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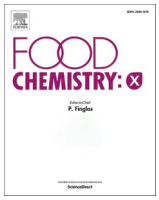

Effect of freeze-thaw treatment on the yield and quality of tiger nut oil

Zhenshan Zhang *, Xinyi Xie, Huijie Jia, Wu Le, Pengfei Xiang

College of Food Science and Technology, Henan University of Technology, Zhengzhou 450001, PR China

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ABSTRACT

To investigate the effect of freeze-thaw (FT) process on the yield and quality of tiger nut oil, tiger nuts were subjected to 0–12 cycles of FT treatment. Results indicated that FT treatment ruptured the cell structure of tiger nut, resulting in an increase in oil yield. Acid value (2.09–2.42 mg KOH/g) and peroxide value (0.40–0.42 mmol/kg) increased with the number of FT cycles, but the increments were small. Likewise, slight differences in fatty acid composition and thermal properties between control and FT-treated samples were observed. FT treatment remarkably increased the bioactive components (e.g., vitamin E, sterols, chlorophyll and carotenoids) in the oil and extended the oxidation induction time from 1.2 to 5.57 h. FT treatment altered the volatile composition of tiger nut oil, increasing the relative content of heterocycles and pyrazines such as 2-methoxy-4-vinylphenol, trimethylpyrazine and tetramethylpyrazine. It was suggested that FT treatment prior to oil extraction was beneficial to improve the oil yield and quality.

1. Introduction

Tiger nut is also known as ground almond, chufa, Zulu nut and rush nut in different countries and regions (Zhang & Sun, 2023). In fact, tiger nut is not a nut but rather a tiny tuber of the perennial sedge plant (*Cyperus esculentus* L). The tuber is the size of a chickpea and has a yellow, brown, red or black outer skin, depending on the variety (Rebezov et al., 2021). The name "Tiger Nut" comes from the stripes on the tuber, which resemble tiger stripes. Tiger nut has a unique chemical composition that combines the features of both nuts and tubers. It contains more water and carbohydrates and less protein and fat than nuts (Sanchez-Zapata, Fernandez-Lopez, & Angel Perez-Alvarez, 2012). Compared to other tubers: potato, sweet potato, yam, yacon and cassava, it contains less water, much more fat, fiber and protein (Sanchez-Zapata et al., 2012). Literature shows that tiger nut typically contains 22–45% lipids, 23–48% starch, 8–15% fiber and 3–8% protein (Yu et al., 2022). Carbohydrates are the primary nutrient in tiger nut, mainly in the form of starch and fiber. Tiger nut, even after drying, contains fewer calories than other nuts. Fresh tiger nut provides approximately 270 kcal per100 g, while dried tiger nut is approximately 430 kcal (Codina-Torrella, Guamis, & Trujillo, 2015). Valuable ingredients of tiger nut are phytosterols, mainly beta-sitosterol (approx. 50%), stigmasterol (approx. 20%) and campesterol (approx. 15%) (Rebezov et al., 2021). Their high concentration increases the value of tiger nut as food. In addition, tiger nut also contains many beneficial bioactive substances such as vitamin E, vitamin C, phenols, and minerals including potassium, phosphorus, sodium, calcium magnesium, manganese, iron, copper and zinc (Rebezov et al., 2021; Yu et al., 2022).

Tiger nut has a pleasant almond-coconut flavor and can be a valuable component of the diet. The history of the tiger nut as a foodstuff can be traced back 6000 years to ancient Egypt. Today, it is widely cultivated in Africa, Europe, North America and Asia including Ghana, Spain, Mexico and China (Ezeh, Gordon, & Niranjan, 2016; Sanchez-Zapata et al., 2012). In Spain, tiger nut is very popular to prepare a cold drink called "horchata de chufa". In Ghana, tiger nut is eaten raw as a snack or crushed and cooked into a delicious porridge (Yeboah, Mitei, Ngila, Wessjohann, & Schmidt, 2012). In addition, tiger nut can be used in the production of edible oil, biscuits, gluten-free bread, candy and pharmaceutical standards (Rebezov et al., 2021; Yu et al., 2022). The consumption of tiger nut can reduce the risk of colon cancer, heart disease, obesity, thrombosis and erectile dysfunctions (Rebezov et al., 2021; Sanchez-Zapata et al., 2012). Tiger nut is considered as a "superfood" that has not yet been fully developed.

In China, tiger nut is a new oil resource to replace soybean, as its oil yield per unit area is about four times that of soybean. Tiger nut oil is a high-quality edible oil with bright color and aromatic flavor. It shares a similar fatty acid profile with olive oil, hazelnut, macadamia nut, and avocado, and is widely regarded as a suitable alternative to olive oil (Ezeh, Gordon, & Niranjan, 2016; Rabail et al., 2021). The high level of monounsaturated fatty acids (>60%), mainly oleic acid, imparts a high

* Corresponding author.
E-mail address: zzsan010@haut.edu.cn (Z. Zhang).

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oxidative stability to tiger nut oil, making it suitable for frying processes. The abundant bioactive components, such as tocopherol, phytosterols, and phenolic substances, further enhance the oxidative stability and nutritional value of tiger nut oil. Studies show that the consumption of tiger nut oil is beneficial for antioxidation, blood sugar and blood lipids reduction, improvement in blood circulation and regulation of physiological metabolism (Rebezov et al., 2021; Rosello-Soto et al., 2018; Yu et al., 2022). In addition to being processed into frying oils, blending oils, and margarine for food applications, tiger nut oil can also be utilized for industrial purposes such as biodiesel, paint, cosmetics, and pharmaceutical (Rabail et al., 2021; Zhang & Sun, 2023). Therefore, tiger nut oil has great development value and broad market prospects.

Freeze-thaw (FT) treatment is a promising pretreatment method that uses ice crystals formed during the freezing process to destroy plant tissues and cell membranes, thereby increasing drying efficiency, reducing energy consumption or improving yield of products. For example, Zhang, Yu, Arun, and Zhou (2022) combined FT treatment with variable-temperature drying technique to enhance the drying rate of lotus roots by approximately 1.4 times, while reducing total energy consumption by about 22%. The study conducted by Jiao, Li, Chang, and Xiao (2018) demonstrated a significant enhancement in the yield of carotenoids in corn gluten meal (approximately 14 times higher than untreated) and an improvement in its antioxidant activity due to FT treatment. Moreover, Lee et al. (2020) showed that the oil yield of FT-treated perilla seeds was 2.5 times higher than that of untreated seeds. Checking the literature, no studies have been reported on the effect of freezing or FT treatment on the quality of tiger nut oil.

The purpose of this study was to investigate the effect of FT treatment on the yield and quality of oil extracted from tiger nuts. In this study, fresh tiger nuts were treated with 0–12 cycles of FT treatment. Subsequently, tiger nut oil was obtained by mechanical pressing. The microstructure of tiger nut with different FT treatments was observed by scanning electron microscopy (SEM). The quality of tiger nut oils was assessed by physicochemical indexes (acid value, peroxide value, and K_{232} and K_{268}), fatty acid composition, bioactive components (vitamin E, sterol, total phenol, carotenoids and chlorophyll), oxidative stability, thermal properties and volatile components.

2. Materials and methods

2.1. Materials

Fresh tiger nuts were purchased from the Henan New Crop Breeding Centre, China. The tiger nuts were carefully handpicked to remove impurities, broken and shriveled ones. Then they were sealed in a self-sealing bag and stored at 4 °C for future use.

The standards, including fatty acid methyl esters (FAMEs), sterols, tocopherols (TP) and tocotrienols (TT), were purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China). Other reagents and chemicals used in this study were of at least analytical purity.

2.2. FT treatment

FT treatment was conducted following the method outlined by Lee et al. (2020) with minor modifications. In brief, 500 g of tiger nuts were packed into self-sealing bags and frozen at −30 °C for 12 h. Subsequently, they were thawed at 15 °C for 12 h. The above steps were repeated for 2, 4, 6, 8, 10, and 12 cycles. The unfrozen tiger nuts were used as a control (CT). After treatments, all samples were dried at 37 °C until the moisture content reached approximately 8%. Finally, the dried samples were sealed and stored at 4 °C.

2.3. Microstructure of tiger nut

The morphological alterations of tiger nuts were observed using a Quanta-250 scanning electron microscope (FEI Co., Ltd., Oregon, USA). Tiger nuts with different FT cycles were sliced thinly and degreased with petroleum ether. Next, the slices were placed on an aluminum stub and sputtered with gold prior to examination under vacuum condition, with an accelerating voltage of 20 kV. The images were observed at 2000 × and 4000 × magnification, respectively.

2.4. Extraction of tiger nut oil

The oil extraction was completed using a hydraulic press (Bafang Machinery & Equipment Co., Ltd., Zhengzhou, China). The tiger nuts were crushed into powder before oil extraction. The powder was wrapped in skimmed gauze and pressed at room temperature with a pressure of 45 MPa for 30 min, repeating this process three times. The collected oil was centrifuged at 5000*g* for 20 min. The purified oil was filled into dark glass bottles and stored at 4 °C for further analysis. The oil yield was calculated using the following formula.

$$Oil\ yield(\%) = \frac{\text{weight of oil extracted}}{\text{weight of tiger nut sample}} \times 100 \quad (1)$$

2.5. Physicochemical characteristics

The peroxide value and acid value of tiger nut oil were measured using AOCS official methods Cd 8b-90 and Cd 3d-63, respectively. The extinction coefficients at 232 and 268 nm (K_{232} and K_{268}) were measured following the standard method of ISO 3656: 2002.

2.6. Fatty acid composition

The fatty acid composition of tiger nut oil was determined according to the method described in our recently published work (Zhang et al., 2023). In brief, fatty acids were derivatized to FAMEs, and then analyzed on an Agilent 7890B gas chromatograph equipped with a flame ionization detector (Agilent Technologies, Wilmington, USA). FAMEs were separated on an HP-88 capillary column (100 m × 0.25 mm i.d × 0.20 μm) with an injection volume of 1 μL and a split ratio of 30:1. The column temperature was held at 140 °C for 5 min, then increased to 240 °C at 4 °C/min and maintained for an additional 10 min. Helium was used as the carrier gas. The injector and detector temperature were set at 250 °C and 280 °C, respectively. The quantitative analysis of fatty acids was conducted using the peak area normalization method.

2.7. Vitamin E composition

The composition and content of vitamin E were determined using the method of Zhang et al. (2023b). A 0.5 g sample of tiger nut oil was weighed and mixed with 10 mL of *n*-hexane. The mixture was then filtered through a 0.22 μm organic membrane before HPLC analysis. The sample was analyzed on a Waters e2695 HPLC system (Waters Corporation, Milford, USA) equipped with a Waters X Bridge column (4.6 mm × 250 mm, 5 μm particle size) and a fluorescence detector. The mobile phase consisted of *n*-hexane: isopropanol (99:1, *v*/v) at a flow rate of 1 mL/min, while the column temperature was maintained at 35 °C. Excitation wavelength was set at 298 nm and emission wavelength at 325 nm for detection purposes. Quantification of vitamin E components relied on an external calibration curve using standards.

2.8. Sterol composition

The sterol composition of tiger nut oil was determined according to the method described by Zhang, Kang, and Che (2019). The analysis was performed on an Agilent 7890B gas chromatograph (Agilent Technologies, Wilmingston, USA) equipped with a flame ionization detector and a HP-5 column (ID 30 m × 0.32 mm, film thickness 0.25 μm). The column temperature was initially set at 285 °C for 30 min and then raised to 300 °C for 5 min. The injector temperature was 300 °C, while the

detector temperature was 360 °C. An injection volume of 1 μL and a spilt ratio of 20:1 was used. Nitrogen gas served as the carrier gas with a flow rate of 1.0 mL/min. Sterols were identified by comparing their retention times with standards, and the results were expressed as milligram per 100 g of oil (mg/100 g).

2.9. Carotenoids and chlorophyll

The content of carotenoids and chlorophyll in tiger nut oil was determined according to the method of Suri, Singh, and Kaur (2022). In brief, 1.5 g of tiger nut oil was accurately weighed and dissolved thoroughly in 5 mL of cyclohexane. The absorbance values at 470 nm and 670 nm were measured to calculate the content of carotenoids and chlorophyll using the following equations:

$$\text{Carotenoids}(\text{mg/kg}) = \frac{Abs_{470} \times 10^6}{2000 \times 100 \times density} \quad (2)$$

$$\text{Chlorophyll}(\text{mg/kg}) = \frac{Abs_{670} \times 10^6}{613 \times 100 \times density} \quad (3)$$

The density was obtained by calculating the ratio of mass to volume in the solution.

2.10. Total phenols content

The total phenols content was determined using the Folin-Ciocalteu method described by Zhang et al. (2023b). Briefly, 10 g of tiger nut oil were dissolved in 25 mL of *n*-hexane, and extracted three times with a 60% methanol solution (*v*/v). The supernatant obtained after centrifugation was separated and concentrated under nitrogen flow. Then, 0.3 mL of the concentrate was mixed with 3 mL of saturated sodium carbonate solution and 1 mL of Folin-Ciocalteu reagent. After standing at 45 °C for 90 min away from light, the absorbance at 720 nm was measured. The results were expressed as gallic acid equivalents (mg/kg) based on the calibration curve of gallic acid.

2.11. Oxidative stability

The oxidative stability of tiger nut oil was assessed using a Rancimat instrument Model 743 (Metrohm, Herisau, Switzerland). Specifically, 5 g of oil sample was heated at 120 °C with an airflow rate of 20 L/h. The result was automatically calculated by the instrument software and presented as the induction time in hours.

2.12. Thermal analysis

The thermal analysis of tiger nut oil was conducted using a Q20 differential scanning calorimeter (TA Instruments Ltd., New Castle, USA). A 10 g sample of the oil was enclosed in an aluminum pan and another empty sealed aluminum pan was used as a reference. The sample was equilibrated at 40 °C for 3 min, then cooled to −80 °C at a rate of 10 °C/min and held isothermal for 3 min before being heated back to 40 °C at the same rate. Nitrogen (99.999%) was used as the purge gas with a flow rate of 50 mL/min. The thermal characteristics including peak temperature (T_p) and enthalpy (ΔH) during cooling and heating were analyzed using TA Universal Analysis 2000 software (Version 4.5 A, TA instruments).

2.13. Volatile compounds

The volatile compounds were analyzed following the method outlined in our recent publication (Zhang et al., 2023b). Briefly, tiger nut oil was subjected to simultaneous distillation extraction (SDE) to collect volatile compounds, which were then analyzed using gas chromatography–mass spectrometry (GC–MS). The GC–MS conditions were as follows: an initial temperature of 40 °C was held for 3.5 min, followed by a gradual increase to 230 °C at a rate of 4 °C/min and held for 8 min. Finally, the temperature was raised to 280 °C at 10 °C/min and maintained for 5 min. Helium was the carrier gas with a flow rate of 1.8 mL/min. The electron ionization source operated at 70 eV and the ion source temperature was 230 °C. Full-scan mode was adopted with a scanning range of 30–500 *m/z*. Detected compounds were compared against the NIST17 library, retaining only those with a similarity greater than or equal to 90%. The retained compounds were further identified based on their retention indices (RI). Quantification of volatile components was accomplished by area normalization method (Sun, Zhang, Han, Wei, & Liu, 2022). The results were expressed as relative percentage.

2.14. Statistical analysis

The experiments were conducted in triplicate, and the results were presented as mean ± standard deviation. Analysis of variance (ANOVA) and Duncan's test ($p < 0.05$) of data was performed using SPSS statistics 24.0 software (International Business Machines Corporation, New York, USA).

3. Results and discussion

3.1. Oil yield

Oil yields from untreated control and FT-treated tiger nuts are shown in Fig. 1. It can be found that the FT treatment significantly affected the oil yield of tiger nuts ($p < 0.05$). As the number of FT cycles increased, the oil yield of tiger nuts gradually increased from 17.05% at the 0th FT cycle to 19.23% at the 12th FT cycle. The increase could be attributed to the physical damage caused by the formation of ice crystals during the freezing process. It is widely acknowledged that plant cells typically contain a certain amount of moisture, and freezing leads to an expansion in the volume of water. In addition, the elasticity of materials is reduced in the frozen state. Consequently, the formation of ice crystals disrupted the cellular structure of the tiger nut, such as the cell wall and cell membrane. With the increased number of FT cycles, the repeated formation and melting of ice crystals disrupted the tissue structure to a greater extent, facilitating easier release of oils from vesicles and thereby increasing oil yield (Phothiset & Charoenrein, 2014). This finding aligns with the report of Lee et al. (2020), who found that FT-treated perilla seeds had an oil yield 2.5 times higher than untreated seeds.

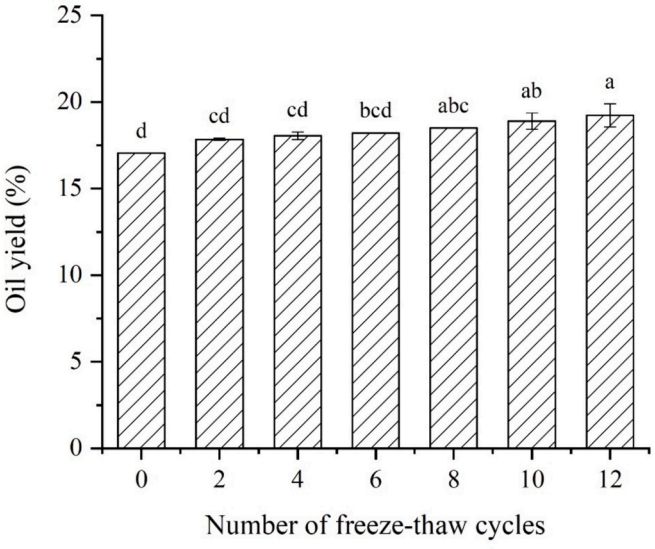

Fig. 1. Effect of freeze-thaw treatment on the oil yield of tiger nuts.

3.2. Microstructure of tiger nut

Fig. 2 illustrates the microstructure of tiger nuts with different numbers of FT cycles. The untreated tiger nuts exhibited intact cellular structures with oval to rounded starch granules that had smooth surfaces. However, after undergoing FT treatment, the surface of the starch granules became rough, microporous structures formed, and fragments of starch granules were observed. These variations were more pronounced with an increase in the number of FT cycles. This was probably due to the uneven moisture content inside and outside the starch granules. Upon freezing, the formation of ice crystals exerted a certain mechanical force on the surface of starch granules, resulting in compression and crushing that made their surface rougher. The melting of the ice crystals redistributed water within pores. The repeated formation and melting of ice crystals resulted in the appearance of more microporous structures on the surface of the starch granules (Liu et al., 2019; Tao, Zhang, Wu, Jin, & Xu, 2016). The breakdown of cellular structure through FT treatment could explain the increased oil yield observed in treated tiger nuts. Wang et al. (2020) also observed a similar disruption in microstructure for FT-treated potato starch along with destruction of its crystalline structure, decreased paste viscosity, and increased in vitro digestibility.

3.3. Physicochemical properties of tiger nut oil

Both the acid value and peroxide value play crucial roles in determining the quality of vegetable oil. The acid value reflects the content of free fatty acids in oils, while the peroxide value indicates the extent of primary oxidation. As shown in Table 1, tiger nut oil exhibited an increase in both acid value and peroxide value with an increasing number

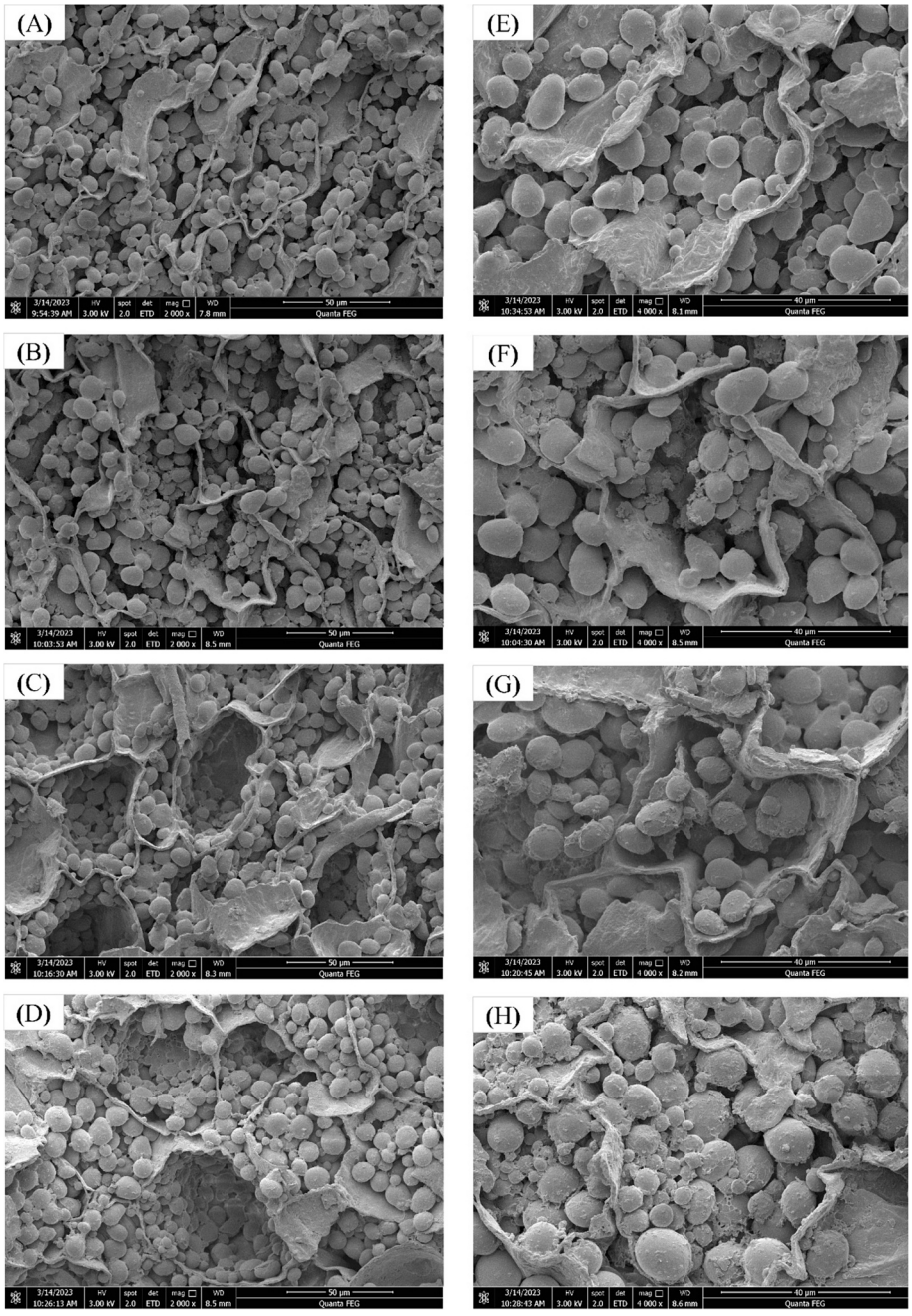

Fig. 2. SEM images of untreated and freeze-thaw treated tiger nuts (A, E: untreated; B, F: 4 cycles; C, G: 8 cycles; D, H: 12 cycles; A-D: magnification 2000×; *E*-H: magnification 4000×).

Table 1
Effect of freeze-thaw treatment on the physicochemical properties of tiger nut oil.

Parameters	Number of freeze-thaw cycles						
	0	2	4	6	8	10	12
AV(mg KOH/g)	2.18 ± 0.07^{cd}	2.09 ± 0.01^{d}	2.14 ± 0.01^{d}	2.26 ± 0.04^{bc}	2.35 ± 0.01^{ab}	2.40 ± 0.04^{a}	2.42 ± 0.07^{a}
PV(mmol/kg)	0.41 ± 0.01^{ab}	0.40 ± 0.00^{b}	0.40 ± 0.00^{b}	0.41 ± 0.00^{ab}	0.41 ± 0.01^{ab}	0.42 ± 0.00^{a}	0.42 ± 0.00^{a}
K_{232}	1.12 ± 0.01^{ab}	1.09 ± 0.00^{b}	1.10 ± 0.04^{b}	1.15 ± 0.03^{a}	1.15 ± 0.00^{a}	1.16 ± 0.00^{a}	1.16 ± 0.01^{a}
K_{268}	0.11 ± 0.01^{c}	0.10 ± 0.00^{c}	0.13 ± 0.00^{b}	0.14 ± 0.00^{b}	0.15 ± 0.00^{a}	0.15 ± 0.00^{a}	0.16 ± 0.00^{a}

Note: Different letters in the same row indicate significant differences ($p < 0.05$).

of FT cycles, particularly when exceeding 6 cycles. This may be attributed to the disruption of the cellular structure caused by FT treatment, which allowed for greater interaction between oil and intrinsic enzymes such as lipase and lipoxygenase, thereby enhancing hydrolysis and oxidation. Additionally, the compromised cellular structure enhanced exposure of the oil to air, thereby facilitating its further oxidation (Zhang et al., 2023b).

In addition, the oxidation degree of oils can also be assessed by measuring the specific extinction coefficients at 232 and 268 nm (K_{232} and K_{268}), which reflects the level of conjugated dienes and conjugated trienes resulting from primary and secondary oxidation of polyunsaturated fatty acids, respectively. As shown in Table 1, FT treatment had a significant effect ($p < 0.05$) on the values of K_{232} and K_{268}, and they gradually increased with the number of FT cycles. This further demonstrated that FT treatment can damage the structure of tiger nuts and encourage the oxidation of their contained oils. It should be emphasized that although these changes were induced by FT treatment, they were relatively limited in magnitude. In a previous study conducted by Lee et al. (2020), it was reported that FT treatment did not have a significant effect on the acid value and peroxide value of perilla seed oil. The conflicting conclusions may be due to the small number of FT cycles they used.

3.4. Fatty acid composition

Fatty acid composition has an important influence on the physical properties, stability and nutritional value of vegetable oils. As shown in Fig. S1 and Table 2, seven fatty acids were identified in tiger nut oils. The main fatty acid was oleic acid (71.42–72.02%), followed by palmitic acid (13.44–14.03%), linoleic acid (10.82–11.19%), and stearic acid (2.40–2.44%). There are also small amounts of palmitoleic acid (~ 0.3%), arachidic acid (~ 0.2%), and linolenic acid (~ 0.2%). The results are consistent with those reported by Guo, Wan, Huang, and Wei (2021), who extracted tiger nut oil using mechanical expression or/with critical fluid extraction. The abundance of oleic acid, an important monounsaturated fatty acid, indicated that tiger nut oil has excellent thermal stability and functional properties such as the prevention of cardiovascular disease (Ezeh, Gordon, & Niranjan, 2016).

As shown in Table 2, slight differences in fatty acid composition were observed between the control and FT-treated samples. Compared to the control group, the FT-treated samples exhibited higher levels of saturated fatty acids (SFA) and monounsaturated fatty acids (MUFA), but lower levels of polyunsaturated fatty acids (PUFA). The decrease in PUFA could be attributed to the oxidation of multiple double bonds in linoleic acid and linolenic acid (Cui et al., 2020). On the contrary, Lee et al. (2020) found no significant effect of FT treatment on the fatty acids of perilla seed oil.

Table 2
Effect of freeze-thaw treatment on the fatty acid composition of tiger nut oil.

Fatty acid (%)	Number of freeze-thawing cycles						
	0	2	4	6	8	10	12
C16:0	13.44 ± 0.01^{d}	13.53 ± 0.01^{c}	13.62 ± 0.03^{b}	13.48 ± 0.01^{d}	14.03 ± 0.01^{a}	13.47 ± 0.02^{de}	13.47 ± 0.01^{de}
C16:1	0.31 ± 0.00^{b}	0.31 ± 0.01^{ab}	0.31 ± 0.01^{ab}	0.32 ± 0.00^{b}	0.32 ± 0.00^{b}	0.32 ± 0.00^{b}	0.32 ± 0.00^{b}
C18:0	2.42 ± 0.00^{b}	2.44 ± 0.01^{a}	2.40 ± 0.00^{c}	2.42 ± 0.00^{b}	2.43 ± 0.01^{a}	2.44 ± 0.00^{a}	2.41 ± 0.00^{c}
C18:1	71.70 ± 0.01^{d}	71.93 ± 0.02^{b}	71.70 ± 0.01^{d}	71.98 ± 0.01^{ab}	71.42 ± 0.00^{e}	71.84 ± 0.06^{c}	72.02 ± 0.01^{a}
C18:2	11.19 ± 0.08^{a}	10.92 ± 0.01^{c}	11.09 ± 0.01^{b}	10.96 ± 0.01^{c}	10.97 ± 0.01^{c}	11.08 ± 0.00^{b}	10.82 ± 0.01^{d}
C20:0	0.22 ± 0.01^{a}	0.20 ± 0.00^{bc}	0.22 ± 0.00^{a}	0.20 ± 0.00^{bc}	0.21 ± 0.01^{ab}	0.21 ± 0.00^{ab}	0.20 ± 0.00^{c}
C18:3	0.22 ± 0.01^{a}	0.20 ± 0.00^{bc}	0.22 ± 0.00^{ab}	0.20 ± 0.00^{bc}	0.21 ± 0.01^{ab}	0.22 ± 0.00^{ab}	0.20 ± 0.00^{c}
SFA	16.25 ± 0.02^{d}	16.35 ± 0.02^{c}	16.41 ± 0.03^{b}	16.28 ± 0.01^{d}	16.84 ± 0.01^{a}	16.29 ± 0.02^{d}	16.27 ± 0.01^{d}
MUFA	72.00 ± 0.02^{d}	72.24 ± 0.03^{b}	72.01 ± 0.02^{d}	72.30 ± 0.01^{ab}	71.74 ± 0.00^{e}	72.16 ± 0.06^{c}	72.34 ± 0.01^{a}
PUFA	11.41 ± 0.09^{a}	11.12 ± 0.01^{c}	11.30 ± 0.00^{b}	11.16 ± 0.01^{c}	11.18 ± 0.01^{c}	11.30 ± 0.00^{b}	11.03 ± 0.00^{d}
UFA	83.41 ± 0.11^{ab}	83.36 ± 0.04^{ab}	83.32 ± 0.02^{b}	83.46 ± 0.02^{a}	82.92 ± 0.02^{c}	83.46 ± 0.06^{a}	83.37 ± 0.01^{ab}

Note: SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; UFA, unsaturated fatty acids; Different letters in the same row indicate significant differences ($p < 0.05$).

3.5. Vitamin E composition

Vitamin E is a natural fat-soluble antioxidant that is effective in preventing cardiovascular disease, inflammation and various cancers (Aggarwal, Sundaram, Prasad, & Kannappan, 2010). It cannot be synthesized in the body and must therefore be obtained from the diet, with edible oils being their most important source (Ma et al., 2023). Vitamin E is composed of eight naturally occurring isomers: four tocopherols (α-, β-, γ-, and δ-TP) and four tocotrienol (α-, β-, γ-, and δ-TT). Among them, α-TP has the strongest antioxidant capacity and activity (Nielsen & Hansen, 2008). As shown in Fig. S2 an Table 3, all eight isomers of vitamin E were detected in tiger nut oil, with a total amount ranging from 155.20 to185.19 mg/kg. Of these, α-TP was the most abundant, followed by β-TP, which accounted for approximately 70% and 22% of the total amount, respectively. These results are consistent with the report of Yeboah et al. (2012) who found that tiger nut oil contained α-TP (86.73 mg/kg) and β-TP (33.37 mg/kg), making a total tocopherol content of 120.1 mg/kg. Ezeh, Niranjan, and Gordon (2016) extracted tiger nut oil using four different methods and obtained tocopherols ranging from 142 to 205 mg/kg. Table 3 shows that vitamin E content increased significantly ($p < 0.05$) with an increasing number of FT cycles. The content reached a maximum value (185.19 mg/kg) at the 12th FT cycle, which was higher by19.32% compared to that of untreated sample. The increase in vitamin E content can be explained by the disruption of cellular structure and the expansion of intercellular gaps in the presence of ice crystals. It was demonstrated that repeated FT treatment can promote the release of more vitamin E from tiger nut.

Table 3
Effect of freeze-thaw treatment on the vitamin E composition of tiger nut oil.

Vitamin E(mg/kg)	Number of freeze-thaw cycles						
	0	2	4	6	8	10	12
α-TP	107.53 ± 2.92^{e}	112.05 ± 1.89^{d}	112.28 ± 1.42^{d}	110.20 ± 1.05^{de}	117.20 ± 1.21^{c}	123.00 ± 1.19^{b}	129.38 ± 1.69^{a}
α-TT	1.84 ± 0.10^{c}	1.24 ± 0.14^{d}	1.04 ± 0.08^{d}	3.56 ± 0.19^{a}	1.32 ± 0.10^{d}	3.06 ± 0.27^{b}	3.79 ± 0.33^{a}
β-TP	34.14 ± 0.25^{c}	34.23 ± 1.11^{c}	39.02 ± 1.14^{ab}	37.35 ± 1.03^{b}	38.31 ± 1.60^{ab}	37.27 ± 1.25^{b}	40.29 ± 0.77^{a}
γ-TP	3.60 ± 0.32^{ab}	3.56 ± 0.04^{ab}	3.21 ± 0.24^{bc}	3.86 ± 0.09^{a}	3.57 ± 0.09^{ab}	3.33 ± 0.24^{ab}	2.79 ± 0.30^{c}
β-TT	2.33 ± 0.15^{b}	2.56 ± 0.01^{b}	2.14 ± 0.01^{b}	3.40 ± 0.25^{a}	3.48 ± 0.43^{a}	2.49 ± 0.14^{b}	2.46 ± 0.11^{b}
γ-TT	3.03 ± 0.02^{e}	3.14 ± 0.06^{e}	3.55 ± 0.16^{cd}	4.22 ± 0.26^{a}	3.18 ± 0.04^{bc}	3.94 ± 0.12^{ab}	3.36 ± 0.18^{de}
δ-TP	0.69 ± 0.11^{b}	0.68 ± 0.03^{b}	0.68 ± 0.01^{b}	0.88 ± 0.13^{b}	0.69 ± 0.05^{b}	1.14 ± 0.14^{a}	0.90 ± 0.11^{b}
δ-TT	2.36 ± 0.24^{a}	2.17 ± 0.03^{a}	2.16 ± 0.09^{a}	2.40 ± 0.14^{a}	2.15 ± 0.05^{a}	2.18 ± 0.12^{a}	2.23 ± 0.19^{a}
ΣVE	155.20 ± 3.56^{e}	159.62 ± 2.97^{de}	164.06 ± 2.31^{cd}	165.87 ± 1.67^{cd}	170.54 ± 2.32^{bc}	176.41 ± 3.20^{b}	185.19 ± 2.67^{a}

Note: TP: tocopherol; TT: tocotrienol; ΣVE: total vitamin E. Different letters in the same row indicate significant differences ($p < 0.05$).

3.6. Sterol composition

Sterols, a natural active ingredient, have been found to possess the ability to reduce cholesterol absorption, boost immunity, and prevent cardiovascular diseases (Nattagh-Eshtivani et al., 2022). As shown in Fig. S3 and Table 4, three major sterols were detected in the oil obtained from untreated tiger nuts: β-sitosterol, campesterol and stigmasterol. Among them, β-sitosterol had the highest concentration (~136 mg/100 g), followed by campesterol (~36 mg/100 g) and stigmasterol (~34 mg/100 g). This finding is consistent with previous studies (Hu et al., 2020; Rosello-Soto et al., 2018; Yeboah et al., 2012). However, it should be noted that these studies reported varying total sterol content due to differences in tiger nut varieties, cultivation environments, and extraction methods. For example, Hu et al. (2020) showed that different extraction methods resulted in a total sterol content range of 580–673 mg/100 g for tiger nut oil. Rosello-Soto et al. (2018) reported a total sterol content range of 72.63–96.21 mg/100 g for tiger nuts from six different countries.

Table 4 reveals that FT treatment had a significant effect ($p < 0.05$) on sterol content in tiger nut oil. The sterol content positively correlated with an increase in the number of FT cycles. After undergoing 12 cycles of FT treatment, the total sterol content increased to 239.14 mg/100 g, which was 16.28% higher than the untreated sample. Furthermore, it was observed that the initial four cycles of FT treatment contributed most significantly to the increase in total sterol content, while the subsequent cycles showed a trend of decreasing efficiency. It can be explained that the first few FT cycles caused the most damage to the cellular structure of tiger nuts.

3.7. Carotenoids and chlorophyll

Carotenoids and chlorophyll are common natural pigments found in vegetable oils, and their consumption is associated with the reduction of non-communicable diseases such as cancer, diabetes and obesity (Cortez, Luna-Vital, Margulis, & Gonzalez de Mejia, 2017). As depicted in Fig. 3, the oil extracted from untreated tiger nuts exhibited a carotenoids content of 4.75 mg/kg and a chlorophyll content of 0.36 mg/kg. Statistical analyses revealed that FT treatment had a significant effect ($p < 0.05$) on the carotenoids and chlorophyll content of tiger nut oil. Both the chlorophyll and carotenoids content increased gradually with an increasing number of FT cycles. However, unlike chlorophyll, there was no significant increase in carotenoids content when the number of FT cycles exceeded 8 times. The maximum values of carotenoids and chlorophyll after FT treatment were 5.41 mg/kg and 0.66 mg/kg, respectively. Apart from the destructive effect of ice crystals on the cellular structure, the collapse or rupture of protein and starch was partially responsible for the increase in carotenoids and chlorophyll content (Jiao et al., 2018; Wang et al., 2020). These results matched those observed in earlier studies, where Jiao et al. (2018) found that FT treatment on corn gluten meal increased the extraction yield (up to 14-fold) of carotenoids and that the yield was influenced by factors such as FT temperature, number of FT cycles, and moisture content.

3.8. Total phenols

Total phenols, including phenolic acids and flavonoids, are secondary metabolites of plants and occur naturally in a variety of foods (Han et al., 2020). They have many biological activities such as antioxidation, anti-inflammation, antimicrobial activity, antitumor and cardiovascular regulation (Zhang et al., 2022). In addition, these compounds can inhibit lipid oxidation by scavenging free radicals and converting phenolic radicals into non-oxidative forms (Zhan, Zhu, & Sun, 2019). As shown in Fig. 3, the total phenol content decreased with an increasing number of FT cycles, especially after >4 cycles. The decrease in total phenols was partly attributed to the oxidation of polyphenols and partly probably due to the loss of certain water-soluble polyphenols during the thawing process of ice crystals (Bassey, Sun, Esua, & Cheng, 2023). The relatively stable total phenol content during the initial FT cycles may be a result of a balance between polyphenol release caused by cell structure damage and their subsequent loss. In recent studies conducted by VanderWeide et al. (2020), it was reported that freezing disrupted cell vacuoles of grape seed and increased the extraction of total phenolics. Oszmianski, Wojdylo, and Kolniak (2009) investigated the effect of FT treatment on the polyphenol content in frozen strawberries and found that strawberries lost 4.5–33.6% of their polyphenols after freezing, with significant variations among different varieties. Therefore, the effect of FT treatment on total phenol content is dependent on both the specific products being treated as well as the FT conditions such as temperature and number of cycles.

Table 4
Effect of freeze-thaw treatment on the sterol composition of tiger nut oil.

Sterol(mg/100 g)	Number of freeze-thaw cycles						
	0	2	4	6	8	10	12
Campesterol	35.51 ± 0.62^{e}	38.14 ± 0.16^{d}	41.65 ± 0.29^{bc}	42.00 ± 0.50^{ab}	42.55 ± 1.52^{ab}	40.17 ± 0.02^{c}	43.48 ± 0.27^{a}
Stigmasterol	34.12 ± 0.27^{e}	36.27 ± 0.47^{d}	36.73 ± 0.71^{d}	38.39 ± 0.05^{c}	39.06 ± 0.84^{c}	46.75 ± 1.09^{a}	41.44 ± 0.16^{b}
β-Sitosterol	136.04 ± 0.62^{e}	141.30 ± 1.51^{d}	147.07 ± 0.22^{c}	147.12 ± 0.34^{c}	152.78 ± 0.16^{a}	149.74 ± 0.55^{b}	154.22 ± 0.36^{a}
Total sterols	205.66 ± 1.52^{d}	215.72 ± 1.82^{d}	225.46 ± 0.63^{c}	227.51 ± 0.78^{c}	234.39 ± 2.20^{b}	236.67 ± 1.66^{ab}	239.14 ± 0.79^{a}

Note: Different letters in the same row indicate significant differences ($p < 0.05$).

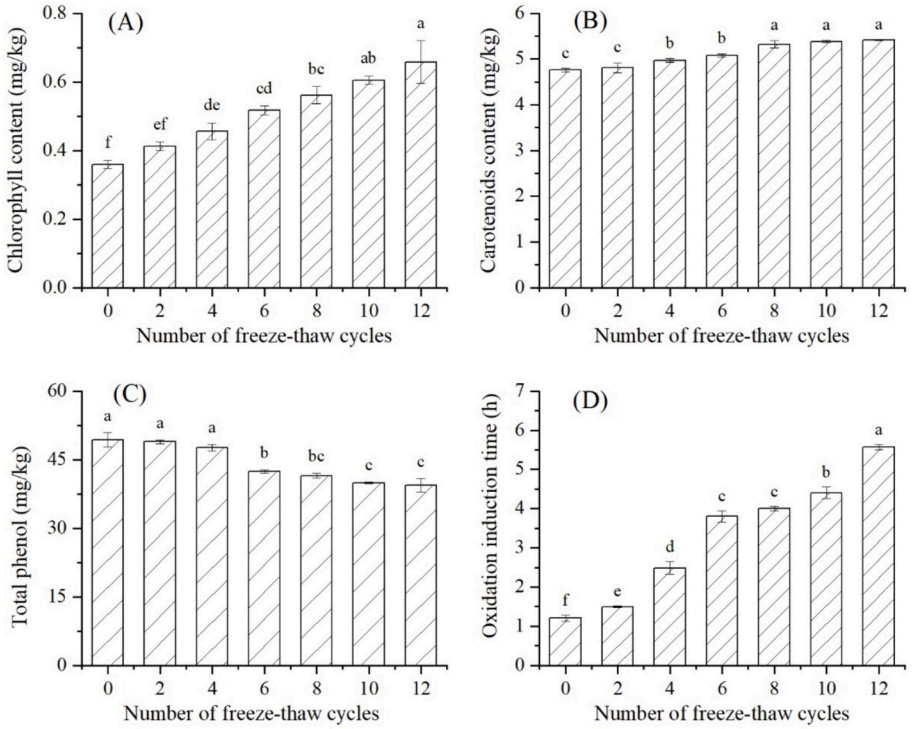

Fig. 3. Effect of freeze-thaw treatment on the chlorophyll, carotenoids and total phenol content, and oxidation induction time of tiger nut oil.

3.9. Oxidative stability

The oxidative stability of oil reflects its ability to resist oxidative deterioration during storage and use, which can be evaluated by the oxidation induction time (OIT). In general, a longer OIT means better oxidative stability of the oil. As shown in Fig. 3, the OIT of tiger nut oil significantly increased with an increasing number of FT cycles. The OIT of the oil extracted from untreated tiger nut was 1.2 h. In contrast, the OIT of oil extracted from FT-treated tiger nut was in the range of 1.50–5.57 h, which increased by 0.25–3.64 times compared to untreated samples. The oxidative stability of oils is also closely related to their fatty acid composition, antioxidant content, and the positional distribution of different fatty acids in triglycerides. In this study, the increase of OIT may be attributed to the fact that oil samples from frozen-thawed tiger nut contained more antioxidant components such as vitamin E, carotenoids. It should be noted that vitamin E and carotenoids had both antioxidant and pro-oxidant properties, depending on their concentration. Shadyro, Sosnovskaya, and Edimecheva (2020) demonstrated that the addition of 5 mg of β-carotene per 100 g of flaxseed oil inhibited the formation of oxidation products. However, when carotenoids concentration exceeded 10 mg/100 g, the oxidation process was significantly accelerated.

3.10. Thermal properties

Fig. 4 shows the crystallization and melting curves of tiger nut oil extracted from tiger nut with different number of FT cycles. As shown in Fig. 4(A), three exothermic peaks appeared on the crystallization curves of tiger nut oil. The first peak was obtained at around −14 °C (T_p), which can be attributed to the crystallization of oil fraction consisting mainly of saturated fatty acids such as palmitic acid and stearic acid. The shallow peak at −35 °C may be caused by a transition in the crystalline form of triacylglycerols. The largest peak observed around −50 °C probably resulted from the oil fraction containing large amounts of unsaturated fatty acids, which had an enthalpy of 23.36–24.44 J/g. FT treatment resulted in a slight shift of the crystallization peak towards higher temperatures and an increase in crystallization enthalpy. This may be due to oils subjected to FT treatment containing more micronutrients, such as phytosterol, vitamin E and pigments, whose presence interfered with the crystallization process of triacylglycerols. However, there was no significant difference in the crystallization curves among oil samples subjected to different number of FT cycles.

As shown in Fig. 4(B), the melting curves of tiger nut oil consisted of one exothermic peak at approximately −29 °C and two endothermic peaks at around −4.5 °C and 6.5 °C, respectively. The exothermic peak may be resulted from the transition/rearrangement of triacylglycerol polymorphic crystals into more stable forms (Zhang, Zhang, Xie, & Che, 2019). The major and minor endothermic peaks were related with the melting of unsaturated triacylglycerols and saturated triacylglycerols, respectively. Notably, Fig. 4(B) shows that the FT treatment had a minimal effect on the melting curves of tiger nut oil, indicating that the quality of the oil extracted from FT-treated tiger nut remained excellent.

3.11. Volatile compounds

The gas chromatograms of volatile compounds in tiger nut oil with different FT cycles are shown in Fig. S4. A total of 28 volatile compounds were identified in tiger nut oils, as listed in Table 5. These compounds were classified into 4 hydrocarbons, 16 aldehydes, 2 ketones, 3 phenols and 3 heterocyclic compounds. The main volatile compounds with a relative content of >5% included (E,E)-2,4-decadienal, nonanal (E,Z)-2,4-decadienal, (E)-2-decenal, and 2-undecenal. In addition, the content of octane, hexanal, (E)-2-heptenal, octanal all exceeded 2%.

FT treatment had a significant effect on the volatile composition of tiger nut oil. A similar phenomenon was also found in the study conducted by Lee et al. (2020), where they investigated the impact of FT treatment on perilla seed oil. Comparison to the untreated samples, the FT-treated samples exhibited higher levels of 2-methoxy-4-vinylphenol, trimethylpyrazine and tetramethylpyrazine, while showing lower amounts of nonanal, (E,Z)-2,4-decadienal and (E,E)-2,4-decadienal. 2-Methoxy-4-vinylphenol was detected as the predominant phenolic substance in the volatiles of tiger nut oil, which is widely found in various

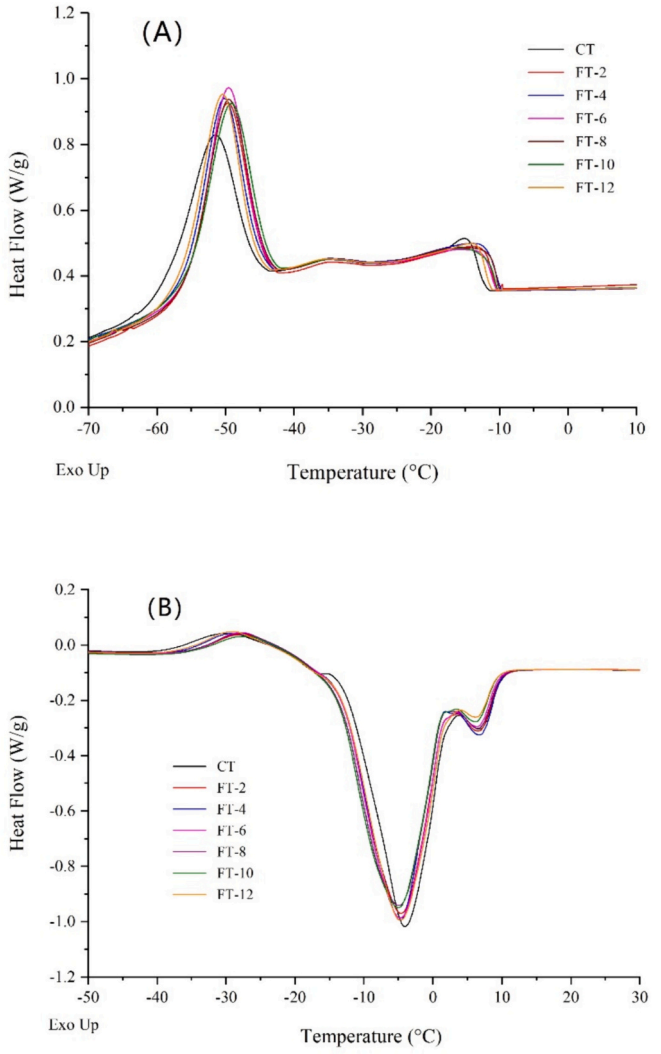

Fig. 4. Effect of freeze-thaw treatment on the thermal properties of tiger nut oil.

plant seed oils and especially in their roasted oil (Yin et al., 2021). In previous reports, trimethylpyrazine and tetramethylpyrazine were mainly found in oils prepared by thermal pretreatment, while they were rarely detected in untreated oils (Yin et al., 2021). This is the first report of the abundant presence of trimethylpyrazine and tetramethylpyrazine in the FT-treated tiger nut oil. In addition, Calva-Estrada, Utrilla-Vazquez, Vallejo-Cardona, Roblero-Perez, and Lugo-Cervantes (2020) reported that trimethylpyrazine and tetramethylpyrazine were the primary pyrazine components in the volatiles of chocolate, with their odor described as cocoa, roasted nuts, peanuts, coffee and earthy. Therefore, the oil derived from FT-treated tiger nut could potentially serve as an ingredient in the production of chocolate.

4. Conclusions

The present study investigated the physicochemical properties, fatty acid composition, bioactive compounds, oxidation stability, thermal properties and volatile profile of oil obtained from FT-treated tiger nuts and compared them with those from untreated tiger nuts. Our finding revealed that FT treatment obviously increased the oil yield from tiger nuts by 4.5% to 12.8%. Although there were slight adverse effects observed in terms of acid value, peroxide value and total phenol content, these were compensated by a considerable enhancement in oxidative stability and levels of vitamin E, sterols, chlorophyll and carotenoids. In

Table 5
Effect of freeze-thaw treatment on the volatile components of tiger nut oil (%).

No.	Volatile compounds	RI	Molecular formula	Number of freeze-thaw cycles		
				0	6	12
	Hydrocarbons					
1	Heptane	707	C_7H_{16}	0.43 ± 0.04^{c}	2.35 ± 0.12^{a}	0.86 ± 0.04^{b}
2	1-Octene	803	C_8H_{16}	0.15 ± 0.01^{a}	ND^{c}	0.06 ± 0.00^{b}
3	Octane	811	C_8H_{18}	2.29 ± 0.04^{c}	3.29 ± 0.08^{a}	2.65 ± 0.13^{b}
4	Dodecane	1215	$C_{12}H_{26}$	0.83 ± 0.02^{a}	ND^{c}	0.28 ± 0.00^{b}
	Aldehydes					
5	Pentanal	711	$C_5H_{10}O$	1.00 ± 0.09^{b}	1.87 ± 0.09^{a}	0.61 ± 0.02^{c}
6	Hexanal	815	$C_6H_{12}O$	4.00 ± 0.35^{b}	5.23 ± 0.10^{a}	2.63 ± 0.04^{c}
7	(E)-2-Hexenal	871	$C_6H_{10}O$	0.11 ± 0.03^{b}	0.33 ± 0.06^{a}	0.07 ± 0.02
8	Heptanal	917	$C_7H_{14}O$	1.11 ± 0.00^{b}	2.33 ± 0.07^{a}	0.85 ± 0.02^{c}
9	(E)-2-Heptenal	974	$C_7H_{12}O$	2.11 ± 0.14^{b}	3.05 ± 0.01^{a}	1.36 ± 0.01^{c}
10	Benzaldehyde	982	C_7H_6O	0.03 ± 0.01^{b}	0.14 ± 0.05^{a}	0.09 ± 0.01^{ab}
11	Octanal	1020	$C_8H_{16}O$	2.32 ± 0.20^{a}	4.25 ± 0.11^{a}	2.50 ± 1.14^{a}
12	5-Ethylcyclopent-1-enecarboxaldehyde	1049	$C_8H_{12}O$	0.31 ± 0.02^{a}	0.27 ± 0.03^{a}	ND^{b}
13	(E)-2-Octenal	1077	$C_8H_{14}O$	1.43 ± 0.04^{a}	1.49 ± 0.31^{a}	0.98 ± 0.02^{a}
14	Nonanal	1123	$C_9H_{18}O$	22.88 ± 1.21^{a}	14.16 ± 0.27^{b}	12.46 ± 0.40^{b}
15	(E)-2-Nonenal	1180	$C_9H_{16}O$	0.63 ± 0.01^{b}	0.93 ± 0.10^{a}	0.44 ± 0.01^{c}
16	Decanal	1225	$C_{10}H_{20}O$	0.99 ± 0.13^{a}	ND^{c}	0.55 ± 0.08^{b}
17	(E)-2-Decenal	1282	$C_{10}H_{18}O$	7.63 ± 0.26^{b}	10.68 ± 0.11^{a}	5.63 ± 0.21^{c}
18	(E,Z)-2,4-Decadienal	1317	$C_{10}H_{16}O$	12.61 ± 0.32^{a}	6.73 ± 0.49^{c}	9.60 ± 0.02^{b}
19	(E,E)-2,4-Decadienal	1342	$C_{10}H_{16}O$	28.51 ± 0.41^{a}	20.60 ± 0.04^{b}	20.04 ± 0.23^{b}
20	2-Undecenal	1386	$C_{11}H_{20}O$	6.54 ± 0.44^{b}	11.15 ± 0.22^{a}	5.21 ± 0.12^{c}
	Ketones					
21	Acetoin	726	$C_4H_8O_2$	ND^{b}	ND^{b}	3.76 ± 0.10^{a}
22	2-Heptanone	907	$C_7H_{14}O$	0.17 ± 0.01^{a}	0.24 ± 0.04^{a}	ND^{b}
	Phenols					

(*continued on next page*)

Table 5 (*continued*)

No.	Volatile compounds	RI	Molecular formula	Number of freeze-thaw cycles		
				0	6	12
23	2-Methoxy-4-vinylphenol	1351	$C_9H_{10}O_2$	1.63 ± 0.53^c	5.93 ± 0.08^b	18.96 ± 0.09^a
24	2,6-Di-t-butylphenol	1470	$C_{14}H_{22}O$	0.28 ± 0.00^a	0.41 ± 0.18^a	0.35 ± 0.03^a
25	2,4-Di-tert-butylphenol	1551	$C_{14}H_{22}O$	0.47 ± 0.28^a	0.26 ± 0.15^a	0.51 ± 0.10^a
	Heterocyclic compounds					
26	Trimethylpyrazine	1022	$C_7H_{10}N_2$	ND^b	ND^b	1.46 ± 0.04^a
27	Tetramethylpyrazine	1087	$C_8H_{12}N_2$	0.21 ± 0.00^c	2.49 ± 0.17^b	7.23 ± 0.08^a
28	2-pentylfuran	1007	$C_9H_{14}O$	1.31 ± 0.00^b	1.82 ± 0.12^a	0.88 ± 0.02^c

addition, FT treatment had a limited effect on the fatty acid composition and thermal properties of tiger nut oil, but noticeably altered its volatile compound composition. FT treatment can be utilized as a pretreatment technique to enhance the oil yield from tiger nut and to produce tiger nut oil of superior quality.

CRediT authorship contribution statement

Zhenshan Zhang: Writing – review & editing, Resources, Funding acquisition. **Xinyi Xie:** Writing – original draft. **Huijie Jia:** Writing – original draft, Investigation, Data curation. **Wu Le:** Software, Formal analysis. **Pengfei Xiang:** Visualization, Software.

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.2024.101733.

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