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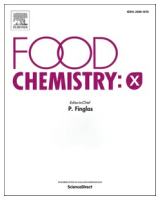

Exploring the oxidative rancidity mechanism and changes in volatile flavors of watermelon seed kernels based on lipidomics

Xiongwei Yu [a,c,d], Bin Li [a], Hui Ouyang [c], Weijian Xu [c], Ruru Zhang [c], Xing Fu [a], Sihai Gao [b,*], Shugang Li [c,d,*]

[a] College of Food Science and Technology, Huazhong Agricultural University, Wuhan 430070, China
[b] Tongji Hospital, Tongji Medical College, Huazhong University of Science and Technology, Wuhan 430030, China
[c] Engineering Research Center of Bio-process, Ministry of Education/Key Laboratory for Agricultural Products Processing of Anhui Province/School of Food and Biological Engineering, Hefei University of Technology, Hefei 230601, China
[d] Wuhan Xudong Food Co Ltd, Wuhan 430000, China

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ABSTRACT

Watermelon seed kernels (WSK) are prone to oxidative rancidity, while their evaluation biomarkers and changes in volatile flavor are still unknown. The research tracked the changes in volatile compounds and lipid components before and after rancidity using HS-SPME-GC-O-MS and lipidomic techniques. The results showed the flavor of watermelon seed kernels changed significantly before and after rancidity, from mild aroma to rancidity. A total of 42 volatile compounds were detected via GC-O-MS, and a total of 220 lipid molecules were detected via lipidomic technology. 55 lipids with significant differences were screened via multivariate statistical analysis. Combining the above analysis, it found that glycerol phospholipid and glyceride pathways were the most important metabolic pathways and 1-Pentanol and styrene could be used as potential biomarkers to judge the rancidity process of watermelon seed kernels. The research could provide powerful technical support for the storage, transportation and freshness preservation of watermelon seed kernels.

Introduction

Watermelon seed, also known as seed watermelon (*Citrullus lanatus* var.), is a variety of watermelon (PEPO) in *Cucurbitaceae*. It is widely planted in regions of Xinjiang, Gansu and Inner Mongolia of China (Li et al., 2020). Its seed kernels are rich in oil, protein and unsaturated fatty acids (Obi, 2016), which can reduce the risk of developing cardiovascular diseases such as hyperlipidemia and hypercholesterolemia (Wani, Sogi, Singh, & Götz, 2013). However, high unsaturated fatty acids can cause watermelon seed kernels to be prone to oxidative rancidity during storage, leading to quality deterioration (Li et al., 2020). At present, acid value and peroxide value are commonly chosen as indicators to characterize the oxidative rancidity of nuts in production process (Carvalho, Leite, Morais, Lima, & Teixeira, 2019). Since the evaluation accuracy of the above indicators is relatively general, a single indicator cannot objectively and comprehensively define the oxidative rancidity process of watermelon seed kernels. Besides, problems with quality control and quality stability are also universal in storage stage and processing process. Therefore, it is vital and significant to identify more accurate evaluation indicators for the oxidative rancidity process of watermelon seed kernels, and further to build more effective storage and freshkeeping techniques.

Nuts contain high levels of unsaturated fatty acids, making them susceptible to oxidation during storage, which can result in flavor deterioration. The main reason for flavor deterioration is the changes in volatile compounds. At present, basic oxidation indicators such as iodine value, acid value and peroxide value were often used in production to judge the oxidation and rancidity process in combination with sensory evaluation of flavor (Thewes et al., 2021). In order to further distinguish the oxidation process of nuts accurately and efficiently, Headspace-Solid Phase Microextraction-Gas Chromatography-Olfactometry-Mass Spectrometry (HS-SPME-GC-O-MS) was widely used in the detection of volatile flavor compounds. Su et al., 2022 analyzed the aroma components of hops under various drying methods by HS-SPME-GC-O-MS and chemometrics, and found that β-Laurene, linalool and geraniol belonged to high-intensity aroma compounds in all samples (Su et al., 2022). Nadya Mara Adelina et al analyzed the volatile substances of two kinds of grafted tricholoma matsutake under different baking conditions through

* Corresponding authors.
E-mail addresses: sihaigao73@163.com (S. Gao), lishugang2020@hfut.edu.cn (S. Li).

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HS-SPME-GC-O-MS combined with electronic nose and found that D-limonene, as the most abundant substance, provided the overall fragrance of citrus for the sample (Adelina, Wang, Zhang, & Zhao, 2021).

In recent years, due to the rapid development of mass spectrometry in the field of lipid detection and analysis, lipidomic technology came into being, and has been widely used in exploring the type, distribution and function of lipids and their dynamic changes in physiological metabolism and pathological states (Mohamed, Molendijk, & Hill, 2020). By combining HS-SPME-GC-O-MS and lipidomics, Jia et al characterized the chemical components of fermented brown goat milk, identified 108 metabolites and 174 flavor related lipids, and identified the mechanism of characteristic flavor formation (Jia, Liu, & Shi, 2021). Sun and Planque et al compared and analyzed the lipid difference between fresh hazelnut oil and oxidized hazelnut oil, and summarized the rule of flavor deterioration and the mechanism of oxidative failure (Sun et al., 2022; Planque et al., 2019). A large number of studies found that HS-SPME-GC-O-MS and lipidomics were the most effective means to explore lipid oxidation and characteristic flavor, but their application in the field of watermelon seed kernel was still limited.

Therefore, the study aimed to: (a) explore the internal correlation between volatile components and lipid molecules in watermelon seed kernels under different storage conditions; (b) reveal oxidative rancidity biomarkers and volatile flavor changes of watermelon seed kernels; (c) analyze potential mechanisms for the formation of oxidative rancidity biomarkers. In addition, the study continued to analyze the mechanism of oxidative rancidity of watermelon seed kernel, and it could provide theoretical support for product stability and high-quality development of watermelon seed kernels.

Materials and methods

Materials and chemicals

Watermelon seeds were purchased from Kuitun City, Xinjiang Uygur Autonomous Region (Kuitun, China), which were sealed in PA-PE bags at − 20 ℃. HPLC grade cyclohexanone was purchased from Sigma-Aldrich (Missouri, USA). Other chemicals used in this experiment were analytical grade chemicals and were not purified before use.

Sample treatment

500 g watermelon seed kernel was placed in a constant temperature incubator at 60℃ for accelerated oxidation experiment, and the oxidation end point was taken as the peroxidation value and acid value of walnut kernel reached the maximum allowed in China National Standard GB 19300–2014 (peroxide value $\leq$ 0.5 g /100 g, acid value $\leq$ 3 mg /g). Watermelon seed kernels before and after oxidation were extracted, crushed, and soaked in petroleum ether for 24 h, filtered and removed by rotary evaporator to obtain oil samples.

Determination of physical and chemical indexes

The related physical and chemical indexes were determined by the following methods: Acid value-AV was determined by GB 5009.229–2016; Peroxide value-PV was determined by GB 5009.227–2016; Anisidine value-AV and the total oxidation value were determined by GB/T 24304–2009; Malondialdehyde-MDA was determined by GB 5009.181–2016; Conjugated diene and conjugated triene were determined by GB/T 22500–2008.

Determination of antioxidant activity

2′-Azinobis-3-ethylbenzoline-6-sulfonic acid(ABTS)assay

Referring to the method of Buthelezi et al with slight modifications (Buthelezi, Tesfay, & Magwaza, 2021), mixed 7 mmol/L ABTS solution and 2.45 mmol/L potassium persulfate solution with the ratio of 1:1, and reacted for 12–16 h at room temperature in darkness to obtain $ABTS^+$ stock solution. Then diluted the stock solution with 0.2 M phosphate buffer solution (PBS, pH 7.4) to the absorbance of 0.7 ± 0.02 to obtain ABTS working solution. Chose 200 μL PBS solution as the blank group, 180 μ L $ABTS^+$ working fluid and 20 μL PBS solution as the control group, and 180 μL $ABTS^+$ working fluid and 20 μL sample solution as the experimental group. All these sample solutions were kept at room temperature in a 96 well plate for 6 min, and the absorbance value of the reaction system at 734 nm was measured. The calculation formula of $ABTS^+$ free radical scavenging capacity was as follows:

$$ABTS^+ \text{ Clearance Rate } \% = \left[1 - \left(\frac{A_i - A_0}{A_1 - A_0}\right)\right] \times 100\% \quad (1)$$

where Ai was the absorbance value of the experimental group; A_0 was the absorbance value of the blank group; and A_1 was the absorbance value of the control group.

2′-Diphenyl-1-picrylhydrazyl(DPPH)assay

Referring to the method of Duduzile Buthelezi et al with slight modifications (Duduzile Buthelezi, Samukelo Magwaza, & Zeray Tesfay, 2019), mixed the sample solution and 0.1 mmol/L DPPH alcohol solution at the ratio of 1:1, then let them react in darkness for 30 min. Took absolute ethanol in place of the sample solution as the blank control group, and measured the absorbance at 517 nm. DPPH radical scavenging capacity was calculated as follows:

$$DPPH \text{ Clearance Rate } \% = \left[\frac{A_0 - A_1}{A_0}\right] \times 100\% \quad (2)$$

where A_0 was the absorbance value of the blank control group; A_1 was the absorbance value of the experimental group.

Determination of total phenols (TP)

The determination of TP was determined using Folin Ciocalteu colorimetry according to the method of Oliveira Alves *et al* with slight modifications (Oliveira-Alves et al., 2020).

Method of electronic nose (E-nose) analysis

Referring to the method of Cai et al with slight modifications (Cai et al., 2021), PEN3.5 E-nose was used to analyze the volatile compounds of the sample. The analyzer consisted of 10 sensors and the different response types of each sensor as well as the corresponding description of the E-nose were listed in Table S1. During the E-nose analysis: accurately weighed 2.0 g of ground watermelon seed sample and placed it in a 20 mL headspace bottle, covered and sealed it, and then balanced it for 15 min under 60 ℃ water bath condition, as well as collecting the volatile substances of the sample. Kept the measurement phase last for 80 s, so as to sufficiently allow the sensor to reach a stable signal value. The period of sensor cleaning time was 100 s, and the carrier gas flow rate was 400 mL/min.

Gas chromatography–olfactometry-mass spectrometry (GC-O-MS)

Extraction of volatile compounds

Volatile compounds were extracted by HS-SPME (headspace solid phase microextraction), and the experiment was repeated three times in parallel. Accurately weighed 2.0 g of ground watermelon seed kernel sample, placed it into a 20 mL headspace vial, and added 5 μL internal standard (cyclohexanone, 18.94 μ G/μ L), then sealed it immediately, and then balanced it for 20 min under 50 ℃ water bath condition. Took SPME manual sampling probe fiber tip (50/30 μ m CAR/PDMS/DVB fiber, 1 cm; Bellefonte, PA) to pretreat the fiber at 250 ℃ in the sampling port of Agilent 7890A gas chromatograph (Agilent Technologies, Santa

Clara, CA) for 30 min. After desorption, inserted the injection probe into the sample headspace bottle (the depth was 2 cm away from the surface of the sample), extracted at 50 ℃ for 40 min, then quickly inserted it into the gas chromatograph injection port and desorbed at 250 ℃ in the non-split flow mode for 5 min.

Identification of aroma-active compounds using GC-O-MS

The volatile compounds in watermelon seed kernel samples were analyzed using Headspace-Solid Phase Microextraction-Gas Chromatography-Olfactometry-Mass Spectrometry (HS-SPME-GC-O-MS) technology. Samples were separated in DB-WAX chromatographic column (30 mm × 0.25 mm × 0.25 μm). The distribution ratio of gas chromatography effluents between mass spectrometer and olfactory detector was 1:1. The temperature rise procedure of chromatographic column was as follows: the initial temperature of the column temperature box was 40 ℃, and the temperature was raised to 200 ℃ at 5 ℃/min and maintained for 2 min, and then to 230 ℃ at 5 ℃/min as well as maintaining for 2 min. The mass spectrometer detector conditions were as follows: electron bombardment (EI) ion source, electron energy 70 eV, quadrupole temperature was 150 ℃, ion source temperature was 230 ℃, and the mass scanning ranged 40–450 *m/z*.

UHPLC-MS/MS (Ultra high performance liquid chromatography-tandem mass spectrometry)

Sample pretreatment

Took 10–15 mg sample, added 2 mL of methanol, precipitated protein at 20 ℃ overnight; then added 2 mL of dichloromethane with internal standard 100 uL (10 ug/mL), vortexed for 1 h; next added 2 mL of dichloromethane and 1.6 mL of ultrapure water in turn, vortexed centrifugation, took down the clear solution, nitrogen blowing; then added 4 mL of dichloromethane vortex centrifugation, took down the clear solution, repeated the above procedure twice; and then combined the lower clear solution for three times, using nitrogen to blow dry, redissolved with 1 mL of dichloromethane/methanol (1:1), vortexed for 10 s, the organic filter passing 0.22 uL shall be standby.

UHPLC-MS/MS data acquisition

Chromatographic system: Shimadzu UPLC LC-30A; Chromatographic column: Phenomenex Kinetex C18 column (100 × 2.1 mm, 2.6 μm); Injection volume: 1 μ L; Flow rate: 0.4 mL/min; Column temperature: 60° C; Sample chamber temperature: 4° C. Phase A: the ratio among water, methanol and acetonitrile was 1:1:1 (containing 5 mM ammonium acetate). Phase B: the ratio between isopropanol and acetonitrile was 5:1 (containing 5 mM ammonium acetate); Gradient elution condition: 0.5 min, 20 % phase B; 1.5 min, 40 % phase B; 3 min, 60 % phase B; 13 min, 98 % phase B; 13.1 min, 20 % phase B; 17 min, 20 % phase B. Mass spectrum system: AB Science TripleTOF ® 6600, ESI ion source, positive and negative modes. Mass number range of mass spectrum collection was *m/z* 100–1200; mass spectrum conditions were as follows: Curtain Gas: 35.000 psi; Ion Source Gas1: 50.000; Ion Source Gas2: 50.00; IonSpray Voltage: 5500.00 V(+) /-4500 V(-); Temperature: 600 °C。.

Data processing and statistical analysis

The experiment was conducted in triplicate. All these parallel experimental data were analyzed by one-way ANOVA and expressed as mean ± standard deviation. SPSS 26.0 (SPSS Inc., Chicago, IL, USA) analysis was used to analyze the difference significance, and $P < 0.05$ was considered statistically significant. GC-O-MS and lipidomics data were all analyzed using online tool Metabo Analyst 5.0 (https://www.metaboanalyst.ca/). PCA analysis, correlation heat map, radar map and volcano map were drawn using Origin 2021 software (OriginLab Inc., USA). PLSR (Partial least squares regression) analysis was performed using Unscrambler 10.4 (CAMOASA, Oslo, Norway).

Results and analysis

Study on the oxidation stability of watermelon seed kernel before and after oxidative rancidity

Lipid oxidation could continuously accumulate primary products, including hydroperoxides, which were extremely unstable and would further decompose into small molecule secondary products such as aldehyde, ketone and acid (Gao et al., 2022). Furthermore, the deterioration degree of watermelon seed quality could be evaluated by acid value (AV), peroxide value (PV), malondialdehyde (MDA) and anisidine (p-AV) values for the detection of oxidation products. Compared with the samples before oxidation (Table 1), AV, PV, MDA and p-AV increased significantly after oxidation ($p < 0.05$), with the increase amplitude of 30.04 %, 10.26 %, 21.03 % and 179.52 % respectively. After constant temperature storage, the total phenol (TP) content, ABTS and DPPH of the sample decreased significantly ($p < 0.05$), with the decrease amplitude of 32.28 %, 3.91 % and 6.77 % respectively. The reduction of TP content would further reduce the antioxidant capacity of the sample. It was found that the phenolic compounds in coffee leaves gradually decreased during storage, further reducing the total phenol content and antioxidant activity (Sun, Huang, Lu, & Chen, 2022). The indexes of oxidation deterioration in the samples increased significantly, and the antioxidant activity decreased significantly, which indicated that the quality of watermelon seed kernels deteriorated after constant temperature storage.

Result of electronic nose (E-nose) analysis

Electronic nose, a kind of machine that imitates human olfactory organs, is very sensitive to the odor information of samples, and any small changes in volatile compounds may lead to differential responses of electronic nose sensors (Chen et al., 2023). In this experiment, the overall flavor of watermelon seed samples before and after constant temperature storage was analyzed by E-nose (Fig. 1A). The response of watermelon seed samples to W1W and W1S sensors was significant, and increased significantly after constant temperature storage. This might be because the concentration of some volatile compounds of watermelon seed increased after constant temperature storage, and the corresponding responder indicated that it might be aldehyde ketone volatile compounds. For better visualization, the data of electronic nose was analyzed by PCA. In the PCA diagram, PC1 and PC2 explained 99.7 % of the total variance, which was much higher than 85 %, indicating that the PCA diagram could explain the E-nose data well. In combination with the PCA analysis of the E-nose in Fig. 1B, the study determined that the volatile compounds in watermelon seeds before and after oxidative rancidity were significantly different. In addition, it was speculated that the changes in volatile compounds in watermelon seeds before and after the thermostatic storage might be caused by complex biochemical reactions, such as lipid degradation and the interaction between lipids.

Analysis of volatile components in watermelon seeds by HS-SPME-GC-O-MS

Identification of volatile compounds

The flavor of watermelon seed kernels is determined by the type and content of their volatile compounds, which served as the material basis for analyzing the flavor change of watermelon seeds. In this experiment, HS-SPME-GC-O-MS was used to analyze the volatile flavor substances in watermelon seed kernels before and after constant temperature storage (Table 2). A total of 42 volatile substances were identified from the samples, including 10 alcohols, 15 alkenes, 5 acids, 4 benzene rings, 3 alkanes, 2 ethers and esters, and 1 other compound. It could be seen from Table 2 that after constant temperature storage, the volatile compounds in watermelon seed kernels displayed significant changes ($p < 0.05$). In this study, alkenes, benzene rings and alcohols were the main

Table 1
Analysis of quality deterioration and oxidation stability of watermelon seeds before and after oxidation rancidity.

	AV(mg/g)	PV(g/100 g)	MDA(mg/kg)	p-AV	$E\frac{1\%}{1cm232}$	$E\frac{1\%}{1cm268}$	TP(mg/kg)	DPPH(ug/ml)	ABTS(mmol/g)
BW	2.33 ± 0.05^{a}	0.39 ± 0.05^{a}	16.55 ± 0.01^{a}	0.83 ± 0.06^{a}	0.298 ± 0.001^{a}	0.760 ± 0.001^{b}	56.10 ± 0.98^{b}	89.37 ± 1.36^{b}	21.93 ± 1.32^{b}
OW	3.03 ± 0.02^{b}	0.43 ± 0.01^{b}	20.03 ± 0.03^{b}	2.32 ± 0.04^{b}	0.562 ± 0.001^{b}	0.641 ± 0.001^{a}	37.99 ± 6.50^{a}	85.46 ± 1.81^{a}	15.16 ± 0.68^{a}

Note: Data are expressed as means ± SD (n = 3). Numbers with different letters (a-d) are significantly different from one another in each column according to the Duncan test ($p < 0.05$). BW: watermelon seed samples before oxidation rancidity; OW: watermelon seed samples after oxidation rancidity; AV: Acid value; PV: Peroxide value; MDA: Malondialdehyde; pAV: p-anisidine value.

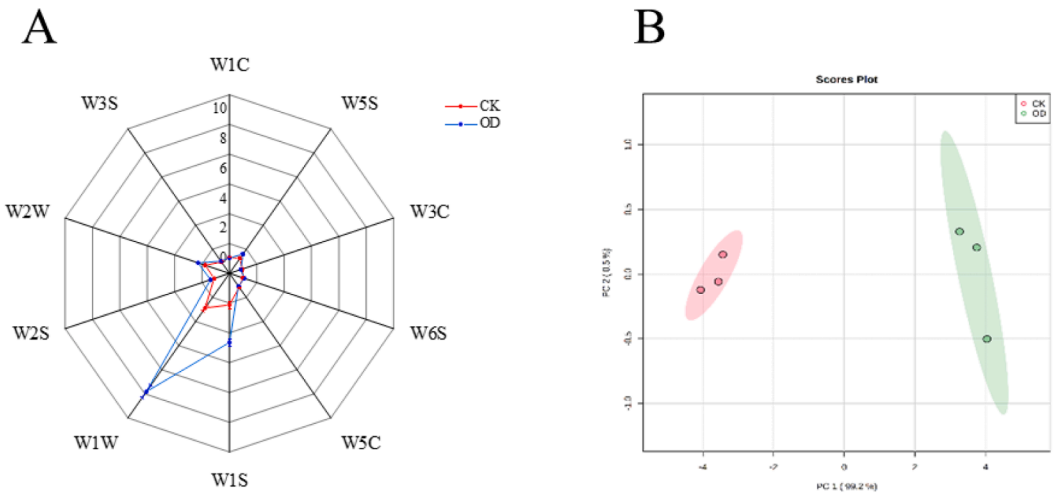

Fig. 1. Characteristic odor analysis of watermelon seeds before and after constant temperature storage: electronic nose radar (A) and principal component analysis (PCA) (B).

volatile flavor compounds in CK group (referring to the control group that was not treated by accelerated oxidation), accounting for 74.95 %, 11.86 % and 4.46 %, respectively, which was similar to the response value of E-nose. According to flavor descriptions, these volatile compounds mainly provided green, citrus, mint, and lemon smell to watermelon seed kernels, delivering a refreshing flavor; After constant temperature storage, the types and contents of these main volatile compounds in watermelon seed kernels also changed, of which the contents of alkenes, acids, alcohols and benzene rings accounted for 28.75 %, 25.59 %, 18.88 % and 15.95 %, respectively. At this stage, sample watermelon seed kernels delivered the taste of acetic acid and rancidity. This result might be related to the significant changes in the type and content of volatile compounds in the sample after constant temperature storage. For instance, 1-amyl alcohol, styrene and acetic acid with the taste of rancidity appeared after constant temperature storage, the contents of which were 121.23 ng/g, 424.96 ng/g and 466.10 ng/g, respectively; while the content of volatile substances in D-limonene and β-terpene that provided a refreshing, mint and citrus flavor to watermelon seed kernels decreased from 4662.22 ng/g to 1187.63 ng/g, and 1722.37 ng/g to 0 ng/g, respectively, after constant temperature storage. Therefore, it was speculated that substances such as 1-pentanol, styrene, and acetic acid could contribute greatly to the production of rancidity flavor of watermelon seed kernels.

It could be seen from Table 2 that the content of alcohols in watermelon seed kernels before and after constant temperature storage changed significantly, accounting for 4.48 % and 18.88 % of the total amount of aroma substances in CK and OD group (referring to the experimental group that was treated by accelerated oxidation) samples respectively. 1-pentanol, as the substance appearing after constant temperature storage provided the sample with the taste of rancidity of acetic acid (Ivanova-Petropulos et al., 2015) due to its lower threshold value. In addition, after constant temperature storage, the content of alkenes decreased from 75.29 % to 28.75 % of the total aroma substances, in which Alkene hydrocarbons such as sabinene, D-limonene and β- Pinene provided the CK group samples with citrus, mint and green fragrance (Fu et al., 2020; Liu, Fan, & Li, 2022). At the same time, styrene was detected in OD group, and because of its lower threshold value, styrene could provide the samples with acetic acid, gasoline and other bad smells (Liu et al., 2022), which was probably due to the thermal degradation and dehydrogenation of lipids during the accelerated oxidation process. It could be concluded that styrene might have no effect on the production of oxidative rancidity flavor in watermelon seed kernels. After constant temperature storage, the content of alcohols in watermelon seed kernels significantly increased ($p < 0.05$), which was consistent with the data from E-nose. Moreover, the overall flavor of watermelon seed kernels shifted from light aroma to sourness, which was also consistent with sensory evaluation. Based on this, 1-pentanol could be used as a key substance for detecting the rancidity process of watermelon seed kernels.

Lipid composition changes in watermelon seed kernels before and after rancidity using lipidomics analysis

Mass spectrum analysis of watermelon seed kernel fat

Lipids were the material basis for changes in volatile compounds in watermelon seed kernels. In order to further identify the potential biomarkers of watermelon seed kernel oxidation, a comprehensive lipidomics analysis was conducted using UHPLC-QTOF-MS on watermelon seed kernel samples before and after rancidity. A total of 220 lipids were detected: 85 were in negative ion mode and 45 were in positive ion mode. Five categories and 13 subclasses of lipids were detected, majorly glycerol esters (GL), glycerol phospholipids (GP), sphingolipids (SP), fatty acyls (FA), and sterol glycolipids (PG), among which 7 GPs, 3 GLs, and 1 FA, 1 SP, and 1 PG were contained, respectively (Fig. 2). In total, the number of GL was the most (103), including 109 TG, 23 DG and 3 DGDG. The second was GP (57), which accounted for the most lipid

Table 2
Changes of volatile compounds in watermelon seed samples before and after oxidation rancidity.

C ode	RT (min)	Compounds	Identity	CAS	Threshold(ng/g)		OAV		Aroma
					CK	OD	CK	OD	
Alcohols	4.799	Ethanol	RI、MS	000064–17-5	151.70 ± 35.10	27.11 ± 1.31	244.68	45.85	sweet
	12.152	1-Pentanol	RI、MS	000071–41-0	0	121.23 ± 4.57	–	837.51	balsamic
	14.869	1-Hexanol	RI、MS	000111–27-3	135.92 ± 5.86	305.94 ± 10.70	339.80	791.61	resin, flower, green
	19.526	2,3-Butanediol	RI、MS	000513–85-9	129.90 ± 70.04	168.73 ± 66.58	1.30	1.02	fruit, onion
	19.688	Linalool	RI、MS	000078–70-6	11.53 ± 1.09	0	4803.32	–	flower, lavender
	20.733	Propylene Glycol	RI、MS	000057–55-6	0	279.30 ± 7.20	–	0.84	–
	22.031	dimethyl-Silanediol	RI	001066–42-8	210.57 ± 47.25	97.75 ± 4.34	–	–	–
	26.956	Benzyl alcohol	RI、MS	000100–51-6	20.32 ± 0.71	96.68 ± 5.72	8.00	40.31	sweet, flower
	27.683	Phenylethyl Alcohol	RI、MS	000060–12-8	0	45.90 ± 1.76	–	3678.45	honey, spice, rose, lilac
	28.925	2,2′-oxybis-Ethanol	RI	000111–46-6	24.11 ± 2.72	31.50 ± 4.13	0.10	0.15	–
Terpenes	6.338	(-)-α-Pinene	RI	007785–26-4	360.94 ± 107.92	0	3609.38	–	–
	6.451	alpha-thujene	RI、MS	002867–05-2	215.19 ± 63.19	33.12 ± 3.18	–	–	wood, green, herb
	8.088	β-pinene	RI、MS	000127–91-3	76.48 ± 19.12	0	63.73	–	pine, resin, turpentine
	8.455	Sabinene	RI、MS	003387–41-5	2947.48 ± 842.25	74.22 ± 4.79	1473.74	39.51	pepper, turpentine, wood
	9.259	3-Carene	RI、MS	013466–78-9	0	68.42 ± 19.62	–	9.47	lemon, resin
	9.915	β-myrcene	RI、MS	000123–35-3	233.95 ± 59.66	0	2079.58	–	balsamic, must, spice
	10.056	α-Terpinene	RI、MS	000099–86-5	227.16 ± 51.74	0	–	–	lemon
	10.6	D-Limonene	RI	005989–27-5	4662.44 ± 1260.14	1187.63 ± 57.56	41260.53	11019.38	citrus, mint
	10.84	beta-terpinene	RI、MS	000099–84-3	1722.37 ± 451.35	0	1435.31	–	–
	11.609	trans-.beta.-Ocimene	RI、MS	003779–61-1	137.58 ± 21.88	0	7357.08	–	sweet, herb
	11.898	.gamma.-Terpinene	RI、MS	000099–85-4	163.31 ± 33.47	0	163.31	–	gasoline, turpentine
	12.067	(Z)-3,7-dimethyl-,1,3,6-Octatriene	RI、MS	003338–55-4	138.05 ± 13.84	0	4060.40	–	citrus, herb, flower
	12.202	1,3,5,7-Cyclooctatetraene	RI	000629–20-9	516.95 ± 201.16	0	–	–	–
	12.223	Styrene	RI、MS	000100–42-5	0	424.96 ± 9.20	–	6679.50	balsamic, gasoline
	12.928	Terpinolene	RI、MS	000586–62-9	87.54 ± 4.03	0	437.69	–	pine, plastic
Ethers	22.518	Estragole	RI、MS	000140–67-0	158.68 ± 27.74	101.38 ± 3.37	9917.33	6125.51	licorice, anise
	25.919	Anethole	RI、MS	000104–46-1	0	39.04 ± 1.32	–	438.58	–
Benzodiazepines	6.726	Toluene	RI、MS	000108–88-3	1024.54 ± 268.36	948.70 ± 106.55	3415.12	3517.51	paint
	8.68	Ethylbenzene	RI、MS	000100–41-4	111.98 ± 23.52	43.15 ± 5.18	153.39	66.21	–
	10.219	p-Xylene	RI、MS	000106–42-3	109.73 ± 38.08	0	109.73	–	–
	12.568	o-Cymene	RI、MS	000527–84-4	571.36 ± 108.57	0	–	–	–
Alkanes	7.276	3-methyl-Decane	RI	013151–34-3	35.05 ± 6.07	0	–	–	–
	7.869	Undecane	RI	001120–21-4	299.17 ± 61.81	146.99 ± 30.25	29.92	17.72	alkane
	13.514	Tridecane	RI	000629–50-5	0	65.94 ± 2.11	–	1.52	alkane
Esters	21.523	Butyrolactone	RI、MS	000096–48-0	38.21 ± 9.44	242.39 ± 7.78	38.21	250.17	caramel, sweet
	22.342	nonyl ester Chloroacetic acid	RI	005451–96-7	19.09 ± 1.35	0	–	–	–
Acids	17.36	Acetic acid	RI、MS	000064–19-7	0	466.10 ± 2.33	–	4.73	sour
	27.994	Imidazole-4-acetic acid	RI	000645–65-8	0	1125.66 ± 77.19	–	–	–
	32.467	Octadecanoic acid	RI	000057–11-4	463.09 ± 15.22	0	23.15	–	–
	33.138	Nonanoic acid	RI、MS	000112–05-0	97.94 ± 10.93	0	21.29	–	green, fat
	38.042	Oleic Acid	RI	000112–80-1	70.14 ± 22.39	0	1.59	–	fat

(*continued on next page*)

Table 2 (*continued*)

C ode	RT (min)	Compounds	Identity	CAS	Threshold(ng/g)		OAV		Aroma
					CK	OD	CK	OD	
Other compounds	24.494	methoxy-phenyl-_Oxime-	RI	1000222–86-6	157.77 ± 28.55	78.34 ± 10.04	–	–	–

Note: Threshold: Odor thresholds of compounds in water reported in the literatures.
The watermelon seed samples in control group (CK) were not treated by accelerated oxidation and the samples after accelerated oxidation treatment were experimental group (OD).
Identification methods of each aroma compound: MS, RI, and OAV represent being identified by mass spectra, retention indices, odor activity value and standard agent, respectively.
-: None.

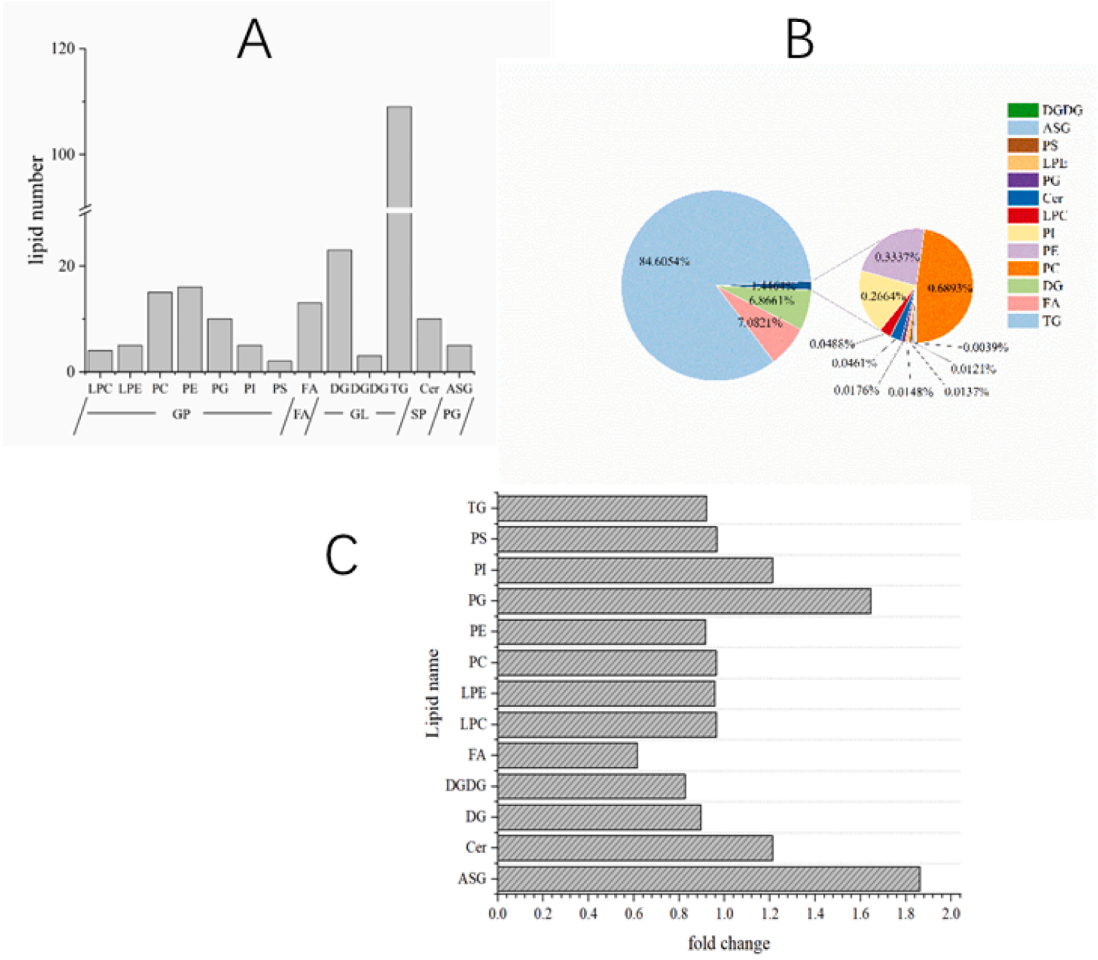

Fig. 2. Histogram of the content, relative percentage and change among different subclasses of lipids in watermelon seeds.

subclasses, including 16 PE, 15 PC, 10 PG, 5 PI, 5 LPE, 4 LPC and 2 PS. The rest were 13 FA, 10 Cer and 5 ASG (acyl sterol glycosides).

The quantitative analysis results showed that the total lipid concentration of the fresh watermelon seed kernel oil sample was 304038.6753 ng/g, and the percentage of lipid subclasses could be obtained according to its concentration and the number of lipid subclasses (Fig. 2B). The proportion of TG in the oil sample was the highest (>84.6054 %); followed by the proportion of FA (>7.0821 %); then followed by DG, PC, PE and PI, accounting for 6.8661 %, 1.4464 %, 0.6893 % and 0.3337 %, respectively (Fig. 2B); and the content of other lipid subclasses was less. It indicated that the number of lipid molecules among different lipid subclasses varied significantly, and TG obtained the most number.

In order to explore the effect of watermelon seed kernel rancidity on its oil content, the research carried out relevant analysis on the change of lipid molecules before and after rancidity. It was found that after constant temperature storage, the total lipid content decreased to 89.93 % of the fresh sample, in which the content of ASG, Cer, PG and PI increased 1.86 times, 1.21 times, 1.64 times and 1.21 times, respectively; the rest lipid subclasses such as DG, DGDG, FA, LPC, LPE, PC, PE, PS and TG decreased to different degrees, respectively; especially the change in FA was the most significant, fell to 61.55 % level of the fresh sample (Fig. 2C). FA was the raw material of other compounds, which could esterify cholesterol, reduce cholesterol and triglycerides in blood, improve brain cell activity, and promote memory and thinking ability (Goepfert & Poirier, 2007). The research found that the metabolism of glyceride and glycerol phospholipid were the main metabolic pathways during the storage of watermelon seed kernels. Therefore, the degradation of glyceride and glycerol phospholipid as well as the further degradation derived from the above degraded products might be one of

the reasons for the occurrence of PI, DG and other lipid contents (Wang, Wang, Qiu, & Li, 2020). Meanwhile, DG was a structured lipid formed by substituting hydroxyl groups in a fatty acid of glycerol salts. Studies proved that millet with high DG content had better effects on reducing visceral fat and blood lipids and inhibiting weight gain, so it was considered a safe and healthy edible lipid (Mai et al., 2020). Lipidomic data indicated that the lipids stored in watermelon seed kernels mainly existed in the form of TG (a series of species with the same total acyl carbon number and total double bonds). The decrease of TG content might be due to DG's degradation and other lipid molecules' decrease during the change of watermelon seed kernel lipids. DG could not only be used as a substrate to synthesize PC and PE through Kennedy pathway, but also be bound with protein kinase as the second messenger of signal transduction (Athenstaedt & Daum, 2006). It was the joint effort of the changes of various lipids that led to the decrease of TG content. Cer, a kind of decomposition product of sphingomyelin in the biofilm bilayer, was recognized a second messenger and played an extensive and important role in cell growth, proliferation, differentiation, apoptosis and damage (Zhang et al., 2021). PC was the main component of biomembrane, and during the process of oxidative rancidity, the content of PC was easily caused to decrease due to that watermelon seed kernels were subject to the influence of active free radicals, high temperature and/or strong light induction and other factors to undergo single bond cleavage and hydrogen rearrangement (Fu et al., 2020; Hu et al., 2022). These above data indicated that there was a significant difference between the oxidized and non-oxidized lipid subclasses in watermelon seed kernels.

Multivariate statistical analysis of lipid composition

To identify the changes of lipids in watermelon seed kernel before and after oxidative rancidity, methods of unsupervised principal component analysis (PCA) and partial least squares discriminant analysis (OPLS-DA) were used to analyze the composition of 220 matched lipids. PCA results showed that the lipid composition in CK and OD was significantly different (Fig. 3A). In OPLS-DA analysis, PCA1 was 50.3 % and PCA2 was 17.5 %, with a total of 88.2 %. CK and OD could be clearly distinguished. These results showed that there were significant differences in lipid composition before and after oxidative rancidity.

In order to further clarify the difference of lipid changes in watermelon seed kernels before and after oxidative rancidity, the lipid profiles at different stages of rancidity were obtained based on UPLC-QTOF-MS method, and the OPLS-DA model was established after the data were normalized. According to the threshold VIP > 1, the lipids with significant differences could be screened (the higher the VIP score of OPLS-DA model, the more likely it was to screen the lipid molecules as potential biomarkers) (Fig. 3B).

Table S2 showed the final screening results: there were 55 distinct lipids in total, including 27 TG, 7 DG, 8 PE, 6 PC, 2 LPE, 2 FA, 1 PG, 1 LPC and 1 PS, which could be used as potential biomarkers to distinguish watermelon seed kernel oxidative rancidity. It was seen from the table, during constant temperature storage, most of the significantly different lipids were down regulated, among which PE (34:1 | PE 16:0_18:1) displayed the most obvious change (down to 70.25 % of the fresh sample), then followed by TG (70:5 | TG 34:1_18:2_18:2) (down to 71.31 % of the fresh sample). In addition, the contents of these five lipid molecules significantly increased after oxidative rancidity, which were PC (35:3 | PC 17:1_18:2), PE (34:3 | PE 16:0_18:3), PG (O-36:3 | PG O-18:1_18:2), LPE (18:1) and DG (42:3 | DG 24:0_18:3), respectively. The main reason for the increase of lipid contents was due to the oxidative degradation of fatty acids. The results showed that during the storage period of watermelon seed kernels, their lipid contents showed an overall downward trend due to the influence of processes such as

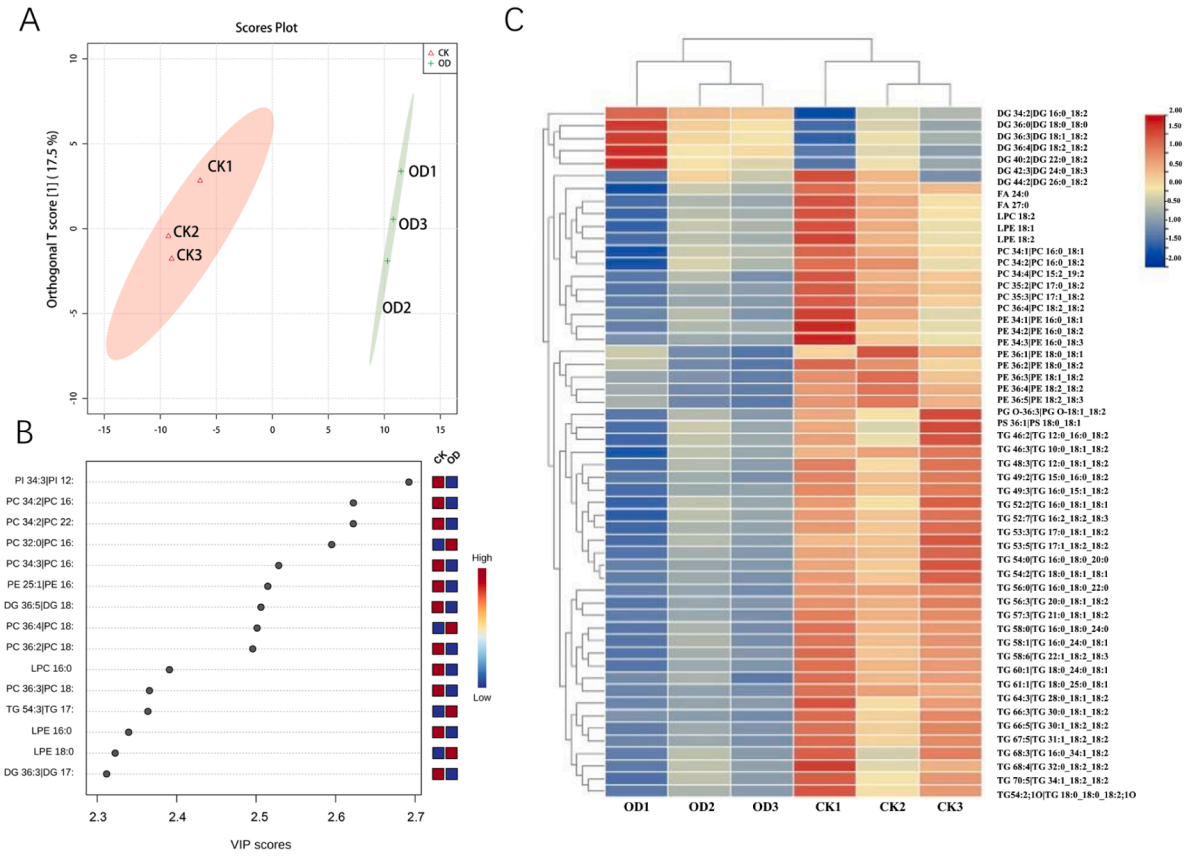

Fig. 3. Distribution of the content and relative percentage of different lipid subclasses in watermelon as well as the change histogram.

enzymatic oxidation and free radical chain reaction. However, due to the complexity of lipid oxidation and the continuous degradation of fatty acids, some lipids' contents increased simultaneously.

Correlation analysis between watermelon seed kernel lipids and flavor change

In this study, a total of 56 lipids with significant differences were screened, of which 5 lipids were significantly up-regulated and 51 lipids were significantly down-regulated. Regarding the relationship between these significantly changed lipids and the underlying changes in watermelon seed kernel lipids and flavor, the path enrichment analysis of GO and KEGG was conducted. As shown in Fig. 4, the metabolic pathways of lipid changes were mainly including metabolism of linoleic acid, glycerol phospholipid metabolism, the metabolism of glycine, serine and threonine, linolenic acid metabolism, sphingolipids metabolism, arachidonic acid metabolism, autophagy-others and glycosylphosphatidylinositol (GPI)-anchor biosynthesis, etc, among which, glycerol phospholipid metabolism and sphingolipid metabolism were the dominant metabolic pathways. Combined with the changes of significantly different lipids and the results of KEGG analysis, the experimental result predicted that the changes in watermelon seed kernel lipids before and after oxidative rancidity were mainly characterized by the changes of glycerides (TG) and glycerides (PC, PE).

During the rancidity process of watermelon seed kernels, the permeability of cell membrane increased or was destroyed, and the substances in cells were lost with the degradation or change of lipids. In this process, lipid change was a dynamic process: in the presence of phospholipase and lipase, glycerol phospholipids and glycerides were hydrolyzed to produce free fatty acids. However, ethanolamine (Etn) and choline (Cho) in watermelon seed kernels combined with diacylglycerol (DAG) could produce PE and PC (Liu et al., 2018) under the catalysis enzymes of 1,2-diacylglycerol ethanolamine phosphotransferase (CEPT1) and choline phosphotransferase (CHPT1). Meanwhile, PE could also be converted into PC under the action of phosphatidylethanolamine methyltransferase. In addition, DG released from TG degradation could be used as the substrate to synthesize PC and PE through Kennedy pathway as well (Athenstaedt & Daum, 2006).

The composition and changes of glycerol phospholipid had a great impact on the storage, processing and consumption of watermelon seed kernels. Yoon, Rico, Koh, and Kang (2012) found that one of the factors causing rice quality deterioration was that PC (phosphatidylcholine) in rice bran was easily degraded to phosphatic acid by phospholipase D, then led to the oxidative decomposition of free unsaturated fatty acids (mainly oleic acid and linoleic acid). In addition, PE and PC could be hydrolyzed by phospholipase A2G6 (PLA2G6) in organisms to produce free fatty acids (FFA). Zhang *et al* explored the changes of rice lipids in fresh and storage rice and proved that PC and PE would hydrolyze during rice storage (Zhang, Duan, Shang, Hong, & Sun, 2021).

During storage, the flavor of watermelon seed kernels would change significantly, which was closely related to its lipid changes. Based on exploration of changes in volatile compounds before and after watermelon seed kernel rancidity, 1-amyl alcohol and styrene were found to play a key role in the formation of watermelon seed kernel rancidity flavor; and the formation of these compounds was originated from the degradation of glycerol esters and glycerol phospholipids, in which the effect of glycerol phospholipid degradation on flavor was greater than that of glycerol ester degradation, and the main reason was due to the comparably higher proportion of unsaturated fatty acids (such as arachidonic acid) in glycerol phospholipids (Farmer & Mottram, 1990).

In the oxidative rancidity process of watermelon seed kernels, the glycerol ester and glycerol phospholipid were hydrolyzed to produce free fatty acids under the catalysis of lipase, and the conjugated hydroperoxyl fatty acids were further produced under the action of lipoxygenase. These acids were converted into volatile compounds such as carbonyl compounds under the action of hydroperoxide dehydratase, hydroperoxide lyase, hydroperoxide epoxidase and other enzymes (Ghnimi, Budilarto, & Kamal-Eldin, 2017). These carbonyl compounds could also be further degraded into alcohols (*trans*-2-hexenol, pentanol, etc.) with stronger flavor effects (Shahidi & Hossain, 2022). For instance, linoleic acid could generate 9-and 13 hydroperoxides under the action of oxygen in the environment. These hydroperoxide-derived alkoxy radicals cut C—O bonds could eventually produce various volatiles (Shahidi & Oh, 2020), among which linoleic acid was mainly originated from the degradation of glycerol phospholipids. In addition, the carbonyl compounds generated by lipid degradation could decarboxylate the amino acids in watermelon seed kernels and convert them into corresponding amines (Capozzi et al., 2017), and these amines could be further affected by the carbonyl compounds, and converted into corresponding Strecker aldehydes or olefins through elimination reaction, an example of the conversion of phenylalanine into styrene via oxidized lipids (Hidalgo & Zamora, 2007). By comparing the lipid changes and lipid metabolism pathways before and after watermelon seed kernel oxidative rancidity, the research found that glycerol ester

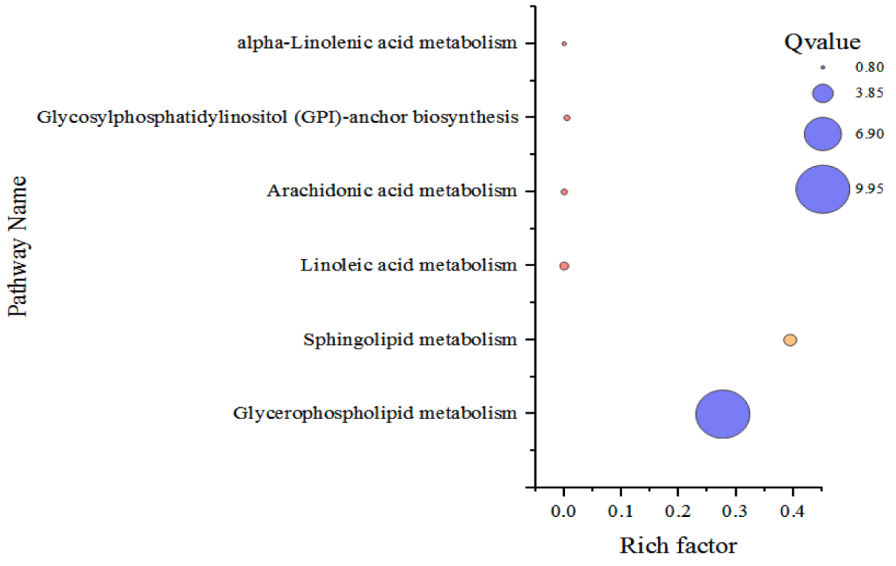

Fig. 4. Bubble diagram of KEGG metabolic pathway.

and glycerol phospholipid displayed significant changes in the process of watermelon seed kernel rancidity and showed direct impact on the flavor change of watermelon seed kernels. Combined with E-nose and GC-O-MS analysis of volatile compounds before and after watermelon seed kernel rancidity, it proved that 1-amyl alcohol and styrene had significant effects on the flavor of watermelon seed kernel rancidity and could be used as biomarkers for testing watermelon seed kernel rancidity.

Conclusion

The study explored the volatile compounds and lipid components in watermelon seed kernels before and after oxidative rancidity by means of E-nose, HS-SPME-GC-O-MS combined with UPLC-Q-Extractive orbitrap mass spectrometry. The results of E-nose and HS-SPME-GC-O-MS showed that the flavor of watermelon seed kernels changed significantly after oxidative rancidity. A total of 42 volatile compounds were identified, in which 1-pentanol and styrene had significant effects on the flavor of watermelon seed kernels; a total of 220 lipid molecules were identified by UPLC-Q-Extractive orbitrap mass spectrometry; 56 lipid molecules with significant differences were screened through multivariate statistical analysis; 9 metabolic pathways related to lipid changes were identified through the analysis of their correlation and the related metabolic pathways, among which glycerol phospholipid metabolism and glycerol metabolism were the main dominant pathways. The study also analyzed the changes of flavor and lipid in watermelon seed kernels before and after oxidative rancidity and clarified that 1-pentanol and styrene could be used as the biomarkers of oxidative rancidity of watermelon seed kernels, which could provide a theoretical basis for the identification of oxidative process during the storage of watermelon seed kernels and the development of new fresh-keeping technology. Further exploration on the molecular mechanism and regulation technology of watermelon seed kernel oxidative rancidity should be given more consideration in future.

CRediT authorship contribution statement

Xiongwei Yu: Writing – original draft, Investigation, Data curation, Conceptualization. **Bin Li:** Writing – review & editing, Methodology, Conceptualization. **Hui Ouyang:** Methodology, Investigation, Formal analysis. **Weijian Xu:** Validation, Formal analysis, Data curation. **Ruru Zhang:** Formal analysis, Data curation. **Xing Fu:** Methodology, Formal analysis. **Sihai Gao:** Software, Formal analysis, Data curation. **Shugang Li:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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.

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.2023.101108.

References

Adelina, N. M., Wang, H., Zhang, L., & Zhao, Y. (2021). Comparative analysis of volatile profiles in two grafted pine nuts by headspace-SPME/GC-MS and electronic nose as responses to different roasting conditions. *Food Research International, 140*, Article 110026.

Athenstaedt, K., & Daum, G. (2006). The life cycle of neutral lipids: Synthesis, storage and degradation. *Cellular and Molecular Life Sciences, 63*(12), 1355–1369.

Buthelezi, N. M. D., Tesfay, S. Z., & Magwaza, L. S. (2021). Influence of roasting on antioxidants, fatty acids, sensory properties and oxidative stability of macadamia nuts. *Scientia Horticulturae, 278*.

Cai, J. S., Zhu, Y. Y., Ma, R. H., Thakur, K., Zhang, J. G., & Wei, Z. J. (2021). Effects of roasting level on physicochemical, sensory, and volatile profiles of soybeans using electronic nose and HS-SPME-GC-MS. *Food Chemistry, 340*, Article 127880.

Capozzi, V., Fragasso, M., Romaniello, R., Berbegal, C., Russo, P., & Spano, G. (2017). Spontaneous food fermentations and potential risks for human health. *Fermentation, 3*(4), 49.

Carvalho, L. C., Leite, M. L., Morais, C. L. M., Lima, K. M. G., & Teixeira, G. H. A. (2019). Non-destructive assessment of the oxidative stability of intact macadamia nuts during the drying process by near-infrared spectroscopy. *Lwt, 103*, 101–107.

Chen, L., Ning, F., Zhao, L., Ming, H., Zhang, J., Yu, W., … Luo, L. (2023). Quality assessment of royal jelly based on physicochemical properties and flavor profiles using HS-SPME-GC/MS combined with electronic nose and electronic tongue analyses. *Food Chemistry, 403*.

Duduzile Buthelezi, N. M., Samukelo Magwaza, L., & Zeray Tesfay, S. (2019). Postharvest pre-storage processing improves antioxidants, nutritional and sensory quality of macadamia nuts. *Scientia Horticulturae, 251*, 197–208.

Farmer, L. J., & Mottram, D. S. (1990). Interaction of lipid in the maillard reaction between cysteine and ribose: The effect of a triglyceride and three phospholipids on the volatile products. *Journal of the Science of Food and Agriculture, 53*, 505–525.

Fu, M., Shen, X., Peng, H., Zhou, Q., Yun, J., Sun, Y., … Hou, R. (2020). Identification of rancidity markers in roasted sunflower seeds produced from raw materials stored for different periods of time. *Lwt, 118*.

Gao, Y., Cui, N., Liu, J., Ma, Q., Zhao, T., Yang, Z., … Liang, L. (2022). Application of metabolomics to explore the automatic oxidation process of hazelnut oil. *Food Research International, 162*.

Ghnimi, S., Budilarto, E., & Kamal-Eldin, A. (2017). The new paradigm for lipid oxidation and insights to microencapsulation of omega-3 fatty acids. *Comprehensive Reviews in Food Science and Food Safety, 16*(6), 1206–1218.

Goepfert, S., & Poirier, Y. (2007). Beta-oxidation in fatty acid degradation and beyond. *Current Opinion in Plant Biology, 10*(3), 245–251.

Hidalgo, F. J., & Zamora, R. (2007). Conversion of phenylalanine into styrene by 2,4-decadienal in model systems. *Journal of Agricultural and Food Chemistry, 55*(12), 4902–4906.

Hu, Q., Zhang, J., He, L., Xing, R., Yu, N., & Chen, Y. (2022). New insight into the evolution of volatile profiles in four vegetable oils with different saturations during thermal processing by integrated volatolomics and lipidomics analysis. *Food Chemistry, 403*, Article 134342.

Ivanova-Petropulos, V., Mitrev, S., Stafilov, T., Markova, N., Leitner, E., Lankmayr, E., & Siegmund, B. (2015). Characterisation of traditional Macedonian edible oils by their fatty acid composition and their volatile compounds. *Food Research International, 77*, 506–514.

Jia, W., Liu, Y., & Shi, L. (2021). Integrated metabolomics and lipidomics profiling reveals beneficial changes in sensory quality of brown fermented goat milk. *Food Chemistry, 364*, Article 130378.

Li, Z., Chu, S., Wang, P., Gao, S., Li, S., & Yu, X. (2020). Effects of irradiation treatment on protein structure and digestion characteristics of seed-watermelon (Citrullus lanatus var.) kernel protein. *Food Science and Biotechnology, 29*(9), 1201–1211.

Li, S., Li, Z., Li, X., Wang, P., Yu, X., Fu, Q., & Gao, S. (2020). Effect of AAPH oxidation on digestion characteristics of seed watermelon (Citrullus lanatus var) kernels protein isolates. *Food Science and Human Wellness, 9*(4), 402–410.

Liu, Y., Cong, P., Li, B., Song, Y., Liu, Y., Xu, J., & Xue, C. (2018). Effect of thermal processing towards lipid oxidation and non-enzymatic browning reactions of Antarctic krill (Euphausia superba) meal. *Journal of the Science of Food and Agriculture, 98*(14), 5257–5268.

Liu, Y., Fan, L., & Li, J. (2022). Flavor and compositional analysis of macadamia nuts during long-term storage. *Journal of Food Processing and.* Preservation.

Mai, Y., Huo, K., Yu, H., Zhou, N., Shui, L., Liu, Y., … Wang, L. (2020). Using lipidomics to reveal details of lipid accumulation in developing Siberian apricot (Prunus sibiricaL.) seed kernels. *GCB Bioenergy, 12*(7), 539–552.

Mohamed, A., Molendijk, J., & Hill, M. M. (2020). lipidr: a software tool for data mining and analysis of lipidomics datasets. *Journal of Proteome Research, 19*(7), 2890–2897.

Obi, O. F. (2016). Evaluation and modeling of the aerodynamic characteristics of watermelon seed of different varieties. *International Journal of Food Properties, 19*(10), 2165–2174.

Oliveira-Alves, S. C., Pereira, R. S., Pereira, A. B., Ferreira, A., Mecha, E., Silva, A. B., … Bronze, M. R. (2020). Identification of functional compounds in baru (Dipteryx alata Vog.) nuts: Nutritional value, volatile and phenolic composition, antioxidant activity and antiproliferative effect. *Food Research International, 131*, Article 109026.

Planque, M., Arnould, T., Delahaut, P., Renard, P., Dieu, M., & Gillard, N. (2019). Development of a strategy for the quantification of food allergens in several food products by mass spectrometry in a routine laboratory. *Food Chemistry, 274*, 35–45.
Shahidi, F., & Hossain, A. (2022). Role of lipids in food flavor generation. *Molecules, 27* (15), 16.
Shahidi, F., & Oh, W. Y. (2020). Lipid-derived flavor and off-flavor of traditional and functional foods: An overview. *In)*.
Su, X., Hurley, K., Xu, Z., Xu, Y., Rutto, L., O'Keefe, S., … Yin, Y. (2022). Performance of alternative drying techniques on hop (Humulus lupulus L.) aroma quality: An HS-SPME-GC-MS-O and chemometrics combined approach. *Food Chemistry, 381*, Article 132289.
Sun, J., Hu, P., Lyu, C., Tian, J., Meng, X., Tan, H., & Dong, W. (2022). Comprehensive lipidomics analysis of the lipids in hazelnut oil during storage. *Food Chemistry, 378*, Article 132050.
Sun, Y., Huang, Y., Lu, T., & Chen, X. (2022). Temporal kinetics of changes in color, phytochemicals, γ-aminobutyric acid, enzyme activity and antioxidant activity of coffee leaves during postharvest storage. *Scientia Horticulturae, 304*.
Thewes, F. R., Both, V., Thewes, F. R., Brackmann, A., Wagner, R., Ribeiro, S. R., … Rossato, F. P. (2021). Pecan storage: Effects of 1-MCP on the overall quality and volatile compounds profile of shelled and unshelled pecans. *Lwt, 145*.
Wang, L. J., Wang, L. B., Qiu, J., & Li, Z. G. (2020). Effects of superheated steam processing on common buckwheat grains: Lipase inactivation and its association with lipidomics profile during storage. *Journal of Cereal Science, 95*, 8.
Wani, A. A., Sogi, D. S., Singh, P., & Götz, A. (2013). Impacts of refining and antioxidants on the physico-chemical characteristics and oxidative stability of watermelon seed oil. *Journal of the American Oil Chemists' Society, 90*(9), 1423–1430.
Yoon, M. R., Rico, C. W., Koh, H. J., & Kang, M. Y. (2012). A study on the lipid components of rice in relation to palatability and storage. *Journal of the Korean Society for Applied Biological Chemistry, 55*(4), 515–521.
Zhang, D., Duan, X. L., Shang, B., Hong, Y., & Sun, H. (2021). Analysis of lipidomics profile of rice and changes during storage by UPLC-Q-extractive orbitrap mass spectrometry. *Food Research International, 142*, 8.
Zhang, H., Wang, J., Zhao, J., Sun, C., Wang, J., Wang, Q., … Feng, Z. (2021). Integrated lipidomic and transcriptomic analysis reveals lipid metabolism in foxtail millet (Setaria italica). *Frontiers in Genetics, 12*, Article 758003.