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Characterization of flavor volatiles in raw and cooked pigmented onion (*Allium cepa* L) bulbs: A comparative HS-GC-IMS fingerprinting study

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ABSTRACT

Variations in volatile flavor components in pigmented onion bulbs (purple, white, and yellow) before and after cooking were characterized by headspace gas chromatography-ion migration spectrometry (HS-GC-IMS) to investigate their odor traits. Results showed that 39 and 45 volatile flavor compounds were identified from pigmented onion bulbs before and after cooking via the HS-GC-IMS fingerprinting, respectively. Sulfurs (accounting for 50.65%–63.42%), aldehydes (13.36%–22.11%), and alcohols (11.32%–17.94%) ranked the top three prevailing compound categories in all pigmented onions (both raw and cooked). Compared to the raw colored onion bulbs, the relative proportion of sulfurs in cooked onions decreased, whereas the relative proportion of alcohols, esters, pyrazines, and furans increased. Two reliable prediction models were established through orthogonal partial least squares-discriminant analysis (OPLS-DA), and 8 and 22 distinctive odor compounds were sieved out by variable importance in projection (VIP>1.0) as volatile labels, respectively. Both principal component analysis (PCA) and clustering heatmap exhibited favorable distinguishing effects for various pigmented onion bulbs before and after cooking. These results might offer insights into understanding the odor characteristics of different pigmented onions.

1. Introduction

Onion (*Allium cepa* L) is an extensively improved and grown vegetable species on planet earth (Wang et al., 2019). Onions are bulbous plants with layers of fleshy leaves that are usually white, yellow, purple, or red in color, and they have a papery outer skin (Kate et al., 2022). Bulb is the main edible part of onion usually versatile as a spice and food ingredient, particularly because of its unique odor and taste (Yuasa et al., 2022; Patil et al., 1995; Fernandes et al., 2020). More and more evidence proved that consumption of onions in diet could contract a lot of bio-activities, like antioxidant, anti-platelet, immune enhancing, etc (Moreno-Ortega et al., 2020; Park et al., 2017).

Mankind mainly consume onions raw, baked, grilled, sautéed, fermented, or caramelized, and their flavor can range from pungent and sharp to sweet and mild, depending on the variety and how they are prepared (Cavagnaro et al., 2007; Villière et al., 2015). The odor of onions is primarily due to volatile compounds that are released when the onion is chopped. The most notable odor chemical responsible for the characteristic odor of onions is syn-propanethial-S-oxide. Once an onion is chopped, the chemical is emitted and reacts with the oxygen, forming

Abbreviations: HS-GC-IMS, headspace gas chromatography-ion migration spectrometry; OPLS-DA, orthogonal partial least squares-discriminant analysis; VIP, variable importance in projection; PCA, principal component analysis; HS-SPME-GC-MS, headspace solid-phase microextraction gas chromatograph-mass spectrometry; GC-O, gas chromatograph-olfactometry; VOCs, volatile organic compounds; RT, retention time; RI, retention index; DT, drift time.

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sulfenic acid, which further decomposes into various sulfur compounds that contribute to the characteristic odor of onions (Cozzolino et al., 2021; Järvenpää et al., 1998; Ueda et al., 1994).

Nowadays, the detection of food volatile odor compounds is a hot topic in food research. Headspace solid-phase microextraction gas chromatograph-mass spectrometry (HS-SPME-GC-MS), gas chromatograph-olfactometry (GC-O), headspace gas chromatography-ion migration spectrometry (HS-GC-IMS), etc. are widely used to assay the odor volatiles in many agricultural products (Jin et al., 2021; Zhao et al., 2021). Kallio, H & Salorinne (1990) compared the odor chemicals in several onion varieties by headspace gas chromatography-mass spectrometry. Fernandes et al. (2020) assessed the odor profiles of onions from various places based on HS-SPME-GC-MS and chemometric tools. Contrasted to HS-SPME-GC-MS, the HS-GC-IMS has been proven superior advantages like fastness, high resolution, and visualization with simple operation (Zhang et al., 2023; Jin et al., 2023a, b). Besides, distinctive odor chemicals in varied samples could be sieved out through chemometrics (Jin et al., 2023a, c). In recent years, the HS-GC-IMS is frequently utilized to assay aroma fingerprints in various agricultural products of different varieties, processing, and keeping environments (Song et al., 2021), whereas the volatile profiles of onions identified through the HS-GC-IMS tool were rarely uncovered.

Odor traits are important olfactory profiles for classifying onions, which is intimately connected with nutrients, freshness and geographical location, thus influencing the preference and buying desire of people of all ages. As onion bulbs are usually white, yellow, purple, or red in color, plenty of studies about colored onions have focused on bio-active ingredients and their health-promoting effects (Brandwein, 1965; Moreno-Ortega et al., 2020; Marotti & Piccaglia, 2002). Özcan et al. (2022) determined the contents of macro- and micro-element in several parts of three different colored onions. Nile and Park (2013) investigated the phenolics, bio-activities of pigmented onions (*Allium cepa* L.). Wang et al. (2022) identified 61 odor chemicals from several pigmented onions by the HS-SPME-GC-MS approach. However, little documentation was to demonstrate the odor profiles of pigmented onions through the emerging HS-GC-IMS technology.

Previous studies have successfully profiled the differences of various pigmented cereals using the HS-GC-IMS and chemometrics (Jin et al., 2023a, c, d). Although the flavor volatiles of colored onions both raw or cooked were investigated by the HS-SPME-GC-MS (Fernandes et al., 2020; Lee et al., 2016; Järvenpää et al., 1998), the emerging HS-GC-IMS-based volatile fingerprinting in pigmented onions was not investigated and compared. Herein, the objective of this research is to reveal the distinctness of flavor volatiles in different pigmented onions (purple, white, and yellow) before and after cooking for the first time with the HS-GC-IMS fingerprinting to compare their odor characteristics. Furthermore, the distinctive odor chemicals are undermined via multivariate statistics, which may offer extra insights into the odor profiles of colored onions academically and industrially.

2. Materials and methods

2.1. Material and standard chemicals

Three colored onions with variety names of Baibilong (white-colored, with total flavonoid content of 0.16 ± 0.02 mg/g, total phenolic content of 0.11 ± 0.03 mg/g, anthocyanin content of 0.61 ± 0.04 μg/g, and carotenoids content of 0.010 ± 0.002 μg/g), Hongyou No.1 (purple-colored, with total flavonoid content of 0.18 ± 0.01 mg/g, total phenolic content of 0.55 ± 0.08 mg/g, anthocyanin content of 5.79 ± 0.13 μg/g, and carotenoid content of 0.033 ± 0.005 μg/g), and Jinke No. 7 (yellow-colored, with total flavonoid content of 0.19 ± 0.02 mg/g, total phenolic content of 0.69 ± 0.06 mg/g, anthocyanin content of 0.55 ± 0.03 μg/g, and carotenoids content of 0.015 ± 0.003 μg/g) were collected from the same geographic site in Suzhou district of Gansu province (Jiuquan, China). Fig. S1 illustrated their appearance and transverse images of pigmented onion varieties. The onion bulbs were peeled and kept at 4 °C. Six analytical level n-ketones (2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, 2-octanone, and 2-nonanone, purity≥99 %) were provided from Haineng Instrumental Co., Ltd. (Jinan, China).

2.2. Preparation of raw and cooked onion bulbs

The three colored onion bulbs were ground into pieces in an electric grinder (Jiuyang Electric Co., Ltd. China), weighed accurately (250 g), put in a self-sealed bag at 4 °C, and labeled as raw onion, respectively. For cooked onion, the three raw onions in sealed bottles were roasted at 120 °C for 6 min in a RSKP1811 electric oven (Royalster, China), respectively, referenced and modified slightly from Cattivelli et al. (2021). Both raw and cooked onion samples were kept at 4 °C less than 5 h before analysis.

2.3. HS-GC-IMS quantitation for volatile organic compounds

The volatile organic compounds (VOCs) in pigmented onion samples (raw and cooked) were measured on an HS- GC-IMS instrument (FlavourSpec®, Germany), according to the procedures of Zhao et al. (2021). Colored onion bulbs were ground evenly, accurately weighed (2.0 g), and transferred to a headspace vial (20 mL). Then 500.0 μL headspace gas nitrogen (purity ≥99.99%) was injected into the injector after incubation at 60 °C for 15 min and then detected by the instrument. The gas chromatographic separation was performed on the MXT-5 column (15 m × 0.53 mm) at 60 °C with nitrogen (purity≥99.99%) as a carrier gas for 20 min. The start-up gas flow rate was 2.0 mL/min, maintained for 2 min, linearly enlarged to 10 mL/min within 10 min, and then linearly expanded to 100 mL/min within 20 min. The IMS was performed with 45 °C IMS detector temperature, 150 mL/min nitrogen (purity ≥99.99%) flow rate, and analyzed for 30 min. The six n-ketones listed previously were employed as external standards to acquire the relative content of volatile compounds in the colored onions, based on the retention time (RT), retention index (RI) and drift time (DT) provided by the library of the instrument (Jin et al., 2023a).

2.4. Statistical analysis

All data were expressed as the mean ± standard deviation (n = 3). Characterization of VOCs was performed by the NIST 2014 and IMS databases. The analysis of variance (ANOVA) was applied through Tukey's test by SPSS 22.0 Software Package (SPSS, Inc., Chicago, IL, USA), with a significance level set as $p < 0.05$. PCA, OPLS-DA, cross validation, and VIP values were analyzed by SIMCA 14.1. The PCA plot and cluster heatmap of differential volatiles were visualized through an online R package for data visualization (https://biit.cs.ut.ee/clustvis/).

3. Results and discussion

3.1. HS-GC-IMS spectrum of various pigmented onion bulbs

The VOCs in various pigmented onion bulbs (raw and cooked) were measured by the HS-GC-IMS. Fig. 1 shows the two-dimensional (2D) spectra of different pigmented onion bulbs, respectively. The volatile compounds were marked as flaws on the spectrum, and colored intensity denoted the signal extent (Zhao et al., 2021; Song et al., 2021). Fig. 1 A and B illustrates the vertical GC-IMS topographic maps, which is difficult to compare the variations in odor profiles in the pigmented onion samples. The diminution maps for analogy were also demonstrated using purple onions (both raw and cooked) as a reference, and the volatile chemicals in three colored onion samples could be differentiated by the comparison 2D GC-IMS (Fig. 1C and D). The relative variations for VOCs in three colored onion samples (both raw and cooked) differ in the exclusive maps owing to the variations in the levels of bio-active ingredients such as anthocyanin (Brandwein, 1965; Zhang et al.,

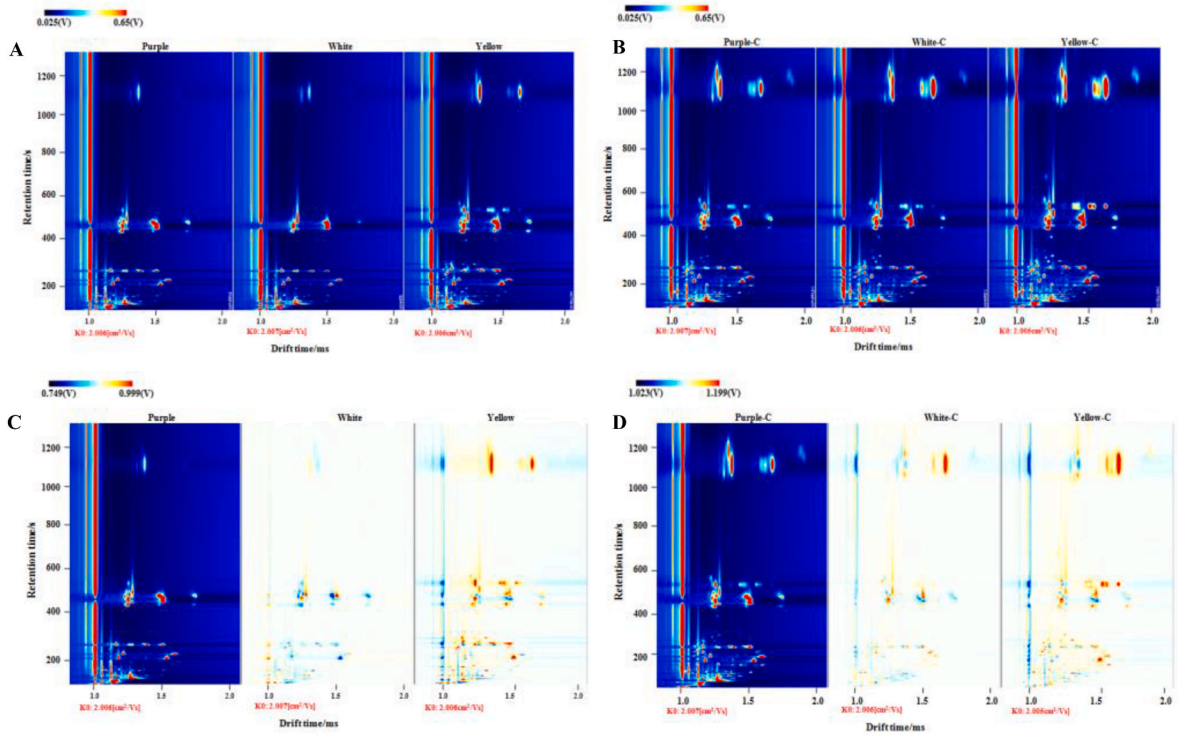

Fig. 1. Two-dimentional GC-IMS vertical topographic maps (A, B) and comparison maps (C, D) of three pigmented onions before and after cooking. A, C for raw onions. B, D for cooked onions.

2016), flavoniods (Marotti and Piccaglia, 2002; Park et al., 2017), thiosulfinate (Ueda et al., 1994), and phenolics (Nile and Park, 2013; Cozzolino et al., 2021), which deserve further correlation analysis with qualification of potential volatile compounds.

3.2. Qualification of odor volatiles in various pigmented onions

Six N-ketones (2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, 2-octanone, and 2-nonanone) were calibrated as foreign standards to obtain the retention index of odor chemicals by contrasting the parameters like retention index (RI), retention time (RT), and drift time (DT) (Wang et al., 2023; Zhang et al., 2023). The qualification spectra of all onions were illustrated in Fig. S2. Totally, 39 volatile chemicals (monomers and dimers) were detected among the raw colored onion bulbs, including 15 sulfurs, 8 aldehydes, 5 alcohols, 4 ketones, 3 acids, 2 pyrazines, 1 ester, and 1 furan. The detailed information about specific volatile compounds in raw onion were shown in Table S1. Among these volatile compounds, 2-methylpentanal is the highest chemical in raw colored onion bulbs, which display the smell of grass, and green (Table S1). Meantime, 45 volatile substances were detected among the cooked colored onion bulbs, including 16 sulfurs, 10 aldehydes, 5 alcohols, 6 ketones, 4 acids, 2 pyrazines, 1 ester, and 1 furan. The detailed information about specific volatile compounds in cooked onion were demonstrated in Table S2. Among these volatile compounds, (*Z*)-1-propenylallyl disulfide smells like fish, and cabbage, which is the highest odor chemicals among cooked colored onion bulbs (Table S2). Wang et al. (2019) pointed out that acetone, dimethyl disulfide, and hexanal ranked the most abundant volatiles in onion bulbs using the SPME-GC-MS, which were different from present HS-GC-IMS results. These variations may be caused by methodology, varieties, and geographic origins (Fernandes et al., 2020; Moreno-Ortega et al., 2020). The present results in specific volatile compounds (Table S1 and Table S2) may lead to the variations in odor characteristics of various pigmented onions (raw and cooked).

3.3. Dactylograms of various pigmented onions

Gallery dactylograms were developed by the instrumental software to exhibit variations of gaseous substances in three colored onion bulbs (raw and cooked) with 3 parallel determinations (Qi et al., 2024; Zhao et al., 2021). All odor compounds and pigmented onions were listed either columns or rows (Fig. 2). For raw colored onion bulbs, the relative concentrations of distinctive odor components in yellow-colored onion bulbs, such as dimethyl disulfide, benzoic acid, 2-methyl pentanal, allyl methy trisulfide, rhodinol, etc., were relatively higher (Fig. 2A). It is totally different from the volatile profiles of purple, and white-colored onion bulbs. Fig. 2A also demonstrates that the volatile profiles of purple-colored and white-colored onions are more similar to each other. At the same approach, Fig. 2B also showed that the relative concentrations of exclusive odor components in cooked yellow onion bulbs, such as dimethyl disulfide, benzoic acid, 2-methyl pentanal, allyl methy trisulfide, rhodinol, etc., were relatively higher. It is also different from the volatile profiles of cooked purple, and white-colored onion bulbs, while the overall volatile profiles of purple-colored and white-colored onions share much similarities (Fig. 2B). Both raw and cooked colored onions, there were at least 12 compounds absent in purple and white onions. A similar study of 27 odor chemicals measured by the SPME-GC-MS in yellow onions also confirmed that 13 odorants were first found in yellow onions (Wang et al., 2019).

Fig. 2C also compared the effects of cooking on volatile organic compounds of the three colored onion bulbs. Compared with raw colored onions, the relative proportions of ethyl trisulfide, rhodinol, (E)-1-propenylmethyl disulfide-D, 2-hexanone, allyl propyl sulfide-D, hexanal, and 2-furancarboxylic acid increased, while the relative proportion of allyl propyl sulfide, and methyl-1-propenyl disulfide decreased. Apart from those common differences, the variations in volatile compounds for yellow-colored onions are still significant before and after cooking. For example, the relative proportion of heptanal, cyclohexanone, 2-propenyl methyl disulfide-D, benzoic acid, dihydroeugenol, allyl methyl trisulfide, 1-propene-3-methylthio, 2,3-diethyl

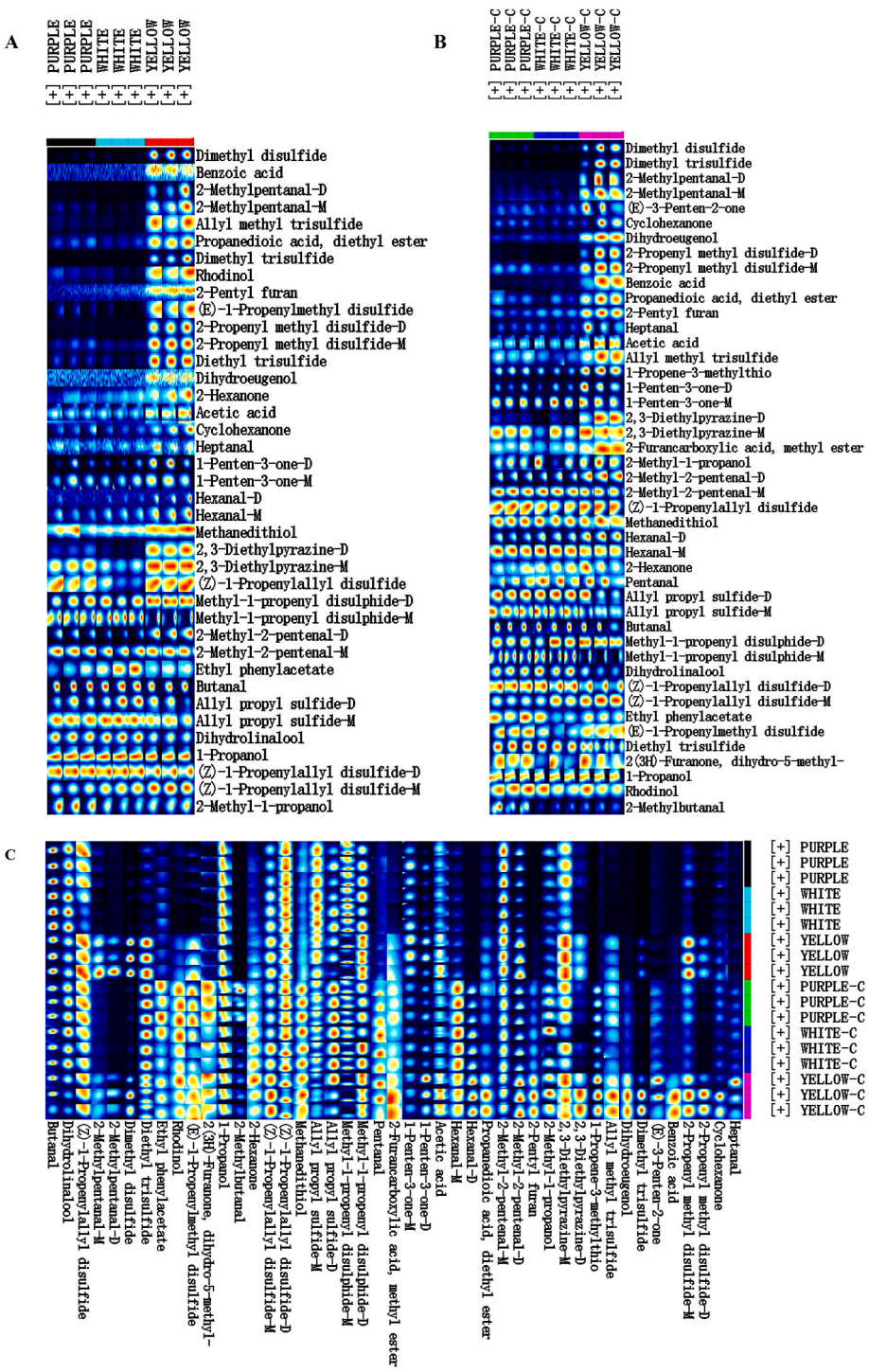

Fig. 2. Gallery dactylograms of volatile odor compounds in three pigmented raw onions (A), cooked onions (B), and all onions (C).

pyrazine-D increased greatly, while dimethyl disulfide, dimethyl trisulfide, and 2-methyl pentanal diminished (Fig. 2C). Cooking treatment for onions experience a complicated progression of odor chemicals together with the autoxidation, the thermal decomposition, and the initiation of Maillard-type compounds between amino groups and carbonyl groups (Villière et al., 2015). Although the odor dactylograms of three pigmented onions (raw and cooked) are extremely complex, the HS-GC-IMS technique can still be used as a rapid tool to compare the flavor volatiles for both raw and cooked onions. A case study of odor profiles in several pigmented quinoa seeds (raw and cooked) by the HS-GC-IMS was also published by Yang et al. (2021).

To clearly display the differences of volatile profiles in colored onion bulbs before and after cooking, the signal volumes of different compounds categories on the dactylograms were aligned to depict the analogous concentrations of odor kinds in three colored onion bulbs (Fig. 3). As demonstrated, the odor substances of various pigmented raw onion bulbs were composed of sulfurs (accounting for 57.18%–63.42%), aldehydes (13.36%–21.49%), alcohols (11.32%–15.03%), acids (2.16%–2.2%), ketones (1.79%–2.54%), esters (1.07%–1.61%), and furans (0.05%–0.09%), respectively. The flavor volatiles of the three colored cooked onion bulbs were made of sulfurs (accounting for 50.65%–56.98%), aldehydes (17.26%–22.11%), alcohols (15.82%–

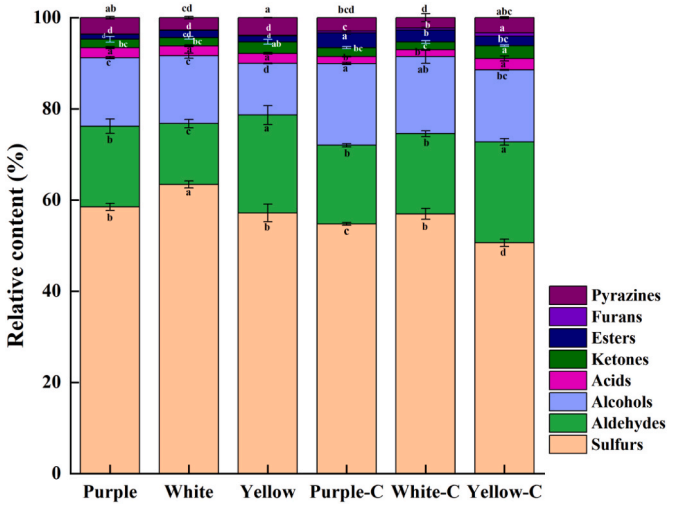

Fig. 3. The relative proportion of every category of odor chemicals in raw and cooked pigmented onions. Different lowercase letters beside bars represent significant differences ($p < 0.05$).

17.94%), acids (1.45%–2.48%), ketones (1.71%–2.83%), esters (2.10%–3.29%), furans (0.34%–0.68%), and pyrazines (2.26%–3.32%), respectively (Fig. 3). Compared to the raw colored onion bulbs, the relative proportion of sulfurs in cooked counterparts decreased, whereas the relative proportion of alcohols, esters, pyrazines, and furans increased. The relative proportion of aldehydes, acids, and ketones showed fluctuations as affected by the colors of onion bulbs (Fig. 3).

Fig. 3 also demonstrates that the prevailing volatiles for raw and cooked onions were sulfurs, aldehydes, and alcohols. Previous documentations pointed out that the majority of volatiles in onions were volatile sulfur-containing compounds via the HS-SPME-GC-MS method (Fernandes et al., 2020; Cozzolino et al., 2021; Järvenpää et al., 1998), and present results indicated that over 50% of volatile organic compounds are sulfurs (Fig. 3). Sulfurs in onions primarily derived from the interplay of alliinase through promoting the decomposition of S-alk (en) lyL-cysteine sulfoxide to emit sulfur chemicals (Cozzolino et al., 2021; Saviano et al., 2019). These sulfur compounds have a pungent and unpleasant smell, but they exhibit many bio-active functions, such as tumor fighting, antimicrobial, etc. (Saviano et al., 2019). The relative proportions of sulfurs in colored onions decreased when cooked, as shown in Fig. 3 for the three cooked colored onions. Cooking or heating can destroy sulfur-containing compounds in onions, thus decreasing pungency and unpleasant flavor of raw onions (Villière et al., 2015; Cavagnaro and Galmarini, 2012; Cavagnaro et al., 2007). The present results were consistent with these above-mentioned reports.

Aldehydes ranked the second odorant category in various pigmented onions (raw and cooked) (Fig. 3). The analogous content of aldehydes were the maximal in yellow-colored onions, compared to those in white- and purple-colored onions. The majority of the aldehydes contain six to nine carbons (C6–C9), as the C6–C9 fatty acids are the base materials of lipoxygenase and hydroperoxide lyase, which correlated with aldehyde emission (Cozzolino et al., 2021; Ioku et al., 2001). 2-methylpentanal (monomer and dimer) ranked the top, which has the distinctive aroma of grass, and green, subsequent for heptanal exhibiting odor of citrus, fat, green, and nut (Table S1).

Ketones and alcohols originated from the oxidative dissociation of lipids, and their threshold value were greater than that of aldehydes, possessing a certain floral and fruity fragrance (Wang et al., 2022). The most abundant ketone in colored onions was 1-penten-3-one (monomer and dimer), which smells like fish, green, and pungent (Table S1). Esters were mainly the chemical reaction products between acids and alcohols, which can provide smells of sweet and fragrance in onions (Ioku et al., 2001). Meanwhile, the relative proportion of esters in raw colored onions increased significantly after cooking (Fig. 3). The relative proportion of pyrazines were found higher in all cooked colored onions than those in raw colored onions, which was consistent with the cases of pyrazines formed during the heating process of foods (Ren et al., 2024).

In a former study based on HS-SPME-GC-MS to identify the odor chemicals in three colored onions, a total of 61 volatiles were detected, including 15–25 sulfurs (47.53%–64.01%) (Wang et al., 2022). The types of odor chemicals were very close to our results, whereas the quantity and percentage of different categories of odorants (sulfurs, aldehydes, alcohols, ketones, etc.) were obviously distinctive, because of the variation of analytical method and treatment conditions. The present study found that the relative amount of (*Z*)-1-propenylallyl disulfide, and diethyl trisulfide were relatively higher in both raw and cooked onions than other sulfurs. Compared to raw onions, the relative amount of methyl-1-propenyl disulfide were higher in cooked onions (Table S1 and Table S2). Cozzolino et al. (2021) detected 31 volatiles in four Southern Italian onions based on HS-SPME-GC-MS method, including 19 sulfur metabolites that dipropyl disulfide, propyl trans-1-propenyl disulfide, dipropyl trisulfide, and methyl propyl disulfide were more abundant. Fernandes et al. (2020) found 86 volatiles in onions from different geographical regions through HS-SPME-GC-MS approach, including 36 sulfur compounds that phenylethylthiol, dipropyl disulfide, dimethyl trisulfide, and methyl propyl disulfide were more abundant in peak area. Many papers have confirmed that the HS-GC-IMS was relative susceptible than the prevailing GC-MS approach, especially in measuring minor odor chemicals (Zhang et al., 2023; Jin et al., 2023a, b, c). Therefore, the present results from HS-GC-IMS can also provide a rapid tool and enrich the volatile profiles of colored onions in the future.

3.4. Multivariate statistical analysis

The signal magnitude was employed to construct the PCA plot of odor chemicals in colored onion bulbs. To classify the odor chemicals between raw and cooked onions, the PCA scattering diagram is shown in Fig. 4A, and the aggregated donation ratio of PC1 (57.1%) and PC2 (21.7%) was 78.8%. The raw and cooked onions were isolated individually on the PCA score plot. This phenomenon proved that the odor characteristics of raw onions and cooked onions varied greatly (Yang et al., 2021), implying that the odor traits of colored onions were substantially modified by cooking.

A supervised OPLS-DA simulation was also carried out, discriminating the colored onions between "raw" and "cooked". Fig. 4B depicts that the fine classifying of the OPLS-DA. The examination indexes, namely an R^2X of 0.788, R^2Y of 0.985 and Q^2 (cum) of 0.98, implying the superior forecast capacity of the simulation. The raw and cooked onion bulbs were also better scattered by the OPLS-DA simulation. The output of vexed calibration (Fig. 4C) said that all Q^2 data were not higher than the initial data, and the restoration band of Q^2 cut the ordinate scale at negative value (−0.665). Therefore, the simulation can offer superior properties to the data, and not over-fitted.

Similarly, the PCA, OPLS-DA, and cross validation for raw and cooked colored onions were also performed. The aggregated donation ratio of PC1 (72.6%) and PC2 (13.1%) for raw colored onions was 85.7% (Fig. 4D). Fig. 4E demonstrated that the fine classifying of the three raw onion bulbs derived from OPLS-DA simulation. The examination indexes, namely an R^2X of 0.949, R^2Y of 0.976 and Q^2 of 0.894, also implying the superior forecast capacity of the simulation. The three raw onion bulbs were also well isolated via OPLS-DA plot. The output of vexed calibration (Fig. 4F) indicated that all Q^2 data were also not higher than the initial data, and restoration band of Q^2 cut the ordinate scale at negative value (−0.85). Meantime, the aggregated donation ratio of PC1 (62.6%) and PC2 (13.1%) for cooked colored onions was 75.7% (Fig. 4G). Fig. 4H also showed the fine classifying of the three cooked onion bulbs derived from OPLS-DA. The examination indexes, namely an R^2X of 0.754, R^2Y of 0.947 and Q^2 (cum) of 0.849, also implying the superior forecast capacity of the simulation. The three

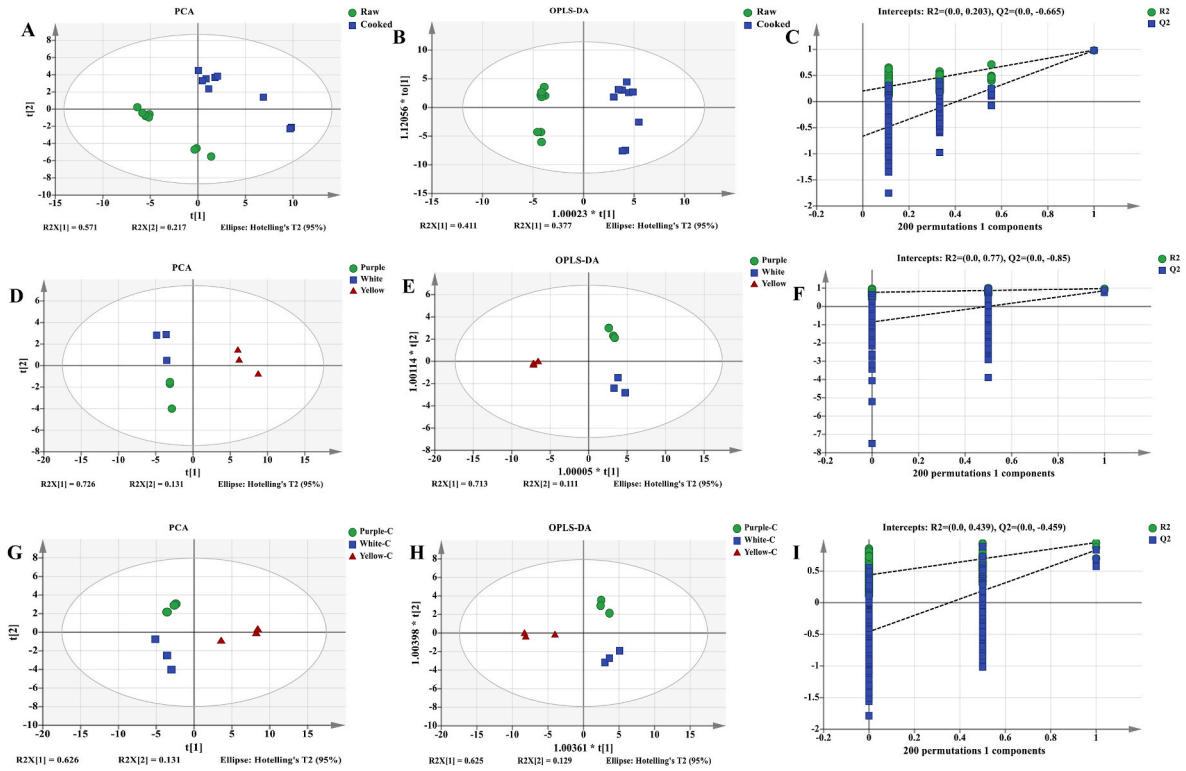

Fig. 4. Scatter maps of PCA, OPLS-DA, and cross validation test with the flavor volatiles measured from all pigmented onions (A, B, C), raw onions (D, E, F), and cooked onions (G, H, I).

cooked onion bulbs were also well scattered by OPLS-DA plot. The output of vexed calibration (Fig. 4I) illustrated that all Q^2 were also not higher than the initial data, and the restoration band of Q^2 cut the ordinate scale at negative value (−0.459), all implying the fine fitting model for raw and cooked colored onions not over-fitted (Song et al., 2021, 2021a, 2021b;b).

3.5. Sieving of potential marker odor chemicals in various pigmented onion bulbs

According to Qi. (2024), after visualization of 39 and 45 volatile components in different colored onion bulbs before and after cooking through their corresponding fingerprints, the participation of every volatile compound in classification was quantified by the variable importance in projection (VIP) through the reliable OPLS-DA simulation above (Fig. 5). For all colored onions (including raw and cooked), there were 22 odor chemicals measured from the raw and cooked pigmented onion bulbs (VIP>1), including six sulfurs (methanedithiol, 1-propene-3-methylthio, allyl propyl sulfide-M, allyl methyl trisulfide, allyl propyl sulfide-D, and (*E*)-1-propenylmethyl disulfide), six aldehydes (hexanal-M, pentanal, hexanal-D, heptanal, butanal, and 2-methylbutanal), four ketones (2(3H)-Furanone, (*E*)-3-penten-2-one, 2-hexanone, and 1-penten-3-one-M), three alcohols (rhodinol, 2-methyl-1-propanol, and dihydroeugenol), 1 furan (2-pentyl furan), 1 ester (ethyl phenylacetate), and 1 acid (2-furancarboxylic acid) (Fig. 5A). In all onions model (including raw and cooked), the VIP value distribution was shown in Fig. 5A, with six sulfurs (methanedithiol, 1-propene-3-methylthio, allyl propyl sulfide-M, allyl methyl trisulfide, allyl propyl sulfide-D, and (*E*)-1-propenylmethyl disulfide), six aldehydes (hexanal-M, pentanal, hexanal-D, heptanal, butanal, and 2-methylbutanal), four ketones (2(3H)-furanone, (*E*)-3-penten-2-one, 2-hexanone, and 1-penten-3-one-M), three alcohols (rhodinol, 2-methyl-1-propanol, and dihydroeugenol), 1 furan (2-pentyl furan), 1 ester (ethyl phenylacetate), and 1 acid (2-furancarboxylic acid) (VIP value > 1.0). Similarly, there were 8 marker volatile compounds for colored raw onions, including 2-methyl-1-propanol, butanal, ethyl phenylacetate, (*Z*)-1-propenylallyl disulfide-M, (*Z*)-1-propenylallyl disulfide, dihydroeugenol, 2-methyl-2-pentenal-M, and 2,3-Diethylpyrazine-M (VIP value > 1.0) (Fig. 5B). There were 22 volatile compounds for colored cooked onions, including 2-methylbutanal, 2(3H)-furanone, (*E*)-1-propenylmethyl disulfide, pentanal, (*Z*)-1-propenylallyl disulfide, ethyl phenylacetate, allyl methyl trisulfide, rhodinol, (*Z*)-1-propenylallyl disulfide-M, (*Z*)-1-propenylallyl disulfide-D, hexanal-D, 2-propenyl methyl disulfide-M, 2-pentyl furan,1-propene-3-methylthio, propanedioic acid, dihydrolinalool, 2,3-diethylpyrazine-D, 2-methyl-2-pentenal-D, 2-methylpentanal-M, etc. (VIP value > 1.0) (Fig. 5C). Many researchers have successfully utilized this approach and screened out volatile odor markers from various samples through HS-GC-IMS fingerprinting technique (Qi et al., 2024; Jin et al., 2023a). Although these differential odor chemicals in pigmented onions were screened out, the specific odor profiles need further assay based on sensory evaluation and the GC-O technique.

Our previous results showed that the distinctive odor substances screened out through OPLS-DA and VIP>1.0 could be employed to discriminate flavor volatiles in different cereals (raw or cooked) (Jin et al., 2023a, c, d). The present results also performed the PCA and clustering heatmap analysis of the screened label volatile chemicals (VIP>1.0) to distinguish pigmented onion samples (Fig. 6). The PCA score plot of 22 marker compounds (Fig. 5A) can discriminate raw onions from the cooked ones, as depicted by the aggregated donation ratio of PC1 (72.1%) and PC2 (11.2%) was 83.3% (Fig. 6A). The signal intensities of these compounds both in raw and cooked onions were further illustrated through clustering heatmap as shown in Fig. 6B, which demonstrated that the relative proportion of methanedithiol, 1-propene-3-methylthio, allyl methyl trisulfide, allyl propyl sulfide-D, (*E*)-1-propenylmethyl disulfide, hexanal-M, pentanal, hexanal-D, heptanal, 2-methylbutanal, 2(3H)-furanone, (*E*)-3-penten-2-one, 2-hexanone, 1-penten-3-one-M, rhodinol, 2-methyl-1-propanol, dihydroeugenol, 2-pentyl furan, ethyl phenylacetate, and

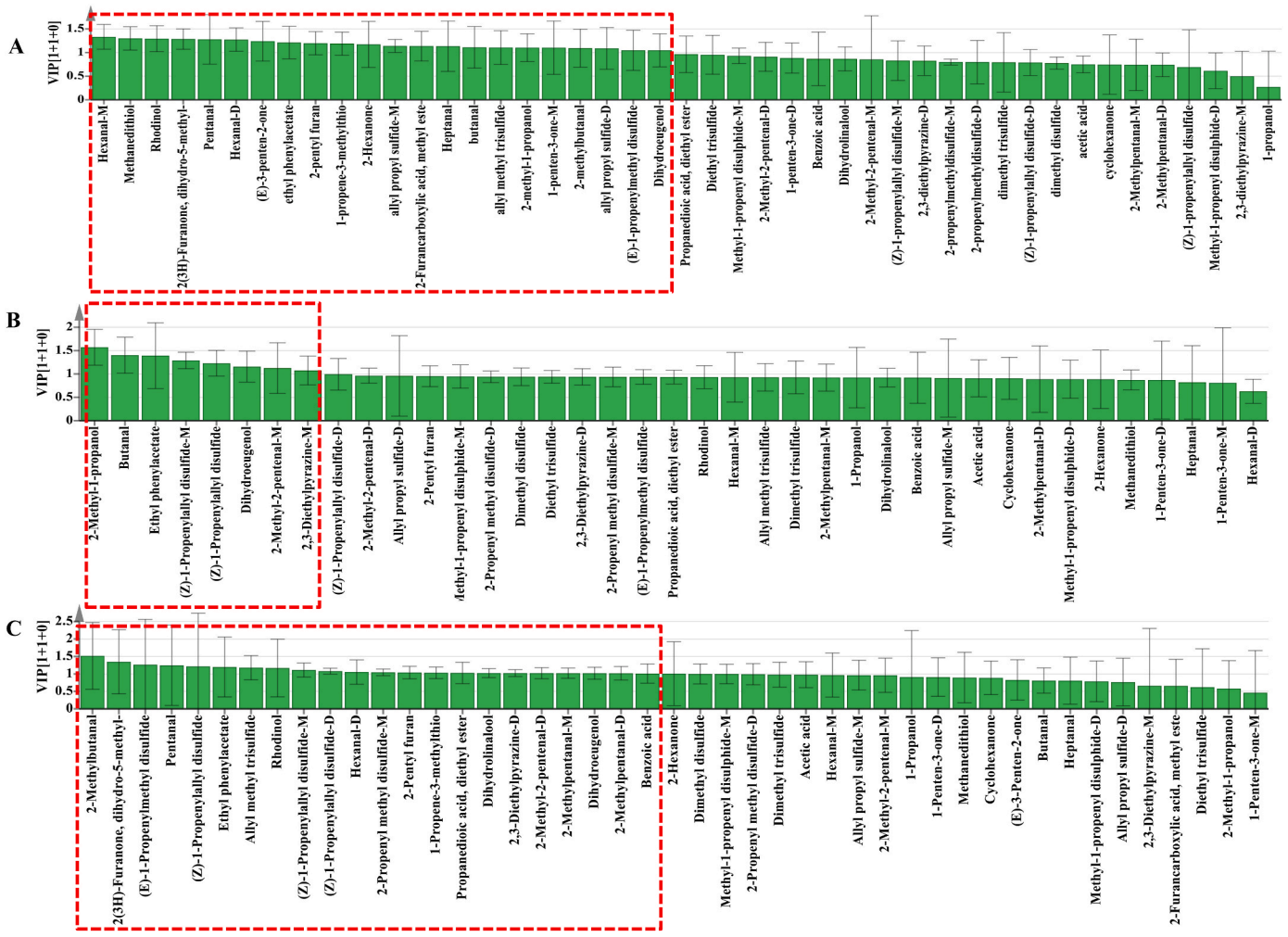

Fig. 5. VIP distributions of the flavor volatiles measured from all pigmented onions (A), raw onions (B), and cooked onions (C). Red rectangles denote the label odor chemicals with VIP values above 1.0. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2-furancarboxylic acid were obviously greater than the raw onion bulbs (Fig. 6B). Likewise, the PCA, and cluster heatmap of these marker volatiles were also performed for raw and cooked onions, respectively (Fig. 6C–F). Fig. 6C demonstrated that the aggregated donation ratio of PC1 (57.8%) and PC2 (36.4%) was 94.2% for raw colored onions. Fig. 6E demonstrated that the aggregated donation ratio of PC1 (71.9%) and PC2 (18.4%) was 90.3% for cooked colored onions. The characteristic marker volatiles were also illustrated on the cluster heatmap for raw onions (Fig. 6D) and cooked onions (Fig. 6F), both indicating the favorable classification effects of odor profiles in pigmented onions (raw and cooked). Thus, the characteristic marker compounds might be selected to discriminate the odor profiles of raw onion bulbs from that of the cooked ones, raw onions and cooked onions with different bulb colors, respectively. Similar studies of marker volatile flavor compounds in colored quinoa seeds (raw and cooked) (Yang et al., 2021), foxtail millets (Jin et al., 2023d), and rice (Jin et al., 2023a) were also reported previously. However, the key aroma traits of pigmented onions (raw and cooked) deserve further investigations and validations through HS-SPME-GC-MS and GC-O technologies.

4. Conclusions

In summary, 39 and 45 volatile flavor compounds were identified from pigmented onion bulbs (raw and cooked) through the HS-GC-IMS fingerprinting, respectively. Sulfurs, aldehydes, and alcohols ranked the prevailing compound categories in pigmented onions (both raw and cooked). Compared to the raw onion bulbs, the relative proportion of sulfurs in cooked onions decreased, whereas the relative proportion of alcohols, esters, pyrazines, and furans increased. Two reliable prediction models were established through OPLS-DA, and 8 and 22 distinctive odor substances (VIP>1) were sieved out as flavor labels for distinguishing the three pigmented onion bulbs (raw and cooked), respectively. Thus, the fingerprints of volatile profiles in pigmented onion bulbs before and after cooking were established. These results may expand the information upon the odor characteristics of pigmented onion bulbs. Future work about the odor characteristics via GC-O, sensory evaluation, phenolic profiles and antioxidant activities of raw and cooked pigmented onions will be reported elsewhere.

CRediT authorship contribution statement

Wengang Jin: Investigation, Methodology, Visualization, Writing – original draft, Project administration. **Shibo Zhao:** Methodology, Data curation. **Xiaohua Chen:** Methodology, Data curation. **Haiyan Sun:** Chemometrics, Visualization. **Jinjin Pei:** Chemometrics, Visualization. **Kaihua Wang:** Supervision, Writing – review & editing. **Ruichang Gao:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financialinterestsor personal relationships that could have appeared to influence

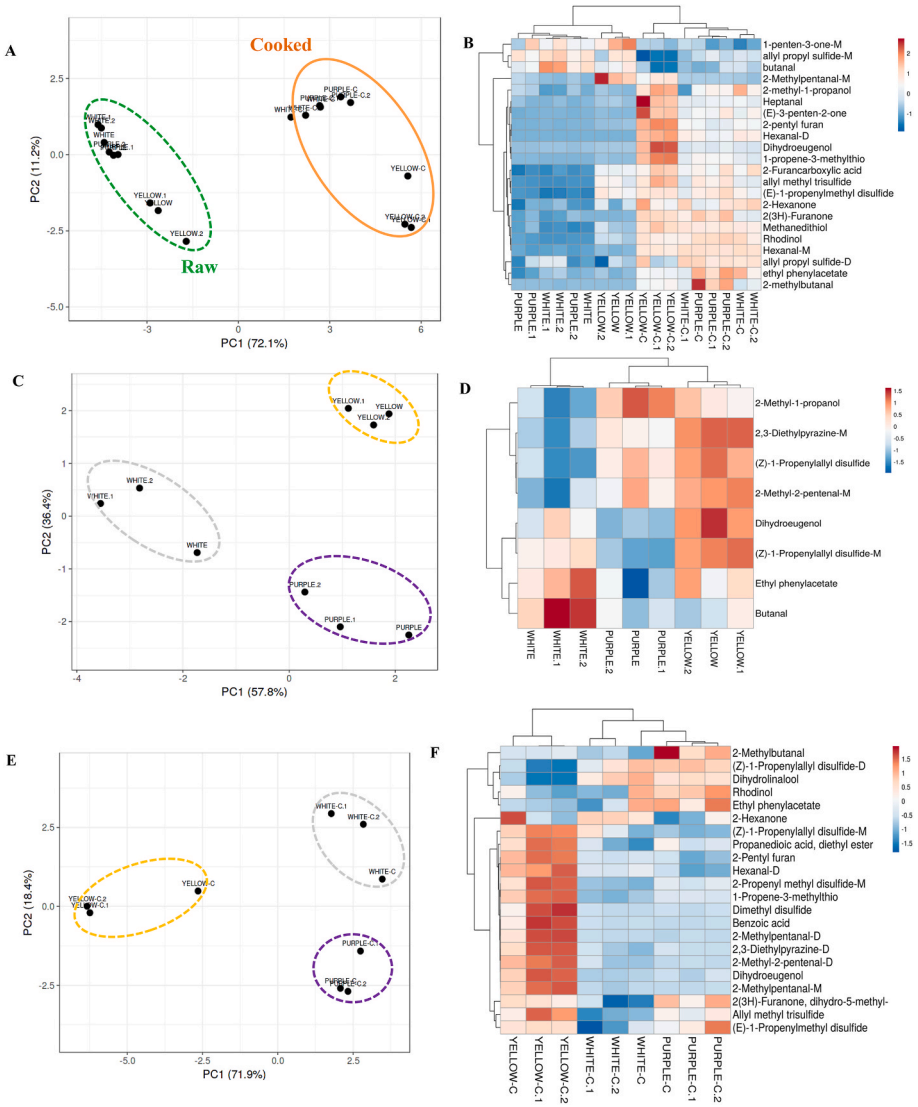

Fig. 6. PCA, and cluster heatmap of marker volatiles based on VIP values acquired from raw and cooked pigmented onions (A, B), raw onions (C, D), and cooked onions (E, F).

the work reported in this paper.

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.crfs.2024.100781.

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