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Daily assessment of malting-induced changes in the volatile composition of barley (*Hordeum vulgare* L.), rye (*Secale cereale* L.), and quinoa (*Chenopodium quinoa* Willd.)

Cynthia Almaguer | **Hubert Kollmannsberger** | **Martina Gastl** | **Thomas Becker**

Lehrstuhl für Brau- und Getränketechnologie, Technische Universität München Weihenstephan, Freising, Germany

Correspondence
Cynthia Almaguer, Lehrstuhl für Brau- und Getränketechnologie, Technische Universität München Weihenstephan, Weihenstephaner Steig 20, 85354 Freising, Germany.
Email: Cynthia.Almaguer@tum.de

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Abstract: Barley (*Hordeum vulgare* L.) is the traditional malting cereal and is primarily used for beverages, whereas rye (*Secale cereale* L.) is mainly used in baked goods. Conversely, quinoa (*Chenopodium quinoa* Willd.) is a gluten-free pseudocereal, rich in starch and high-quality proteins, and can be used in a similar manner to cereals. The sharp bitterness of unprocessed rye and the earthy aroma of native quinoa interfere with the acceptance and development of food products. Malting of barley is known to improve its processing properties and enhance its sensory quality. Therefore, the effect of germination and kilning on malt quality (e.g., viscosity) as well as the volatile composition of barley, rye, and quinoa were monitored. Moreover, temporal changes on the volatile patterns of rye and quinoa at the different stages of malting were compared to barley. In total, 34 volatile compounds were quantified in the three (pseudo)cereals; the alcohol group dominated in all unprocessed samples, in particular, compounds contributing grassy notes (e.g., hexan-1-ol). These grassy compounds remained abundant during germination, whereas kilning promoted the formation of Maillard reaction volatiles associated with malty and roasted notes. The volatile profiles of kilned barley and quinoa were characterized by high concentrations of the malty Strecker aldehyde, 3-methylbutanal. In contrast, green, floral notes imparted by phenylacetaldehyde remained dominant in rye malt. Hierarchical cluster analysis of the volatile data discriminated the samples into the different stages of malting, confirmed the similarities in the volatile patterns of barley and rye, and indicated clear differences to the quinoa samples.

KEYWORDS
aroma, barley, daily modifications, malting, quinoa, rye, (pseudo)cereals

Practical Application: In this study, the effect of germination and kilning on the chemical and volatile composition of barley, rye, and quinoa was examined. Temporal changes on the volatile patterns of rye and quinoa at different stages of malting were compared to barley. Understanding the differences among the

(pseudo)cereals as well as the influence of processing on malt quality and aroma development can help find new food applications.

1 | INTRODUCTION

Barley (*Hordeum vulgare* L.) and rye (*Secale cereale* L.) are genetically related temperate cereals belonging to the same tribe (i.e., Triticeae) of the Poaceae grass family (Wrigley, 2019). Conversely, quinoa (*Chenopodium quinoa* Willd.) is a gluten-free pseudocereal of the Amaranthaceae family, indigenous to the Andean region of South America (Graf et al., 2015). Quinoa is a dicotyledonous plant, and therefore, not a true cereal (i.e., monocotyledonous); however, due to its starch-rich perispermic seeds (69.0%–75.8%) (Kozioł, 1992; Wright et al., 2002), it is referred to as pseudocereal, it can be milled into flour and used similarly to cereals (Hager et al., 2014). The protein content (12.5%–16.7%) (Bruin, 1964; Kozioł, 1992; Vega-Gálvez et al., 2010) in quinoa is higher than in most cereals and further characterized by high levels of lysine (5.8%–6.4%) (Kozioł, 1992; Wright et al., 2002), a limiting essential amino acid in cereals (Mahoney et al., 1975; Ruales & Nair, 1992). In barley, the protein content ranges from 8.0% to 13.0% (Lásztity, 1996), and in malting barley, it should ideally be between 9.0% and 11.0% (Fox, 2010). The content of protein reported in rye cultivars, grown in different countries, ranged from 9.0% to 15.8% (Hansen et al., 2004; Nyström et al., 2008; Sapirstein & Bushuk, 2016; Shewry et al., 2010). In both cereals, starch is mainly found in the endosperm, contents between 51.3%–68.0% and 54.9%–65.6% have been reported in barley and rye, respectively (Czuchajowska et al., 1998; Hansen et al., 2004; Holtekjølen et al., 2006; Nyström et al., 2008; Sapirstein & Bushuk, 2016; Shewry et al., 2010).

The term (pseudo)cereal is used henceforth to collectively refer to cereals as well as pseudocereals. (Pseudo)cereals are valuable raw materials for the production of human consumption products, such as fermented beverages and baked goods. Barley remains the traditional malting and brewing cereal, consequently, its attributes are considered the industry standard for brewing purposes. Rye is mainly used to produce a variety of baked goods, including sourdough bread, crispbread, and pumpernickel. Rye is also used in fermented beverages, such as kvass, whiskey, vodka, and beer (Wrigley, 2019). Quinoa seeds are primarily consumed in a similar manner to rice but can also be used to produce soups and breads as well as the traditional beverage, chicha. Other food products made from quinoa are porridge, desserts, pasta, and beverages (Bojanic, 2011; Simmonds, 1965; Tapia, 2021; Valencia-Chamorro, 2003; Weber, 1978). A major challenge for the development of rye or quinoa-based food products is making them palatable and widely acceptable to consumers due to their sharp bitterness. The high nonstarch polysaccharide (i.e., dietary fiber: 18.7%–22.2% (Andersson et al., 2009); e.g., arabinoxylan) and saponin (up to 4.65% (Scanlin & Lewis, 2017)) levels in rye bran and quinoa pericarp, respectively, produce the bitter taste which interferes with their acceptance (Jonsson et al., 2018; Miranda-Villa et al., 2019; Suárez-Estrella et al., 2018). Moreover, rye extracts are very viscous due to the high nonstarch polysaccharides (Bengtsson & Åman, 1990), and the aroma of unprocessed quinoa is often described as unpleasant due to its grassy and earthy notes (Hager et al., 2014; Scanlin & Lewis, 2017). Consequently, rye or quinoa-based food products could benefit from preprocessing methods such as malting.

In barley, malting improves the processing properties (e.g., low viscosity) and, in addition, generates distinct color, taste, and aroma. Moreover, the contribution of barley to food flavor is mostly developed through the malting process (Bettenhausen et al., 2018). During germination, hydrolytic enzymes catalyze structural modifications in the kernel resulting in the degradation of the storage macromolecules into free amino acids, fermentable sugars, and other micro as well as macro components. Germination is followed by the drying process (i.e., kilning), color and aroma are typically formed by heat-induced reactions. The most important is the Maillard reaction in which interactions between the available amino acids and reducing sugars yield new substances, in particular, nonenzymatically formed, odor-active volatiles (Briggs, 1998). Some of the most common volatile products of the Maillard reaction are the Strecker degradation products (i.e., Strecker aldehydes), formed by the decarboxylation and deamination of amino acids (Filipowska et al., 2021; Parker et al., 2000). Lipid degradation products are another important source of malt volatiles (Peppard et al., 1981; Sucan & Weerasinghe, 2005). Depending on the precursor pool (e.g., amino acids and reducing sugars) generated during malting, it is possible to create different malt qualities and aroma profiles. This, in turn, will influence the sensory profile and acceptance of finished food products (Bettenhausen et al., 2020).

In this study, the volatile composition of unprocessed barley, rye, and quinoa as well as the volatile development in their corresponding standard malts (M) were examined. The produced (pseudo)cereal malts, however,

aimed to remain within the accepted processing quality range of commercial barley malts. To better understand the effect of malting and volatile formation in the different (pseudo)cereals, the volatile patterns of rye and quinoa at different stages of malting were monitored and compared to barely. Characterization of the chemical and volatile composition was first done in the unmalted (UM) (pseudo)cereals. Subsequently, the temporal changes and effect of germination time (i.e., days; d) on malt quality indicators (e.g., soluble protein) as well as volatile composition were monitored daily. Finally, the impact of kilning on malt quality and volatile formation was assessed in the three standard malts. Barley remains the main malting cereal, therefore, the impact of germination and kilning on the composition and volatile formation in the rye and quinoa samples were compared to barley.

2 | MATERIALS AND METHODS

2.1 | Grain material

Two-row spring barley (hulled variety Grace; Ackermann Saatzucht GmbH & Co. KG, Irlbach, Germany) with 11.4% moisture and a protein content of 12.2% dry matter (d.m.) was kindly provided by Weyermann® (Bamberg, Germany). Winter rye (variety Dukato; Hybro Saatzucht GmbH & Co. KG, Schenkenberg, Germany) with 9.6% moisture and 10.0% protein (d.m.) was generously donated by SAATEN-UNION GmbH (Isernhagen, Germany). The measured starch is 62.0% and 62.6% (d.m.) in barley and rye, respectively. Organic white quinoa (variety unknown) with 9.4% moisture, 9.1% protein (d.m.), and 65.8% starch (d.m.) was purchased from Ziegler & Co. GmbH (Wunsiedel, Germany).

2.2 | Chemicals

Chemicals were purchased from the following sources: dichloromethane (≥99.8%), ethanol p.a. (≥99.8%), ammonia (25.0%), and sodium chloride (NaCl; ≥99.0%) from Sigma−Aldrich (Sigma−Aldrich Chemie GmbH, Schnelldorf, Germany). Reference standards of aroma compounds, 2-methylpropanal (≥99.5%), 3-methylbutanal (97.0%), 2-methylbutanal (95.0%), 3-(methylsulfanyl)propanal (≥97.0%), phenylacetaldehyde (≥90.0%), benzaldehyde (≥99.0%), pentanal (97.0%), hexanal (98.0%), 1-heptanal (95.0%), (*E*)-hex-2-enal (98.0%), (*E*)−2-nonenal (97.0%), (*E*,*Z*)−2,6-nonadienal (95.0%), (*E*,*E*)−2,4-decadienal (≥90.0%), 3-methylbutan-1-ol (≥98.0%), 2-methylbutan-1-ol (≥99.0%), 2-phenylethan-1-ol (≥99.0%), pentan-1-ol (≥99.0%), hexan-1-ol (98.0%), octan-1-ol (≥99.5%), (*Z*)-hex-3-en-1-ol (≥96.0%), (*E*)-hex-2-en-1-ol (97.0%), oct-1-en-3-ol (98.0%), (*E*)-non-2-en-1-ol (≥95.0%), pentan-2-one (99.5%), heptan-2-one (≥98.0%), 6-methylhept-5-en-2-one (≥98.0%), (*E*)-β-damascenone (≥98.0%), 2,5-dimethylpyrazine (≥98.0%), 2-ethyl-3,5(6)-dimethylpyrazine (≥98.0%), 2,3,5,6-tetramethylpyrazine (≥98.0%), furan-2-carbaldehyde (≥98.0%), 2-acetylfuran (99.0%), γ-nonalactone (≥98.0%), methyl butanoate (99.0%), and methyl heptanoate (≥99.8%), were purchased from commercial sources: Alfa Aesar (Alfa Aesar GmbH & Co. KG); Merck (Merck KGaA); or Sigma−Aldrich (Sigma−Aldrich Chemie GmbH).

2.3 | Malting

All malting trials were produced in 1 kg batches in the malting facility at the Institute of Brewing and Beverage Technology, Technische Universität München (Freising, Germany) as standardized by the Mitteleuropäische Brautechnische Analysenkommision e.V. (MEBAK; R-110.00.008 [2016-03]) (Jacob, 2016). The malting parameters used for the standard barley, rye, and quinoa malts are shown in Table 1. For the first two days, steeping was done in a stainless-steel steeping tank, 5 and 4 h on day 1 and day 2, respectively. After each steeping period, the grains were left to germinate in a climatic chamber with 95%–98% relative humidity. On the third day, the moisture was adjusted by spraying when deviations occurred. Once the final steep moisture was reached, all samples were turned twice a day until concluding the germination period. To monitor the daily modifications, samples were collected every 24 h (e.g., Bar-1d), stored at −20°C, and then freeze-dried using the BETA 1–8 LSCplus freeze dryer (Martin Christ GmbH, Osterode am Harz, Germany) to a moisture below 8.5%. To produce the standard malts (e.g., Bar-M), a sample was also kilned (50°C/16 h; 60°C/1 h; 70°C/1 h; and 80°C/5 h) after the last day of germination. After drying, rootlets and acrospires were removed, and samples were transferred into hermetic glass jars, and stored in a dry and dark location until further analysis. All samples used in this study were produced in three biological replicates.

The malting regimes required to produce the standard malts (i.e., Table 1 samples) were determined in separate studies. Design-Expert® Software (version 8.0.6; Stat-Ease, Inc.) was used to create a face-centered, central composite design. This experimental design (data not shown) investigates the effect of steep moisture, germination temperature, and germination time on malt quality indicators (e.g., extract) in barley, rye, and quinoa. To cover a broad range of modification, all malting parameters were tested at three different levels. Each series was malted twice and consisted of 25 samples, the factorial and

TABLE 1 Overview of malting regimes for experimental standard malts.

Sample code	Steep moisture [%]	Temperature [°C]	Time [d]
Bar-M	43	15	6
Rye-M	45	12	8
Qui-M	46	16	6

Abbreviations: Bar, barley; d, day; M, standard malt; Qui, quinoa.

center points were included in duplicate and triplicate, respectively. For each malting series, the experimental data of the analyzed malt quality indicators were statistically evaluated using analysis of variance (ANOVA, $p < 0.05$). Subsequently, multiple regression analyses of the experimental data were done to calculate statistical models (e.g., quadratic). Different tests were used to validate the statistical models; these include the *F*-value ($p < 0.05$), the coefficient of determination ($R^2 > 80\%$), and the lack-of-fit ($p > 0.05$) to assess the significance, the reliability, and the adequacy of the fitted model, respectively (Muñoz-Insa et al., 2016; Myers et al., 2016). These models evaluate the interaction of the three malting parameters and their effect on malt modification. Subsequently, these were used to determine the standard malting regime for each (pseudo)cereal. The selected regimes aimed to improve their quality and processing properties and were, therefore, set to yield high extract and soluble protein as well as low viscosity malts.

2.4 | (Pseudo)cereal and malt standard analyses

The moisture of the samples was determined following the MEBAK method R-200.18.020 [2016-03] (Jacob, 2016). To assess the malt modification, the malts were isothermally mashed at 65°C for 1 h as outlined in the MEBAK method R-207.00.002 [2016-03] (Jacob, 2016). The resulting laboratory worts were used to measure the pH, extract, total protein, soluble protein, free amino nitrogen (FAN), and viscosity of the produced malts. All analyses were carried out in technical triplicates according to the MEBAK methods (Jacob, 2016).

2.5 | Isolation of volatiles—Steam distillation

Prior to steam distillation, 50 g of finely ground sample (Laboratory Disk Mill DLFU; Bühler Group) was suspended in 200 mL of distilled water (dH_2O). After stirring for 30 min, the sample-dH_2O suspension was centrifuged at 9000 rpm for 20 min (20°C), and the supernatant was then transferred to a 150 mL volumetric flask. The internal standards, methyl butanoate and methyl heptanoate (1 mL, c = 10 mg/L), were added for quantification. Subsequently, the volatile fraction was isolated using a Büchi distillation unit K-355 (BÜCHI Labortechnik GmbH) as previously described by Herrmann et al. (2007). After steam distillation, 22.5 g NaCl, 4 mL ammonia (25.0%), and 1 mL dichloromethane were added to 80 mL distillate; shaken for 30 min (Turbula®, Willy A. Bachofen AG) and centrifuged at 2400 rpm for 15 min (0°C.) The organic phase was then transferred to a 300 µL glass vial and concentrated to 150 µL. Three replications of each extraction were carried out.

2.6 | Gas chromatography-flame ionization detector (GC-F-ID) parameters

Malt volatile compound analysis was done with a Hewlett-Packard 5890 Series II Plus gas chromatograph (Agilent Technologies Germany GmbH & Co. KG) with two flame ionization detectors. Volatile compounds were separated using two capillary columns with different polarities. A polyethylene glycol, highly polar, HP-INNOWax (60 m × 0.25 mm inner diameter, i.d., 0.25 µm film thickness; Agilent Technologies Germany GmbH & Co. KG) and a (5%-phenyl)-methylpolysiloxane, nonpolar, HP-5 (60 m × 0.25 mm i.d., 0.25 µm film thickness; Agilent Technologies Germany GmbH & Co. KG). Column carrier gas was hydrogen at a constant flow of 1.9 mL/min. The injector temperature as well as the transfer line temperature was 250°C. Using an autosampler, 4 µL of the concentrated volatile extract was injected (1:7 split). The temperature program as described in MEBAK method 2.23.5 was used (Jacob, 2013). The initial temperature was 50°C and maintained for 4 min; subsequently, the heating rate was 4°C/min until reaching a final temperature of 210°C and was held for 36 min. Peak area detection was performed in Agilent ChemStation B.04.03 [16] (Agilent Technologies Germany GmbH & Co. KG, Waldbronn, Germany). Concentrations were calculated from external calibration with commercial reference standards.

2.7 | Statistical analysis

Statistical analyses were performed using JMP® Pro (version 16.0.0; SAS Institute Inc., Cary, NC, USA). Normality of the analytical data was examined using the Shapiro–Wilk W test ($\alpha > 0.05$). Significant differences of normally distributed data were identified using one-way ANOVA ($p < 0.05$). For post hoc analysis ($p < 0.05$), the Tukey–Kramer HSD-test and Student's *t*-test were conducted for group means and pair means, respectively. OriginPro® 2023 (version 10.0.0.154; OriginLab Corp., Northampton, MA, USA) was used for two-way hierarchical cluster analysis and figures.

3 | RESULTS AND DISCUSSION

3.1 | (Pseudo)cereal quality parameters

To monitor the daily malting modifications of the (pseudo)cereals, samples were collected every 24 h (e.g., Bar-1d), stored at −20°C, and then freeze-dried to fix the composition of the samples rapidly while minimizing changes caused by heating (i.e., kilning) (Briggs, 1998). Unlike cereals in which the storage macromolecules are located in the endosperm, quinoa starch is found primarily in the perisperm, which is located in the center of the seed (Wolf et al., 1950), whereas proteins are stored mostly in the endosperm and embryo (Prego et al., 1998). Malting increased the amylolytic activity (i.e., extract), promoted storage protein degradation, and reduced the viscosity of all (pseudo)cereals (see Table 2).

The starch content is comparable in both unprocessed cereals; however, the different endosperm cell structure as well as cell wall morphology and composition determine the rate of starch mobilization and hydrolysis during germination (Dornez et al., 2011; Heneen & Brismar, 1987; Pomeranz, 1972; Wijngaard et al., 2007). Moreover, the higher total protein in Bar-UM is often associated with lower malt extract (Howard et al., 1996); the extract in barley malt and Rye-M is 84.0% and 92.2%, respectively. Conversely, the extract levels of Qui-M were considerably lower despite the higher starch content and lower total protein in unmalted quinoa. However, it was recently reported that the starch hydrolysis capacity of quinoa is significantly lower than that of cereals (Hager et al., 2014). While processing caused the total protein to decrease in both cereals, it increased in Qui-M. This effect has been reported in germinating quinoa seeds and attributed to total weight loss (i.e., dry matter) due to starch and lipid utilization during germination (Maldonado-Alvarado et al., 2023; Pilco-Quesada et al., 2020). After the first day of steeping, the soluble protein in all (pseudo)cereals diminished, these substances are commonly lost by leaching (Briggs, 1998). Subsequently, the soluble protein and FAN progressively increased until the last day of germination. The highest soluble protein and FAN were measured in Qui-M followed by Rye-M and Bar-M. Although the soluble protein levels of both cereal malts are comparable, these are considerably lower than in quinoa malt. The higher soluble protein in quinoa is likely associated with its smaller seed size, thus, resulting in faster germination and storage protein mobilization as well as higher protein hydrolysis (Zarnkow et al., 2007). These changes were accompanied by a gradual decrease in viscosity, resulting from enzymatic degradation of proteins and, primarily, nonstarch polysaccharides (e.g., β-glucan) (Pomeranz, 1972). Compared to barley and quinoa, the viscosity of Rye-M is markedly higher due to the higher content of water-soluble pentosans (e.g., arabinoxylan) found in the cell wall matrix of rye (Henry, 1987).

Compared to the recommended quality range for commercial barley pale malt for brewing purposes (Back et al., 2019), the extract of Qui-M is lower, the soluble protein of all (pseudo)cereals is higher, and the viscosity of Rye-M is considerably higher. The structural modifications caused by germination not only improve the quality (e.g., high soluble protein) and processing properties (e.g., low viscosity) of the (pseudo)cereals, but they also provide a rich source of precursors (i.e., reducing sugars and amino acids) for the aroma generating reactions occurring upon further processing. Thermal heating of the (pseudo)cereals will produce Maillard reaction, Strecker degradation, and lipid peroxidation products (Peppard et al., 1981; Sucan & Weerasinghe, 2005); the newly formed volatile compounds (e.g., Strecker aldehydes, pyrazines) in kilned barley malts are typically associated with malty and roasted aromas.

3.2 | Comparison of volatile profiles in unprocessed (pseudo)cereals and kilned malts

The effect of germination and kilning on the volatile compound composition of barley, rye, and quinoa is shown in Figure 1. In total, 34 known (pseudo)cereal volatile compounds were quantified in three (pseudo)cereals using gas chromatography-flame ionization detector; 13 aldehydes, 10 alcohols, four ketones, four pyrazines (i.e., *N*-heterocyclic), two furans, and a lactone. The alcohol and the aldehyde group were dominant in all unprocessed (pseudo)cereals and kilned malts, respectively. Of the quantified volatiles, hexan-1-ol was most abundant in Bar-UM; whereas, 2-phenylethan-1-ol was dominant in unmalted rye and quinoa. After germination and kilning,

TABLE 2 Means and standard deviations ($n = 9$) of the standard analyses[a] of unmalted (pseudo)cereals, daily freeze-dried germinated samples, and kilned malts[b] ($n = 3$).

Sample	Moisture[c] [%]	pH[c]	Extract[c] [%, d.m.]	Total protein[c] [%, d.m.]	Soluble protein[c] [mg/100 g, d.m.]	FAN[c] [mg/100 g, d.m.]	Viscosity (8.6%)[c] [mPa × s]
Barley							
Pale malt[d]	*n.d.*	*5.80–6.00*	*> 81.0*	*9.0–11.5*	*570–670*	*100–140*	*< 1.60*
Bar-UM	11.4 ± 0.0^{a}	5.83 ± 0.01^{c}	67.1 ± 1.2^{e}	12.2 ± 0.2^{a}	354 ± 6^{f}	36 ± 1^{f}	10.21 ± 0.97^{a}
Bar-1d	8.4 ± 0.1^{b}	5.86 ± 0.01^{c}	66.8 ± 0.1^{e}	10.1 ± 0.1^{c}	317 ± 4^{g}	40 ± 4^{f}	8.54 ± 0.02^{b}
Bar-2d	8.3 ± 0.1^{b}	5.82 ± 0.03^{c}	76.3 ± 0.4^{d}	10.2 ± 0.1^{bc}	411 ± 6^{e}	62 ± 2^{e}	4.73 ± 0.02^{c}
Bar-3d	8.1 ± 0.1^{bc}	5.98 ± 0.01^{ab}	80.2 ± 0.1^{c}	10.4 ± 0.1^{bc}	567 ± 5^{d}	94 ± 2^{d}	2.74 ± 0.01^{d}
Bar-4d	7.8 ± 0.1^{c}	5.97 ± 0.02^{ab}	81.8 ± 0.8^{bc}	10.2 ± 0.1^{c}	693 ± 4^{c}	120 ± 2^{c}	1.80 ± 0.02^{d}
Bar-5d	8.0 ± 0.1^{c}	6.00 ± 0.01^{a}	83.4 ± 0.1^{ab}	10.7 ± 0.1^{b}	709 ± 7^{c}	131 ± 4^{b}	1.63 ± 0.01^{d}
Bar-6d	7.8 ± 0.1^{c}	6.01 ± 0.02^{a}	83.6 ± 0.0^{ab}	10.2 ± 0.1^{c}	746 ± 6^{b}	146 ± 1^{a}	1.55 ± 0.01^{d}
Bar-M	6.1 ± 0.1^{d}	5.93 ± 0.01^{b}	84.0 ± 0.1^{a}	10.0 ± 0.1^{c}	785 ± 2^{a}	141 ± 1^{ab}	1.55 ± 0.00^{d}
Rye							
Rye-UM	9.6 ± 0.0^{a}	6.46 ± 0.05^{a}	63.2 ± 1.2^{f}	10.0 ± 0.0^{a}	476 ± 6^{e}	40 ± 0^{f}	11.52 ± 0.11^{b}
Rye-1d	8.5 ± 0.1^{b}	6.43 ± 0.04^{a}	71.8 ± 2.8^{e}	9.2 ± 0.1^{b}	466 ± 8^{e}	44 ± 1^{f}	12.50 ± 0.08^{a}
Rye-2d	8.4 ± 0.1^{b}	6.30 ± 0.02^{b}	80.2 ± 0.8^{d}	9.1 ± 0.1^{bc}	498 ± 8^{e}	49 ± 5^{ef}	12.28 ± 0.10^{a}
Rye-3d	8.3 ± 0.1^{b}	6.26 ± 0.01^{b}	84 ± 0.8 ^{cd}	8.9 ± 0.1^{bcd}	627 ± 17^{d}	64 ± 3^{e}	9.65 ± 0.21^{c}
Rye-4d	7.9 ± 0.1^{c}	6.22 ± 0.02^{bc}	86.8 ± 0.8^{bc}	9.1 ± 0.1^{bc}	714 ± 8^{c}	87 ± 3^{d}	7.22 ± 0.09^{d}
Rye-5d	7.7 ± 0.1 ^{cd}	6.16 ± 0.01 ^{cd}	88.2 ± 0.8^{abc}	8.7 ± 0.1 ^{cd}	807 ± 6^{ab}	121 ± 6^{c}	5.37 ± 0.11^{e}
Rye-6d	7.4 ± 0.1^{d}	6.13 ± 0.01 ^{cd}	88.7 ± 0.1^{ab}	8.5 ± 0.1^{d}	837 ± 11^{a}	155 ± 2^{b}	4.17 ± 0.07^{f}
Rye-7d	7.7 ± 0.1 ^{cd}	6.14 ± 0.01 ^{cd}	89.7 ± 0.1^{ab}	9.1 ± 0.2^{bc}	835 ± 2^{a}	140 ± 4^{b}	3.98 ± 0.01^{fg}
Rye-8d	7.4 ± 0.1^{d}	6.08 ± 0.01^{de}	89.4 ± 0.3^{ab}	9.1 ± 0.1^{bc}	838 ± 1^{a}	153 ± 5^{b}	3.60 ± 0.02^{gh}
Rye-M	5.8 ± 0.1^{e}	6.02 ± 0.01^{e}	92.2 ± 0.5^{a}	7.9 ± 0.1^{e}	788 ± 11^{b}	171 ± 6^{a}	3.52 ± 0.05^{h}
Quinoa							
Qui-UM	9.4 ± 0.0^{a}	6.29 ± 0.03^{a}	34.6 ± 0.45^{e}	9.1 ± 0.18^{c}	597 ± 2^{e}	46 ± 0^{e}	3.36 ± 0.14^{ab}
Qui-1d	6.0 ± 0.3^{bc}	6.21 ± 0.04^{ab}	36.5 ± 3.2^{e}	12.0 ± 0.4^{ab}	464 ± 31^{f}	59 ± 8de	3.49 ± 0.05^{a}
Qui-2d	6.3 ± 0.2^{b}	6.09 ± 0.05^{bc}	47.1 ± 1.1^{d}	12.1 ± 0.2^{ab}	681 ± 18^{d}	78 ± 3 ^{cd}	3.33 ± 0.01^{ab}
Qui-3d	6.2 ± 0.3^{b}	6.01 ± 0.02 ^{cd}	54.0 ± 2.2 ^{cd}	12.7 ± 0.1^{ab}	802 ± 18^{c}	102 ± 5^{bc}	3.11 ± 0.11^{bc}
Qui-4d	6.1 ± 0.3^{bc}	5.94 ± 0.03 ^{cd}	58.3 ± 0.9^{bc}	13.0 ± 0.1^{a}	846 ± 6^{abc}	122 ± 4^{b}	3.04 ± 0.03^{bc}
Qui-5d	6.1 ± 0.4^{bc}	5.84 ± 0.01^{de}	63.3 ± 1.6^{b}	13.1 ± 0.4^{a}	826 ± 18^{bc}	162 ± 4^{a}	2.85 ± 0.06 ^{cd}
Qui-6d	5.8 ± 0.1^{bc}	5.69 ± 0.05^{e}	71.0 ± 1.6^{a}	12.6 ± 0.2^{ab}	901 ± 11^{a}	182 ± 4^{a}	2.53 ± 0.16^{d}
Qui-M	5.2 ± 0.1^{c}	5.50 ± 0.09^{f}	74.9 ± 1.3^{a}	11.2 ± 0.9^{b}	883 ± 17^{ab}	180 ± 13^{a}	1.92 ± 0.05^{e}

Abbreviations: Bar, barley; d, day; d.m., dry matter; FAN, free amino nitrogen; M, standard malt; n.d., not defined; Qui, quinoa; UM, unmalted.

[a]Analyses done on laboratory worts produced by isothermal 65°C mashing as described in MEBAK (Jacob, 2016).

[b]Malting regimes are described in Table 1.

[c]Different superscript letters in a column indicate significant differences in data sets (ANOVA followed by Tukey–Kramer HSD-test, $p < 0.05$). Data sets grouped by (pseudo)cereal.

[d]Recommended quality range for commercial barley pale malt measured in isothermal 65°C mash (Back et al., 2019).

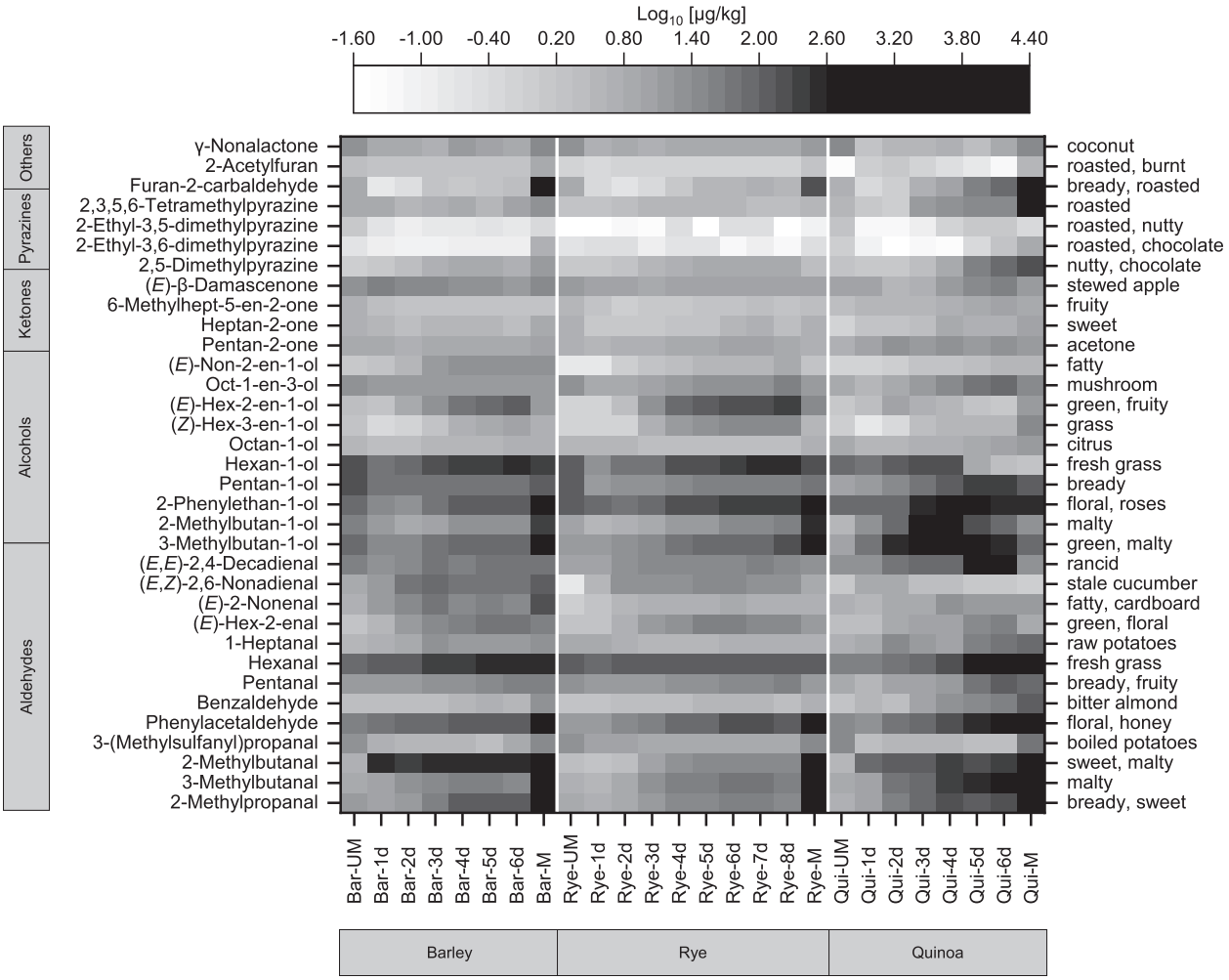

FIGURE 1 Heatmap showing the mean ($n = 9$) Log_{10} concentration [µg/kg] of the measured volatile compounds for each (pseudo)cereal sample at the different stages of malting. Volatile compound analyses done as described in MEBAK method 2.23.5 (Jacob, 2013). High and low concentrations are shown in black and white, respectively. Odor descriptions as perceived at the sniffing port are listed on the right (Almaguer et al., 2023). Rectangles on the left grouped compounds by chemical class; both furans and the lactone included in others. Bar, barley; d, day; M, standard malt; Qui, quinoa; UM, unmalted.

3-methylbutanal was the major volatile in Bar-M and Qui-M, and phenylacetaldehyde in rye malt. These Strecker aldehydes deliver characteristic malty and floral notes to malts and are the breakdown products of leucine and phenylalanine, respectively. In the unmalted samples, the highest total concentration was measured in barley and the lowest in quinoa. After processing, the total volatile concentration significantly increased in all (pseudo)cereals, the most abundant total volatile composition was measured in Qui-M followed by Bar-M. The concentration of 26 volatile compounds increased in all kilned malts and only the behavior of eight compounds varied among the three (pseudo)cereals. In the alcohol group, pentan-1-ol and oct-1-en-3-ol decreased in barley and rye but increased in quinoa. Conversely, hexan-1-ol decreased in Qui-M and increased in both cereals. Although the alcohol behavior was similar in both cereals, different behaviors were recorded in the ketone group. All ketones decreased in rye after malting, increased in Qui-M, and except for 6-methyl-5-hepten-2-one, these also increased in barley malt; whereas, the lactone only increased in Bar-M.

3.3 | Effect of steeping and germination on the temporal volatile composition

Temporal changes on the volatile composition of the (pseudo)cereals during malting were also monitored. During steeping, many physical and chemical activities which influence grain modification, volatile development, and the resulting malt quality take place (Brookes et al., 1976). After the first day of steeping (e.g., Bar-1d), the total volatile compound concentration of both cereals decreased, conversely, it increased in quinoa. In barley,

similar concentrations to Bar-UM were reached after 2 days of steeping (i.e., Bar-2d). In contrast, the germination rate and structural modification of rye were slower despite the rapid water uptake during steeping (Briggs, 1998). Therefore, it was only in Rye-4d that higher total volatile concentrations than the unmalted rye sample were reached. In Rye-1d, all compound groups decreased; in Bar-1d and Qui-1d, however, only the pyrazine, furan, and lactone groups decreased, whereas the aldehyde and ketone groups increased. The alcohol group decreased in barley but increased in quinoa. Of the quantified volatiles, 14 compounds decreased in all (pseudo)cereals after the first day of steeping, including all pyrazines, furans, and the lactone. Most alcohols decreased and only the concentrations of pentanal and 3-(methylsulfanyl)propanal (i.e., methional) were lower than in the unmalted samples. The concentration of five aldehydes increased with initial steeping of the (pseudo)cereals, of which the degradation product of isoleucine, 2-methylbutanal, was significant.

With germination, the aldehyde group increased in all (pseudo)cereals, except for (*E*,*Z*)−2,6-nonadienal which decreased in quinoa. In barley, most aldehydes increased in Bar-1d and reached their maximum in Bar-5d, followed by a slight decrease on the last day of germination (i.e., Bar-6d). Compared to barley, the Strecker aldehydes required an extra germinating day to reach the highest concentration in rye (i.e., Rye-6d) before decreasing again in the final stages of germination. The linolenic acid-derived aldehydes, however, reached their highest on Rye-5d, whereas the linoleic acid degradation products increased progressively until the last day of rye germination. In quinoa, the highest concentrations of 2-methylpropanal and (*E*)-2-nonenal were recorded on Qui-4d, whereas all other aldehydes continued to increase until the last day of germination. On Qui-5d, however, a significant increase in the lipid oxidation compounds, hexanal and (*E*,*E*)−2,4-decadienal, was recorded.

Another abundant group in all (pseudo)cereals during germination is the alcohol group. Although alcohols in food can be present in relatively large amounts, their contribution to the overall aroma is likely to be lower than that of the aldehyde group due to their higher odor thresholds (120–1200 μg/L). Unsaturated alcohols have lower threshold values, and therefore, compounds such as oct-1-en-3-ol, which delivers a distinctive mushroom note, and the grassy smelling (*Z*)-hex-3-en-1-ol, may contribute to the characteristic (pseudo)cereal aromas (Czerny et al., 2008; Mottram, 1991). Unlike the aldehydes, the alcohols in barley decreased on Bar-1d, followed by a progressive increase until the last day of germination. Except for 2-methylbutan-1-ol and 2-phenylethan-1-ol which reached their maximum in Bar-5d, whereas germination of barley caused pentan-1-ol and oct-1-en-3-ol to diminish. Unlike barley, all alcohols increased until the last day of germination in rye, except octan-1-ol. Similar to barley, 3-methylbutan-1-ol, 2-phenylethan-1-ol, hexan-1-ol, and (*E*)-hex-2-en-1-ol were the most abundant alcohols in germinating rye, these contribute green, grassy, and floral notes (Almaguer et al., 2023). In quinoa, all alcohols increased with germination, except (*E*)-hex-2-en-1-ol. Moreover, compared to both cereals, significantly lower concentrations were recorded for all green, grassy C_6 alcohols in quinoa. The most abundant alcohols in the quinoa samples were 3-methylbutan-1-ol and 2-methylbutan-1-ol followed by 2-phenylethan-1-ol. The methyl alcohols deliver malty notes and reached their highest concentration on Qui-4d, whereas an additional germination day was required for 2-phenylethan-1-ol. Alcohols were the major quantitative volatile group in germinating rye and quinoa, whereas the volatile composition of germinating barley was dominated by aldehydes. Changes in the aldehyde and alcohol profile of the (pseudo)cereals during germination were significant. Conversely, the variation of the ketone, pyrazine, and furan groups in the germinating (pseudo)cereals was low; these are mainly formed during thermal processing.

3.4 | Impact of kilning on volatile formation

The grassy notes in barely are indicative of low amounts of Maillard reaction products (Bettenhausen et al., 2021). In malting, Maillard reaction, Strecker degradation, and thermal reaction compounds are formed during the kilning step (Peppard et al., 1981; Sucan & Weerasinghe, 2005). Upon thermal treatment, the Strecker aldehydes and 1-heptanal increased in all (pseudo)cereals, these evoke distinctive malty and bready notes. Conversely, the concentrations of pentanal and the grassy C_6 aldehydes declined; this behavior for both C_6 aldehydes was previously reported in barley (Dong et al., 2013). The lipid-derived carbonyls, (*E*,*Z*)−2,6-nonadienal, (*E*)−2-nonenal, and (*E*,*E*)−2,4-decadienal, which contribute stale and fatty notes decreased in rye and quinoa malt but increased in Bar-M. In the alcohol group, octan-1-ol and 2-phenylethan-1-ol increased in all (pseudo)cereals after thermal processing, whereas hexan-1-ol and (*E*)-non-2-en-1-ol decreased. Similar to the C_9 aldehydes, (*E*)-non-2-en-1-ol evokes fatty odors and was characteristic in barley malt. In both cereals, a similar behavior was recorded for the remaining alcohols. The highly volatile alcohols, 3-methylbutan-1-ol, 2-methylbutan-1-ol, and pentan-1-ol, increased in barley and rye but despite their high concentrations in Qui-6d, these decreased in quinoa after kilning. In sharp contrast,

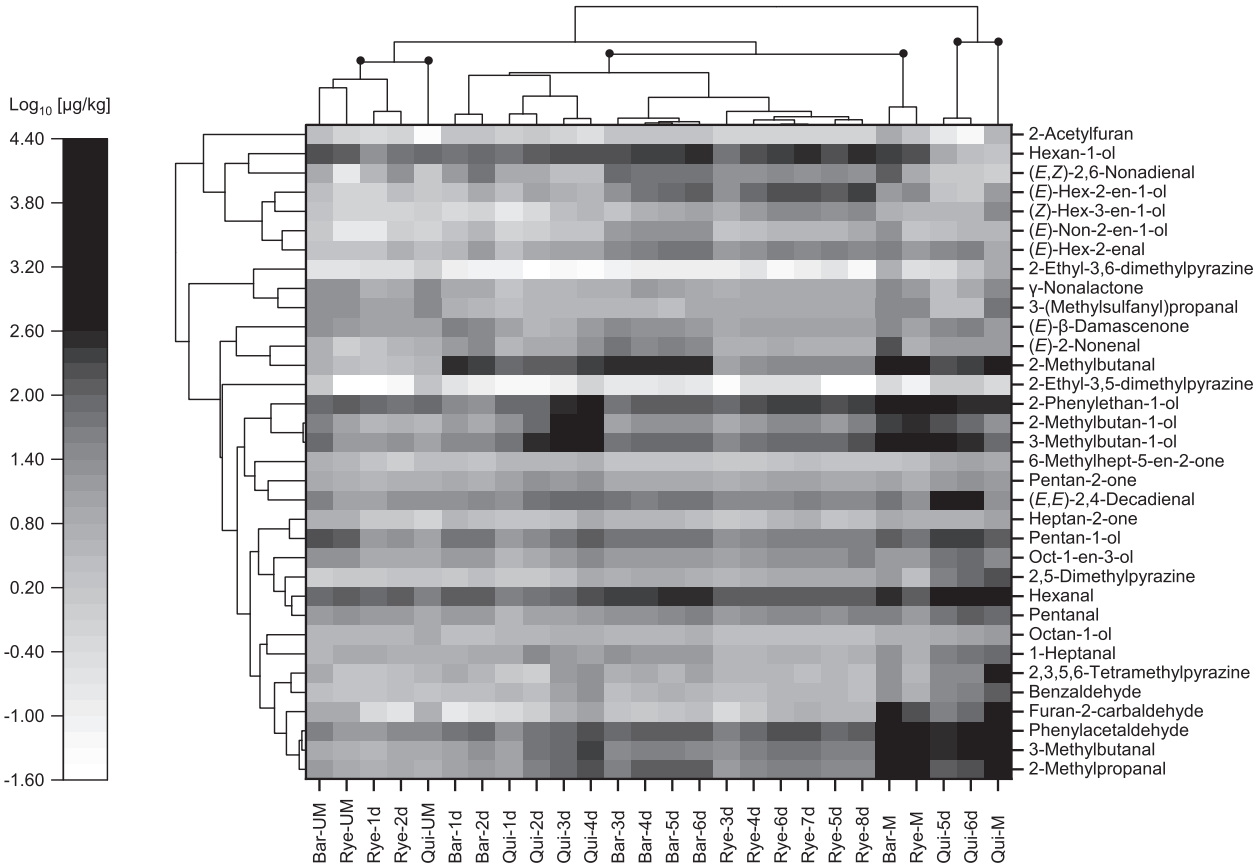

FIGURE 2 Two-way hierarchical clustering of the mean ($n = 9$) Log_{10} concentration [µg/kg] of the measured volatile compounds for each (pseudo)cereal sample during malting. Volatile compound analyses done as described in MEBAK method 2.23.5 (Jacob, 2013). High and low concentrations are shown in black and white, respectively. Cutoff level set to 55% similarity for six clusters (•). Bar, barley; d, day; M, standard malt; Qui, quinoa; UM, unmalted.

both C_6 unsaturated alcohols decreased in the cereal malts and increased in Qui-M.

Compared to the aldehydes and alcohols, the concentration of the ketone and pyrazine groups is significantly lower in all (pseudo)cereals. The ketones deliver sweet, fruity notes to the kilned malts; (*E*)-*β*-damascenone, typically formed by thermal reactions, was characteristic in barley malt. Germination and kilning had little impact on the concentration of 6-methylhept-5-en-2-one in both cereals, but favored its development in quinoa. Most pyrazines are known for their extremely low odor recognition thresholds, therefore, even at low concentrations, their contribution of roasted, nutty aromas to (pseudo)cereals is important. As expected, the concentration of these *N*-heterocyclic compounds increased in all (pseudo)cereals after kilning. However, 2,5-dimethylpyrazine and 2,3,5,6-tetramethylpyrazine were characteristic of Qui-M, the former favored by the high lysine levels in unmalted quinoa (Cha et al., 2019). While pyrazines are characteristic Maillard reaction products, furans are typical sugar dehydration products (Parker et al., 2000). Furan-2-carbaldehyde (i.e., 2-furfural) and 2-acetylfuran also deliver roasted notes and are well-known heat indicators in barley malt (Krahl et al., 2009). Germination had little impact on the accumulation of both compounds; however, thermal treatment promoted the formation of furan-2-carbaldehyde in all (pseudo)cereals. The highest concentrations were recorded in Bar-M and Qui-M. Another known heat indicator in barley malt is the linoleic acid oxidation product, *γ*-nonalactone. Similar to the furans, its concentration increased after kilning and was dominant in barley malt. Despite their pleasant contribution to malt aroma, high concentrations of the three previously mentioned compounds are undesirable since these are known malt-derived beer aging indicators (Vanderhaegen et al., 2003, 2006).

3.5 | Hierarchical cluster analysis of volatile compounds

Hierarchical clustering was performed on the volatile data to visualize the variations and similarities among the samples (see Figure 2). Of the six clusters, the distance

between the unmalted (pseudo)cereals and the corresponding kilned malts is the greatest. Although both clusters merge, the unmalted cereals (i.e., cluster 1; $n = 4$) are not grouped with Qui-UM (i.e., cluster 2; $n = 1$). Similarly, Bar-M and Rye-M were grouped together (i.e., cluster 4; $n = 2$) but adjacent to quinoa malt (i.e., cluster 6; $n = 1$). Characteristic of the kilned malts are the high concentrations of 2-methylpropanal, 3-methylbutanal, and phenylacetaldehyde. The total volatile concentration of Rye-1d and Rye-2d were comparatively low and were, thus, clustered with the unmalted cereals. Cluster 3 ($n = 16$) is the largest and most of the germination stage samples are grouped together. Similar patterns were obtained for barley and quinoa during the early stages of malting (e.g., steeping, Bar-1d). However, as germination proceeded (e.g., Bar-3d), similarities among the barley and rye samples were recorded. In barley and rye, a marked shift in their volatile profiles occurred once steeping was completed, whereas, in quinoa, it was recorded toward the end of germination. The aldehyde concentration markedly increased as of Qui-5d (i.e., cluster 5; $n = 2$) resulting in similar volatile patterns to quinoa malt and merging clusters. Malting changed the volatile patterns of the (pseudo)cereals; although all volatiles were quantified in the three (pseudo)cereals, their concentrations varied. Hierarchical clustering further confirmed the similarities in the volatile compositions of both cereals and the differences to the volatile profile of quinoa.

4 | CONCLUSION

In this study, temporal changes on malt quality as well as volatile composition of three (pseudo)cereals during malting were monitored daily. At the different stages of malting, similarities among them were observed but (pseudo)cereal-specific behaviors were also evident. The alcohol group dominated in all unprocessed samples, in particular, compounds contributing to the grassy notes. These green and grassy compounds remained abundant during germination, whereas kilning promoted the formation of the Maillard reaction and Strecker degradation volatiles associated with malty and roasted notes. High aldehyde concentrations were common in the volatile patterns of all kilned malts. The volatile profiles of Bar-M and Qui-M were characterized by high concentrations of 3-methylbutanal which delivers desirable malty aromas. In contrast, green, floral notes delivered by phenylacetaldehyde remained dominant in rye malt. Throughout the malting process, high concentrations of the C_9 aldehydes, (*E*)-non-2-en-1-ol, and (*E*)-β-damascenone were exclusive in barley; only in Bar-M, both C_9 aldehydes significantly increased following thermal treatment. Slower structural modification delayed volatile development in rye. In contrast, quinoa seeds germinated very fast, this promoted high volatile formation from the onset of the malting process. In both cereals, hexanal was a major volatile in the early stages of malting, however, as germination proceeded, high concentrations of the corresponding alcohol, hexan-1-ol, were measured. The opposite behavior was recorded in quinoa seeds for both C_6 compounds. Hierarchical cluster analysis of the volatile data grouped the samples into the different stages of malting, confirmed the similarities in the volatile pattern of both cereals, and indicated clear differences to the quinoa samples. Moreover, these results provide a better understanding on the volatile changes occurring at the different stages of malting as well as the impact of germination and kilning on volatile formation. Malting improved the processing properties and pleasant malty or floral aromas were intensified in the kilned malts. Since (pseudo)cereals are a major source of aroma and flavor in finished food products, understanding the influence of germination and kilning on their chemical composition and flavor properties can help find new food applications, enhance their aroma and flavor profiles, and improve their acceptance.

AUTHOR CONTRIBUTIONS

Cynthia Almaguer: Conceptualization; methodology; investigation; formal analysis; data curation; visualization; validation; writing — original draft; writing — review & editing. **Hubert Kollmannsberger**: Data curation; writing — review & editing. **Martina Gastl**: Funding acquisition; supervision; writing — review & editing. **Thomas Becker**: Supervision; resources; writing — review & editing.

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CONFLICT OF INTEREST STATEMENT

The authors have no conflict of interest to declare that are relevant to the content of this article.

ORCID

Cynthia Almaguer https://orcid.org/0000-0002-5926-5172

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