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### Original Research Article

# Physicochemical properties, sugar profile, and non-starch polysaccharides characterization of old wheat malt landraces

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#### ABSTRACT

Craft beers produced by small breweries are becoming increasingly popular worldwide due to their unique composition, taste, and flavour. Wheat malt is a traditional brewing raw material with great potential to improve beer properties such as mouthfeel, foam, haze, and flavour. In this study, the malting quality of eight wheat varieties (four common and four durum) was evaluated to explore the feasibility of producing 100 % wheat malt beer from old landraces. The physicochemical characteristics such as friability, Kolbach index, viscosity, and colour, of the wheat malts indicated a better degree of modification in the common wheat varieties when compared to that of the durum wheat varieties. The wheat malts showed a proper enzymatic pattern, and significant differences in the enzyme activities were observed in durum and common wheat malts which affected the non-starch and starch polysaccharide content. The sugar content, profile, and extract levels of the congress worts were comparable to those of commercial malts. This study could be a use-ful resource that enables small brewing and malting to extend their portfolio and promote the use of old landraces to produce beers with unique tastes and profiles.

#### 1. Introduction

Malt is cereal that is germinated and then dried under controlled conditions, is commonly used in baking, brewing, and whisky production. The growing interest in new raw materials suitable for the malting industry is highlighted by the increasing number of published articles, such as studies on rice, teff, and einkorn malt, as well as studies on the behaviour of sorghum, buckwheat, quinoa, and amaranth malt for gluten-free beer production (Bravi et al., 2012; Ceccaroni et al., 2019a, 2019b; de Meo et al., 2011; Di Ghionno et al., 2017b, 2017a; Marconi et al., 2013; Mayer et al., 2016, 2014, 2011).

Recently, a preliminary evaluation and screening of old durum wheat landraces were carried out to evaluate their malting performance, and the results showed the suitability of some landraces in the malting industry (Alfeo et al., 2018a, 2018b). Old landraces are characterised by high rusticity and environmental adaptability, representing the ideal raw material for the development of short supply chains under low input or organic farming regimes.

Furthermore, several researchers have pointed out the increasing interest in different wheat varieties with lower protein for malting and brewing at low viscosity levels (Faltermaier et al., 2014). Protein levels play a key role in cereal malting. In particular, high protein content is related to low protein solubility and a reduced degree of modification, which can be enhanced by extending the germination phase (Jin et al., 2011). On the other hand, extensive protein degradation leads to a high Kolbach Index (KIs values and high respiration rates with increasing malting losses) (Jin et al., 2014). The physicochemical properties brews, such as wort viscosity, are mainly affected by the non-starch polysaccharide (NSP) content in malt and the polymerisation degree (Krahl et al., 2009).

The NSPs are represented by arabinoxylans and  $\beta$ -glucans in wheat, similar to that of other cereals. However, the  $\beta$ -glucan con-

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tent in wheat is less than that in other cere als and wheat  $\beta$ -glucan has a regular structure that makes it less water soluble. In contrast to  $\beta$ glucans, arabinoxy lans can reach approximately 7% of the whole kernel weight of wheat and are mainly responsible for changes in the physicochemical properties of wort and beer (Alfeo et al., 2018a; Cui et al., 2000). Wheat arabinoxy lans consist of a  $\beta$ -Dxy lopy ranose linear backbone at the O-3 or both at O-2 and O-3  $\alpha$ -L-arabinofuranose sidechains. Brewers consider arabinoxy lans to be responsible for a higher body and mouthfeel in beer rather than  $\beta$ -glucans (Li et al., 2019; 2020). Further more, the protein composition of wheat malt improves beer properties such as foam stability and colloidal haze in cloudy beers (Hu et al., 2019).

To the best of our knowledge, an accurate and comprehensive dataset of traditional cereal malting quality has not been reported previously. The present study is the first to evaluate the unmalted, malted, and wort quality traits of different old common and durum wheat landraces. The malting quality parameters, protein and starch degradation processes, and starch- and NSP-degrading enzyme activities were studied. Furthermore, the comparison and evaluation of the wort sugar profiles of various common and durum wheat malts is presented to assess their suitability as raw materials for brewing.

#### 2. Materials and methods

#### 2.1. Raw materials

In the 2018–2019 season, four old common wheat varieties (Maiorca, Maiorcone, Cuccitta, and Romano) and four durum wheat landraces (Bufala nera lunga, Bufala nera corta, Bufala rossa lunga, and Bufala Bianca), were grown in Italy at the "Stazione Consorziale Sperimentale di Granicoltura per la Sicilia' farm in Caltagirone (Lat.  $37^{\circ}14'$  Long.  $14^{\circ}30'$ , 350 m above sea level, sandy clay soil). The exact agro-technical protocols were applied to all the wheat crops, cultivated in two field plots of 100 m<sup>2</sup> each. The sowing of 350 viable seeds per m<sup>2</sup> was carried out in duplicate in December 2018, supplying 40 kg ha<sup>-1</sup> of N and 90 kg ha<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>. Samples were harvested in June 2019 and stored at 4–6 °C prior to malting.

#### 2.2. Malting conditions

Malting tests were performed in triplicate in an automatic malting system (Custom Laboratory Products, Milton Keynes, UK). Samples of eight wheat landraces were cleaned to remove the glumes and husks, or, if present, external contaminants. Prior to malting, the sample grains were sieved and the portion retained by a 2.5 mm sieve was used for subsequent tests. Malting processes were carried out according to the conditions proposed by Alfeo et al. (2018a,b). For each wheat sample, 500 g of grains were steeped in water at 15 °C for 5 h, followed by 8 h of air-rest, and further 4 h in water, reaching a steeping-out moisture of 42 %. The germination occurred after 120 h at 15 °C and 95 % of relative humidity, then the samples were dried and kilned for 34 h as follow: 3 h at 55 °C, 12 h at 60 °C, 10 h at 65 °C, 5 h at 70 °C, and 4 h at 75 °C. The roots and acrospires were removed at the end of the malting process.

#### 2.3. Quality attributes of unmalted and malted wheat

The analyses were performed in triplicate according to the Analytica European Brewery Convention (EBC) (2007). In particular, the moisture (%) of raw and corresponding malted grains were determined by EBC methods 3.2 and 4.2, respectively. The germination energy (GE, %) was calculated by EBC method 3.6.2 and the thousand corn weight (TCW, g dry basis, db) was measured for wheat and malts by EBC methods 3.4 and 4.4, respectively. Proteins and soluble proteins were calculated as total nitrogen (TN, db%) or soluble nitrogen (SN,

db%), obtained using the EBC method 3.3.1 for wheat, and EBC method 4.3.1, and 4.9, respectively, for malt, then multiplied by 5.7. The KI (%) is the S/N ratio. Malt colour was estimated using EBC method 4.7.1. The malt friability (%), wholly unmodified grains (WUG, %), or partly unmodified grains (PUG, %) were estimated using a friabilimeter (Pfeuffer GmbH, Kitzingen, Germany) according to EBC method 4.15.

The Megazyme assay kit (Megazyme International, Ireland) was used for total starch content (db%) determination following the AOAC method 996.11 (2005). The total starch assay had a low detection limit of 0.18 g 100 g<sup>-1</sup> of total starch "as is" and a linearity over the range of 4–100 µg of D-glucose. The degraded starch (defined as delta " $\Delta$ " starch, db%) during the malting process was calculated for each wheat sample as the difference between the average wheat (W) and malt (M) starch content ( $\Delta$  starch % = W – M) according to Alfeo et al. (2018b). The malt extract (db%) from wheat malts was measured using EBC method 4.5.1, fermentability (%) was measured using EBC method 4.11.1, pH was measured using EBC method 4.5.1, and free amino nitrogen (FAN, mg 100 g<sup>-1</sup> db) was measured using EBC method 4.10. The wort viscosity (mPa.s) was determined using a falling ball micro viscometer (Anton Paar GmbH, Graz, Austria) following EBC method 4.8.

#### 2.3.1. Enzyme activities

The NSP-degrading enzymes were measured by  $\beta$ -glucazyme and xylazyme tablets (Megazyme International), respectively, for endo- $\beta$ -glucanase and endo-1,4- $\beta$ -D-xylanase activities. A malt amylase assay kit (Megazyme International) was used to quantify  $\alpha$  and  $\beta$  amylases in malt flours. The enzyme activities were measured by reading the assay absorbance using a Varian Cary 100 UV–vis spectrophotometer (Palo Alto, California, United States) and reported as units per gram of dry matter (U g<sup>-1</sup>). One unit of activity is defined as the amount of enzyme required to release 1  $\mu$ mol of reducing sugar equivalents per minute under the defined assay conditions.

#### 2.3.2. Non-starch polysaccharides

 $\beta$ -glucan levels were measured for the wheat (BG), malts (MBG), and congress worts (WBG) according to EBC methods 3.10.1., 4.16.1 and 8.13.1, respectively, using the Megazyme assay kit (Megazyme International).

Total wheat arabinoxylans (AX) and malt water-extractable arabinoxylans (WEAX) were extracted according to the methods reported by Marconi et al. (2020) and Alfeo et al. (2018b), respectively. For the purification of the AX, WEAX, and wort arabinoxylans (WAX), the samples were milled to pass through a 0.5 mm screen, and 500 mg of the sample was added to 10 ml of acetate buffer (pH 5.2), and then 200 µL of α-amylase (Megazyme International, 3000 U mL<sup>-1</sup>) was added during continuous stirring at 80 °C for 15 min, followed by the subsequent addition of 23 µL of amyloglucosidase (Megazyme, 3260 U mL<sup>-1</sup>) with stirring at 60 °C for 15 min. The solution was adjusted to pH 7 using 1 M NaOH, then 4 mg pancreatin and 20 µL lichenase were added, and the solution was stirred at 40 °C for 1 h. The addition of 30 ml of pure ethanol allowed the precipitation of the purified pellet, and the tubes were left on ice for 30 min. Samples were centrifuged (2000 g, 10 min), the supernatant fraction was discarded, and the pellet was washed by adding 10 ml of ethanol (85 % v v $^{-1}$ ) and again centrifuged 10 min at 2000 g to discard the supernatant fraction. Acetone (20 mL) was added to the pellet, the solution was mixed, and centrifuged at 2000 g for 10 min, after which the uncapped test tube was left at 80 °C for 15 min to allow solvent evaporation. Acid hydrolysis was carried out by adding 5 ml of 12 M sulfuric acid to the pellet, and the solution was continuously stirred at 35 °C for 1 h. Then, 25 ml of deionised water was added and the mixture was boiled for 30 min before dilution (1:3 ratio).

For quantification of AX, WEAX, and WAX, 10 ml of a pentosanspecific reagent (phloroglucinol) was added to the sample, which was boiled for 22 min, cooled on ice for 10 min, and left at 20 °C for 5 min. The absorbance versus blank reagent was read using a Varian Cary 100 UV–vis spectrophotometer (Palo Alto, California, United States) at 510 nm and subtracted from the absorbance at 552 nm (Douglas, 1981).

#### 2.3.3. Congress wort sugars profile

The sugar profile was obtained by HPLC using a Shodex-NH<sub>2</sub>P-50, 250 mm polymeric amino column (Shodex Inc., Tokyo, Japan) following the method proposed by Floridi et al. (2001). An evaporative light scattering detector (ELSD C-650, BÜCHI, Flawil, Switzerland) was used with a drift tube temperature of 110 °C and 2.21 min<sup>-1</sup> of nitrogen flow. The gradient was obtained by low-pressure mixing of acetonitrile/water using a pump, ternary gradient mixer, and 3-line degasser (Jasco Corporation, Tokyo, Japan). The eluent flow rate was 1 ml min<sup>-1</sup>, and the mixture was maintained for the first 10 min after injection at 75 % (v v<sup>-1</sup>) of acetonitrile, then decreased to 50 % acetonitrile in 15 min and maintained at this concentration for 5 min. Five minutes were required to restore the initial conditions.

#### 2.3.4. Statistical analysis

The analysis of variance (one-way ANOVA,  $p \le 0.05$ ) using Tukey's post hoc test was performed using the Matlab R2015a software (Math-Works Inc., Nutick, Massachusetts, United States). The Pearson correlation coefficients at three levels of significance (p values, 0.05, 0.01, and 0.001) were obtained using the IBM SPSS statistics software (SPSS Inc., Chicago, Illinois, United States). To understand the effect of wheat landrace on the modification degree, as well as the NSP content and the resulting wort viscosity better, a principal component analysis (PCA) was performed using the Matlab R2015a software (MathWorks Inc.).

#### 3. Results and discussion

#### 3.1. Quality parameters of raw wheat grains

Table 1 summarises the main quality parameters of the wheat malts. The moisture content in our study was in the optimal range to prevent fungal development during storage (Laitila, 2015). Total corn weight (TCW) is a parameter that controls seed size. A low value (<30 g db) indicates the presence of empty or diseased seeds. The genetic diversity of the old landraces caused a high variability in the TCW values, ranging from 36.88 g (db) in the Maiorca variety to 49.25 g (db) in the Cuccitta variety (Table 1). The durum and common wheats showed on average similar TCW levels, and the results were in line with those reported previously, as well as with the Italian Brewing Research Centre database for wheat malt (Alfeo et al., 2018b; Ciccoritti et al., 2011). Although the different wheat varieties were grown in the same field plot with exact input levels, the protein content showed high heterogeneity, mainly due to the landraces effect, which was in accordance with the results of other studies on wheat storage proteins (Branlard et al., 2001). The protein content was higher than the optimal value for malting cereals in our study, which could lead to technological problems during malting, such as a low degree of modification and haze formation during brewing. No relevant differences were observed between the average protein content of durum and common wheat. Germination energy was in the optimal range for all the samples, with an average score of 98 % for common wheat and 97.25 % for durum wheat (Table 1).

#### 3.2. Quality parameters of wheat malt

The moisture content was optimal for both common and durum wheat (3.81 and 4.11 % on average, respectively). The reduction of the TCW between wheat and malt represents malting losses due to kernel respiration. The average TCW of the common wheat decreased from 42.77 g (db) to 35.86 g (db) with a loss of 6.91 g (db), while for the durum wheat it dropped from 43.25 g (db) to 37.10 g (db) with a loss of

Table 1	
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Wheat and malt quality parameters

	Moisture (% w w <sup>-1</sup> )	TCW (g db)	Proteins (% db)	Sol. Proteins (% db)	Starch (% db)	GE (%)	Friability (%)	WUG (%)	PUG (%)
Wheat									
Triticum aes	stivum L.								
Maiorca	$11.6 \pm 0.35^{a}$	$36.9 \pm 1.20^{a}$	$11.8 \pm 0.10^{a}$	-	$66.8 \pm 1.33^{b}$	$97.0 \pm 1.00^{a}$	-	-	-
Maiorcone	$12.4 \pm 0.37^{b}$	$39.6 \pm 0.01^{b}$	$13.8 \pm 0.10^{\circ}$	-	$67.8 \pm 0.79^{b}$	$98.0 \pm 1.00^{a}$	-	-	-
Cuccitta	$12.9 \pm 0.42^{b}$	$49.2 \pm 0.50^{d}$	$14.7~\pm~0.00^d$	-	$61.8 \pm 1.82^{a}$	$99.0 \pm 1.00^{a}$	-	-	-
Ro ma no	$12.9 \pm 0.39^{b}$	$45.3 \pm 0.80^{\circ}$	$12.3~\pm~0.10^{b}$	-	$62.9 \pm 1.25^{a}$	$98.0 \pm 1.00^{a}$	-	-	-
Triticum tur	gidum ssp durum desf.								
BNL	$11.1 \pm 0.33^{A}$	$43.2 \ \pm \ 0.80^{B}$	$12.5~\pm~0.10^{\rm A}$	-	$67.3 \pm 0.01^{B}$	$98.0\ \pm\ 1.00^{B}$	-	-	-
BNC	$12.3 \pm 0.49^{B}$	$48.0 \pm 0.30^{\circ}$	$13.6 \pm 0.60^{B}$	-	$69.2 \pm 0.18^{\circ}$	$98.0 \pm 1.00^{B}$	-	-	-
BRL	$12.8 \pm 0.38^{B}$	$42.3 \pm 0.80^{B}$	$12.7~\pm~0.20^{\rm A}$	-	$65.5 \pm 0.67^{A}$	$94.0~\pm~1.00^{\rm A}$	-	-	-
BB	$11.8 \pm 0.35^{A}$	$39.4 \pm 0.50^{A}$	$14.9 \pm 0.40^{\circ}$	-	$66.9 \pm 0.86^{B}$	$99.0 \pm 1.00^{B}$	-	-	-
Malt									
Triticum aes	tivum L.								
Maiorca	$3.80 \pm 0.10^{a}$	$31.6 ~\pm~ 2.10^{a}$	$11.5 \pm 0.35^{a}$	$5.61 \pm 0.05^{d}$	$58.1 \pm 1.29^{bc}$	-	$77.5 \pm 0.50^{d}$	$0.45 \ \pm \ 0.05^{b}$	$0.60~\pm~0.10^a$
Maiorcone	$3.75 \pm 0.05^{a}$	$32.8 ~\pm~ 0.50^{a}$	$13.7~\pm~0.05^{\rm b}$	$4.42 \pm 0.15^{b}$	$54.3 \pm 1.61^{a}$	-	$69.5 \pm 1.50^{b}$	$0.80~\pm~0.01^{c}$	$1.00~\pm~0.40^{ab}$
Cuccitta	$3.85 \pm 0.05^{a}$	$40.7~\pm~0.20^{c}$	$14.0~\pm~0.40^{\rm b}$	$4.13 \pm 0.05^{a}$	$59.9 \pm 0.09^{\circ}$	-	$55.5 \pm 0.50^{a}$	$0.35\ \pm\ 0.05^{a}$	$1.15 \pm 0.25^{b}$
Romano	$3.85 \pm 0.05^{a}$	$38.3~\pm~1.05^{\mathrm{b}}$	$11.8 \pm 0.15^{a}$	$4.67 \pm 0.20^{\circ}$	$56.7\ \pm\ 0.12^{b}$	-	$72.5 \pm 0.50^{\circ}$	$0.30 \ \pm \ 0.01^{a}$	$0.65 ~\pm~ 0.15^{a}$
Triticum tur	gidum ssp durum desf.								
BNL	$3.90 \pm 0.01^{A}$	$35.8~\pm~1.05^{\text{AB}}$	$12.0~\pm~0.20^{\rm A}$	$5.04 \pm 0.15^{B}$	$59.7 \pm 0.21^{B}$	-	$47.5 \pm 0.50^{\circ}$	$1.90~\pm~0.20^{\rm A}$	$3.15 \pm 0.05^{B}$
BNC	$4.15 \pm 0.15^{AB}$	$41.2 \pm 0.40^{\circ}$	$12.8 \pm 0.01^{B}$	$4.96 \pm 0.10^{B}$	$56.6 \pm 0.53^{A}$	-	$47.0 \pm 0.00^{\circ}$	$1.85 \pm 0.65^{A}$	$1.95 \pm 0.35^{A}$
BRL	$4.20\ \pm\ 0.20^{B}$	$36.2 \pm 0.05^{B}$	$12.6 \pm 0.60^{B}$	$4.10 \ \pm \ 0.25^{A}$	$61.0 \ \pm \ 0.60^{B}$	-	$20.0~\pm~2.00^{\text{A}}$	$44.1 \pm 3.95^{\circ}$	$7.25 \pm 0.15^{\circ}$
BB	$4.20\ \pm\ 0.10^{B}$	$35.1 \pm 0.40^{A}$	$14.7~\pm~0.10^{\rm C}$	$4.87 \pm 0.05^{B}$	$58.6\ \pm\ 3.02^{AB}$	-	$37.5 \pm 1.50^{B}$	$6.25\ \pm\ 0.85^{B}$	$8.70~\pm~0.20^{\rm D}$

BNL = Bufala nera lunga; BNC = Bufala nera corta; BRL = Bufala rossa lunga; BB = Bufala bianca; TCW = thousand corn weight; GE = germination energy; WUG = wholly unmodified grains; PUG = partly unmodified grains; db = dry basis; (-) = not available; for each class of samples, values in the same column followed by different lowercase letters for common, and uppercase letters for durum wheat, are statistically different ( $p \le 0.05$ ).

6.15 g (db). These differences were probably due to the different degrees of modification between common and durum wheat. This hypothesis was confirmed by the results of the friability, where the average for common and durum wheat malts were 68.75 % and 38.00 %, respectively. This significant difference in friability values could be due to the vitreous character of durum wheat varieties. The hardness of wheat is associated to the fracture along the interphase starch/protein, whereas in durum wheat, the adhesion on the interphase starch/protein is higher and is located at the cell limits and is greatly due to the aleurone layer (Osborne et al., 2007; Ponce-García et al., 2016). Friability values may predict the lautering performance and wort viscosity (Bathgate, 1983). As expected, common wheat showed much higher levels of friability than durum wheat, as confirmed by the low WUG and PUG levels. Among the durum wheat malts, the Bufala rossa lunga (BRL) variety was poorly modified with 20 % of friability and 44 % of unmodified kernels, as shown in Table 1. Soluble proteins are often used in malting as guidelines to determine the extent of modification; the soluble protein content was in the range 4.10–5.60 % db for common wheat and 4.10-5.04 % db for durum wheat in our study, which is lower than that reported in other studies (Alfeo et al., 2018b; Guo et al., 2014). Furthermore, protein solubilisation and degradation is greatly affected by endopeptidase activity during malting, which is mainly influenced by landraces (Jones, 1998; Jones and Budde, 2005). Fig. 1 shows the trend of protein and starch degradation, expressed as KI and  $\Delta$  starch.

The protein and starch degradation are good indicators of the degree of modification that occurs during malting. In common wheat malts, the KI was in the range 29.47-48.64 % for the Cuccitta and Maiorcone varieties, while for that of the durum wheat malts ranged between 32.43 % in the BRL and 41.94 % in Bufala nera lunga (BNL) variety. The common wheat malts showed an average KI of 37.46 %, which was slightly higher than that found in common wheat malts. These results are consistent with those of other studies on wheat malts (Depraetere et al., 2004). The  $\Delta$  starch levels showed high heterogeneity among samples and ranged from 1.88 to 13.5% for the Cuccitta and Maiorcone varieties, while that of the durum wheat malts ranged between 4.51 % in the BRL and 12.58 % in Bufala nera corta (BNC) variety. On average, the durum wheat malts showed higher starch degradation (approximately 8.25 %) than common wheat malts (approximately 7.56 %), with an opposite trend compared to KI. The Cuccitta and BRL samples had the lowest  $\Delta$  starch values, probably due to the larger kernel size. The  $\Delta$  starch can be enhanced by lengthening germination (Alfeo et al., 2018b).

#### 3.3. NSP- and starch-degrading enzymes

A complete enzymatic pattern is essential for the quality of malt and its brewhouse performance. Barley malt is the most used raw material in beer production because of its excellent diastatic power, which allows the production of high-yielding extracts without the addition of exogenous enzymes. The first group of enzymes studied were the debranching enzymes endo-\beta-glucanases and endo-1,4-β-D-xylanases (Table 2). These enzymes, in combination with endo-1,3- $\beta$ -glucanase, endo-1,3:1,4-β-glucanase, endo-1,4-β-glucanase, β-D-xylosidase, and  $\alpha$ -L-arabinofuranosidase, are essential for hydrolysing the NSPs that are not attacked by  $\alpha$ - and  $\beta$ -amylases (Prentice, 1976). To obtain the best performance from amylases during mashing, the endosperm cell walls must be degraded by  $\beta$ -glucanases and xylanases to increase the availability of starch and facilitating amylase activities. The endo- $\beta$ glucanases in barley increase by 100-200 times during germination and quickly decrease during kilning. For these reasons, malting is a crucial production step for proper grain modification (De Sá and Palmer, 2004). Durum wheat on average showed higher endo-1,4-β-Dglucanases activity than common wheat, respectively 64.36 and 21.39 U kg<sup>-1</sup>. Additionally, the BNC and BNL varieties showed significantly higher endo- $\beta$ -glucanase activity among the durum wheat malts, while those of the BRL and Bufala Bianca (BB) varieties were similar to the levels observed in common wheat malts (Table 2). Levels of endo-βglucanase in common wheat malts were in the range 3.34-35.66 U kg<sup>-1</sup>, respectively, for the Maiorca and Romano varieties. The endo- $\beta$ glucanase levels observed in this study were higher than those of other studies carried out for wheat malt, which was probably due to the different landraces used for the tests (Alfeo et al., 2018b; Jin et al., 2014). The endo-1,4-β-D-xylanase activity increases during malting to cut the  $\beta$ -1,4-glycosidic bonds of the arabinoxylans solubilized from the endosperm cell walls (Mendis and Simsek, 2015). Common and durum wheat malts showed comparable endo-1,4-β-D-xylanase levels on average, respectively 0.36 and 0.37 U g<sup>-1</sup>. Among the common wheat malts, Maiorca and Romano varieties showed significantly higher endo-1,4-β-D-xy lanase levels, while the BNC variety reached the highest activity, followed by the BNL and BB varieties among the durum wheat malts. These results are in line with the literature regarding the endo-1,4-β-D-xy lanase levels observed in wheat malts as well as in barley malt (Alfeo et al., 2018a; Hattingh et al., 2014).

Malt amylases play a key role in mashing, as shown in Table 2.  $\beta$ -Amylases are present in free, insoluble, and latent forms in wheat, and the insoluble and latent forms are released during malting, while  $\alpha$ -amylase is synthesised in the aleurone cells during germination



**Fig. 1.** Degradation trend observed for protein and starch expressed respectively as Kolbach index and  $\Delta$  starch (n = 3; error bars = SD). BNL = Bufala nera lunga; BNC = Bufala nera corta; BRL = Bufala rossa lunga; BB = Bufala bianca; Bar followed by different lowercase letters for common, and uppercase letters for durum wheat, are statistically different (p ≤ 0.05).

#### Table 2

Main NSP- and Starch-degrading enzyme activities detected in wheat malts.

	endo-β- glucanases (U kg <sup>-1</sup> db)	Endo-1,4-β-D- xy la nase (U g <sup>-1</sup> db)	β-am ylas e (BU g <sup>-1</sup> db)	α-am ylas e (CU g <sup>-1</sup> db)	
Triticum aes	stivum L.				
Maiorca	$3.34 \pm 0.45^{a}$	$0.49 \pm 0.07^{b}$	$25.1 \pm 0.75^{a}$	$214 \pm 22.8^{\circ}$	
Maiorcone	$14.2 \pm 8.84^{b}$	$0.27 \pm 0.03^{a}$	$38.2 \pm 1.43^{\circ}$	$118 \pm 4.27^{\mathrm{b}}$	
Cuccitta	$32.3 \pm 5.32^{\circ}$	$0.23 ~\pm~ 0.03^{a}$	$33.1 \pm 0.14^{b}$	$87.7 \pm 2.17^{a}$	
Romano	$35.7 \pm 3.39^{\circ}$	$0.45~\pm~0.01^b$	$25.9~\pm~0.44^a$	$238~\pm~6.85^d$	
Triticum tur					
BNL	$84.8 \pm 9.19^{B}$	$0.37 \pm 0.06^{B}$	$28.8 \pm 0.51^{B}$	$105 \pm 3.25^{A}$	
BNC	$110.1 \pm 19.5^{B}$	$0.55 \pm 0.01^{\circ}$	$26.6 \pm 0.16^{A}$	$113 \pm 10.3^{A}$	
BRL	$32.5 \pm 2.35^{A}$	$0.16 \ \pm \ 0.02^{A}$	$26.7 \pm 0.48^{A}$	$167 \pm 8.10^{B}$	
BB	$29.9 \pm 16.40^{\text{A}}$	$0.38 \pm 0.01^{B}$	$29.8 \pm 1.76^{B}$	$221 \pm 8.31^{\circ}$	

BNL = Bufala nera lunga; BNC = Bufala nera corta; BRL = Bufala rossa lunga; BB = Bufala bianca; db = dry basis; Values in the same column followed by different lowercase letters for common, and uppercase letters for durum wheat, are statistically different ( $p \le 0.05$ ).

(Faltermaier et al., 2014). In particular,  $\beta$ -amylases cut alternate  $\alpha$ -1,4 linkages from the non-reducing end of the starch molecule, and  $\alpha$ amylase cuts the  $\alpha$ -1,4 linkages from the inside, degrading amylose and amylopectin to dextrins. In our study, common wheat malts showed higher activity values for both  $\beta$ - and  $\alpha$ -amylases on average, indicating a better degree of modification than durum wheat malts. The Maiorcone variety had a  $\beta$ -amylase activity of 38.2 BU g<sup>-1</sup>, which was significantly higher when compared to the other common wheat malts, while the Maiorca variety had the weakest activity. In durum wheat malts, the  $\beta$ -amylase activity was in the range 26.6–29.2 BU g<sup>-1</sup>, respectively, for the BNC and BB varieties. These results are comparable with the levels of  $\beta$ -amylase activity reported in literature for durum and common wheat malts (Alfeo et al., 2018b; Jin et al., 2011). The activity of a-amylases observed in the Romano wheat malt was significantly higher than that of the other common wheat malts, as well as that of the BB variety among the durum wheat malts (Table 2). Interestingly, the levels of  $\alpha$ -amylases observed in our study for all the samples were higher than those reported in the literature for wheat malts and were comparable to barley malt (Alfeo et al., 2018b; Faltermaier et al., 2014; Hattingh et al., 2014).

#### 3.4. NSP in wheats, malts and worts

Arabinoxylans and  $\beta$ -glucans form the cell walls of different tissues in wheat, such as the starchy endosperm and the aleuronic layer. The arabinoxylan content and structure in wheat are influenced by the genotype and grain tissues, while the  $\beta$ -glucans are less represented than in other cereals and show lower water solubility, probably because of their regular molecular structure (Cui et al., 2000). The AX level of the common wheat malts was 2.61 g per 100 g (db) on average, and the Romano variety showed the highest AX content while no significant differences were observed among samples for the other varieties (Table 3). In durum wheat, the AX content was significantly lower than that of the other wheat samples, being even lower than 2.0 g per 100 g (db) for the BB and BNL varieties.

The same trend was observed for WEAX values, with common wheat malts showing higher water solubility, and the Maiorca variety reached the highest level. The average WEAX of durum wheat malt was 0.17 g per 100 g, and the BB variety showed the lowest WEAX content among all the tested wheat malts that were comparable to the WEAX levels observed in barley malts (Marconi et al., 2020). The WAX content was 523 mg L<sup>-1</sup> on average for the common wheat malt. The Maiorca, Romano, and Maiorcone varieties had higher and comparable WAX content. In durum wheat malts, the WAX content was 352 mg L<sup>-1</sup> on average, and as expected, the BB variety showed the lowest content (Table 3). Overall, the contents of AX, WEAX, and WAX of the landraces studied were lower than the levels reported in the literature for common and durum wheat malts (Alfeo et al., 2018b; Ciccoritti et al., 2011; Li et al., 2005).

The higher  $\beta$ -glucanase activity found in the durum wheat malts (Table 2) did not lead to increased degradation of  $\beta$ -glucans during malting. Although durum wheat had the lowest BG content (1.83 g per 100 g-) when compared to common wheat (2.59 g per 100 g), more  $\beta$ glucans were observed at the end of the malting process and even in the wort. The Maiorca variety had the highest BG content, and the  $\beta$ glucanases degraded  $\beta$ -glucans to a level lower than 0.40 g per 100 g (db) during malting, that represents the average MBG level found in durum wheat malts (Table 3). Although BNL and BNC were the landraces with lower BG content, these malts showed higher MBG content and  $\beta$ -glucanase activity at the end of the malting process. The average WBG was 294 mg L<sup>-1</sup> for the durum wheat malts and 285 mg L<sup>-1</sup> for the common wheat malts, and with the exception of BB among the durum wheat malts, no significant differences were observed among the samples. These results highlight how β-glucanase inhibition occurs during malting and mashing of durum wheat, which is probably due to the presence of proteinaceous inhibitors (York et al., 2004).

#### 3.5. Congress wort characteristics

The malt extract represents a key quality parameter, and the malt extract levels measured in our samples are listed in Table 4. The durum

#### Table 3

Arabinoxylan and betaglucan content of wheat, malts and worts.

		Wort (mg $L^{-1}$ )	)	Malt (g 100 g $^{-1}$ db)	Wheat (g 100 g $^{-1}$ db)				
	WBG	WAX	MBG	WEAX	BG	AX			
						rum L.	Triticum aestiv		
	$270 \pm 9.06^{a}$	$576 \pm 40.51^{b}$	$0.35 \pm 0.01^{\circ}$	$0.58 \pm 0.03^{\circ}$	$3.09 \pm 0.15^{\circ}$	$2.51 \pm 0.02^{a}$	Maiorca		
	$271 \pm 15.10^{a}$	$522 \pm 26.28^{ab}$	$0.20 \pm 0.00^{a}$	$0.39 \pm 0.01^{b}$	$2.41 \pm 0.12^{a}$	$2.47 \pm 0.22^{a}$	Miorcone		
	$282 \pm 51.42^{a}$	$470 \pm 49.51^{a}$	$0.27 \pm 0.02^{b}$	$0.37 \pm 0.03^{b}$	$2.17 \pm 0.11^{a}$	$2.64 \pm 0.27^{a}$	Cuccitta		
	$314 \pm 60.00^{a}$	$523 \pm 55.98^{ab}$	$0.36~\pm~0.02^c$	$0.18~\pm~0.01^a$	$2.67~\pm~0.13^{\rm b}$	$2.80~\pm~0.06^a$	Ro ma no		
						lum ssp durum desf.	Triticum turgid		
	$281 \pm 7.97^{AB}$	$347 \pm 23.66^{AB}$	$0.44 \pm 0.00^{BC}$	$0.20 \pm 0.05^{\circ}$	$1.59 \pm 0.08^{\text{A}}$	$1.98 \pm 0.09^{A}$	BNL		
	$321 \pm 25.87^{B}$	$414 \pm 53.78^{B}$	$0.37 \pm 0.02^{AB}$	$0.19~\pm~0.01^{\text{BC}}$	$1.71 \pm 0.09^{\text{A}}$	$2.13 \pm 0.10^{AB}$	BNC		
	$309 \pm 24.35^{B}$	$331 \pm 37.72^{A}$	$0.49 \pm 0.00^{\circ}$	$0.14 \pm 0.01^{AB}$	$2.00 \pm 0.10^{B}$	$2.37 \pm 0.09^{B}$	BRL		
	$263 \pm 26.08^{\text{A}}$	$316 \pm 23.78^{A}$	$0.30~\pm~0.09^{\rm A}$	$0.13~\pm~0.03^{\rm A}$	$2.03~\pm~0.10^{\scriptscriptstyle B}$	$1.84 \pm 0.18^{A}$	BB		
	$\begin{array}{r} 271 \ \pm \ 15.10^a \\ 282 \ \pm \ 51.42^a \\ 314 \ \pm \ 60.00^a \end{array}$ $\begin{array}{r} 281 \ \pm \ 7.97^{AB} \\ 321 \ \pm \ 25.87^B \\ 309 \ \pm \ 24.35^B \\ 263 \ \pm \ 26.08^A \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{l} 0.39 \ \pm \ 0.01^{\rm b} \\ 0.37 \ \pm \ 0.03^{\rm b} \\ 0.18 \ \pm \ 0.01^{\rm a} \end{array}$	$\begin{array}{rrrr} 2.41 \ \pm \ 0.12^a \\ 2.17 \ \pm \ 0.11^a \\ 2.67 \ \pm \ 0.13^b \end{array}$	$\begin{array}{rrrr} 2.47 \ \pm \ 0.22^a \\ 2.64 \ \pm \ 0.27^a \\ 2.80 \ \pm \ 0.06^a \end{array}$ lum ss p durum desf. 1.98 \ \pm \ 0.09^A \\ 2.13 \ \pm \ 0.10^{AB} \\ 2.37 \ \pm \ 0.09^B \\ 1.84 \ \pm \ 0.18^A \end{array}	Mi or cone Cuccitta Roma no <i>Triticum turgid</i> BNL BNC BRL BB		

AX = total arabinoxylans; BG = total  $\beta$ -glucans; WEAX = water extractable arabinoxylans; MBG = malt  $\beta$ -glucans; WAX = wort arabinoxylans; WBG = wort  $\beta$ -glucans; BNL = Bufala nera lunga; BNC = Bufala nera corta; BRL = Bufala rossa lunga; BB = Bufala bianca; db = dry basis; Values in the same column followed by different lowercase letters for common, and uppercase letters for durum wheat, are statistically different (p  $\leq$  0.05).

Table	- 4
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Quality	7 attributes	of the	EBC	congress	worts.
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	Extract (% db)	рН	Colour (EBC unit)	Viscosity (mPa.s)	Ferm entability (%)	FAN (mg L <sup>-1</sup> )
Triticum aestivum L.						
Maiorca	$85.6 \pm 0.05^{d}$	$6.05 \pm 0.01^{a}$	$6.35 \pm 0.15^{\circ}$	$1.64 \pm 0.01^{\circ}$	$82.2 \pm 0.05^{b}$	$181 \pm 2.00^{\circ}$
Maiorcone	$81.2 \pm 0.01^{b}$	$6.14 \pm 0.02^{b}$	$4.95 \pm 0.05^{b}$	$1.59 \pm 0.01^{a}$	$81.8 \pm 0.05^{a}$	$146 \pm 0.50^{b}$
Cuccitta	$80.8 \pm 0.10^{a}$	$6.13 \pm 0.06^{b}$	$4.05 \pm 0.05^{a}$	$1.70 ~\pm~ 0.01^{d}$	$81.8 \pm 0.15^{a}$	$132 \pm 0.01^{a}$
Romano	$83.0 \pm 0.01^{\circ}$	$6.18 \ \pm \ 0.01^{\rm b}$	$5.10~\pm~0.01^b$	$1.61 \ \pm \ 0.01^{b}$	$82.6 \pm 0.15^{\circ}$	$180~\pm~0.01^{\circ}$
Triticum turgidum	ssp durum desf.					
BNL	$84.7 \pm 0.01^{D}$	$6.12 \pm 0.07^{A}$	$3.65 \pm 0.05^{\text{D}}$	$1.78 \pm 0.01^{B}$	$81.5 \pm 0.60^{B}$	$146 \pm 0.00^{\circ}$
BNC	$83.6 \pm 0.05^{\circ}$	$6.10 \pm 0.00^{A}$	$3.35 \pm 0.05^{B}$	$1.75 \pm 0.01^{A}$	$81.9 \pm 0.10^{B}$	$143 \pm 4.00^{BC}$
BRL	$82.7 \pm 0.10^{B}$	$6.22 \pm 0.02^{B}$	$3.10 \pm 0.10^{A}$	$1.77 \pm 0.01^{B}$	$79.3 \pm 0.40^{\text{A}}$	$105 \pm 0.50^{A}$
BB	$81.9 \pm 0.20^{A}$	$6.22 \pm 0.01^{B}$	$3.30 \pm 0.10^{B}$	$1.74 \pm 0.01^{A}$	$82.1 \pm 0.10^{B}$	$141~\pm~0.50$

FAN = free amino nitrogen; BNL = Bufala nera lunga; BNC = Bufala nera corta; BRL = Bufala rossa lunga; BB = Bufala bianca; db = dry basis; values in the same column followed by different lowercase letters for common, and uppercase letters for durum wheat, are statistically different ( $p \le 0.05$ ).

wheat malts showed a slightly higher extract (83.2 % on average, db) than the common wheat malts (82.7 % on average, db). These results are consistent with recommended brewing values (Depraetere et al., 2004; Faltermaier et al., 2014). The wort pH values were higher than those measured in barley malt congress and were similar to those observed in previous studies (Alfeo et al., 2018b; Jin et al., 2011, 2012). The colour formation during the kilning of the malt is due to the melanoidins formed by the condensation of amino acids and reducing sugars, which are precursors of the Maillard reaction. Thus, a higher degree of modification during germination leads to higher formation of colour compounds. The colour of common wheat malts was higher than that of durum malts (Table 4) despite the similar soluble protein content and KI values. Among the common wheat samples, the Maiorca variety was the darkest coloured malt, with the highest KI, friability, and FAN content (Table 4). The higher degree of modification in the Maiorca variety could be due to the low protein content and TCW, two factors that positively influence water uptake during steeping (Chandra et al., 1999). The durum wheat malts showed an average colour of 3.35 EBC unit, and BRL was the palest malt.

Viscosity is a key quality parameter for both wort and beer. A high wort viscosity can lead to problems of wort filterability, low extract, and haze formation in wort and beer. Several authors have reported the ability of β-glucans and arabinoxylans to increase wort viscosity (Jin et al., 2004). However, recent studies have highlighted that the reduction in the  $\beta$ -glucan and arabinoxylan content is not sufficient to exclude mash filtration problems, which could be due to molecular and hydrodynamic properties, such as molecular weight distributions, gyration radii, intrinsic viscosity, and Mark-Houwink parameters (Izydorczyk and Dexter, 2008; Marconi et al., 2020, 2014; Sadosky et al., 2014). The viscosity was found to be lower in common wheat samples than in the durum wheat malts (Table 4),1.63 and 1.76 mPa.s on average, respectively; these results are in line with those reported in literature (Alfeo et al., 2018b; Jin et al., 2011, 2014, 2012). Furthermore, no correlation was found between the viscosity and NSP content in both common and durum wheat malt.

In addition to the determination of  $\alpha$ -amylase activity, many brewers ask the maltsters the measurement of fermentability or apparent attenuation limit, which better emulates the brewing process on a small scale. Although the fermentability is more predictive than diastatic power, some authors have reported that even the determination of fermentability may not always provide an accurate prediction of malt fermentability performance in brewery production (Gibson et al., 1995). In our study, all the wheat malts showed similar fermentability, with values ranging from 79.3 %–82.6 % on average, and 82.1 % and 81.2 %, respectively, for common and durum wheat malts. Despite the low friability (20 %) and the high WUG content (44 %), the fermentability of the BRL variety was optimal, confirming the difficulty in evaluating the quality of a malt using only a few parameters and the importance of carrying out several analyses before using it. The FAN content indicates the amount of free amino nitrogen, which is key in yeast nutrition. The average FAN content was 160 mg  $L^{-1}$  for common wheat and 134 mg  $L^{-1}$  for durum wheat, demonstrating a higher degree of protein degradation in common wheat. The Maiorca and Romano landraces had the highest FAN levels (Table 4), which were higher than those reported in other studies on wheat malt, and these levels were also more than the FAN level of 100–140 mg  $L^{-1}$  required for proper yeast growth and fermentation performance (Alfeo et al., 2018b; Ceccaroni et al., 2019a; Guo et al., 2014; Hill and Stewart, 2019). The BRL variety showed the lowest FAN level (Table 4), demonstrating low protein degradation during malting and mashing, probably due to the vitreous kernel of durum wheat and a short germination time of 5 days instead of 5.5 or 6, as reported for some wheat malts to reach the optimal FAN level (Guo et al., 2014).

Principal component analysis (PCA) was carried out to evaluate the influence of the wheat landraces on the monitored quality parameters of endosperm modification, such as friability, PUG, WUG, and KI, as well as the malt extract, NSP, and wort viscosity. A biplot of the score and loading of the PCA is shown in Fig. 2. Two principal components were selected, where 52.91 % of the variance was from principal component 1 (PC1), and 23.45 % of the variance was from PC2, explaining 76.36 % of the total variance. The PC1 spreads the sample scores according to the degree of endosperm modification. The sample scores on the positive side of PC1 were common wheat malts with higher endosperm modification and WAX content.

Durum wheat malts were plotted on the negative side of PC1, and their relative positions reflect the presence of under-modified and glassy endosperms with high WBG and viscosity levels, as reported in a similar study (Alfeo et al., 2018b; Faltermaier et al., 2015). The PC2 separates the sample scores according to the malt extract and extent of protein degradation. The samples plotted on the positive side were the BNL, BNC, and BRL varieties, showing higher extract levels, even if they were under-modified malts. Furthermore, the Maiorca variety was the only common wheat malt plotted on the positive side of PC2, as it had the highest extract and KI values observed among all the samples. The samples in the first quadrant of the biplot were the over-modified malts (KI > 45 %); only the Maiorca variety showed these characteristics among the common wheat samples, while we could observe the durum wheat malts that showed proper extract and protein degradation even if under-modified, as highlighted by the level of PUG, WUG, WBG, and viscosity, in the second quadrant. These results are in line with those of previous studies on wheat malts (Faltermaier et al., 2014; Guo et al., 2014; Jin et al., 2011, 2014). The score of the BB variety was plotted in the third quadrant as this sample had the lowest WBG level, viscosity, and extract among the durum wheat malts. Most of the common wheat malts were in the fourth quadrant, such as the Cuccitta and Maiorcone varieties, which were characterised by low extract and protein degradation, although they showed higher friability levels, while the Romano variety showed intermediate characteristics, with proper



**Fig. 2.** Biplot for scores and loading of the principal component analysis (PCA). (**Square** = loadings; **circle** = durum wheat scores; **triangle** = common wheat scores) BNL = Bufala nera lunga; BNC = Bufala nera corta; BRL = Bufala rossa lunga; BB = Bufala Bianca.

extract level, protein degradation, and friability, and was plotted closer to the first quadrant.

## 3.6. Sugar composition

The wort sugar composition is an important parameter for evaluating the quality of malt (Table 5). In particular, well-modified malts show high levels of fermentable sugars, such as maltose, glucose, and sucrose, and to a lesser extent, fructose. In a studies involving 12 Plato worts brewed from barley malt, the simple sugars consist of 8–10 g L<sup>-1</sup> glucose, 0–2 g L<sup>-1</sup> fructose, 3–5 g L<sup>-1</sup> sucrose, and 54–64 g L<sup>-1</sup> maltose (De Francesco et al., 2018; Mayer et al., 2016; Meilgaard, 1976). The wort sugar profiles of the studied wheat malts showed statistically significant differences. The level of simple sugars in the common wheat malts was in the range of 43.6–48.7 g L<sup>-1</sup>, respectively, for the Cuccitta and Romano varieties (Table 5), obtained as the sum of fructose, glu-

#### Table 5

Sugar profile of the EBC congress wort (g  $L^{-1}$ ).

Sugar	Triticum aestivum L.				Triticum turgidum ssp durum desf.			
	Maiorca	Maiorcone	Cuccitta	Romano	BNL	BNC	BRL	BB
Fructose	$0.61 \pm 0.01^{a}$	$0.63 \pm 0.01^{a}$	$0.81\ \pm\ 0.12^{b}$	$0.93 \pm 0.03^{\circ}$	$1.20 \pm 0.22^{\circ}$	$0.69\ \pm\ 0.07^{AB}$	$0.54 \pm 0.08^{A}$	$0.91 \pm 0.07^{B}$
Glucose	$5.61 \pm 0.44^{a}$	$4.83 \pm 0.11^{a}$	$4.80 \pm 0.08^{a}$	$8.55 \pm 0.97^{b}$	$5.83 \pm 0.93^{B}$	$5.69 \pm 0.30^{B}$	$4.19 \pm 0.19^{A}$	$6.05 \pm 0.08^{B}$
Sucrose	$4.29 \pm 0.56^{\circ}$	$2.79 ~\pm~ 0.02^{ab}$	$2.27 ~\pm~ 0.15^{a}$	$3.91 \pm 1.28^{bc}$	$2.53 \pm 0.27^{A}$	$2.53 \pm 0.28^{A}$	$2.53 \pm 0.07^{A}$	$2.96 \pm 0.36^{A}$
Maltose	$33.9 \pm 2.47^{a}$	$37.0 \pm 0.97^{a}$	$35.7 \pm 1.47^{a}$	$35.2 \pm 8.11^{a}$	$39.4 \pm 1.67^{A}$	$38.5 \pm 5.43^{A}$	$38.0 \pm 2.75^{A}$	$38.3 \pm 0.07^{A}$
tot simple sugars	44.4 ± 3.49a	45.2 ± 1.07a	<b>43.5</b> ± 1.65 <i>a</i>	48.7 ± 8.46a	49.0 ± 2.54A	47.5 ± 5.34A	45.3 ± 2.56A	48.2 ± 0.30A
D3 (maltotriose)	$9.24 \pm 0.81^{ab}$	$7.44 \pm 0.43^{a}$	$7.77 \pm 0.97^{a}$	$10.80 \pm 2.65^{b}$	$9.06 \pm 1.15^{A}$	$8.95 \pm 1.01^{A}$	$8.34 \pm 0.73^{A}$	$7.89 \pm 0.19^{A}$
D4 (maltotetraose)	$1.67 \pm 0.06^{bc}$	$1.48 \pm 0.25^{b}$	$2.04 \pm 0.22^{c}$	$0.97 \pm 0.21^{a}$	$1.12 \pm 0.06^{B}$	$1.65 \pm 0.13^{D}$	$1.39 \pm 0.07^{\circ}$	$0.95 \pm 0.08^{A}$
D5 (maltopentaose)	$0.73~\pm~0.10^{a}$	$0.70~\pm~0.08^{a}$	$0.81~\pm~0.02^{a}$	$0.75 ~\pm~ 0.19^{a}$	$0.68 \pm 0.06^{B}$	$0.49 \pm 0.01^{A}$	$0.45 \pm 0.07^{A}$	$0.60 \pm 0.05^{B}$
D6 (maltohexaose)	$1.10 ~\pm~ 0.09^{b}$	$1.17~\pm~0.02^{\rm b}$	$0.91~\pm~0.07^{a}$	$1.25 \pm 0.15^{b}$	$0.64 \pm 0.11^{A}$	$0.79 \pm 0.05^{A}$	$0.76 \pm 0.04^{A}$	$0.90 \pm 0.21^{A}$
D7 (maltoeptaose)	$0.97~\pm~0.07^{\rm b}$	$0.67 \pm 0.11^{a}$	$0.71 ~\pm~ 0.01^{a}$	$1.14 \pm 0.05^{\circ}$	$0.67 \pm 0.08^{A}$	$0.71 \pm 0.06^{A}$	$0.79 \pm 0.13^{A}$	$0.81 \pm 0.07^{A}$
D8	$0.77 ~\pm~ 0.10^{a}$	$0.70 ~\pm~ 0.07^{a}$	$0.73~\pm~0.03^{a}$	$0.80~\pm~0.13^{a}$	$0.91 \pm 0.11^{B}$	$0.93 \pm 0.13^{B}$	$0.56 \pm 0.08^{A}$	$0.54 \pm 0.02^{A}$
D9	$0.58 \pm 0.01^{b}$	$0.66 \pm 0.06^{b}$	$1.05 \pm 0.02^{c}$	$0.44 \pm 0.08^{a}$	$0.69 \pm 0.03^{A}$	$0.80 \ \pm \ 0.02^{B}$	$0.89 \pm 0.04^{\circ}$	$0.64 \pm 0.03^{A}$
D10	$0.07~\pm~0.01^a$	$0.12 ~\pm~ 0.01^{b}$	$0.26 \pm 0.03^{c}$	$0.07 \pm 0.03^{a}$	$0.10 \ \pm \ 0.01^{\text{A}}$	$0.08 ~\pm~ 0.01^{A}$	$0.07 \pm 0.01^{A}$	$0.08 \pm 0.03^{A}$
D11	$0.08 \pm 0.01^{b}$	$0.06 \pm 0.01^{a}$	$0.06 \pm 0.01^{a}$	$0.07 ~\pm~ 0.01^{ab}$	$0.05 \pm 0.02^{A}$	$0.06 \pm 0.02^{A}$	$0.07 \pm 0.01^{A}$	$0.13 \pm 0.01^{B}$
D12	$0.12 ~\pm~ 0.01^{a}$	$0.11 ~\pm~ 0.02^{a}$	$0.10 \ \pm \ 0.02^{a}$	$0.10 ~\pm~ 0.01^{a}$	$0.11 ~\pm~ 0.01^{\text{A}}$	$0.12 \ \pm \ 0.02^{A}$	$0.15 \pm 0.03^{A}$	$0.12 \pm 0.01^{A}$
D13	$0.14 ~\pm~ 0.05^{a}$	$0.13 ~\pm~ 0.01^{a}$	$0.09 ~\pm~ 0.01^{a}$	$0.09 ~\pm~ 0.02^{a}$	$0.14 \pm 0.01^{B}$	$0.15 \ \pm \ 0.02^{B}$	$0.13 \pm 0.02^{B}$	$0.10 \pm 0.01^{A}$
D14	$0.06 \pm 0.02^{a}$	$0.12~\pm~0.02^{b}$	$0.14~\pm~0.04^{b}$	$0.06 \pm 0.03^{a}$	$0.12 \ \pm \ 0.02^{A}$	$0.11 \ \pm \ 0.01^{A}$	$0.11 \pm 0.03^{A}$	ND
tot dextrins	15.5 ± 1.23a	13.4 ± 0.61a	14.7 ± 0.99a	16.5 ± 3.04a	14.3 ± 1.31B	$14.8 \pm 0.83B$	13.7 ± 0.36AB	$12.8 \pm 0.11A$
Total sugars	$60.0 \pm 4.72^{a}$	$58.6~\pm~0.46^a$	$58.2 \pm 2.64^{a}$	$65.2 \pm 11.5^{a}$	$63.2 \pm 3.85^{A}$	$62.3 \pm 6.17^{A}$	$59.0 \pm 2.91^{\text{A}}$	$61.0 \pm 0.41^{A}$

BNL = Bufala nera lunga; BNC = Bufala nera corta; BRL = Bufala rossa lunga; BB = Bufala bianca; values in the same row followed by different lowercase letters for common, and uppercase letters for durum wheat, are statistically different ( $p \le 0.05$ ).

cose, sucrose, and maltose, Among the common wheat malts, the Romano variety exhibited the highest fructose and glucose levels, while the Maiorca variety showed the highest sucrose level, and no significant differences were observed for maltose and the total simple sugars. The levels of simple sugars among the durum wheat malts ranged between 45.3 in the BRL variety to 49.0 in the BNL variety. The latter showed the highest fructose level, while for glucose, with the exception of the BRL variety, no significant differences were observed among the other samples. The durum wheat samples had similar contents of sucrose and maltose, and no significant differences were observed among the samples. On average, the total simple sugars were equal to 45.5 g  $L^{-1}$  for common wheat and 47.5 g  $L^{-1}$  for durum wheat. The amount of maltose observed was in line with the wort derived from barley malt in a previous study, reaching over 59 % and 62 % of the total sugars on average, respectively, for common and durum wheat malts (Younis and Stewart, 1998) (Table 5).

Regarding the simple sugars, the maltotriose level was similar in all the samples, which was comparable to that in barley malt wort. In particular, the worts from common and durum wheat malts showed similar maltotriose content, 8.81 and 8.56 g L<sup>-1</sup> on average, respectively, accounting for 14.6 % and 13.9 % of total sugars. Brewing wort consists of 75 % fermentables, and the sugar profile shows approximately 10 % glucose, 5% sucrose, 45 % maltose, 15 % maltotriose, 10 % maltotetraose, and 15 % dextrins (over four D-glucose units) (Russel, 2006). In other studies on barley malt, maltotetraose in the derived wort is accounted for approximately 6% of the total sugar content, and the other dextrins account for 22 % (Ragot et al., 1989). In our samples, the total dextrins were 15.0 g L<sup>-1</sup> and 13.9 g L<sup>-1</sup> on average, respectively, for common and durum malts, accounting for 25 % and 23 % of total sugars, respectively. In general, the wort sugar composition of the studied wheat malts was comparable to that of wort derived from barlev malt.

#### 3.7. Pearson correlations

The Pearson correlation coefficients are shown as supplementary materials in Table S1 for the common wheat malts and in Table S2 for the durum wheat malts. Common wheat malt extract was positively correlated with the KI (0.997, p < 0.01), wheat BG content (0.983, p < 0.05), and soluble proteins (0.984, p < 0.05). As expected, according to Maillard reaction kinetics, malt colour was not only positively correlated with the KI (0.951, p < 0.05) and soluble proteins (0.977, p < 0.05), but also with malt BG content (0.987, p < 0.05)and WAX content (0.994, p < 0.01). These correlations could be due to protein release and endosperm modification during the malting tests, which increase the levels of peptides as precursors of the Maillard reaction. Furthermore, the malt proteins showed a positive correlation with PUG level (0.991, p < 0.01) and negatively correlated with levels of FAN (-0.987, p < 0.05),  $\alpha$ -amylase (-0.971, p < 0.05), and xylanase (-0.999, p < 0.001), confirming the inhibitory effect of the protein level on  $\alpha$ -amylase and xylanase activities, which generates poor starch degradation during malting. When the proteins were degraded into low-molecular-weight peptides during malting and mashing, the protein inhibition effects were reduced, as indicated by the positive correlation found between FAN and  $\alpha$ -amylase content (0.986, p < 0.05) and xylanase (0.987, p < 0.05). A strong negative correlation was also found between FAN and PUG levels (-0.998, p < 0.01), confirming that reduced protein degradation led to under-modified wheat malt. Interestingly, friability values showed a positive correlation with WAX content (0.952, p < 0.05), indicating that the solubilisation of arabinoxylans led to better cell wall degradation, as observed in a previous study for barley malt with  $\beta$ -glucan (Lee, 2008). In this regard, two negative correlations were found between PUG and  $\alpha$ -amylase (-0.976, p < 0.05) and xylanase content (-0.993, p < 0.01). Moreover, no correlation was found between friability and proteins, in agreement with Chandra et al. (1999), highlighting that the variations in the proportion and distribution of proteins and  $\beta$ -glucans within the endosperm are more important than the total amount.

Regarding the durum wheat correlation coefficients, the extract was positively correlated with WEAX (0.956, p < 0.05) and negatively correlated with BG content (-0.966, p < 0.05), indicating that the solubilisation of AX during malting led to higher extract levels, while high BG content led to a reduced degree of modification and extract levels. This fact was confirmed by the KI values that were positively correlated with WEAX content (0.969, p < 0.05) and negatively correlated with BG content (-0.991, p < 0.01). Wort fermentability was positively influenced by the extent of protein degradation and negatively influenced by the presence of under-modified grains, as highlighted by the correlation with FAN (0.957, p < 0.05) and WUG content (-0.962, p < 0.05). In contrast to the common wheat malts, soluble proteins of durum wheat malts showed a positive correlation with friability (0.973, p < 0.05) and FAN content (0.998, p < 0.01), while soluble protein level was negatively correlated with WUG (-0.996, p < 0.01), indicating that protein solubilisation and degradation of durum wheat malts alter the structure of the caryopsis by reducing their hardness. The same trend was observed for the FAN content, which was positively correlated with friability (0.957, p < 0.05) and negatively correlated with WUG (-0.957, p < 0.01). As expected, xylanase was positively correlated with  $\Delta$  starch content (0.952, p < 0.05), indicating that endosperm cell wall degradation promotes starch hydrolysis, facilitating amylase activity.

#### 4. Conclusions

The present study involved the evaluation of eight old Sicilian wheat landraces. The results highlighted the potential of these grains to produce 100 % malted wheat beer. However, the wheats protein content was higher than the ideal level for producing beer without adjuncts, especially for industrial targets. The common wheat samples showed higher values for both  $\beta$ -amylases and  $\alpha$ -amylases. The amount of  $\beta$ -glucanases in the durum wheat samples was 3-folds of that in the common wheat samples. In addition, common wheat showed a better degree of modification under the malting conditions used in this study. The common wheat samples had higher colour, lower viscosity, and a greater amount of FAN than the durum wheat samples. The friability results showed that some parameters currently used for barley malt evaluation do not fully indicate the quality of wheat malt. The wheat malt sugar composition assessed in this study contributes to filling the gap in information in the current literature. The total amount of fermentable sugars and dextrins did not show significant differences among the samples despite the different degrees of modification. The characterization of local craft beers will improve from the enhancement of the terroir of the raw materials. This study confirmed the need to carry out as many analytical determinations as possible to better understand the characteristics of a malt. In conclusion, among the eight tested landraces, all the wheat malts appear to be suitable as brewing raw material, and some of these landraces showed excellent characteristics, such as the Romano and Maiorca varieties among the common wheat samples and the BNC and BNL varieties among the durum wheat samples.

#### Authors contributions

For transparency, we encourage authors to submit an author statement file outlining their individual contributions to the paper using the relevant CRediT roles:

Aldo Todaro and Vincenzo Alfeo Conceptualization. Vincenzo Alfeo, Giovanni De Francesco and Valeria Sileoni Data curation. Vincenzo Alfeo, Giovanni De Francesco, Valeria Sileoni and Aldo Todaro Investigation. Vincenzo Alfeo, Aldo Todaro, Sebastiano Blangiforti and Rosa Palmeri Methodology. Aldo To daro, Giusep pe Perretti and Guido Aerts Supervision and Validation. Vincenzo Alfeo and Giovanni De Francesco Writing - review & editing.

#### Uncited references

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfca.2021.103997.

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