Research Article

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Characterization of the aroma profile of quinoa (*Chenopodium quinoa* Willd.) and assessment of the impact of malting on the odor-active volatile composition

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Abstract

Background: Quinoa (*Chenopodium quinoa* Willd.) is a gluten-free pseudocereal, rich in starch and high-quality proteins. It can be used as a cereal. Recently, a variety of nontraditional food products were developed; however, the sharp bitterness and the earthy aroma of unprocessed quinoa interfered with the acceptance of these products. Malting of cereals is known to improve their processing properties and enhance their sensory quality. To evaluate the acceptance and potential of quinoa malt as a raw material for beverage production, malt quality indicators (e.g., soluble protein) and the aroma profiles of different quinoa malts were compared.

Results: Initial sensory assessment of quinoa in its native and malted state identified differences in their aroma profiles and revealed that pleasant nutty and caramel aromas were formed by malting. Subsequently, three complementary isolation techniques and gas chromatography-olfactometry/mass spectrometry (GC-O/MS) were used for volatile analysis. Instrumental analysis detected 34 and 62 odor-active regions in native quinoa and quinoa malt, respectively. In the second part, storage and the impact of three malting parameters on volatile formation were examined. By varying the malting parameters, seven additional odor-active malting byproducts were revealed.

Conclusion: Three naturally occurring methoxypyrazines were identified as important contributors to the characteristic quinoa aroma. In all fresh quinoa malts a similar number of volatile compounds was perceived but their intensity and composition varied. Higher germination temperature promoted the formation of lipid oxidation products. Fatty smelling compounds and carboxylic acids, formed during storage, were classified as aging indicators of quinoa malt.

Keywords: quinoa; malting; aroma; GC-O/MS; cAEDA; methoxypyrazines

INTRODUCTION

Quinoa (*Chenopodium quinoa* Willd.) is a gluten-free pseudocereal of the Amaranthaceae family, indigenous to the Andean region of South America.[1] Quinoa is a dicotyledonous plant and therefore not a true cereal (i.e., monocotyledonous); however, due to its starch-rich seeds (69.0%–75.8%)[2,3] it is referred to as pseudocereal, it can be milled into flour and used in a similar way to cereals (e.g., barley).[4] Quinoa seeds are primarily consumed in a similar manner to rice but can also be used to produce a variety of food products. The main uses are soups and breads as well as the traditional beverage, chicha. Other food products made from quinoa are porridge, desserts, and pasta.[5-9] The protein content (12.5%–16.7%)[2,10] in quinoa is higher than in most cereals and further characterized by high levels of lysine (5.8%–6.4%),[2,3] a limiting essential amino acid in cereals.[11,12] Consequently, quinoa is being introduced in other countries and nontraditional functional food products are being developed. However, the pericarp of quinoa seeds is rich in bitter-tasting saponins, which interfere with the palatability and digestibility of quinoa-based food products. The maximum saponin range for consumer acceptance is 0.06%–0.12%.[13] In an effort to improve the agronomic properties and development of quinoa cultivars with desirable profiles, its genome was recently assembled[14] and the metabolic diversity (e.g., saponins) in 471 quinoa cultivars was determined.[15] Although 90%–95% of saponins can be removed by different

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desaponification methods (e.g., mechanical abrasion, washing),[16] a bitter aftertaste has been reported in quinoa-rich products.[17] Moreover, the aroma of unprocessed quinoa is often described as unpleasant due to its grassy and earthy notes.[4,18] Quinoa-based food products could benefit from an additional steeping (i.e., soaking) step and further processing of the seeds.

In cereals such as barley and rye, malting improves the processing properties (e.g., viscosity) and generates a distinct color, taste, and aroma. During germination, hydrolytic enzymes catalyze structural modifications in the kernel resulting in the degradation of the macromolecules into free amino acids and reducing sugars. Germination is followed by the drying process (i.e., kilning); interactions between the available amino acids and reducing sugars during kilning yield new substances, in particular, nonenzymatically formed, odor-active compounds.[19] Acceptance of new quinoa products has relied on sensory analyses; however, these fail to identify the odor-active compounds responsible for specific aromas. Moreover, the aroma profile of native quinoa remains largely uncharacterized and only limited data are available on quinoa aroma. Volatile compound analysis of quinoa and quinoa products helps understand how they are generated and how to improve the aroma. Recent studies have looked at the odor-active volatiles present in thermally treated quinoa food products such as porridge,[20] bread,[21-23] biscuits,[24] and different colored quinoa seeds (i.e., white, red, black).[25,26]

Hitherto, aroma improvement of quinoa seeds by fermentation[27] has been investigated but not by malting (i.e., germination and kilning). To better understand the effect of malting on quinoa and evaluate its acceptance and potential as a brewing raw material, the malt quality indicators (e.g., soluble protein, viscosity) and aroma profiles of several quinoa malts were examined in this study. In the first part, initial aroma characterization of quinoa in its native and malted state was carried out by trained panelists. Subsequently, sensory profiles of unmalted (UM) quinoa and corresponding standard malt (M) were complemented by instrumental analysis of the volatile compounds. The chemical diversity (e.g., polarity) of the volatile compounds present in quinoa is high; consequently, the choice of extraction method will impact the composition and characterization of the volatile profile. Three complementary isolation techniques, including headspace solid-phase microextraction (HS-SPME) and two solvent extraction methods, simultaneous distillation-extraction (SDE) and solvent assisted flavor evaporation (SAFE), were therefore used to create detailed aroma profiles. Gas chromatography-olfactometry/mass spectrometry (GC-O/MS) was used to analyze, describe, identify, and classify the odor-active compounds in the quinoa volatile isolates.

Depending on the precursor pool generated during malting, it is possible to create different malt qualities and aroma profiles. In part two, therefore, the impact of the malting parameters (i.e., steep moisture, germination temperature, and germination time) on the odor-active volatiles in a diverse set of malts (e.g., high and low modification; Hi and Lo) was investigated. The malts that were produced, however, aimed to be within the accepted processing quality range of commercial barley malts (i.e., malting standard). Gas chromatography-olfactometry/mass spectrometry and comparative aroma extract dilution analysis (cAEDA) were used to determine and compare the flavor dilution (FD) factors of the perceived odor-active volatiles in the quinoa malts. The collected data were used to identify the malting parameters that yield a high quality malt (e.g., high extract) and pleasant caramel aromas. Lastly, the storage (St) effects on the aroma profile of the standard quinoa malt were also investigated by cAEDA.

MATERIALS AND METHODS

Seed material

Organic white quinoa (variety unknown, Bolivia) with 9.4% moisture, 9.1% protein dry matter (d.m.), 65.8% starch (d.m.), and 7.1% fat (d.m.) was purchased from Ziegler & Co. GmbH (Wunsiedel, Germany).

Chemicals

Chemicals were purchased from the following sources: diethyl ether (≥99.5%), ethanol p.a. (≥99.8%), and anhydrous sodium sulfate (Na_2SO_4) (≥99.0%) from Sigma–Aldrich (Taufkirchen, Germany). Reference standards of aroma compounds were purchased from commercial sources: Alfa Aesar (Karlsruhe, Germany); Merck (Darmstadt, Germany); or Sigma–Aldrich.

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 described by the Mitteleuropäische Brautechnische Analysenkommision e.V. (MEBAK) (R-110.00.008 [2016–2103]).[28] An overview of the malting parameters for the different quinoa samples is shown in Table 1. All samples used in this study were produced in three biological replicates, transferred into hermetic glass jars, and stored in a dry and dark location until further analysis.

To determine the malting regimes required to produce the standard malt, as well as malts with high or low modification (i.e., Table 1 samples), Design-Expert® Software (version 8.0.6; Stat-Ease, Inc., Minneapolis, MN, USA) 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, viscosity) in quinoa. To cover a broad range of

Table 1. Overview of malting regimes for experimental quinoa malts

	Sample Code[a]	Steep Moisture (%)	Temperature (°C)	Time (d)	Storage
Unmalted	**Qui-UM**				
Standard	**Qui-M**	46	16	6	
Standard stored	**Qui-St**	46	16	6	18 months
High modification	**Qui-Hi**	46	18	6	
Low modification	**Qui-Lo**	40	12	4	

[a] Qui = quinoa, UM = unmalted, M = standard malt, St = stored standard malt, Hi = high modification, Lo = low modification.

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modification, all malting parameters were tested at three different levels. Each series was malted twice and consisted of 25 samples; the factorial and 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 ANOVA ($P < 0.05$). Subsequently, multiple regression analyses of the experimental data were done to calculate quadratic models. 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.[29,30]

Quinoa and malt standard analyses

The moisture of the samples was determined following MEBAK method R-200.18.020 [2016–2103].[28] To assess the malt modification, the malts were isothermally mashed at 65 °C for 1 h as outlined in MEBAK method R-207.00.002 [2016–2103].[28] 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 using the MEBAK methods.[28]

Sensory characterization of quinoa

Freshly ground (Laboratory Disk Mill DLFU; Bühler Group, Uzwil, Switzerland) quinoa samples (10 g) were presented in a clear glass (⌀ 6.5 cm) and covered with a watch glass. Randomized three-digit number codes were assigned to the samples; the quinoa samples were evaluated by a trained sensory panel consisting of 11 certified beer judges (five female, six male; ages 22–57). All panelists had been trained in weekly sensory sessions for the evaluation of (pseudo)cereal based fermented products (e.g., beverages and bread) following the DLG (Deutsche Landwirtschafts- Gesellschaft e.V.) guidelines (i.e., DIN EN ISO 8586:2014–2105).[31] In preliminary sessions, the panel members generated ten descriptors by descriptive analysis. In the following sessions, the panelists evaluated the odor intensity of six of these attributes as well as the overall intensity on a four-point linear sensory scale ranging from not detectable (0) to extreme (3). To accurately differentiate among the samples, dichotomous assessment was conducted for the remaining descriptors. Finally, each panelist was asked to rate the preference of the samples on a six-point hedonic sensory scale ranging from dislike extremely (0) to like extremely (5). The sensory evaluation of the samples was executed in four independent sessions.

Isolation of volatiles

Headspace solid-phase microextraction. The 50/30 µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS; Supelco Inc., Bellefonte, PA, USA) fiber was selected for volatile analysis because of its highest adsorption capacity across a range of volatile polarities. New fibers were attached to a solid-phase microextraction (SPME) holder for manual sampling and conditioned in a GC injector at 270 °C for 1 h. Manual HS-SPME extraction was conducted as described by Roth *et al.*[32] Prior to adsorption, samples were ground with a mortar and pestle. Freshly ground samples (3 g) in sealed 20 mL headspace vials were equilibrated with the fiber for 30 min at 50 °C before desorption and GC-O/MS analysis. Volatiles were desorbed at 250 °C for 30 s. Before the next analysis, the fiber was reconditioned at 250 °C for 15 min in a GC injector to avoid carry over of compounds from previous samples.

Simultaneous distillation-extraction. The extraction was done using a Likens–Nickerson apparatus as described by Roth *et al.*[32] In a round-bottomed flask, 100 g of finely ground sample (Laboratory Disk Mill DLFU; Bühler Group, Uzwil, Switzerland) was suspended in 350 mL of distilled water (dH_2O) containing an antifoam agent. The sample-dH_2O suspension and 100 mL of diethyl ether were boiled for 2 h. After cooling down to room temperature, the diethyl ether extract was dried over anhydrous sodium sulfate and concentrated to 1 mL using a Vigreux column (30 cm × 1 cm inner diameter; i.d.) at 38 °C. The concentrated extract was stored in 2 mL amber glass vials at −20 °C until use. Three replications of each extraction were carried out.

Solvent assisted flavor evaporation. Prior to distillation, 150 g of finely ground sample (Laboratory Disk Mill DLFU; Bühler Group, Uzwil, Switzerland) was mixed with 200 mL of diethyl ether; 500 µL of methyl decanoate (c = 1.05 g/L) was added for semi-quantification. After 60 min shaking, the organic phase was collected and 60 mL of diethyl ether was added to the grist and the extraction continued for 60 min at room temperature. The combined extract was filtered through a paper filter to remove grist residues, afterwards it was concentrated to 50 mL. Subsequently, the volatile fraction was isolated under high-vacuum by SAFE at 40 °C.[33] The distillate was dried over anhydrous Na_2SO_4 and concentrated to 1 mL using a Vigreux column at 38 °C. The concentrated extract was stored in 2 mL amber glass vials at −20 °C until use. Extractions were conducted at least in triplicate.

Comparative aroma extract dilution analysis. To simulate a serial dilution, 2 µL of the concentrated SAFE malt extract was injected (autosampler injection) in different split modes into the GC, including the splitless mode. The following split ratios were used in this series, 1:5, 1:10, 1:20, 1:40, and 1:80; for the highest dilution, 1 µL was injected in a 1:80 split. The samples were analyzed by GC-O/MS and each odor was assigned an FD factor corresponding to the highest dilution at which the odor was recognized, thus resulting in factors of 1 (splitless), 5, 10, 20, 40, 80, or 160, respectively. In the cAEDA series each extract was first analyzed at the highest dilution (i.e., FD = 160) to avoid false recognition due to memory effects. The peak areas of the internal standard and selected compounds were measured and compared to validate the accuracy and reproducibility of the dilution series.

Separation and identification of volatiles

Gas chromatography-olfactometry/mass spectrometry parameters. Analysis of the aroma extracts was carried out on a Trace 1300 Ultra gas chromatograph (Thermo Fisher Scientific Inc., Waltham, MA, USA) fitted with a TG-5MS (i.e., DB-5) silica capillary column (Thermo Fisher Scientific Inc., Waltham, MA, USA; 60 m × 0.25 mm i.d., 0.25 µm film thickness). Column carrier gas was helium at a constant flow of 1.85 mL/min. The injector temperature and the transfer line temperature were 250 °C. The initial temperature was maintained at 40 °C for 4 min. Subsequently, the heating rate was 5 °C/min until reaching 170 °C, afterwards the rate was increased to 10 °C/min to reach a final temperature of 250 °C and was held for 2 min.

The GC was coupled to a single quadrupole mass spectrometer (ISQ QD, Thermo Fisher Scientific Inc., Waltham, MA, USA) and an olfactory detection port (ODP 3, Gerstel GmbH & Co. KG, Mühlheim an der Ruhr, Germany). The effluent was split into two equal parts with a micro-flow splitter. The sniffing port was heated to 250 °C and flushed with humidified air to avoid dehydration of

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the nasal membranes. Mass spectrometry detection was accomplished with an electron ionization (EI) energy of 70 eV. The analyzed mass range was 35–350 amu in EI mode. Peak detection was performed in Thermo Xcalibur™ 3.1.66.10 (Thermo Fisher Scientific Inc., Waltham, MA, USA). Olfactometric assessment was done at least in triplicate by three panelists trained specifically on cereal, malt, and beverage aromas.

Aroma compound identification. Identification of aroma compounds was based on odor description, linear retention indices (RIs), and comparison with reference substances and mass spectrometric data from the literature, the National Institute of Standards and Technology (NIST) library (NIST 08, version 2.0f), and in-house mass spectral libraries. If the recorded MS data were too weak for unequivocal identification, aroma compounds were tentatively identified based on the remaining criteria. Linear retention indices of the compounds were calculated as described by van Den Dool and Kratz,[34] using a series of *n*-alkanes, C_6–C_{20}, under the same operating conditions outlined above.

Statistical analysis

Statistical analyses were performed using JMP Pro (version 12.2.0; SAS Institute Inc., Cary, NC, USA). The 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 honestly significant difference (HSD) test and Student's *t*-test were conducted for group means and pair means, respectively.

RESULTS AND DISCUSSION

Quinoa quality parameters

Unlike cereals in which the storage macromolecules are located in the cells of the endosperm, quinoa starch is found primarily in the perisperm, which is located in the center of the seed[35]; whereas proteins are stored mostly in the endosperm and embryo.[36] Malting increased the amylolytic activity (i.e., extract), promoted storage protein degradation, and reduced the viscosity of quinoa (see Table 2). However, only the composition of Qui-M was close to the recommended quality range for commercial barley pale malt.[37] The soluble protein content of Qui-Hi was significantly above the range but the extract was much lower. In comparison with the other malts, the malting conditions of Qui-Lo were not favorable for sugar and protein solubility. Although malting of quinoa is not common, the correct malting parameters can enhance its properties. The structural modifications caused by germination not only improve the processing properties of quinoa, they also provide a rich source of precursors (i.e., reducing sugars and amino acids) for the aroma generating reactions. The formation of new odor-active compounds can positively modify the aroma profile, therefore, germination and further processing (i.e., thermal heating) of quinoa were carried out to produce Maillard reaction, Strecker degradation, and thermal reaction compounds.[38,39]

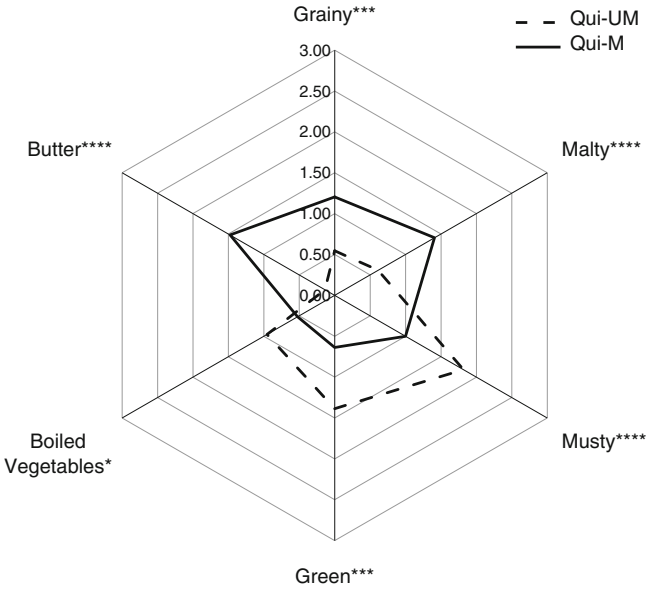

Figure 1. Aroma profile of quinoa. Intensity means ($n = 44$) of the attributes rated by a trained panel ($n = 11$) on a four-point linear sensory scale ranging from not detectable (0) to extreme (3). Hyphenated line represents the unmalted (UM) sample and solid line represents the standard malt (M). Asterisks indicate significant differences in data pairs (ANOVA followed by Student's *t*-test, $P < 0.05$; **** $P < 0.0001$; *** $P < 0.001$; * $P < 0.05$). Malting regime is described in Table 1.

Sensory characterization of quinoa

Initial aroma assessment in freshly ground quinoa samples was carried out by a trained panel. Figure 1 compares the odor intensity of six predefined attributes in quinoa in its native and malted

Table 2. Means and standard deviations ($n = 9$) of the standard analyses[a] of unmalted quinoa and quinoa 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)
Pale malt[d]	*n.d.*	*5.80–6.00*	*>81.0*	*9.0–11.5*	*570–670*	*>140*	*<1.60*
Qui-UM	9.4 ± 0.0[a]	6.29 ± 0.03[a]	34.6 ± 0.45[d]	9.1 ± 0.18[c]	597 ± 2[b]	46 ± 0[c]	3.36 ± 0.14[a]
Qui-M	2.3 ± 0.1[b]	5.46 ± 0.03[b]	79.2 ± 0.22[a]	12.7 ± 0.81[b]	644 ± 45[b]	130 ± 12[b]	2.30 ± 0.27[b]
Qui-Hi	2.1 ± 0.2[b]	6.10 ± 0.20[a]	52.0 ± 3.7[b]	15.9 ± 0.57[a]	844 ± 44[a]	163 ± 16[a]	2.59 ± 0.34[b]
Qui-Lo	2.1 ± 0.1[b]	6.07 ± 0.05[a]	42.0 ± 3.6[c]	15.9 ± 0.24[a]	309 ± 14[c]	70 ± 9[c]	2.70 ± 0.18[b]

Abbreviation: n.d. = not defined.
[a] Analyses done on laboratory worts produced by isothermal 65 °C mashing as described in MEBAK.[28]
[b] Malting regimes are described in Table 1. Qui = quinoa, UM = unmalted, M = standard malt, Hi = high modification, Lo = low modification.
[c] Different superscript letters in a column indicate significant differences in data sets (ANOVA followed by Tukey–Kramer HSD-test, $P < 0.05$).
[d] Recommended quality range for commercial barley pale malt measured in isothermal 65 °C mash.[37]

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Table 3. Mean intensity and preference scores and standard deviations ($n = 44$) of quinoa in its unmalted and malted[a] state as assessed by panelists ($n = 11$) in the sensory evaluation sessions ($n = 4$)

	Scale	Qui-UM	Qui-M[b]
Intensity	(0–3)[c]	1.93 ± 0.76	2.52 ± 0.63***
Preference	(0–5)[d]	1.55 ± 1.00	2.50 ± 1.75**

[a] Malting regime is described in Table 1. Qui = quinoa, UM = unmalted, M = standard malt.
[b] Asterisks indicate significant differences in data pairs (ANOVA followed by Student's *t*-test, $P < 0.05$; *** $P < 0.001$; ** $P < 0.01$).
[c] 4-point linear sensory scale ranging from not detectable (0) to extreme (3).
[d] 6-Point hedonic sensory scale ranging from dislike extremely (0) to like extremely (5).

state. Malting simultaneously increased the intensity of the grainy and malty attributes and decreased the musty character in quinoa. Subsequently, for a more detailed characterization of the malty and musty attributes, the presence of roasted and caramel aromas or boiled potato and mushroom notes, respectively, were assessed. The malty character of Qui-M was both roasty and caramel-like but the caramel odor predominated. The musty attribute had a subtle mushroom aroma in both samples, whereas the boiled potato character was frequently identified in Qui-UM but malting reduced its intensity. The green note markedly decreased after malting while only a minor change in the intensity of the boiled vegetables attribute was perceived. In Qui-M, a marked shift was recorded for the butter descriptor; however, the stronger butter odor did not have a negative impact on the preference rating. The overall odor intensity and preference of Qui-M were rated higher than the unmalted sample (see Table 3).

The aroma profile of native quinoa is characterized by green notes as well as musty and vegetal odors. Malting increased the overall odor intensity and led to the development of the pleasant grainy and malty character in quinoa. The sensory results indicate the presence and influence of volatiles from the kilning process such as pyrazines (e.g., malty) or sugar degradation products (e.g., caramel) on the aroma profile. Sensory-directed investigations coupled with instrumental analysis were therefore conducted to understand the importance of the perceived aroma attributes in quinoa.

Odor-active volatiles in quinoa

The different extraction methods offer a number of individual advantages but also suffer from specific limitations. In complex matrices, the chemical diversity (i.e., volatility, polarity) of the volatile compounds present is high. The choice of extraction method impacts compound selectivity and the composition of the volatile isolate as well as the subsequent identification of odor-active compounds. By using different isolation methods it is therefore possible to achieve a representative classification of the odor-active volatiles in quinoa. As expected from the overall odor intensity values, a higher number of odor-active compounds was detected in the volatile fraction of quinoa malt than in the unprocessed seeds. Using three extraction methods revealed 34 and 62 odor-active regions in Qui-UM and Qui-M, respectively. The detected odor-active compounds and their descriptors are listed and compared in Table 4. In quinoa malt, 28 compounds were detected by all techniques, hence indicating these are not isolation artifacts. Further, the collected GC-O/MS data of the volatile fraction of Qui-UM confirmed 17 of these compounds are native to quinoa and survive the malting and extraction processes. All other odor-active regions were detected by at least one of the extraction methods used, thereby confirming the importance of the isolation technique used and the application of complementary methods. Carbonyl compounds, in particular aldehydes, as well as the *N*-heterocyclic compounds (e.g., pyrazines) were dominant in quinoa. The remaining identified compounds were classified as acids, esters, alcohols, phenols, terpenes, lactones, or sulfur compounds. Unequivocal MS data could not be obtained for 1-penten-3-one, (*Z*)-4-heptenal, 3-(methylsulfanyl)propanal (i.e., methional), 2-acetyl-1-pyrroline, oct-1-en-3-one, (*Z*)-1,5-octadien-3-one, and 3-methyl-1*H*-indole and were, thus, tentatively identified based on their odor description, RI, and comparison with literature data. Seven odor-active regions remain unknown as these could not be identified in the volatile isolates due to their low concentrations and limited MS data.

Only 3-(methylsulfanyl)propanal, three methoxypyrazines, (*E*,*Z*)-2,6-nonadienal, and (*Z*)-4,5-epoxy-(*E*)-2-decenal were detected in all samples. These compounds contribute to the musty character of quinoa and are known for their extremely low odor-recognition thresholds.[40-43] The sensory evaluations revealed their perceived intensity in the ground samples decreased upon malting. Further, the boiled potato note, commonly associated with 3-(methylsulfanyl)propanal, was less frequently recorded in quinoa malt. Several sensory panels have reported the characteristic musty, earthy odor in quinoa food products[44,45] but no compounds have been ascribed to this attribute. In this study, three methoxypyrazines which impart distinctive musty, earthy notes were identified by GC-O/MS in the quinoa volatile isolates. Unlike barley and rye where methoxypyrazine formation is induced by germination,[46] these occur naturally in quinoa. Despite the structural similarities, different intensities and aromas were described for the methoxypyrazines. 2-Methoxy-3-isopropylpyrazine delivers an odor resembling fresh cucumber or asparagus and was often described as 'quinoa', whereas 2-methoxy-3-*sec*-butylpyrazine and 2-methoxy-3-isobutylpyrazine confers a potent bell pepper aroma. The former could be distinguished by the perceived freshness at the sniffing port and the latter by its pungency. The linolenic acid degradation product, (*E*,*Z*)-2,6-nonadienal, also evoked a cucumber note but lacked the crispness of the methoxypyrazine aroma. In contrast, the 4,5-epoxy-(*E*)-2-alkenals delivered a metallic odor; however only the *cis* C_{10} isomer was perceived in all samples. Another compound contributing to the musty character is oct-1-en-3-one, it was perceived in all samples except the SAFE extract of Qui-UM. In addition to the metallic note, the C_8 ketone and its corresponding alcohol, oct-1-en-3-ol, evoke the characteristic mushroom odor. Based on the sensory evaluations, malting did not alter the perception of the mushroom note. Gentle distillation (i.e., SAFE), however, was not favorable for the isolation of ten additional odor-active regions native to quinoa, which also survived the malting process. These include compounds that deliver green notes (e.g., hexanal) as well as compounds that contribute to the roasted, nutty odor (e.g., 2,3-diethyl-5-methylpyrazine) of quinoa. Moreover, the lipid degradation products such as both 2-nonenal isomers were not extracted from Qui-UM by SAFE, these give rise to unpleasant rancid, fatty odors in quinoa.

Eleven malting odor-active byproducts were detected in Qui-M by all sampling techniques; germination was essential for the formation of eight of these. Their absence in the SDE extract of unmalted quinoa confirmed germination is required because heating alone is not enough to release these compounds from their precursors. The contribution of two Maillard reaction

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Table 4. Odor-active volatiles detected in quinoa in its unmalted and malted[a] state by SPME, SDE, and/or SAFE ($n \geq 9$)

				SPME		SDE		SAFE	
No.	RI_{DB-5}[b]	Compound[c]	Odor Descriptor[d]	Qui-UM	Qui-M	Qui-UM	Qui-M	Qui-UM	Qui-M
1	534	Dimethyl sulfide	boiled vegetables		x				
2	551	Butane-2,3-dione	buttery		x	x	x		x
4	649	3-Methylbutanal	malty		x		x		x
5	681	1-Penten-3-one[e]	vegetables, cheesy				x		
7	721	Unknown	sulfury, onion			x	x		
8	755	Ethyl 2-methylpropanoate	fruity		x				x
10	800	Hexanal	fresh grass	x	x	x	x		x
11	810	2-Methylthiazole	garlic, onion				x		
12	824	2-Methylpyrazine	onion, garlic	x	x	x	x		
13	832	3-Methylbutanoic acid	cheesy, vomit		x		x		x
14	842	2-Methylbutanoic acid	cheesy, sweet				x		
15	852	Ethyl 2-Methylbutanoate	fruity, pineapple						x
16	856	Ethyl 3-Methylbutanoate	fruity, berries		x		x		x
17	870	Unknown	musty	x	x	x	x		
18	901	(*Z*)-4-Heptenal[e]	raw potatoes, fishy	x	x	x	x		x
19	910	3-(Methylsulfanyl)propanal[e]	boiled potatoes	x	x	x	x	x	x
20	912	2-Acetylfuran	roasted, burnt			x	x		
21	925	2-Acetyl-1-pyrroline[e]	malty, roasted	x	x	x	x		x
22	940	α-Pinene	pine tree	x	x			x	x
23	963	Ethyl 4-methylpentanoate	fruity, berries					x	x
24	971	5-Methylfurfural	nutty, roasted				x		
25	977	Dimethyl trisulfide	sulfury, onion						x
26	980	Oct-1-en-3-one[e]	mushroom	x	x	x	x		x
27	987	(*Z*)-1,5-Octadien-3-one[e]	geranium		x		x		x
30	1005	Octanal	orange peel, citrus	x	x				
31	1007	2,3,5-Trimethylpyrazine	nutty, roasted		x				x
32	1039	1,8-Cineole	eucalyptus						x
33	1042	4-Hydroxy-5-methyl-3(2*H*)-furanone	caramel, sweet, nutty			x	x		
34	1049	Phenylacetaldehyde	floral, honey		x		x		
35	1057	Unknown	nutshells	x	x	x	x		x
36	1061	(*E*)-2-Octenal	green, fatty						x
37	1069	4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone	caramel, strawberry		x		x		x
38	1083	2-Ethyl-3,6-dimethylpyrazine	roasted, chocolate			x	x		x
39	1089	2-Ethyl-3,5-dimethylpyrazine	roasted, nutty, bread	x	x	x	x		x
40	1095	(*E*)-2,3-Epoxyoctanal	flower peduncle		x				x
41	1098	2-Methoxy-3-isopropylpyrazine	asparagus, cucumber	x	x	x	x	x	x
43	1110	3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone	dehydrated broth						x
44	1121	2-Phenylethan-1-ol	floral, roses		x		x		x
45	1150	(*Z*)-2-Nonenal	fatty, rubber	x	x	x	x		x
46	1159	(*E*,*Z*)-2,6-Nonadienal	stale cucumber	x	x	x	x	x	x
47	1160	2,3-Diethyl-5-methylpyrazine	nutty	x	x	x	x		x
48	1163	(*E*)-2-Nonenal	fatty, cardboard	x	x	x	x		x
49	1170	Unknown	floral, honey	x	x	x	x		x
50	1177	2-Methoxy-3-*sec*-butylpyrazine	fresh bell pepper	x	x	x	x	x	x
51	1186	2-Methoxy-3-isobutylpyrazine	green bell pepper, pungent	x	x	x	x	x	x
52	1197	(*E*)-2,3-Epoxynonanal	fruity, plastic						x
53	1205	Unknown	dusty	x	x				
54	1220	(*E*,*E*)-2,4-Nonadienal	deep fried	x	x	x	x		x
55	1240	1,3-Benzothiazole	malty, dusty		x				x
56	1247	Unknown	fruity, citrus		x		x		x
57	1283	(*E*)-4,5-Epoxy-(*E*)-2-nonenal	mealy, metallic	x	x				x
58	1290	4,5-Epoxy-(*E*)-2-nonenal	mealy, metallic	x	x				x
60	1323	(*E*,*E*)-2,4-Decadienal	rancid cooking oil		x	x	x		x
61	1325	2-Methoxy-4-vinylphenol	clove, spicy		x	x	x		x
62	1345	Unknown	chlorine						x

Table 4. Continued

No.	RI_{DB-5}[b]	Compound[c]	Odor Descriptor[d]	SPME		SDE		SAFE	
				Qui-UM	Qui-M	Qui-UM	Qui-M	Qui-UM	Qui-M
63	1358	Ethyl 3-Phenylpropionate	citrus, strawberry		x				x
64	1379	(*Z*)-4,5-Epoxy-(*E*)-2-decenal	dusty, metallic, chalk	x	x	x	x	x	x
65	1384	(*E*)-4,5-Epoxy-(*E*)-2-decenal	dusty, metallic, dry						x
66	1396	(*E*)-*β*-Damascenone	stewed apple			x	x		
67	1408	3-Methyl-1*H*-indole[e]	fecal			x	x		
68	1478	Ethyl (*E*)-3-Phenylprop-2-enoate	fruity, strawberry		x		x		x
69	1483	5,6-Dihydro-6-pentyl-2*H*-pyran-2-one	soapy, waxy						x

Note: x = perceived.
[a] Malting regimes are described in Table 1. Qui = quinoa, UM = unmalted, M = standard malt.
[b] Retention indices on a DB-5 column.
[c] Identified compounds by retention index, odor description, and mass spectrum obtained in EI.
[d] Odor description as perceived at the sniffing port.
[e] Tentatively identified compounds by retention index, odor description, and comparison with reference substance.

products to the malty character of quinoa is particularly significant. Although compounds that evoke pleasant malty, caramel odors are present in Qui-UM, their interactions with 3-methylbutanal and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (i.e., furaneol) led to higher malty and caramel scores, respectively, in quinoa malt. In sharp contrast, the combined contribution of (*Z*)-1,5-octadien-3-one and 2-phenylethan-1-ol did not intensify the floral perception in Qui-M. In addition to the malty and floral malting byproducts, germination induced the formation of the fruity esters, ethyl 3-methylbutanoate and ethyl (*E*)-3-phenylprop-2-enoate. Conversely, as confirmed by SDE analysis, elevated temperatures sufficed to release butane-2,-3-dione (i.e., diacetyl), (*E*,*E*)-2,4-decadienal, and 2-methoxy-4-vinylphenol (i.e., 4-vinylguaiacol; 4-VG) from the unmalted seeds during SDE isolation. These three compounds are known to increase upon thermal treatment.[47-50] The presence of butane-2,3-dione in all Qui-M isolates confirm the influence of this volatile on the butter descriptor sensory score assigned to the malt sample.

Odor-active volatiles detected by HS-SPME

Initial analysis by HS-SPME provides an overview of the volatile composition of the samples. In Qui-UM and Qui-M, 24 and 42 odor-active regions were perceived at the sniffing port, respectively. Headspace volatile analysis allowed the identification of dimethyl sulfide (DMS) in the malt sample as there is no interference from the solvent peak. Although DMS was only identified in Qui-M by GC-O/MS analysis, the sensory score for the boiled vegetables descriptor was higher in Qui-UM; consequently, indicating that other compounds contribute to this attribute. Two additional compounds native to quinoa were detected by HS-SPME analysis only. However, HS-SPME failed to isolate 2-ethyl-3,-6-dimethylpyrazine, which was identified as a malting byproduct by the other two extraction methods but not by headspace analysis.

Odor-active volatiles detected by SDE

In Qui-UM, the highest number of odor-active volatiles was found in the SDE extract. The gas chromatograms revealed 28 and 41 odor-active regions in Qui-UM and Qui-M, respectively. Nine additional odor-active volatiles were found in the quinoa SDE extracts. Most of these compounds are typical thermal reaction products, which were not perceived by SPME or SAFE; therefore, artifact formation during distillation should not be disregarded. Five compounds were perceived in both SDE extracts but not by the other two isolation techniques. Heating released these volatiles from the unmalted seeds during SDE extraction; the Qui-M SDE data confirmed that these also survived the malting process. 2-Acetylfuran and 4-hydroxy-5-methyl-3(2*H*)-furanone (i.e., norfuraneol) impart roasted, caramel notes. Solvent extraction at higher temperatures also released the stewed apple aroma delivered by (*E*)-*β*-damascenone, a typical thermal reaction product.[51] Although these compounds were not detected by SPME and SAFE, these aromas can form upon further processing (i.e., boiling) of quinoa. In addition to the pleasant aromas, two undesirable compounds (3-methyl-1*H*-indole) formed during extraction at high temperatures. Upon germination and kilning, four additional compounds were extracted by SDE. These include, 5-methylfurfural which delivers a pleasant nutty odor and was previously identified in cooked quinoa (i.e., 100 °C) but not in unprocessed quinoa.[25] This Maillard reaction product was also detected in a selection of gluten-free breads but the highest amount was measured in quinoa bread crust (i.e., 190 °C).[22] Conversely, the malting byproducts, 1-penten-3-one, 2-methylthiazole, and 2-methylbutanoic acid deliver unpleasant notes. As previously mentioned, high temperatures can promote the formation of an array of compounds, yet the thermal alteration of the quinoa volatile fraction isolated by SDE was also confirmed by the absence of the naturally occurring *α*-pinene and five malting odor-active byproducts.

Odor-active volatiles detected by SAFE

In comparison with SPME and SDE, the lowest and highest number of odor-active regions were detected in the SAFE extracts of Qui-UM (eight) and Qui-M (47), respectively. The SAFE extracts revealed ten additional compounds, which were not perceived by the other extraction methods. Except for ethyl 4-methylpentanoate, these compounds were malting odor-active byproducts with low odor recognition thresholds,[42] including dimethyl trisulfide, 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (i.e., sotolon), (*E*)-4,5-epoxy-(*E*)-2-decenal, and 5,6-dihydro-6-pentyl-2*H*-pyran-2-one. In addition, fruity smelling compounds (e.g., ethyl 2-methylbutanoate) as well as compounds contributing to the green note (e.g., 1,8-cineole) in Qui-M were exclusively extracted by SAFE. Another malting byproduct contributing to the green, floral note is phenylacetaldehyde;

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however, the Strecker aldehyde was not detected in the volatile fraction isolated by SAFE. Overall, more compounds were detected in quinoa malt than in Qui-UM and in comparison with the other isolation methods, SAFE produced an extract with the highest number of odor-active compounds. Consequently, in the second part of this study, further aroma characterization was only done on malt using SAFE extraction. Subsequently, cAEDA was carried out to examine and compare the effect of different malting regimes as well as storage of the standard malt on the aroma profiles of the quinoa malts that were produced.

Comparison of odor-active compounds in quinoa malts by cAEDA

Table 5 lists the 56 odor-active regions detected in the quinoa malts and their corresponding FD factors. Variation in the malting parameters resulted in noticeable changes in the volatile composition and intensity of the quinoa malts. Seven additional compounds were detected in Qui-Hi and Qui-Lo but not in Qui-M; and of the perceived compounds, 36 were common to all quinoa malts. In the fresh samples, the highest number of volatile compounds was perceived in the standard quinoa malt (i.e., 47). In Qui-M, only the naturally occurring 2-methoxy-3-isopropylpyrazine and 2-methoxy-3-isobutylpyrazine were assigned the highest FD factor (i.e., FD = 160), whereas 2-methoxy-3-*sec*-butylpyrazine was perceived at a lower intensity (FD = 80). The different malting conditions did not impact the intensity at which the asparagus note, delivered by the former, was perceived. Conversely, varying the malting parameters resulted in weaker intensities for the other two methoxypyrazines. After storage, all methoxypyrazines were perceived at the same intensity as in the fresh standard malt and their odor quality remained unchanged. All 4,5-epoxy-(*E*)-2-alkenals were, generally, perceived at higher intensities in Qui-Hi and Qui-Lo than in Qui-M; in addition, the C_{10} compounds elicited a more intense metallic odor. In the sensory assessment, the musty attribute was further characterized as potato-like or mushroom-like. GC-O/MS analysis revealed 3-(methylsulfanyl)propanal and (*Z*)-4-heptenal contribute to the former and oct-1-en-3-one to the latter. The odor delivered by the Strecker aldehyde was four times stronger and resembled boiled potatoes whereas the lipid degradation product had an earthy taint. The intensity of both potato smelling compounds declined after the storage period; conversely, the mushroom note increased. Although the same FD factor was assigned to 3-(methylsulfanyl)propanal and oct-1-en-3-one in Qui-M; their odor detection thresholds in water are 0.430 μg/L and 0.016 μg/L,[42] respectively, explaining the higher detection frequency of the latter in the sensory sessions.

Malting reduced the intensity of the musty attribute and modified the distinctive green note perceived in the milled seeds. In comparison with the volatiles contributing to the musty character, lower FD factors were assigned to the green and floral volatile compounds. Two natural occurring compounds, hexanal and α-pinene, and two malting odor-active byproducts, 1,8-cineole and (*E*)-2-octenal, deliver characteristic green notes. Subtle differences in their aroma were perceived at the sniffing port. Hexanal delivers a fresh green, grassy note, whereas the other three compounds are characterized by a resinous odor. The intensity of hexanal also increased after storage but both monoterpenes were weakened. Differences in the preferred malting conditions for the production of floral compounds were also reported. The rose and geranium aroma delivered by 2-phenylethan-1-ol and (*Z*)-1,-5-octadien-3-one, respectively, were favored by lower germination temperatures. In sharp contrast, higher temperatures promoted the development of (*E*)-2,3-epoxyoctanal, and an unknown floral compound with a subtle honey note ($RI_{DB\text{-}5}$ = 1170). Hexanal and (*E*)-2,3-epoxyoctanal usually increase during storage and are common indicators of oxidation in quinoa and cereals (e.g., oats).[52,53]

Compared to Qui-UM, the butter attribute followed by malty scored the highest sensory intensity values in the standard quinoa malt. The FD factors assigned by GC-O/MS analysis to butane-2,-3-dione and 3-methylbutanal are 20 and 10, respectively. Although these FD factors lie at the lower end of the dilution series, both attributes received high scores in the sensory assessment. Butane-2,3-dione is a highly volatile compound; the buttery odor is probably among the first compounds to reach the olfactory receptors, thus, higher scores were assigned. Similarly, 3-methylbutanal is highly volatile, however the malty attribute is enhanced by pyrazines and furanones, which give rise to nutty and caramel notes, respectively. The more odor-active 2-ethyl-3,-5-dimethylpyrazine[54] as well as 2,3-diethyl-5-methylpyrazine were already present in perceivable amounts in Qui-UM. Malting enhanced or suppressed the production of these naturally occurring nutty pyrazines but storage did not. Two additional pyrazines, 2,3,5-trimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine, were formed upon malting but their strong roasted aroma decreased during storage. Both caramel furanones are malting odor-active byproducts; 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone evokes a spicy note, whereas 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone delivers a pleasant caramel aroma in thermally processed foods.[55,56] The 3(2*H*)-furanone is considered an important contributor to the overall aroma of colored barley malt[57,58] and wheat and rye breads.[59] In comparison with an array of gluten-free breads and a control wheat bread, higher proportions of this 3(2*H*)-furanone were reported in quinoa bread crust.[22] In Qui-M, it contributes to the frequently perceived caramel-like character in the sensory sessions.

Unlike most perceived compounds, the fruity esters were almost exclusively identified in Qui-M. The malting conditions of Qui-Hi and Qui-Lo caused the naturally occurring ethyl 4-methylpentanoate to disappear and did not allow the development of four fruity volatiles. Except for ethyl hexanoate formed during storage, the perceived intensity of the berry aromas decreased after the storage period. These esters were probably evaporated out of the seed matrix due to their low concentrations and high volatility. Both low volatile esters delivered strawberry notes; ethyl (*E*)-3-phenylprop-2-enoate was only identified in Qui-M but the malting conditions of Qui-Lo favored the formation of ethyl 3-phenylpropionate in quinoa. Conversely, higher germination temperature was favorable for the formation of six additional fruity and fatty compounds in Qui-Hi. In the standard malt, pentanal, octanal, nonanal, and 2-pentylfuran were formed during storage and the intensity of (*E*)-2,3-epoxynonanal and an unknown compound ($RI_{DB\text{-}5}$ = 1247) increased after the storage period. Consequently, these could be classified as high modification as well as quinoa aging indicators. Pentanal has also been reported to be a crucial volatile compound, which helps discriminate among the different colored quinoa seeds,[25,26] whereas nonanal and 2-pentylfuran were identified as important aroma compounds in cooked quinoa porridge (i.e., 100 °C).[20]

In addition to the compounds that deliver pleasant aromas to quinoa, undesirable odors were also reported. The natural occurring lipid derived carbonyls, (*Z*)-2-nonenal, (*E*)-2-nonenal, (*E*,*Z*)-2,6-nonadienal, (*E*,*E*)-2,4-nonadienal as well as the malting byproducts, (*E*,*Z*)-2,4-decadienal and (*E*,*E*)-2,4-decadienal contribute to

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Table 5. Odor-active volatiles and corresponding FD factors ($n \geq 9$) in quinoa malts[a] by cAEDA

No.	RI_{DB-5}[b]	Compound[c]	Odor Descriptor[d]	FD Factor			
				Qui-M	Qui-St	Qui-Hi	Qui-Lo
2	551	Butane-2,3-dione	buttery	20	10	-	-
3	614	Acetic acid	vinegar	-	5	-	-
4	649	3-Methylbutanal	malty	10	-	-	-
6	698	Pentanal	bready, fruity	-	10	10	1
8	755	Ethyl 2-Methylpropanoate	fruity	20	10	-	-
9	791	Butanoic acid	rancid, butter	-	10	-	-
10	800	Hexanal	fresh grass	80	160	160	160
13	832	3-Methylbutanoic acid	cheesy, vomit	10	20	5	5
15	852	Ethyl 2-Methylbutanoate	fruity, pineapple	80	5	-	-
16	856	Ethyl 3-Methylbutanoate	fruity, berries	40	5	-	-
18	901	(*Z*)-4-Heptenal[e]	raw potatoes, fishy	20	10	20	20
19	910	3-(Methylsulfanyl)propanal[e]	boiled potatoes	80	20	20	20
21	925	2-Acetyl-1-pyrroline[e]	malty, roasted	40	5	5	5
22	940	α-Pinene	pine tree	40	20	20	20
23	963	Ethyl 4-Methylpentanoate	fruity, berries	20	5	-	-
25	977	Dimethyl trisulfide	sulfury, onion	20	20	-	-
26	980	Oct-1-en-3-one[e]	mushroom	80	160	160	160
27	987	(*Z*)-1,5-Octadien-3-one[e]	geranium	40	10	5	10
28	993	2-Pentylfuran	fruity, citrus	-	10	10	5
29	999	Ethyl hexanoate	fruity, berries	-	10	5	1
30	1005	Octanal	orange peel, citrus	-	10	40	20
31	1007	2,3,5-Trimethylpyrazine	nutty, roasted	40	10	-	-
32	1039	1,8-Cineole	eucalyptus	40	5	10	10
35	1057	Unknown	nutshells	80	10	160	40
36	1061	(*E*)-2-Octenal	green, fatty	10	10	20	10
37	1069	4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone	caramel, strawberry	80	10	20	5
38	1083	2-Ethyl-3,6-dimethylpyrazine	roasted, chocolate	20	10	5	-
39	1089	2-Ethyl-3,5-dimethylpyrazine	roasted, nutty, bread	80	80	10	10
40	1095	(*E*)-2,3-Epoxyoctanal	flower peduncle	80	160	160	80
41	1098	2-Methoxy-3-isopropylpyrazine	asparagus, cucumber	160	160	160	160
42	1106	Nonanal	floral, citrus	-	1	1	1
43	1110	3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone	dehydrated broth	5	10	5	5
44	1121	2-Phenylethan-1-ol	floral, roses	20	20	10	20
45	1150	(*Z*)-2-Nonenal	fatty, rubber	80	80	80	40
46	1159	(*E*,*Z*)-2,6-Nonadienal	stale cucumber	20	5	1	5
47	1160	2,3-Diethyl-5-methylpyrazine	nutty	80	80	20	20
48	1163	(*E*)-2-Nonenal	fatty, cardboard	40	40	20	20
49	1170	Unknown	floral, honey	5	40	80	40
50	1177	2-Methoxy-3-*sec*-butylpyrazine	fresh bell pepper	80	80	10	5
51	1186	2-Methoxy-3-isobutylpyrazine	green bell pepper, pungent	160	160	10	20
52	1197	(*E*)-2,3-Epoxynonanal	fruity, plastic	10	40	160	40
53	1205	Unknown	dusty	-	80	160	20
54	1220	(*E*,*E*)-2,4-Nonadienal	deep fried	20	20	40	40
55	1240	1,3-Benzothiazole	malty, dusty	10	40	160	10
56	1247	Unknown	fruity, citrus	10	20	10	5
57	1283	(*E*)-4,5-Epoxy-(*E*)-2-nonenal	mealy, metallic	5	5	1	1
58	1290	4,5-Epoxy-(*E*)-2-nonenal	mealy, metallic	20	80	80	160
59	1299	(*E*,*Z*)-2,4-Decadienal	rancid, metallic	-	5	10	10
60	1323	(*E*,*E*)-2,4-Decadienal	rancid cooking oil	20	40	40	80
61	1325	2-Methoxy-4-vinylphenol	clove, spicy	20	-	-	-
62	1345	Unknown	chlorine	5	5	5	20
63	1358	Ethyl 3-Phenylpropionate	citrus, strawberry	10	5	5	20
64	1379	(*Z*)-4,5-Epoxy-(*E*)-2-decenal	dusty, metallic, chalk	80	80	160	160
65	1384	(*E*)-4,5-Epoxy-(*E*)-2-decenal	dusty, metallic, dry	40	160	160	160

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Table 5. Continued

No.	RI_{DB-5}[b]	Compound[c]	Odor Descriptor[d]	FD Factor			
				Qui-M	Qui-St	Qui-Hi	Qui-Lo
68	1478	Ethyl (*E*)-3-Phenylprop-2-enoate	fruity, strawberry	40	5	-	-
69	1483	5,6-Dihydro-6-pentyl-2*H*-pyran-2-one	soapy, waxy	1	10	10	10

[a] Malting regimes are described in Table 1. Qui = quinoa, M = standard malt, St = stored standard malt, Hi = high modification, Lo = low modification.
[b] Retention indices on a DB-5 column.
[c] Identified compounds by retention index, odor description, and mass spectrum obtained in EI.
[d] Odor description as perceived at the sniffing port.
[e] Tentatively identified compounds by retention index, odor description, and in comparison with a reference substance.

the unpleasant rancid, fatty odors in quinoa. Among these aldehydes, (*Z*)-2-nonenal followed by its *trans* isomer, scored the highest FD factors in Qui-M. Storage did not increase the perceived intensity of the 2-nonenal isomers but the malting parameters of Qui-Lo hindered the formation of the more odor-active *cis* isomer. Conversely, these malting conditions favored the development of (*E*,*E*)-2,4-decadienal in quinoa. In previous studies, (*E*,*E*)-2,4-decadienal was identified as a characteristic aroma compound in quinoa porridge[20] and in quinoa breads.[22] The intensity of (*E*,*Z*)-2,6-nonadienal decreased in Qui-St yet both 2,4-decadienal isomers were enriched by storage of Qui-M. Three carboxylic acids also contribute to the off–flavors and were classified as aging indicators. Acetic and butanoic acid were exclusively detected in Qui-St, whereas 3-methylbutanoic acid was also perceived in the fresh malt samples but the unpleasant note was enriched upon storage.

CONCLUSIONS

In the sensory sessions, the panel members characterized the aroma of native quinoa as green and musty. Malting decreased the sensory scores of both attributes and led to the development of the pleasant malty aroma, which was further characterized by its caramel notes. Instrumental analysis by GC-O/MS identified three methoxypyrazines as important aroma compounds in quinoa. These occur naturally in quinoa and impart the distinctive musty, earthy notes. At the sniffing port, the perceived odor of 2-methoxy-3-isopropylpyrazine resembled quinoa the most. Although the methoxypyrazines were detected by all methods, HS-SPME lacked sensitivity for the extraction of nutty-smelling heterocyclic compounds and several artifacts were produced by SDE. Conversely, the highest number of odor-active compounds were perceived in the SAFE extract of quinoa malt and artifact formation was avoided. However, by using different extraction methods, it was possible to achieve a representative classification of the odor-active volatiles present in quinoa, understand their contribution to the characteristic aroma profile, and determine which compounds are naturally occurring in quinoa and which require germination, kilning, or both for their formation.

In the second part of this study, a broader spectrum of malt aromas was obtained by varying the malting parameters. The impact of malt modification and the effect of storage on the odor-active volatiles were examined by cAEDA. A similar number (43–47) of volatile compounds was perceived in all fresh quinoa malts but their intensity and composition varied. The presence of the esters as well as selected malty compounds (e.g., 3-methylbutanal) was exclusive of Qui-M. Higher germination temperature allowed better protein degradation in Qui-Hi but also promoted the formation of lipid oxidation products such as the (*E*)-2,3-epoxyalkanals. In addition, high malt modification resulted in stronger perceived intensities at the sniffing port and the highest FD factor (FD = 160) was most frequently assigned in Qui-Hi to compounds that contribute to the musty character of quinoa. In sharp contrast, the malting conditions of Qui-Lo were not favorable for starch and protein solubility, thus limiting the precursor availability. Consequently, the lowest number of odor-active volatiles was reported in Qui-Lo and the assigned FD factors were generally lower. Although the malty smelling compounds decreased during storage and other compounds were no longer perceived, the highest number of compounds was reported in Qui-St. Fatty smelling compounds as well as the undesirable carboxylic acids were formed upon storage of Qui-M. These were therefore classified as aging indicators of quinoa seeds. Malting changed the odor-active volatile compound composition of quinoa; therefore, understanding the impact of germination and storage on malt quality and aroma properties is fundamental for improving the aroma profile of quinoa. In comparison with unprocessed quinoa seeds, the different malting regimes provided malts with enhanced processing properties and pleasant nutty and caramel aromas. Quinoa malt can, therefore, be used to add desirable aromas and flavors to quinoa-based food products and improve their acceptability.

AUTHOR CONTRIBUTIONS

Cynthia Almaguer: Conceptualization, methodology, investigation, formal analysis, data curation, visualization, writing – original draft, review, and editing. Hubert Kollmannsberger: data curation, writing – review and editing. Martina Gastl: Funding acquisition, supervision, writing – review and editing. Thomas Becker: Supervision, resources, writing – review and editing. All authors have read and agreed to the published version of the manuscript.

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CONFLICT OF INTEREST

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

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