and consequently low friability), as can be seen from Table 2. In 2019, protein levels were high for both types of barley, but hull-less showed maximal levels >15%. However, it seems that soluble protein in malt was not significantly affected by the elevated protein content.

Table 1. Barley quality indicators.

Cultivar	Year	Type	Yield t/ha	Hectoliter Weight (kg)	Protein (%)	Starch (%)	Thousand Kernel Weight (g)	1st Class Grain (%)
Osvit	2016	Hull-less	6.70uv	76.80n	14.08f	65.08n	43.08y	64.83ac
Mandatar	2016	Hull-less	6.80tu	80.78g	14.90c	64.99o	44.74v	86.97q
GZ-184	2016	Hull-less	6.67vw	71.43s	14.03f	64.54qrs	43.74x	64.03ad
Osk.8.26/1–14	2016	Hull-less	6.84t	73.18p	15.18a	63.83x	43.84x	89.76m
Osk.6.24/4–12	2016	Hull-less	6.68v	78.25k	14.58e	64.42t	41.95aa	65.86ab
Barun	2016	Hulled	8.26hi	64.25ab	10.90q	64.48st	43.38y	67.85aa
OsLukas	2016	Hulled	7.96lm	64.30ab	10.50s	64.90p	48.17o	95.19e
Vanessa	2016	Hulled	5.89z	62.85ad	11.65m	65.53kl	48.99m	83.80t
Casanova	2016	Hulled	8.14ij	69.85w	10.58r	66.13j	49.78k	97.86d
Maestro	2016	Hulled	7.75no	62.13ae	11.23p	63.87x	41.78aaab	69.07z
Osvit	2017	Hull-less	8.84e	85.10c	13.25i	66.26i	47.76p	92.78j
Mandatar	2017	Hull-less	7.87mn	84.95d	13.70g	65.55p	47.60l	70.43y
GZ-184	2017	Hull-less	8.44h	85.30b	13.18i	65.53l	48.78n	86.75r
Osk.8.26/1–14	2017	Hull-less	8.41g	82.18f	14.03f	64.85op	45.50t	95.27e
Osk.6.24/4–12	2017	Hull-less	7.99kl	85.38a	14.08f	64.55rs	47.20q	75.03e
Barun	2017	Hulled	10.71a	73.28p	11.18p	65.18m	49.48l	94.84fg
OsLukas	2017	Hulled	10.21b	72.75q	11.15p	65.53k	56.62b	94.42h
Vanessa	2017	Hulled	8.70f	67.43z	13.38i	64.18u	53.74f	86.80qr
Casanova	2017	Hulled	9.31d	71.13t	13.78h	64.12uv	54.50e	86.40s
Maestro	2017	Hulled	9.57c	72.05r	11.45n	65.23m	49.38l	88.45p
Osvit	2018	Hull-less	5.24ab	80.00j	10.93q	69.49a	45.94s	59.01ae
Mandatar	2018	Hull-less	5.13ac	80.50h	11.68m	68.40c	41.69ab	92.90j
GZ-184	2018	Hull-less	5.18ac	78.23k	11.28op	68.53b	46.20r	56.50af

Table 1. *Cont.*

Cultivar	Year	Type	Yield t/ha	Hectoliter Weight (kg)	Protein (%)	Starch (%)	Thousand Kernel Weight (g)	1st Class Grain (%)
Osk.8.26/1–14	2018	Hull-less	5.51a	77.35m	12.08kl	68.00d	45.16u	94.81f
Osk.6.24/4–12	2018	Hull-less	5.51a	82.10f	12.18k	67.83e	44.85v	50.38ag
Barun	2018	Hulled	7.34q	66.48a	9.08v	66.69g	50.52j	89.83m
OsLukas	2018	Hulled	7.31r	70.40m	8.83w	66.95f	54.58d	98.23c
Vanessa	2018	Hulled	7.99kl	67.65y	9.65u	66.78g	57.49a	98.57b
Casanova	2018	Hulled	8.01jk	68.85x	9.80t	66.30i	55.05c	99.54a
Maestro	2018	Hulled	7.64op	70.48u	8.83w	66.55h	48.80mn	94.66g
Osvit	2019	Hull-less	6.03y	80.35i	15.00bc	65.32m	51.72i	74.93w
Mandatar	2019	Hull-less	5.99z	76.38o	15.05ab	64.55s	45.41t	74.30x
GZ-184	2019	Hull-less	6.52w	77.73l	14.75d	64.65q	47.13q	64.71ac
Osk.8.26/1–14	2019	Hull-less	7.62p	80.30i	14.90c	64.09vw	44.62v	81.76u
Osk.6.24/4–12	2019	Hull-less	6.26x	83.60e	14.90c	64.61qr	44.48w	46.51ah
Barun	2019	Hulled	7.63p	62.18ae	11.63m	64.39t	53.25g	88.84o
OsLukas	2019	Hulled	7.45q	61.70af	12.00l	64.41t	57.58a	92.44k
Vanessa	2019	Hulled	7.45q	60.33ag	12.65j	64.00w	55.17c	91.11l
Casanova	2019	Hulled	6.97s	63.55ac	12.70j	64.13uv	52.89h	93.96i
Maestro	2019	Hulled	7.95lm	63.50ac	11.40no	65.10n	54.42de	89.41n

Values are means obtained after three measurements. Values displayed in the same column and tagged with different letters (a–z) are significantly different ($p < 0.05$).

Table 2. Malt quality indicators.

Cultivar	Year	Type	Malt Moisture (%)	Malt Extract (%)	Extract Difference (%)	Friability (%)	Wort Viscosity (mPas)	Soluble Protein (%)	Kolbach Index (%)	Wort Color (EBC)	Wort pH
Osvit	2016	Hull-less	5.55r	81.84p	11.49c	23.48ac	4.45c	4.68bcd	31.91st	5.82c	5.45ij
Mandatar	2016	Hull-less	5.64pqr	81.87p	11.10d	25.23ab	4.97a	4.68bcde	31.33vw	7.01b	5.46ij
GZ-184	2016	Hull-less	5.71pq	82.45l	8.35jk	41.66r	2.79i	4.60bcdef	32.51q	9.88a	5.37j
Osk.8.26/1–14	2016	Hull-less	5.51r	79.40w	13.75a	16.04ah	4.42c	4.40hij	28.85ac	4.71ef	5.47ghij
Osk.6.24/4–12	2016	Hull-less	5.54r	80.65t	13.00b	18.88af	4.65b	4.55defgh	30.23z	6.91b	5.44hij
Barun	2016	Hulled	6.45k	79.46w	4.20v	61.94h	1.65uvw	4.05op	40.70c	4.31kl	5.60fghi
OsLukas	2016	Hulled	6.59k	79.60v	5.63q	47.64p	1.73stu	4.10no	36.77k	4.55hij	5.64cdef
Vanessa	2016	Hulled	6.16mn	79.70v	3.37y	75.38d	1.50y	3.95pq	37.98g	4.14nmo	5.53efghi
Casanova	2016	Hulled	6.39l	80.74t	3.80w	58.80i	1.71tuv	4.15mno	39.15f	4.03opq	5.60cdef
Maestro	2016	Hulled	6.80ij	78.66y	3.39y	54.74k	1.77rst	4.55cdefgh	36.40l	3.63s	5.63cdef
Osvit	2017	Hull-less	7.34bcd	83.76e	9.64g	13.12aj	3.54e	4.65bcde	31.10w	3.49t	5.65cdef
Mandatar	2017	Hull-less	7.57a	83.57ef	8.42j	23.48ac	3.65d	4.75b	31.35v	4.87d	5.64def
GZ-184	2017	Hull-less	6.97ij	81.93p	7.73lm	25.12ab	2.93h	4.55bc	30.85x	3.91q	5.00k
Osk.8.26/1–14	2017	Hull-less	7.01gh	82.59k	8.77i	17.68ag	3.25f	4.50efgh	29.41ab	4.59gh	5.62fghi
Osk.6.24/4–12	2017	Hull-less	7.27bcde	82.23mn	10.82e	13.58a	3.08g	4.55defgh	29.84a	4.03pq	5.62fghi
Barun	2017	Hulled	7.32bcd	80.09u	7.62m	37.60v	2.48jk	3.85pq	31.17w	4.62fgh	5.59def
OsLukas	2017	Hulled	7.41bcde	81.20s	5.16r	33.42y	2.49lmn	4.02mno	33.01o	4.08nop	5.63efghi
Vanessa	2017	Hulled	7.48bc	81.08s	4.87t	37.68v	1.87r	4.35klm	31.87u	4.72fg	5.57fghi
Casanova	2017	Hulled	6.94hi	79.63v	5.89p	35.10w	2.14op	4.45fghi	32.48q	4.27jk	5.62efghi
Maestro	2017	Hulled	7.17def	80.05u	4.64u	39.18s	2.11p	4.60cdefg	32.93p	3.59st	5.58efgh
Osvit	2018	Hull-less	6.26lm	86.42a	7.24n	33.54x	2.64j	4.30jkl	35.25n	4.61fgh	5.62ghij
Mandatar	2018	Hull-less	6.15mn	84.85c	8.33jk	33.40y	3.44e	4.25klmn	32.95p	4.57gh	5.60cdef
GZ-184	2018	Hull-less	6.01n	86.06b	7.83l	38.84t	2.44jkl	4.30ijk	35.98m	4.12mnop	5.65efg

Table 2. *Cont.*

Cultivar	Year	Type	Malt Moisture (%)	Malt Extract (%)	Extract Difference (%)	Friability (%)	Wort Viscosity (mPas)	Soluble Protein (%)	Kolbach Index (%)	Wort Color (EBC)	Wort pH
Osk.8.26/1–14	2018	Hull-less	6.24lmn	84.73cd	7.82l	37.74u	2.45klm	4.30jkl	31.73u	4.42jk	5.61def
Osk.6.24/4–12	2018	Hull-less	5.94o	84.54d	8.91h	23.04ad	2.42mn	4.40hij	32.00rs	4.23lm	5.59efghi
Barun	2018	Hulled	5.94o	82.57k	4.51u	52.52l	1.85rs	3.85q	40.53c	4.68ef	5.63fghi
OsLukas	2018	Hulled	6.09n	81.65q	5.03s	49.25m	2.17o	3.88q	37.78h	4.48hij	5.70bcde
Vanessa	2018	Hulled	5.76op	83.53fg	3.69x	65.78f	1.60vwx	4.20lmn	41.18b	4.51ghi	5.61efghi
Casanova	2018	Hulled	6.09n	82.79j	2.79z	75.98c	1.66vw	3.90q	40.63c	4.87d	5.64cdef
Maestro	2018	Hulled	6.19lmn	80.66t	4.50u	48.34n	1.85r	3.85pq	39.90d	4.02nop	5.63cdef
Osvit	2019	Hull-less	7.08fg	83.39hi	8.27k	27.44a	2.44jkl	4.85bc	32.88p	2.53w	5.87a
Mandatar	2019	Hull-less	6.82ij	84.59d	7.76lm	31.40z	2.76i	4.60bcdef	31.72tu	2.55x	5.90a
GZ-184	2019	Hull-less	7.16efg	83.26i	6.12o	41.70q	1.96q	4.60bcdef	32.06r	4.63fg	5.81a
Osk.8.26/1–14	2019	Hull-less	7.40ab	83.50gh	5.93p	47.74o	2.14op	4.40hij	30.03a	2.77v	5.85ab
Osk.6.24/4–12	2019	Hull-less	6.98ij	82.25m	10.29f	21.90ae	2.39n	4.45ghi	30.48y	3.35u	5.87abc
Barun	2019	Hulled	6.73j	81.33r	2.74z	66.01e	1.59wx	4.43ghij	39.08f	4.15mn	5.81a
OsLukas	2019	Hulled	7.23cde	79.16x	2.60a	57.07j	1.59wx	4.97a	37.06j	4.79de	5.83a
Vanessa	2019	Hulled	6.34lm	82.04o	4.42v	62.68g	1.59wx	4.30jkl	37.55i	3.79r	5.85abc
Casanova	2019	Hulled	5.60qr	82.14no	1.94ab	86.66b	1.50y	4.55cdefgh	39.74e	4.42ijk	5.81ab
Maestro	2019	Hulled	5.89o	83.45h	1.03ac	91.24a	1.50xy	4.50efgh	42.86a	4.59fgh	5.76abcd

Values are means obtained after three measurements. Values displayed in the same column and tagged with different letters (a–z) are significantly different ($p < 0.05$).

Hull-less barely is challenging for maltsters, but several authors have reported very successful malting using hull-less barely, especially regarding friability values [6,7,23–26]. Friability values for hull-less barley malt showed very low values in this research. The minimum value was 13.12% for Osvit in 2017, and the highest value for friability was recorded in Osk.8.26/1–14 in 2019, amounting to 47.74%. Hulled barley varieties maintained more steady values (especially Casanova) and Meastro showed the highest value in 2019 with 91.24%. This shows that the grain modification during malting via adjusted malting conditions is possible. Similar values were obtained by Krstanović et al. [7] who subjected two hull-less varieties Matko and GZ-184 to four different malting procedures. The control samples were subjected to the standard MEBAK micromalting procedure (A). The results showed that the intensification of the process of germination should be combined with the extension of soaking time, which should lead to improvements in the friability of malt and better value for other indicators of malt quality, which is the main guide for future research in this field.

Viscosity values correlate with friability values in such a way that higher friability values make congress wort viscosity lower, which is the case in this research. Namely, the lowest viscosity value was detected in GZ-184 in 2019 and was 1.96%, while the highest viscosity value was 4.97% for Mandatar in 2016. Hulled barley varieties generally showed lower values for viscosity, as can be seen in Table 2. This indicates the connection of deeper grain degradation with different components which causes the increase in wort viscosity values (β-glucans, pentosanes, residual starch) which is in accordance with previous research [7,8,11].

The Kolbach index indicates the level of protein degradation in the malt grain, and optimal values for standard malt range from 38–42% [27]. The results obtained in this research show that hull-less barley varieties have a somewhat lower Kolbach index than the hulled ones. The min value (28.85%) for Kolbach index in hull-less varieties was recorded in Osk.8.26/1–14 in 2016 and the max value (35.98%) was achieved in 2018 in the GZ-184 variety. The results are in accordance with the results of malt hull-less barley varieties in Canada [24]. Similarly, Edney, and Langrell [6] reported Kolbach index values higher than 40% for the hull-less variety CDC Dawn in cases with a longer germination period. Similar results regarding Kolbach index values were described by Krstanović et al. [7] (2015), where the values of the Kolbach index reached 41% in the modified malting process. In a previous study published by Šimić et al. [28], there were also reported differences in malting behavior between hull-less and hulled varieties. Results obtained for the friability, difference in extract yield between finely and coarsely ground malt, wort viscosity and Kolbach index revealed that malting varieties achieved better cytolytic and proteolytic modification than hull-less barley lines.

In order to detect the significant differences between barley types we condensed the data from Tables 1 and 2 into Tables 3 and 4. They show the mean values (sum of quality parameters divided by four years) of barley and malt quality indicators and give a clear insight into statistical difference between data sets. It is visible from Table 3 that starting quality indicators for hull-less and hulled barley show statistical difference. This is especially pronounced for yield, where there is a statistical difference ($p < 0.05$) for every year and between hull-less and hulled barley type. There is a certain overlap in some quality indicators, mostly between hull-less and hull-less and hulled and hulled barley types, but between some years hull-less and hulled showed no statistical difference ($p > 0.05$) in hectoliter weight (hull-less 2016/hulled 2017), 1000 kernel weight (hulled 2019/hull-less 2019/hull-less 2016) and starch content (hulled 2017/ hulled 2019/hull-less 2019/hull-less2016). Protein content was greatly affected by the type of barley and showed higher values for hull-less types, with the max value being 14.92% for hull-less barley in 2019. However, there is no statistically significant difference between hull-less varieties in 2016 and 2017. Hulled varieties showed lower max value, amounting up to 12.19% in 2017. Another important quality indicator is the share of first class grains. Namely, in order to meet the maltsters' quality requirements, barley grains must also have a specific protein level, and high proportion of plump grains [22]. However, research conducted by Magliano et al. [21], showed that thin grains can contain more proteins than plump ones. This would mean that the reduced protein content can originate from a great share of plump grains while the small ones were selected and discarded during sieving. Perhaps hulled barley in 2018, which had 9.24% protein and >96% first class grains, is a good example for this theory. This is something to consider prior future protein content analysis.

Table 3. Mean values for barley quality indicators for each year.

Type	Yield (t/ha)	Hectoliter Weight (kg)	Protein (%)	Starch (%)	Thousand Kernel Weight (g)	1st Class Grain (%)
Hull-less2016	6.74 ^{f}	76.09 ^{bc}	14.55 ^{ab}	64.57 ^{ab}	43.47 ^{cd}	74.29 ^{cd}
Hulled2016	7.60 ^{d}	64.68 ^{e}	10.97 ^{d}	64.98 ^{b}	46.42 ^{d}	82.75 ^{cd}
Hull-less2017	8.31 ^{b}	84.58 ^{a}	13.65 ^{b}	65.35 ^{a}	47.37 ^{bc}	84.05 ^{bc}
Hulled2017	9.70 ^{a}	71.33 ^{c}	12.19 ^{c}	64.85 ^{ab}	52.74 ^{ab}	90.18 ^{ab}
Hull-less2018	5.31 ^{h}	79.64 ^{ab}	11.63 ^{c}	68.45 ^{a}	44.77 ^{cd}	70.72 ^{d}
Hulled2018	7.66 ^{c}	68.77 ^{cd}	9.24 ^{d}	66.65 ^{a}	53.29 ^{a}	96.17 ^{a}
Hull-less2019	6.48 ^{g}	79.67 ^{ab}	14.92 ^{a}	64.64 ^{ab}	46.67 ^{cd}	68.44 ^{d}
Hulled2019	7.49 ^{e}	62.25 ^{de}	12.08 ^{c}	64.41 ^{ab}	54.66 ^{a}	91.15 ^{ab}

Values are mean values of analytical data for each quality indicator for each year. Values displayed in the same column and tagged with different letters (a–h) are significantly different ($p < 0.05$).

Table 4. Mean values malt quality indicators for each year.

Type	Moisture (%)	Extract (%)	Extract Difference (%)	Friability (%)	Viscosity (mPas)	Soluble Protein (%)	Kolbach Index (%)	Wort Color (EBC)	Wort pH
Hull-less2016	5.59 ^{g}	81.24 ^{f}	11.54 ^{a}	25.06 ^{g}	4.26 ^{a}	4.58 ^{ab}	30.97 ^{g}	6.87 ^{a}	5.44 ^{c}
Hulled2016	6.48 ^{c}	79.63 ^{h}	4.08 ^{f}	59.70 ^{b}	1.67 ^{g}	4.16 ^{d}	38.20 ^{c}	4.13 ^{e}	5.60 ^{b}
Hull-less2017	7.23 ^{a}	82.82 ^{c}	9.08 ^{b}	18.60 ^{h}	3.29 ^{b}	4.60 ^{a}	30.51 ^{h}	4.18 ^{e}	5.51 ^{c}
Hulled2017	7.26 ^{a}	80.41 ^{g}	5.64 ^{e}	36.60 ^{d}	2.22 ^{e}	4.25 ^{c}	32.29 ^{e}	4.26 ^{e}	5.60 ^{b}
Hull-less2018	6.12 ^{e}	85.32 ^{a}	8.03 ^{c}	33.31 ^{f}	2.68 ^{c}	4.31 ^{c}	33.58 ^{d}	4.39 ^{f}	5.61 ^{b}
Hulled2018	6.01 ^{f}	82.24 ^{d}	4.10 ^{f}	58.37 ^{c}	1.83 ^{f}	3.94 ^{e}	40.00 ^{a}	4.51 ^{b}	5.64 ^{b}
Hull-less2019	7.09 ^{b}	83.40 ^{b}	7.67 ^{d}	34.04 ^{e}	2.34 ^{d}	4.58 ^{b}	31.43 ^{f}	3.17 ^{f}	5.86 ^{a}
Hulled2019	6.36 ^{d}	81.62 ^{e}	2.55 ^{g}	72.73 ^{a}	1.55 ^{h}	4.55 ^{b}	39.26 ^{b}	4.35 ^{c}	5.81 ^{a}

Values are mean values of analytical data for each quality indicator for each year. Values displayed in the same column and tagged with different letters (a–h) are significantly different ($p < 0.05$).

Table 4 shows the mean values for malt quality indicators from which a recognizable statistical difference can be noted between parameters. Malt samples show a distinct statistical difference between the analyzed data, with no overlaps between barley types and years. Only hull-less barley in 2016 showed on overlap for soluble proteins with both, hull-less and hulled barley in 2019. This is not surprising for hull-less barley in 2019, because it had similar content of protein in grains (14.92%) as 2016 (14.55%) which resulted in equal share of proteins in wort (4.58%). It is, however, interesting that hulled barley contained 12.08% of proteins in 2019 and the amount of soluble proteins in wort amounted to 4.55%, which is very close to the hull-less varieties in 2016 (4.58%). According to Edney Langrell [6], higher levels of soluble protein are detected in "better-modified" malts and could be correlated with higher extract levels. Extract levels for the aforementioned malts (hull-less 2016/2019 and hulled 2019) in this research are higher than 80% but do not represent the maximal extract values (85.32% for hull-less in 2016) in this research. They also show significant differences between all analyzed samples, regardless of being of the hull-less or hulled type. Friability levels vary, but are significantly different for each year and for both types of barley. In general, mean values for hull-less barleys′ friability are circa two-fold lower than for the hulled barley′s for every year (2016—25.06/59.70%; 2017—18.60/36.60%; 2018—33.31/58.37%; 2019—34.04/72.73%). Viscosity mean values generally show increased values for hull-less varieties for every year. In a study conducted by Krstanović et al. [7], a narrow connection between β-glucan content and viscosity was determined, meaning that lower β-glucan content in hull-less barley reduces the viscosity of wort. Hull-less barley is known to have a higher β-glucan content [28] and thus increased viscosity values, which are considered problematic during filtration in the brewing process. Viscosity values are approximately 1.4–1.5 times higher for hull-less barley, with the exception for 2016 where viscosity was 2.5 times higher than in hulled varieties.

To test whether the observed differences in agronomic and quality parameters explored through four growing seasons between different types of cultivars (hulled vs. hull-less) were genotype-specific, and to what extent, the PCA analysis was chosen. The first two PCs explained 56.5% of the variation present in the dataset (Figure 1). Cultivars showed distinct reactions towards forming two major groups at the basic level, meaning hull-less (first and fourth quadrant) vs. hulled (second and third quadrant). Variation among different growing years (seasons) displayed distinctiveness in groupings where cultivars mostly kept to their group defined by the year of cultivation, confounding well the seasonal reactions. Hull-less cultivars were determined by bi-plot vectors indicating mostly quality parameters, however, one must be aware of some vectors/traits having an overall negative impact on quality even though they display an increase in value (viscosity, extract difference, protein content). The best performing year quality-wise for the hull-less cultivars was 2018 (red circle), where the whole group concentrated to the relative proximity of the vector for the extract trait. High protein synthesis seasons were determined to be 2017 (green square) and 2019 (olive x) where these seasonal groups also intermingled between vectors for protein, viscosity, extract difference, and hectoliter. On the other hand, the hulled barley cultivars showed an inclination more towards agronomic traits and some key quality parameters (friability and Kolbach index). The best season in the agronomic sense was 2017 (green square), where the whole group of hulled cultivars swarmed firmly around the grain yield vector. Inversely, the best seasons for quality parameters among hulled cultivars were 2016 (blue cross) and 2018 (red circle). Eigenvalues of parameters explaining at least 10% of variation were the first four (PC1–PC4), eigenvalues of PC5 and up were excluded from further analysis and their influence may be considered negligible in describing variation between the cultivars and/or growing seasons.

In addition, and as a complement to the PCA, the correlation matrix was calculated for better distinction and understanding of inter-trait relationships. As shown in Figure 2, the most significant correlation is stated with extract difference, friability, viscosity, malt soluble protein, and Kolbach index traits. Agronomic traits that showed the most significant correlation were mainly hectolitre and protein content, in addition to traits such as grain yield and 1000 grain weight that display their significance a tad lower on the scale. In a previous study, it was reported that 1000 grain weight has not been an accurate predictor of malting quality attributes between varieties, but when results were observed within varieties, higher 1000 grain weight was correlated with higher extract [29]. Here, we found no correlation between 1000 grain weight and malt extract content, which is in accordance with Swanston et al. [30], who observed no correlation between 1000 grain weight and either extract or predicted spirit yield. The results of this study showed that higher 1000 grain weight positively influenced endosperm cytolytic and proteolytic degradation, indicated through lower extract difference and wort viscosity, and a higher friability and Kolbach index.

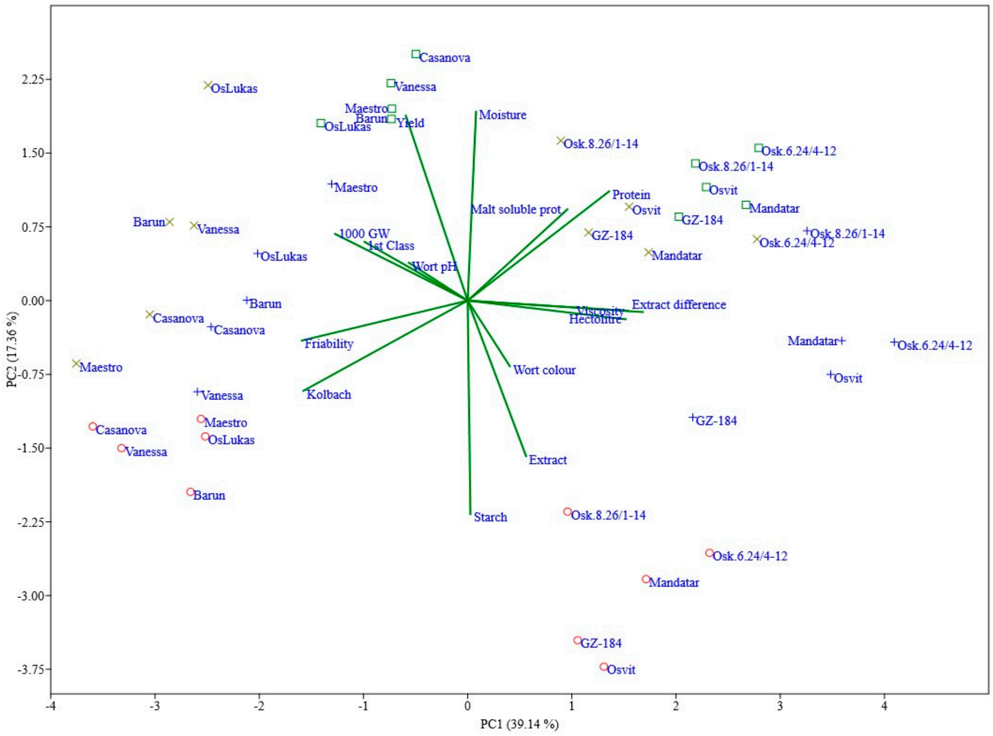

Figure 1. PCA bi-plot of ten winter barley varieties and their respective agronomic and quality traits observed through four growing seasons (2016—blue cross; 2017—green square; 2018—red circle; 2019—olive x).

A positive correlation was determined between viscosity, extract difference, protein content, and malt soluble protein traits, as well as between the Kolbach index and friability. Negative correlations were determined among friability and hectoliter, friability and extract difference, Kolbach index and hectoliter, Kolbach index and protein content, Kolbach index and extract difference, Kolbach index and viscosity, viscosity, and friability.

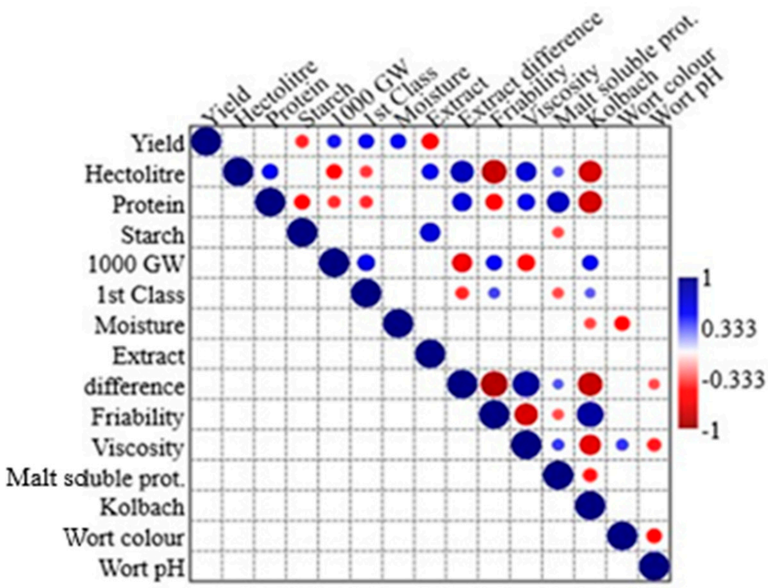

Figure 2. Correlation matrix of agronomic and quality traits for winter barley cultivars observed through four growing seasons (2016–2019) (Note to correlation key and the scale reads: positive—blue, negative—red; smaller circle—lesser significance; bigger circle—greater significance; non-significant values are not shown (blank square)).

4. Conclusions

The results indicate that hull-less barley displays a stronger resistance to grain modification (expressed as lower water absorption during steeping, and very low friability values) than hulled barley varieties. This problem should be addressed in the further selection processes of domestic hull-less barley varieties intended for malting. Additionally, proper modification and optimization (extension of steeping time and decreased temperatures during germination) of the malting process could aid grain modification which should lead to improvements in the friability of malt and better value for other indicators of malt quality. Future aspects should include extensive research on the malting process modifications and optimization which could result in better quality hull-less barley malt. Additional experiments should be addressing the influence of agro-climatic conditions on friability since the results of this research indicate that this could be a significant factor in obtaining acceptable values of friability.

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