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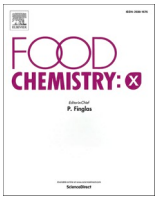

Influence of germination and roasting on the characteristic volatile organic compounds of quinoa using sensory evaluation, *E*-nose, HS-GC-IMS, and HS-SPME-GC-MS

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ABSTRACT

This study aimed to investigate the effects of germination and roasting on the flavor of quinoa. Firstly, the aroma of quinoa and germinated quinoa roasted under different conditions was analyzed using sensory evaluation and electronic nose (*E*-nose). Results showed that the best favorable aroma of quinoa and germinated quinoa was obtained when roasted at 160 °C for 15 min. Then, a total of 34 and 80 volatile organic compounds (VOCs) of quinoa and germinated quinoa roasted at 160 °C for 15 min were determined using headspace-gas chromatography-ion mobility spectrometry (HS-GC-IMS) and headspace solid-phase microextraction gas chromatography–mass spectrometry (HS-SPME-GC–MS), respectively. Germination and roasting effectively reduced the contents of VOCs that produced undesirable flavor. Moreover, germination improved the floral aromas, while roasting mainly produced caramel, cocoa, and roasted nut aromas of quinoa. This study indicated that germination and roasting treatments might serve as promising processing methods to improve the flavor of quinoa.

1. Introduction

Quinoa is a pseudocereal that originated from the Andes region of South America and has been introduced to North America, Asia, Africa, and Europe due to its adaptability to different environments and unique nutritional value (Repo-Carrasco, Espinoza, & Jacobsen, 2003). Quinoa is rich in various macronutrients, such as carbohydrates, fiber, protein, and fats, and micronutrients, such as vitamins, minerals, and polyphenols (Tang et al., 2015; Vilcacundo & Hernandez-Ledesma, 2017). In recent years, the demand for nutritionally balanced foods has improved rapidly. Among them, quinoa has gained immense popularity among consumers due to its unique nutritional value and health-promoting effects. For instance, quinoa consumption has been found to exhibit preventive and alleviative effects on diabetes, obesity, dyslipidemia, and anemia (Navruz-Varli & Sanlier, 2016).

Currently, quinoa is being processed into various products, including pancakes, cookies, cakes, and bread (Brito et al., 2015; Rosell, Cortez, & Repo-Carrasco, 2009). It is reported that several factors influence the flavor quality of quinoa; among which the aroma has the predominant effect. Typically, unprocessed quinoa has unpleasant flavors of grass and earth. In this regard, germination could alter the sensory and nutritional aspects of the grain, serving as a potential method for reducing off-flavors (Almaguer, Kollmannsberger, Gastl, & Becker, 2023). Previous studies have reported the effect of various processing methods, such as cooking and fermentation, on the flavor of quinoa (Brito et al., 2015; Li et al., 2018). Roasting and germination are widely used methods in the processing of quinoa foods. However, the effects of roasting and germination on the aroma characteristics of quinoa and its underlying mechanisms have not yet been fully elucidated.

The electronic noses (*E*-nose) system is comprised of 10 metal oxide sensors and one recognition analysis software that can identify various odors and distinguish between samples effectively. HS-SPME-GC–MS can characterize and quantify the volatile compounds by combining the advantages of gas chromatography (GC) separation capability and mass spectrometry (MS) capability for metabolite identification (Chen et al., 2021). However, it is not sensitive to low concentrations of volatile

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organic compounds (VOCs), resulting in some VOCs not being well identified (Wang et al., 2023). In recent years, headspace-gas chromatography-ion mobility spectrometry (HS-GC-IMS) has been widely applied in the field of food flavor detection due to the combined advantages of the excellent separation efficiency of GC and the high sensitivity of ion mobility spectrometry (IMS) (Hernandez-Mesa et al., 2019). Additionally, this technique allows for rapid detection of volatiles in samples without complex pretreatment (Kaneko & Kumazawa, 2015). Compared to HS-SPM*E*-GC–MS, HS-GC-IMS can detect low concentrations of VOCs (Chen et al., 2020). Unfortunately, rare studies have analyzed the effects of roasting and germination on the volatile flavor of quinoa using the combination of E-nose, HS-GC-IMS, and GC–MS techniques so far.

Therefore, the present study aimed to assess the effects of roasting temperature (100–180 °C) and time (0-20 min) on the flavor characteristics of quinoa by sensory evaluation and E-nose. Then the volatile compounds of quinoa and germinated quinoa roasted at 160 °C for 15 min were detected using HS-SPME-GC–MS and HS-GC-IMS. This study explores the flavor compounds produced by different processing conditions and provides a basis for investigating the mechanisms of flavor formation in germinated and roasted quinoa.

2. Material and methods

2.1. Sample preparation

The white quinoa was obtained from Qinghai Bayanhar Ecological Agriculture Co., Ltd. (Golmud, Qinghai, China). The quinoa was washed to remove the saponins and dried at 55 °C for 16 h (Q). For the germination, after removal of the saponins, quinoa was germinated in water at 30 °C for 90 min and then dried at 55 °C for 16 h (GQ).

Forty grams of the quinoa and germinated quinoa samples were spread on a roasting sheet and then roasted in the oven at 100, 120, 140, 160, and 180 °C for 15 min or at 160 °C for 0, 5, 10, 15, and 20 min, respectively. All the quinoa samples were crushed using a pulverizer (150 T, Xichu, Jinhua, Zhejiang, China). The powder under 60 mesh was collected and used for further analysis. The aroma of quinoa and germinated quinoa roasted at a temperature (100, 120, 140, 160, and 180 °C) and for a time (0, 5, 10, 15, and 20 min) was determined using sensory evaluation and *E*-nose. Then, the VOCs of roasted quinoa (RQ) and roasted germinated quinoa (RGQ) at 160 °C for 15 min were determined using HS-GC-IMS and HS-SPME-GC–MS. In the sensory evaluation, each test was repeated 10 times, while in the E-nose, HS-GC-IMS, and HS-SPME-GC–MS analysis, each test was conducted in triple.

2.2. Sensory evaluation

The quinoa sample was presented in a clear glass and coded randomly. The aroma of the quinoa samples was evaluated by ten sensory experts (aged 21–30 years, five females and five males). All experts had been trained on sensory aspects of pseudo grains according to the Method (GB/T 16291.1–2012). The expert analysis yielded ten aroma descriptors. In the next sensory rating, the experts rated four attributes and overall flavor intensity. Sensory analysis was approved by the College of Food Science and Engineering, Northwest A&F University. All participants received signed informed consent forms.

2.3. E-nose analysis

The quinoa sample (5 g) was placed in the headspace bottle, equilibrated at 25 °C for 50 min, and then analyzed using a PNE3 electronic nose (PEN3 Airsence, Schwerin, Germany). The sensors used for the E-nose were listed in **Table S1**. The technical parameters were as follows: detection time of 60 s, internal flow rate of 400 mL/min, injection flow rate of 10 mL/min, injection time of 5 s, and cleaning time of 300 s.

2.4. HS-GC-IMS analysis

The VOCs of the quinoa sample were analyzed using HS-GC-IMS (FlavourSpec®, G.A.S., Dortmund, Germany) according to the described method (Song et al., 2021) with some adjustments. The quinoa sample (2 g) was placed in 20 mL headspace glass vials and then incubated at 40 °C for 25 min. Then 500 μL of gas was injected into the injector at 85 °C in splitless mode. The headspace gas was separated at 45 °C using an IMS column (MXT-5 capillary column, 15 m × 0.53 mm). Nitrogen gas (99.999%) was used as carrier gas and drift gas. The program of carrier gas was as follows: 2 mL/min for 2 min, increased to 100 mL/min over 10 min, then ramped up to 150 mL/min in 18 min, while the drift gas was set as 75 mL/min. The retention index (RI) of VOCs was calculated by using n-ketones C4-C9 (FlavourSpec®, G.A.S.) as the external parameter. The VOCs were identified by comparing the drift time and RI with the GC-IMS library. The peak intensity of HS-GC-IMS was used to calculate the relative quantification of VOCs.

2.5. HS-SPME-GC–MS analysis

The VOCs of the quinoa sample were further analyzed using HS-SPME-GC–MS according to the described method (Zhang et al., 2018) with some modifications. Two grams of the quinoa sample and 10 μL of 3-heptanone (CATO, Guangzhou, China) were added to the headspace bottle and then cultured in an incubator at 40 °C for 25 min.

Briefly, The SPME (50/30 μm, DVB/CAR/PDMS) fibers are preheated at 250 °C for 1 h. A GC–MS (Shimadzu QP2010, Kyoto, Japan) with a TG-5MS capillary GC column (DB-17MS, 60 m × 0.25 mm × 0.25 μm) was utilized for analyzing and isolating the extracted VOCs. The inlet temperature was set at 270 °C in splitless mode. The column temperature was maintained at 40 °C for 1 min, then programmed to increase at 2 °C/min to 60 °C for 3 min, then at 5 °C/min to 150 °C for 2 min, and finally at 10 °C/min to 180 °C for 1 min. The following conditions for MS are ionization mode, electron shock at 70 eV; transmission line temperature at 230 °C; and the ion source temperature at 230 °C. Set the full scan mode range to 35–600 *m/z*. The compounds were identified and matched with the MS NIST14 library (NIST14, version 2.2, National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.). The concentrations of VOCs were calculated using 3-heptanone as the internal standard.

2.6. Statistical analysis

All samples were measured three times, and the results were reported as mean ± SD. The difference was statistically significant by ANOVA, and Duncan's multipolar difference test was performed by GraphPad Prism 8 software (Chicago, IL, U.S.A.). Radar plots for *E*-nose and sensory evaluation were calculated using OriginPro 2023. “Fingerprint” Gallery Plots were analyzed by the GC-IMS Library Search equipped with the GC-IMS instrument (G.A.S., Dortmund, Germany). Principal component analysis (PCA) was performed using SIMCA-P 14.0 software (Umetrics, Umeå, Sweden). Heat maps were analyzed and generated by the TB tool. The significance level was $P < 0.05$.

3. Results and discussion

3.1. Sensory characterization

The flavor of the quinoa samples was assessed by a trained panel. A previous study has reported that roasting could improve the flavor profile of foods such as coffee and peanuts (Moon & Shibamoto, 2009). In this study, the flavor profiles of the quinoa samples included general flavor, butter, caramel, roasted nut, and burnt. The germination treatment increased the caramel and roasted nut aroma of quinoa. The sensory scales of general flavor, butter, caramel, roasted nut, and burnt of quinoa and germinated quinoa all increased with roasting temperatures

ranging from 100 °C to 180 °C (Fig. 1A and C, **Fig. S1**) and time ranging from 0 to 20 min (Fig. 1B and D, **Fig. S2**). It is reported that a high roasting temperature can destroy the aroma and produce a pronounced burnt flavor (Guo, Ho, Schwab, & Wan, 2021). In our present study, the sensory scores of the burnt flavor of quinoa and germinated quinoa increased slightly with the roasting temperature ranging from 100 to 160 °C ($P > 0.05$) but it increased sharply at 180 °C. As a consequence, the sensory scores of the burnt flavor of quinoa and germinated quinoa at 180 °C were both significantly higher than those at 100 °C ($P < 0.01$). It suggested that excessive roasting temperature, for example, 180 °C, might produce a pronounced burnt aroma of quinoa and germinated quinoa. Similarly, roasting for 20 min also significantly increased the burnt flavor of quinoa ($P < 0.005$) and might bring an unpleasant flavor. In summary, the roasting conditions of 160 °C and 15 min would be appropriate to maintain the sensory flavor quality of quinoa and germinated quinoa.

3.2. E-nose analysis

The effects of germination and roasting on the flavor of quinoa were further determined by E-nose. The principal component analysis (PCA) results showed that the roasting temperature and time significantly influenced the odors of quinoa and germinated quinoa (**Fig. S3**). The 10 sensors in the E-nose system were sensitive to different odors. The response values of the sensors W1W (sulfur compounds) and W5S (nitrogen oxides) significantly increased ($P < 0.05$) with increasing roasting temperature and time, suggesting that roasting mainly increased the contents of sulfur compounds and nitrogen oxides in quinoa and germinated quinoa (Fig. 2). The contents of sulfur compounds and nitrogen oxides in quinoa and germinated quinoa were accumulated rapidly at over 160 °C and 15 min, and their contents at 180 °C were higher than that of 160 °C, while their contents remained similar at 15 min and 20 min. Excessive sulfur compounds would produce a pungent odor. Therefore, similar to the sensory evaluation results, roasting at 160 °C for 15 min was suitable for treating quinoa and germinated quinoa. However, the volatile compounds in the quinoa (Q), germinated quinoa (GQ), roasted quinoa (RQ) and roasted germinated quinoa (RGQ) at 160 °C for 15 min require further characterization.

3.3. HS-GC-IMS analysis of the VOCs of quinoa with different treatments

3.3.1. Identification of the VOCs by HS-GC–IMS

The VOCs in the samples were identified using HS-GC-IMS. The aromatic components in the samples were characterized using comparative modeling. As shown in Fig. 3A, the topography of quinoa sample-1 (Q-1) was selected as the reference. The GQ samples showed some scattered red spots, suggesting that these VOCs were slightly higher than those in the Q samples. The contents of VOCs in the roasted samples increased significantly. Therefore, it was speculated that the high-temperature treatment during roasting could promote the production of aroma compounds and accelerate their release.

Among the 49 detected signal peaks, 34 typical VOCs were successfully identified, including 8 alcohols, 6 ketones, 8 aldehydes, 4 esters, 3 heterocycles, 1 acid, and 4 others (**Table S2**). The VOC fingerprints were compared to analyze the effects of germination and roasting on the VOCs of quinoa visually. As shown in Fig. 3B, after germination and roasting, the contents of n-pentanal were significantly reduced, while the contents of diethyl sulfide, 4-methylthiazole, and

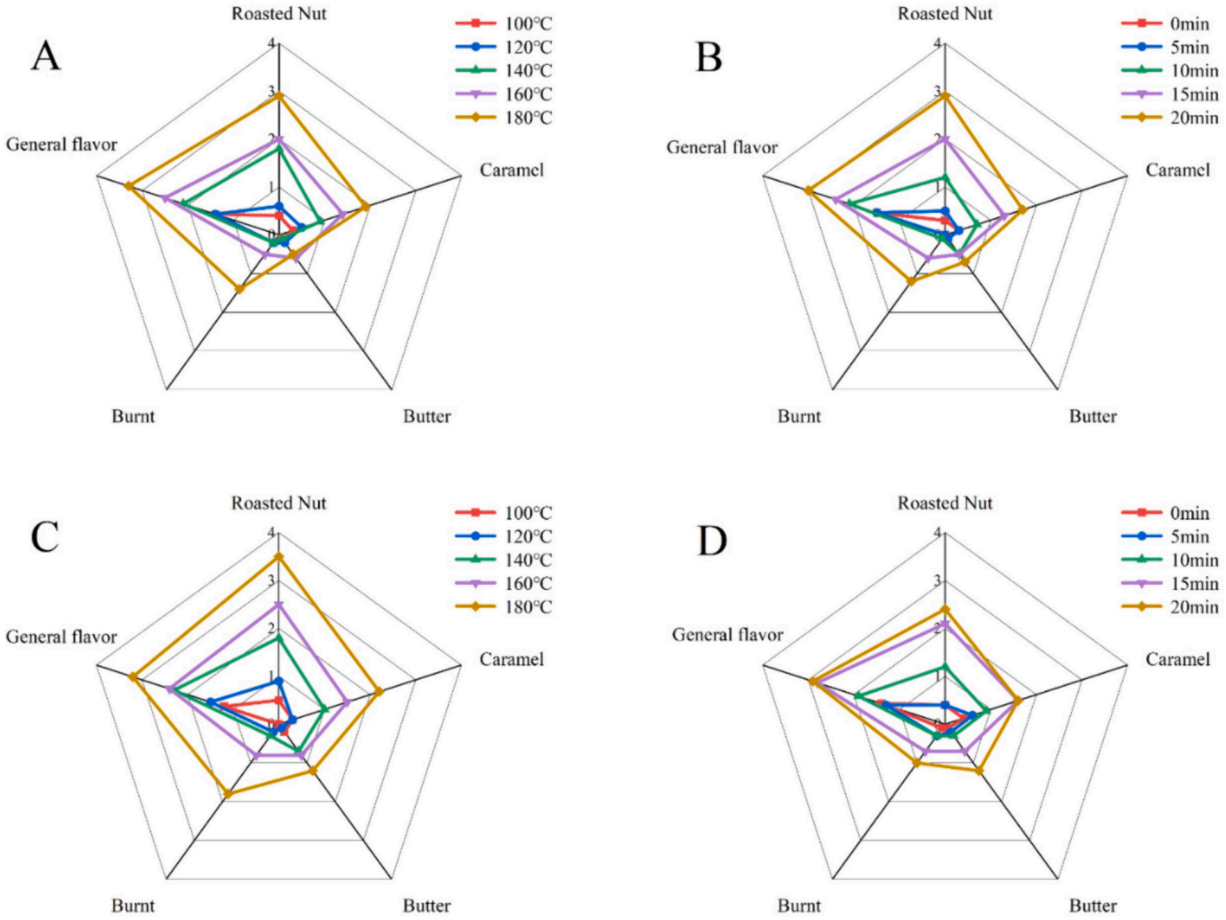

Fig. 1. Radar graph of effects of roasting temperature (A, C) and time (B, D) on the sensory aroma profiles of quinoa (A, B) and germinated quinoa (C, D) by sensory evaluation.

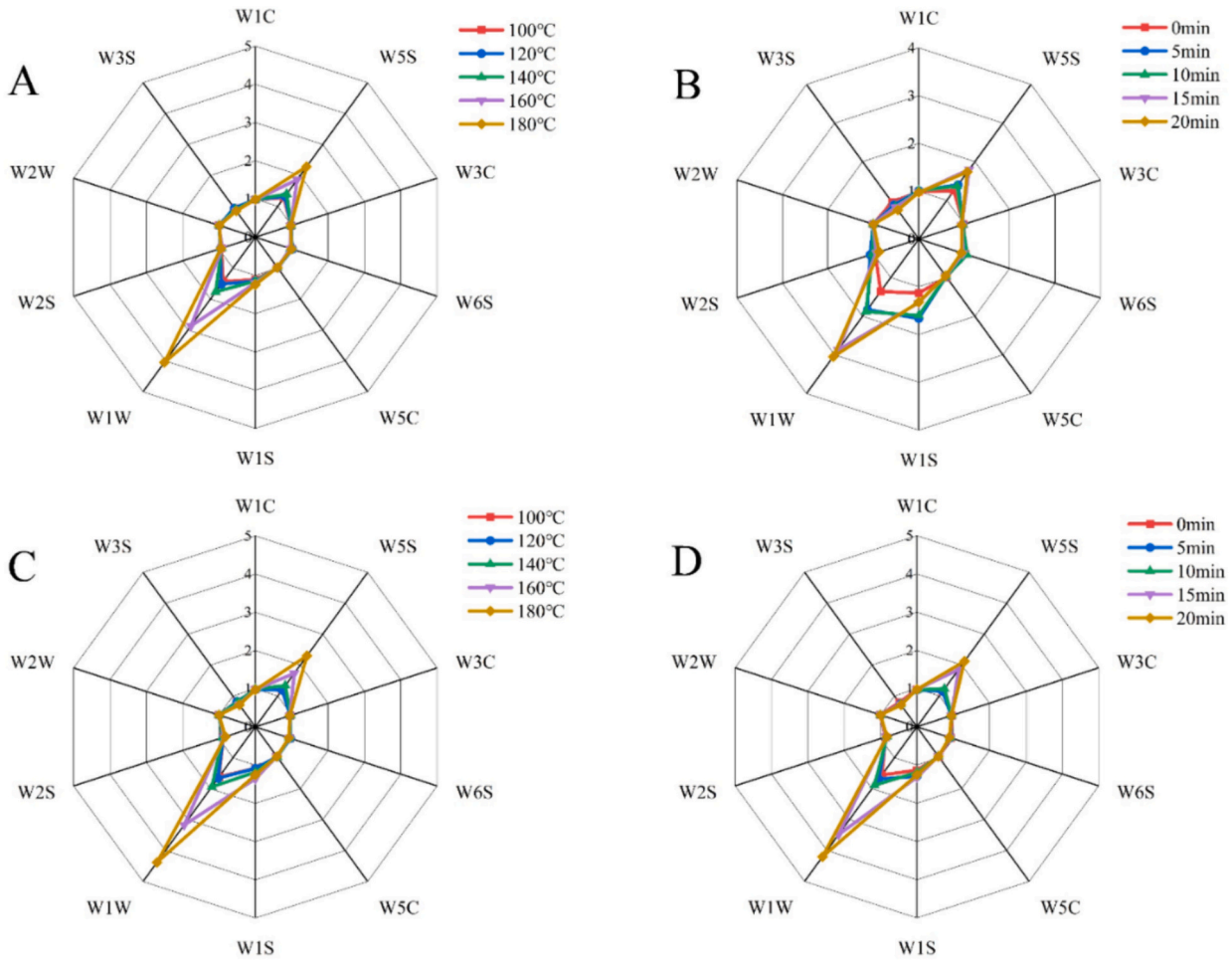

Fig. 2. Radar graph of effects of roasting temperature (A, C) and time (B, D) on the odors of quinoa (A, B) and germinated quinoa (C, D) by E-nose analysis.

acetic acid were significantly increased in the samples. The almond, bitter, oil, and pungent aroma of n-pentanal is considered an unpleasant odor. The content of 1-hexanal (M) was significantly increased ($P < 0.05$) in the GQ and RQ samples, which yielded fatty and fruity aromas. Those might contribute to the improvement of the aroma of quinoa by germination and roasting. The contents of some compounds increased in the GQ samples, such as 1-penten-3-one, ethyl acrylate, dimethylamine, propanal, acetic acid, diethyl sulfide, 4-methylthiazole, and acroleine. Among them, 4-methylthiazole produces green, nut, and roasted meat aromas and diethyl sulfide has coffee and meat aroma.

The RQ samples had high contents of 2-methyl-2-propanol, acetic acid, diethyl sulfide, 4-methylthiazole, 2-heptanone, 2-furaldehyde, pyridine, 2,3-pentandione, and 1-hexanal (D). Compared with the Q samples, the content of metabolite 1-hexanal (apple, fat, fresh, green, oil) improved significantly ($P < 0.05$) in the RQ samples. This might be due to the formation of aldehydes through alcohol oxidation, producing a typical fatty aroma. It is known that aldehydes are the main components of quinoa flavor formation (Yang et al., 2021). 2-furaldehyde is a furan-containing compound produced by the thermal degradation of sugar with almond and spicy aroma (Vazquez-Araujo, Enguix, Verdu, Garcia-Garcia, & Carbonell-Barrachina, 2008). Additionally, the contents of acrolein (acrid, disagreeable) and propional (floral, pungent, solvent) with unpleasant and irritating odor were high in the Q samples, which significantly reduced in the RG and RGQ samples. In contrast, the contents of ketones, such as 2,3-pentandione and 2-heptanone, with typical nutty and buttery aromas, were significantly improved after roasting, which might be due to lipid oxidation and amino acid decomposition, respectively (Yin et al., 2021). The contents of 2,3-pentandione and 2-heptanone were elevated after roasting and exhibited a fatty aroma. It was consistent with the results of the sensory evaluation. These results suggested that roasting could effectively eliminate the undesirable flavors of quinoa and produce a pleasant aroma.

The RGQ samples showed high levels of butanal, 3-methyl butanal, acetic acid methyl ester, 1-butanol 3-methyl (M), 1-butanol 3-methyl (D), 2,3-butanedione, 2-butanone (M), and 2-butanone (D). Among them, 3-methyl butanal, which can be produced by the Maillard reaction, shows chocolate, peach, and fatty aromas (Xiao et al., 2014). Acetic acid methyl ester produces the aromas of ester and green notes, while 2-butanone (M), 2-butanone (D), 1-butanol 3-methyl (M), and 1-butanol 3-methyl (D) produce fruit, pleasant, floral, and malt aromas. The contents of these compounds were significantly increased in the RGQ samples compared to that of the RQ and GQ samples, suggesting that germination combined with roasting accelerated the synthesis and release of these compounds.

Moreover, the RQ and RGQ samples showed high levels of 1-hexanal (M), 1,2-dimethoxyethane, ethanol, 1-butanol (M), 1-butanol (D), and 2,3-dimethyl pyrazine. Pyrazine is mainly formed by the reaction between amino ketones (Wei et al., 2020). It is reported that pyrazine is an important volatile compound for adding roasting flavor to foods (Almaguer et al., 2023). 2,3-dimethyl pyrazine produces caramel, cocoa, peanut butter, and roasted aromas, playing an important role in quinoa aroma. 1-hexanal (alcoholic) and 1-butanol dimer (fruit) are typical flavor substances found in wine (Lakatosová et al., 2016), and the contents of these compounds increased significantly after roasting, improving the aromatic richness of the RQ and RGQ samples.

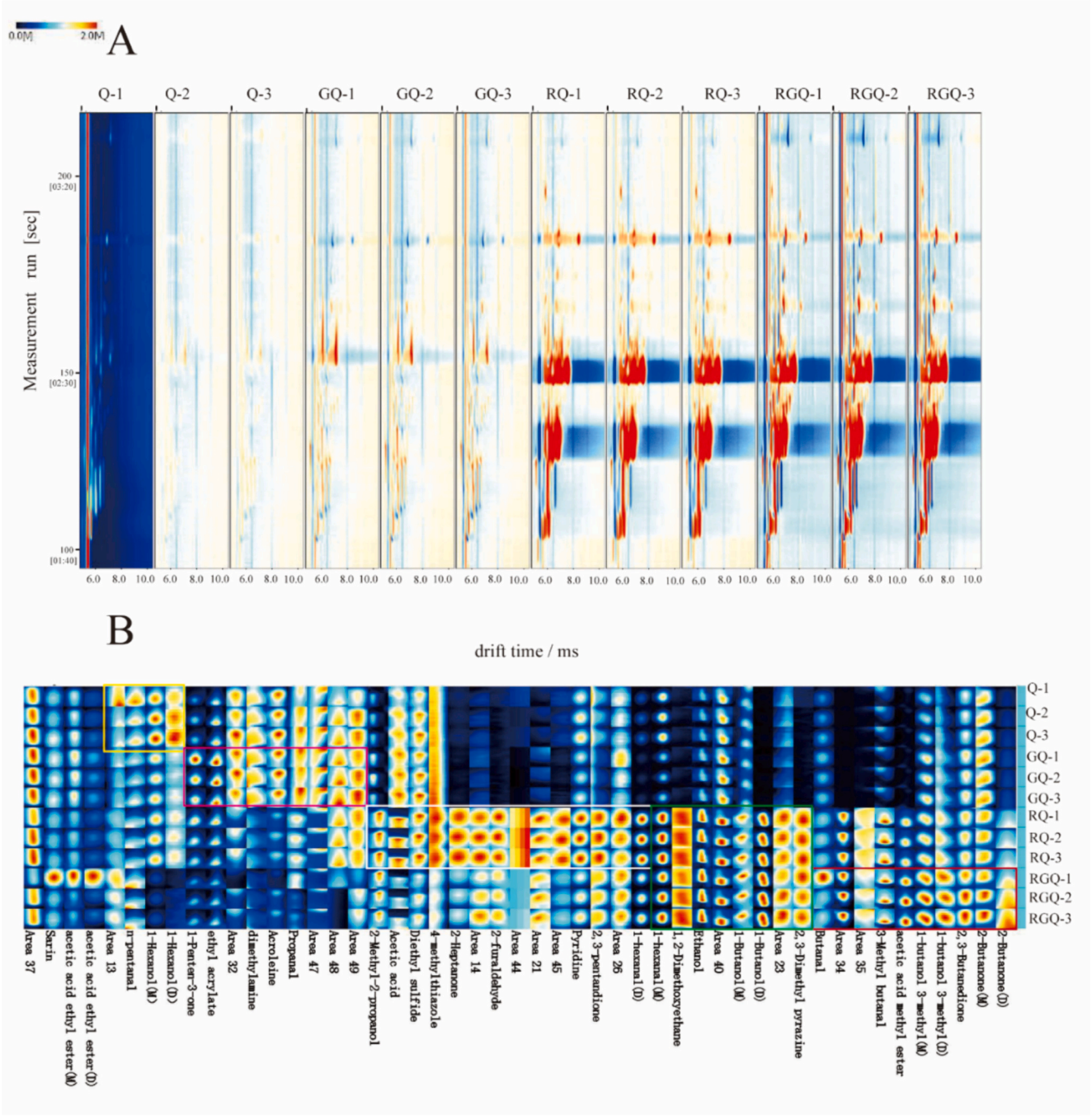

Fig. 3. Top-view plot (A) and gallery plot (B) of the volatile fingerprints of quinoa by HS-GC-IMS.

As shown in **Fig. S4**, 2-heptanone, 2,3-dimethyl pyrazine, 1,2-dimethoxyethane, 1-butanol (D), propanal, 2-furaldehyde, 2-methyl-2-propanol 4-methylthiazole, 2-butanone (D), and acetic acid methyl ester were positively correlated with the roast nut, caramel, butter, and burnt aromas of quinoa. In contrast, sarin, ethyl acrylate, diethyl sulfide, acetic acid ethyl ester (M), 2,3-butanedione, acetic acid ethyl ester (D), 2-butanone (M), acetic acid, ethanol, dimethylamine, and acroleine were negatively correlated with the aroma of quinoa.

3.3.2. *Multivariate statistical analysis*

The flavor profile of different samples was analyzed using OPLS-DA. As shown in Fig. 4A, the first two PCs (71.2% of PC1 and 15.3% of PC2) explained 86.5% of the total variance among the four groups. The results showed that germination and roasting had a significant effect on the volatile profile of quinoa. The model parameters ($R^2Y = 0.984$, $Q^2 = 0.964$) indicated that the model had good explanatory and predictive performance. The 200 permutation tests showed that the model was not overfitted ($R^2 = 0.315$, $Q^2 = -0.971$) (Fig. 4B). As shown in Fig. 4C, the GQ samples were positively correlated with 1-butanol 3-methyl (M), 2,3-pentandione, propanal, butanal, and acetic acid ethyl ester (M), which contributed to the malt, floral, green, aromatic, and fruity aroma. The RQ samples were correlated with 2-heptanone, 1-hexanal (D), 3-methyl butanal, and 2-furaldehyde, which produced almond, roasted potatoes, nuts, spice, and butter odors. Compared with other samples, the RGQ samples had higher levels of 1-butanol (D), 1,2-dimethoxyethane, 2-butanone (D), and acetic acid methyl ester, producing ester, fragrant, fruit, and pleasant odors. Furthermore, the degree of influence and explanatory power of each variable on classification discrimination

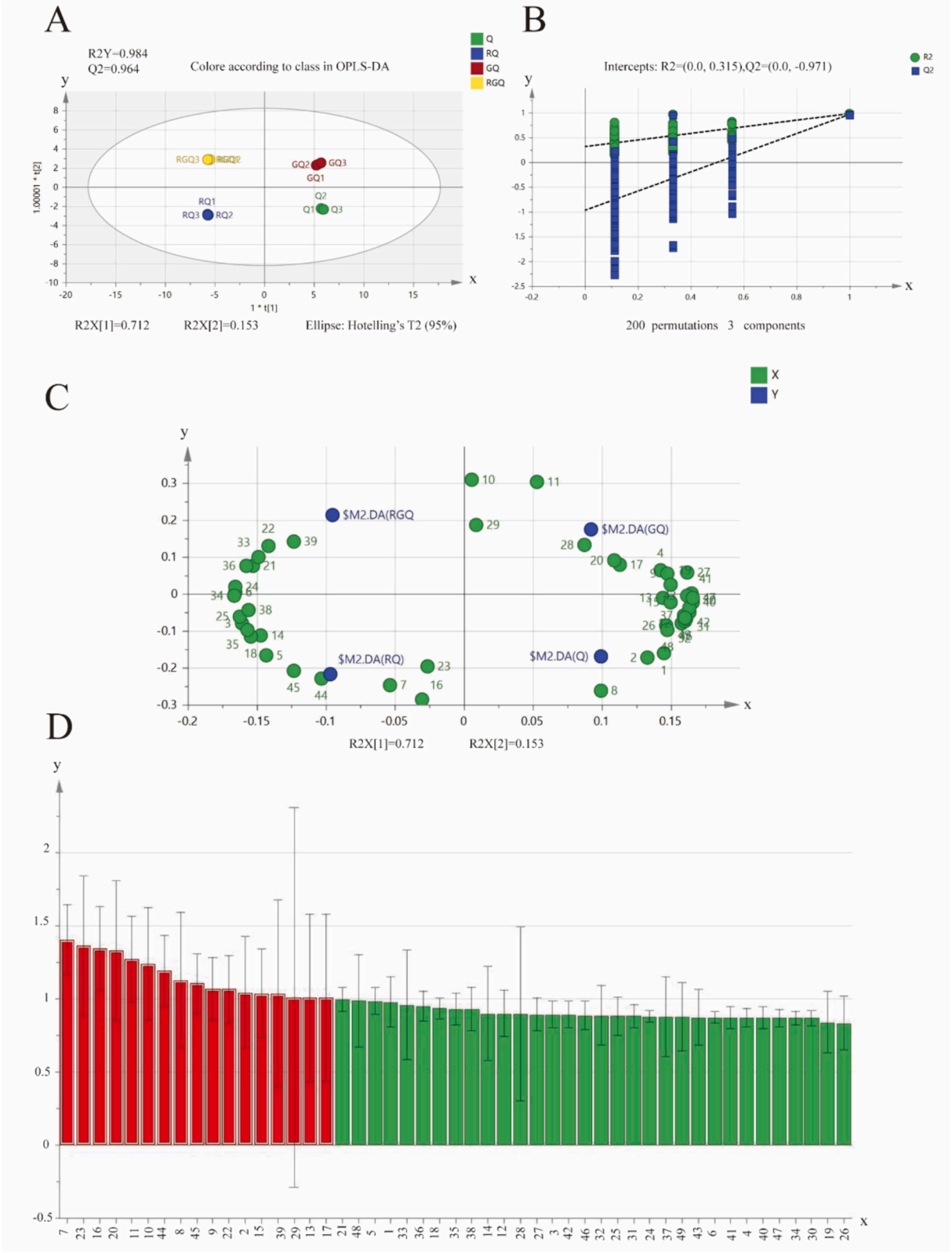

Fig. 4. The OPLS-DA results of quinoa with different treatments by HS-GC–IMS. (A) Score plots of OPLS-DA. (B) Cross-validation plot by 200 permutation tests. (C) Loading plot of OPLS-DA. (D) VIP scores in OPLS-DA.

was analyzed using the variable projected importance (VIP). In this study, 17 compounds with VIP > 1 were observed, mainly including 1-hexanol (D), 1-hexanal (M), pyridine, ethyl acrylate, 1-butanol 3-methyl (D), n-pentanal, 2,3-pentandione, 1-butanol (M), 1-penten-3-one, 1,2-dimethoxyethane, 1-butanol 3-methyl (M), butanal, and ethanol (Fig. 4D). The changes of the contents of those compounds might help to explain the effects of germination and roasting on the flavor of quinoa.

3.4. HS-SPME-GC–MS analysis of the VOCs in quinoa with different treatments

3.4.1. Identification of the VOCs by HS-SPME-GC–MS

The VOCs in different samples were further analyzed using HS-SPME-GC–MS. As shown in **Table S3**, 80 VOCs were detected and classified into 7 groups, including 9 alcohols, 5 aldehydes, 3 ketones, 4 esters, 49 hydrocarbons, 1 pyrazine, 2 furans, 4 heterocyclics, and 3 others. A total of 46, 40, 48, and 57 VOCs were identified in the Q, GQ, RQ, and RGQ samples, respectively, indicating that germination and roasting treatments significantly affected the content of VOCs.

Fig. 5. Relative contents of classified volatile compounds (A) and heat map clustering of volatile compounds (B) of quinoa with different treatments by HS-SPME-GC–MS.

As shown in Fig. 5A, germination and roasting increased the content of VOCs in quinoa. The total content of the VOCs was the highest in the RGQ samples, followed by the RQ samples, and the lowest in the Q samples. Among the VOCs, the contents of hydrocarbons were the highest in all samples. Especially, the Q samples had higher levels of hydrocarbons and heterocyclics, but the GQ samples had higher levels of alcohols, hydrocarbons, and heterocyclics and the RQ samples had higher levels of aldehydes, ketones, and hydrocarbons than the other samples. Interestingly, the RGQ samples had higher levels of alcohols, esters, aldehydes, and hydrocarbons compared to the other samples.

The changes in the concentrations of VOCs in different samples were visualized using a cluster heat map. As shown in Fig. 5B, each row of the graph represents a flavor compound, and each column represents a sample. The Q samples contained high levels of methyl butyrate, linalool, 5-butyl-2-nonane, and 2,6-dimethyldecane, with cheese and floral aromas. After germination, the contents of VOCs of n-hexane, isoheptane, octamethylcyclotetrasiloxane, o-xylene, ether, methyl 2-methylbutyrate, 1-hexanol, 3-heptanol, and 2,5-dimethyldecane were increased significantly. In the GQ samples, 1-hexanol and 3-heptanol, producing flower, banana, and herb odors, might be formed from lipid oxidation catalyzed by alcohol reductase (Zhu et al., 2022). Methyl 2-methylbutyrate, producing fruit and strawberry aromas, might be produced by the esterification of alcohols and acids. There was a significant reduction in acetone (Pungent) content in the GQ samples, indicating that germination eliminated the undesirable flavors of quinoa. Taken together, germination not only promoted the release of pleasant flavor but also reduced the formation of unpleasant flavors of quinoa.

In the RQ samples, the contents of ethanol, dodecane, 4,6-dimethyl, pentanol, nonanal, styrene, (+)-limonene, hexanal, 6-methylhept-5-en-2-one, and 2-amylfuran were increased significantly. Roasting accelerated the release of aldehydes, alcohols, and ketones. Additionally, roasting yielded some unique VOCs. For instance, pentanol, nonanal, and (+)-limonene were only detected in the RQ samples. Pentanol and (+)-limonene contributed to the citrus, fruit, and green aromas. Nonanal, generated by the oxidation of linoleic acid, was reported to be the main contributor to quinoa aroma (Perez, Sanz, Olias, & Olias, 1999; Zhang et al., 2019). It is known that 2-pentylfuran, generated by lipid oxidation, has caramel and nutty aromas (Spada et al., 2021). Nonanal and 2-amylfuran are the key aroma compounds of cooked quinoa porridge (Yang, Pei, Du, & Xie, 2023). 6-methylhept-5-en-2-one has citrus and strawberry aromas and is mainly produced by enzymatic oxidative decarboxylation of fatty acids.

Additionally, the contents of 2-mercaptoethanol, 3-methyl-1-butanol, 2-methylbutan-1-ol, tetrahydrofurfuryl alcohol, methyl isobutyrate, hexyl formate, and 3-methyltetrahydrofuran were significantly increased in the RGQ samples. It is reported that 3-methyl-1-butanol, mainly contributing to the cocoa, malt, and floral odors, has an important effect on the aroma with a low odor threshold. 2-mercaptoethanol and tetrahydrofurfuryl alcohol produce a typical nutty aroma, which were only detected in the RGQ samples. Esters contribute to the characteristic flavor of most grains, producing ester, floral, and fruit aromas (Almaguer et al., 2023). Methyl isobutyrate (flower, fruit) and hexyl formate (fruit) were also only detected in the RGQ samples. 3-methyltetrahydrofuran is the key component of caramel aroma (Aprotosoaie, Luca, & Miron, 2016). Therefore, roasting would promote the formation of some characteristic VOCs from the GQ samples, as well as the Q samples.

The RQ and RGQ samples had high contents of 3-methylbutanal, 2-butanone, isobutyraldehyde, 2-methylbutanl, and 2,5-dimethylpyrazine, which were all positively correlated with the sensory scores of the aroma of quinoa (**Fig. S5**). Therefore, it was speculated that 3-methylbutanal (ethereal aldehydic, chocolate, and peach fatty aromas), 2-butanone (fragrant, fruit, and pleasant aromas), isobutyraldehyde (burnt, caramel, and cocoa aromas), 2-methylbutanl (hazelnut, almond, and cocoa aromas), and 2,5-dimethylpyrazine (cocoa, roast beef, and roasted nut aromas) mainly contributed to the desirable flavor of the RQ

and RGQ samples.

3.4.2. Multivariate statistical analysis

OPLS-DA is effective in distinguishing between groups and identifying the important variables contributing to the differences between groups. The differences and similarities between samples can be analyzed using score plots. In this study, the Q, GQ, RQ, and RGQ samples were dispersed obviously from each other (Fig. 6A). The fitted parameters of the partial least square regression model ($R^2Y = 0.988$, $Q^2 = 0.965$) indicated a good explanatory and strong prediction power.

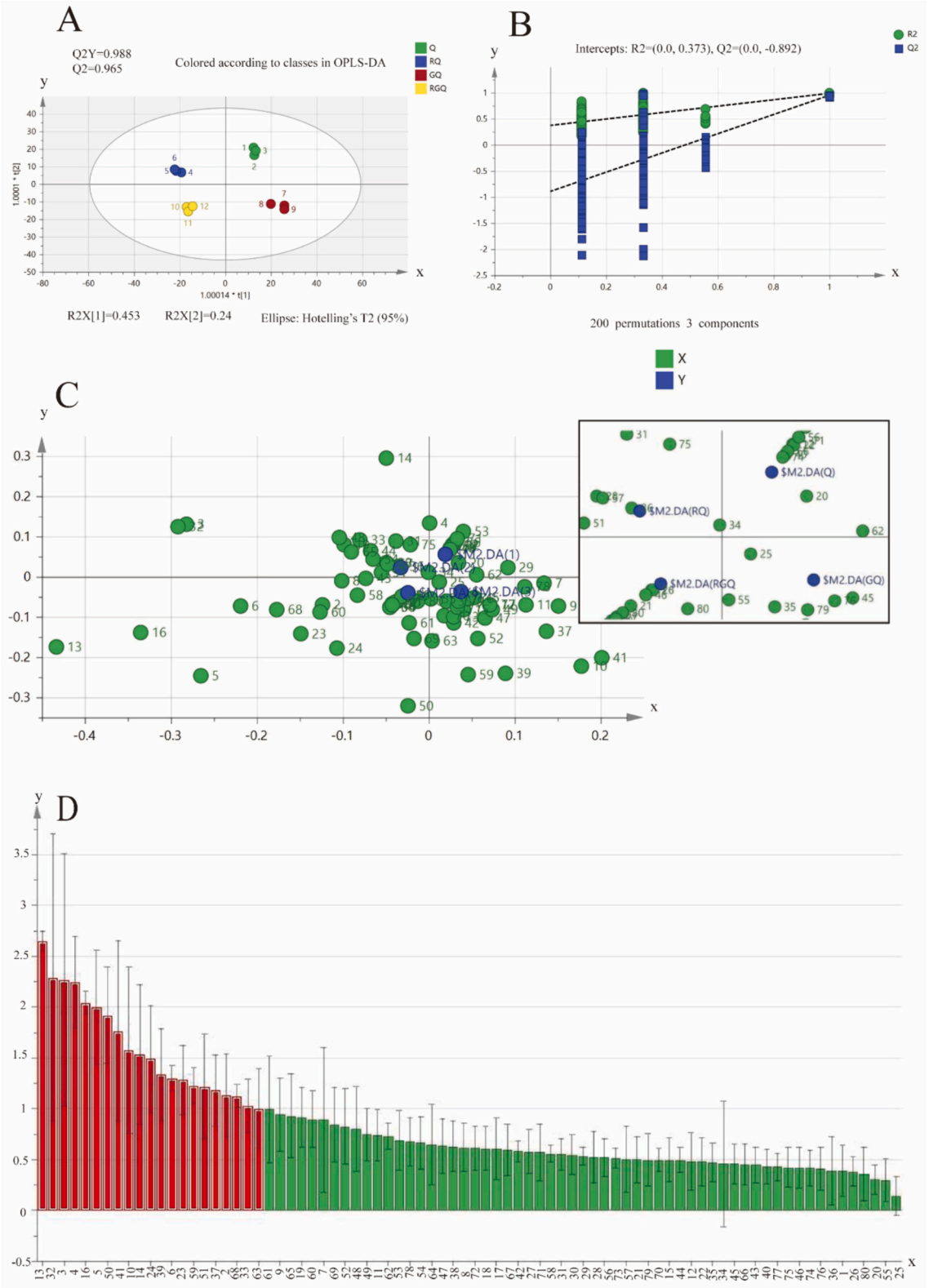

Fig. 6. The OPLS-DA results of quinoa with different treatments by HS-SPME-GC–MS. (A) Score plots of OPLS-DA. (B) Cross-validation plot by 200 permutation tests. (C) Loading plot of OPLS-DA. (D) VIP scores in OPLS-DA.

The feasibility of the model was assessed through 200 replications of the permutation test (Fig. 6B). The intercept of the regression line is <0, indicating that the model is reliable without overfitting ($R^2 = 0.373$, $Q^2 = -0.892$). Additionally, the key compounds responsible for the differences in the aroma profiles of the quinoa samples were analyzed using the load plots (Fig. 6C). For instance, the content of methyl butyrate was higher in the Q samples than that in the other samples. However, the contents of 2,3,6-trimethyloctane, tetradecane, and ether were higher in the GQ samples and the contents of styrene, dodecane,4,6-dimethyl, and heptane were higher in the RQ samples than the other samples. In addition, the contents of 2-mercaptoethanol, 2,3-dimethylnonane, tetrahydrofurfuryl alcohol, and 3-methyltetrahydrofuran were higher in the RGQ samples than the other samples, contributing to the grilled, soup, and nuts aromas. Furthermore, 21 compounds with VIP > 1 were screened, mainly including aldehydes and alcohols, such as ethanol, 3-methyl-1-butanol, 2-methylbutan-1-ol, 1-hexanol, 3-heptanol, isobutyraldehyde, 3-methylbutanal, 2-methylbutanl, hexanal, acetone, pentane, n-hexane, octane, undecane, 3-methyldecane 2,6,6-trimethyldecane, o-xylene, di-methylsulfide borane, and methyldimethoxysilane (Fig. 6D). All those compounds contributed to the desirable improvements of quinoa by germination and roasting.

3.4.3. Odor activity value (OAV) analysis

OAV represents the ratio of the absolute concentration of each compound (ug/kg) and their odor threshold (ug/kg). Generally, the compounds with OAV ≥ 1 are considered as the characteristic VOCs. In the present study, 10 key aroma compounds with OAV ≥ 1 were identified, including 4 aldehydes, 3 alcohols, 1 ester, and 2 heterocyclic compounds (Table 1).

Methyl 2-methylbutyrate (OAV = 14) was the main aroma of the Q samples, as well as the GQ. RQ, and RGQ samples. It was found that, compared with the Q samples, 1-Hexanol (banana, flower, grass, and herb aromas) had a high OAV of 12 in the GQ samples, while 3-methylbutanal, 2-methylbutanl, hexanal, and nonanal had a high OAV of 130, 77, 30, and 16, respectively, in the RGQ samples. Similar results, high OAV of 10, 154, 91, and 10 for 3-methyl-1-butanol, 3-methylbutanal, 2-methylbutanl, and hexanal, respectively, were observed in the RGQ samples. It indicated that quinoa had a fruit aroma and would remain after germination and roasting. However, germination and roasting both improved the herbal flavor of quinoa. Importantly, roasting also produced other desirable flavors such as chocolate, fatty, cocoa, and malt aromas, thus, increasing the richness of the aroma of quinoa.

4. Conclusions

In this study, the sensory evaluation and *E*-nose analysis showed that roasting at 160 °C for 15 min might be appropriate to obtain a desirable flavor of quinoa and germinated quinoa. HS-GC-IMS and HS-SPME-GC–MS analysis indicated that germination and roasting significantly altered the VOC compositions of quinoa. On one hand, germination and roasting both effectively reduced the undesirable flavor components of quinoa. On the other hand, germination improved the floral aromas of quinoa, while roasting mainly produced caramel, cocoa, and roasted nut aromas of quinoa. Overall, this study suggests that germination and roasting could be promising processing methods to improve the flavor of quinoa and will provide a basis for further research on the mechanisms of flavor formation in germinated and roasted quinoa.

CRediT authorship contribution statement

Siwang Peng: Conceptualization, Data curation, Methodology, Writing – original draft. **Yiju Li:** Data curation, Formal analysis, Methodology. **Huan Liu:** Data curation, Formal analysis, Methodology. **Yuanrong Tuo:** Data curation, Methodology. **Jiamin Dang:** Data curation. **Wei Wang:** Data curation. **Haixi You:** Formal analysis. **Shuangkui Du:** Data curation, Supervision. **Liying Wang:** Conceptualization, Funding acquisition, Supervision. **Long Ding:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 1
Odor activity values (OAV) of the volatile organic compounds (VOCs) of quinoa with different treatments by HS-SPME-GC–MS.

No.	Compounds	Odor description	Threshold (μg/kg)	OAV			
				Q	GQ	RQ	RGQ
1	3-Methyl-1-butanol	Burnt, Cocoa, Floral, Malt	4 [e]	–	–	3	10
2	Pentanol	Balsamic, Fruit, Green, Pungent, Yeast	150.2 [f]	–	–	<1	–
3	1-Hexanol	Banana, Flower, Grass, Herb	2.5 [c]	–	12	–	–
4	Linalool	Coriander, Floral, Lavender, Lemon, Rose	6 [b]	2	–	–	–
5	Ethanol	Sweet	100,000 [g]	<1	<1	<1	<1
6	3-Methylbutanal	Ethereal, Aldehydic, Chocolate, Peach, Fatty	1.1 [e]	2	–	130	154
7	2-Methylbutanl	Almond, Cocoa, Fermented, Hazelnut, Malt	1.1 [e]	–	–	77	91
8	Hexanal	Apple, Fat, Fresh, Green, Oil	4.5 [c]	5	1	30	10
9	Nonanal	Fat, Floral, Green, Lemon	1.1 [f]	–	–	16	–
10	6-Methylhept-5-en-2-one	Citrus, Mushroom, Pepper, Rubber, Strawberry	50 [a]	<1	–	<1	<1
11	Dodecane	–	2140 [d]	<1	<1	<1	<1
12	Methyl 2-methylbutyrate	Apple, Fruit, Green Apple, Strawberry	0.25 [d]	14	16	15	14
13	Ether	–	100 [d]	<1	<1	<1	<1
14	Styrene	Floral	65 [f]	–	–	<1	–
15	Toluene	Paint	1000 [d]	<1	–	<1	–
16	2,5-Dimethylpyrazine	Cocoa, Roast Beef, Roasted Nut	1.8 [c]	–	–	3	2
17	2-Amylfuran	Butter, Floral, Fruit, Green Bean	5.8 [e]	5	3	6	5
18	Methyl butyrate	Apple, Banana, Cheese, Ester, Floral	65 [d]	<1	<1	<1	<1

Q, Quinoa; GQ, germinated quinoa; RQ, roasted quinoa; RQG, roasted germinated quinoa.
[a] Odor threshold taken from (Fan et al., 2021).
[b] Odor threshold taken from (Yuan, Peng, Zhong, Zhao, & Lin, 2021).
[c] Odor threshold taken from (Guan, Liu, Li, Wang, & Zhang, 2022).
[d] Odor threshold taken from (Duppeti, Kempaiah, & Manjabhatta, 2022).
[e] Odor threshold taken from (Xu, Shui, Chen, Ma, & Feng, 2022).
[f] Odor threshold taken from (Huang et al., 2022).
[g] Odor threshold taken from (Wen, Yin, Hu, Chen, & Kong, 2022).

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.101441.

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