Food Chemistry: X 19 (2023) 100767

Contents lists available at ScienceDirect

Food Chemistry: X

journal homepage: www.sciencedirect.com/journal/food-chemistry-x

Comparison of volatile and nonvolatile metabolites in green tea under hot-air drying and four heat-conduction drying patterns using widely targeted metabolomics

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A R T I C L E I N F O

Keywords:
Heat-conduction drying
Hot-air drying
Green tea
Volatile metabolites
Nonvolatile metabolites

A B S T R A C T

Hot-air and heat-conduction drying are the most common drying patterns in green tea production. However, the differences between them in terms of the resulting green tea chemical compounds have not been illustrated systematically. In this study, 515 volatile and 204 nonvolatile metabolites were selected to compare the differences between hot-air drying green tea (HAGT) and four heat-conduction drying green teas (HCDGTs) using widely targeted metabolomics. The results showed notable changes in volatile compounds; for example, two kinds of HCDGTs preferred to form chestnut-like and caramel-like key odorants. In addition, 14 flavonol glycosides, 10 catechins, 9 phenolic acids, 8 amino acids, 7 flavonols, and 3 sugars were significantly changed between HAGT and HCDGTs ($p < 0.05$), presenting a tremendous discrepancy in the transformation of nonvolatile compounds. Our results provide clear guidance for the precise manufacturing of green tea by four common heat-drying patterns and hot air-drying patterns.

1. Introduction

Green tea is a globally consumed tea. Usually, the initial processing of green tea involves spreading, fixation, and drying. Drying is a key part of the initial tea making process that removes excess water while forming different sensory qualities. During the drying process, some insoluble substances in tea undergo decomposition and isomerization, which improves the taste, the appearance, and develops the tea's pure aroma (Shao et al., 2022; Wang et al., 2022). According to traditional drying patterns, green tea can be divided into roasted green tea, baked green tea, and solar-dried tea (Kang, 2016). Different drying patterns result in the distinctive flavor of green tea. In recent years, microwave drying, vacuum freeze drying, and far-infrared drying patterns have been successively used in tea drying processes with the rapid development of technology, but hot-air drying and heat-conduction drying are still the most common drying patterns in green tea production, and they produce baked green tea and roasted green tea, respectively (Liu, Wang, Li, Wang, Tang & Li, 2015; Chen, Wang, Wu, & Zhang, 2014).

At present, hot-air drying mainly uses a chain plate pattern by heating the air as a medium to make static tea leaves lose moisture (Fig. 1), and the representative green tea is called Maofeng, which is widely consumed in China. Heat-conduction drying patterns generally refer to flat-frying, carding-frying, roller-frying, and caldron-frying in daily green tea manufacturing and are famous for Longjing, Needle-shaped tea, Fragrant tea, and Bead-shaped tea. Different from hot air-drying, the tea leaves in the heat conduction drying process are in motion. This means the tea leaves move continuously inside the equipment to form a unique movement under different external forces so that the tea leaves are squeezed and penetrated by the heated inner wall of the equipment to achieve drying and shaping (Fig. 1). Furthermore, tea

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https://doi.org/10.1016/j.fochx.2023.100767
Received 20 April 2023; Received in revised form 19 June 2023; Accepted 20 June 2023
Available online 24 June 2023

leaves under heat-conduction drying patterns are subjected to diverse heating methods through different devices, which may reveal unique intrinsic qualities. For instance, it was found that there were great disparities in pyrazines in carding-frying green tea and flat-frying green tea (Yang et al., 2020). In addition, roller-frying was reported to produce roasty-like and burnt-like aroma compounds in green tea processing (Zhu et al., 2021). In a previous study, the influence on tea quality among various drying patterns was researched, while the comparison of green tea metabolites between heat-conduction drying and hot-air drying patterns has not been systematically studied.

The objective of this study was to compare the differences in volatile and nonvolatile metabolites of green tea between the four most commonly used heat-conduction drying patterns (roller-frying, caldron-frying, carding-frying, and flat-frying patterns) and the traditional hot air-drying pattern. This study may reveal the influence of hot-air drying and heat-conduction drying patterns on green tea products and provide academic support for the orthonormal and precision processing of high-quality green teas.

2. Materials and methods

2.1. Chemicals and reagents

2-Octanol was purchased from TCI Chemical Industry Development (Shanghai, China). Optima TM mass spectrometry grade methanol, acetonitrile and formic acid were purchased from Fisher Scientific (Fair Lawn, USA). Mass spectrometry grade ammonium bicarbonate was purchased from Sigma–Aldrich Co. (St. Louis, USA). The isotope labeling internal standard was purchased from Cambridge Isotope Laboratories Inc. (Tewksbury, USA) and Toronto Research Chemicals (Toronto, Canada). Ultrapure water (18.2 MΩ·cm) was prepared using a Milli-Q purified water system (Merck KGaA, Darmstadt, Germany).

2.2. Sample preparation

Tea leaves (one bud with two leaves) [Camellia sinensis (L.) O. Kuntze] of "Fuxuan No.9" were picked from the tea plantation at Yibin, Sichuan, China, in June 2022. The green tea was manufactured as follows: (1) Spreading: Plucked tea leaves were spread at a temperature of 25 ± 3.0 °C with a relative humidity of 70 ± 5.0% until the moisture of tea leaves reached 70%. (2) Fixating: The spread tea leaves were fixed at a temperature of 260 °C. (3) Rolling: The soft leaves were rolled for 40 min. (4) Drying: Hot-air drying and four heat-conduction drying treatments were applied to ensure that the temperature of the rolled tea leaves reached and was maintained at 100 °C until its moisture content reached approximately 6%. Hot air-drying green tea (HAGT), 1 kg/m^2 rolled leaves were uniformly spread out in a chain plate pattern (6CHZ-16; Fujian Jiayou Tea Patternry Intelligent Technologies Inc., Fujian, China) for approximately 20 min. Roller-frying green tea (RFGT), 30 kg rolled leaves were heated in a roller-frying pattern (6CCP-110; Fujian Jiayou Tea Patternry Intelligent Technologies Inc., Fujian, China) for approximately 30 min. Caldron-frying green tea (CalFGT), 20 kg rolled leaves were heated in a Caldron-frying pattern (6CCGQ-50; Fujian Jiayou Tea Patternry Intelligent Technologies Inc., Fujian, China) for approximately 120 min. Carding-frying green tea (CarFGT), 1 kg rolled leaves were heated in a carding-frying pattern (6CMD-6018, Zhejiang Lvfeng Patternry Co., Ltd., Zhejiang, China) for approximately 15 min. Flat-frying green tea (FFGT), 70 g rolled leaves were heated in a flat-frying pattern (6CCB-80ZD, Zhejiang Lvfeng Patternry Co., Ltd., Zhejiang, China) around 6 min (Fig. 1).

Leaves of each sample were ground to powder for further detection, and the experiment was conducted in triplicate.

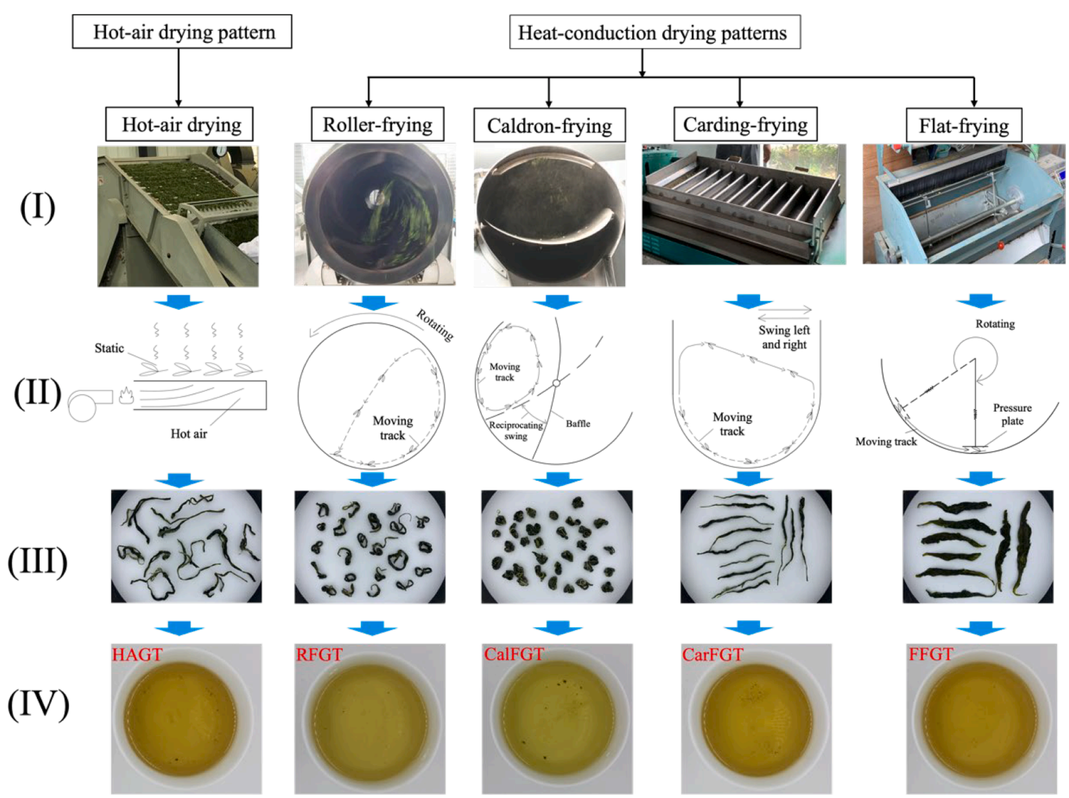

Fig. 1. The illustration of differences between hot-air drying and four types of heat-conduction drying patterns. (I) Physical picture of hot-air drying and four types of heat-conduction drying patterns. (II) Movement trajectory and heating process of green tea. (III) Appearance of green tea products. (IV) The infusions of hot-air drying tea and four types of heat-conduction drying teas. HAGT, hot-air drying green tea; RFGT, roller-frying green tea; CalFGT, caldron-frying green tea; CarFGT, carding-frying green tea; FFGT, flat-frying green tea. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Volatile metabolite analysis

Tea samples (100 ± 5.0 mg) were taken into a 20 mL headspace vial (Agilent Technologies, USA). Five milliliters of saturated NaCl solution and 10.0 μL of 2-octanol (10.0 mg/L stock in dH_2O) were added as internal standards. Then, the vial was incubated in a water bath at 60 °C for 30 min with the DVB/CAR/PDMS fiber head (Supelco) inserted. All samples were repeated three times.

The detection was performed by Biotree Biomedical Technology Co., Ltd. (Shanghai, China) (Hwang, Yang, Lee, & Ha, 2020). All samples were analyzed by a gas chromatograph system coupled with a spectrometer (GC–MS) using an Agilent 7890 gas chromatograph system coupled with a 5977B mass spectrometer. The desorption time was 4 min. The ultrainert capillary column was DB-Wax (30 m × 250 μm × 0.25 μm) and injected in splitless mode. Helium (99.999%) was used as the carrier gas, the front inlet purge flow was 3.0 mL/min, and the gas flow rate through the column was 1 mL/min. The initial temperature was kept at 40 °C for 4 min, then raised to 245 °C at a rate of 5 °C/min, kept for 5 min. The injection, transfer line, ion source and quad temperatures were 250, 250, 230 and 150 °C, respectively. The energy was −70 eV in electron impact mode. The mass spectrometry data were acquired in scan mode with a m/z range of 20–400 and a solvent delay of 0 min.

For qualitative analysis, Chroma TOF 4.3X software of LECO Corporation and NIST database were used for raw peak exacting, data baseline filtering and calibration of the baseline, peak alignment, deconvolution analysis, peak identification, integration, and spectrum match of the peak area (Kind et al., 2009). The relative content of volatile compounds was calculated based on the internal standards.

2.4. Nonvolatile metabolite analysis

Samples (200 ± 2.0 mg) were accurately weighed and placed in a 15 mL plug centrifuge tube (Corning Incorporated, USA), and 5 mL of 70% (v/v) methanol (preheated to 70 °C) was added, stirred, and immediately placed in a 70 °C water bath for extraction for 10 min (stirring every 2 min). Then, the tubes were cooled to room temperature and centrifuged at 1360 × g for 10 min. The supernatant was transferred to 10 mL volumetric flasks, and extraction was performed twice. The combined extracts were mixed, diluted to 10 mL, and filtered through a 0.22-μm membrane. The tea metabolite extract was transferred to the sample flask for metabolomic analysis by liquid chromatography-high-resolution orbital trap mass spectrometry.

The detection was performed by IPhenome Biotechnology (Yun Pu Kang) Inc. (Dalian, China) (Deng et al., 2021). Metabolites were determined by a Thermo Dionex UltiMate 3000™ ultrahigh-performance liquid chromatography system (Thermo Fisher Scientific, USA) coupled with a Q Exactive™ quadrupole-orbitrap high-resolution mass spectrometer (UPLC-HRMS; Thermo Fisher Scientific, USA). Chromatographic conditions: Acquity UPLC HSS T_3 column (2.1 × 100 mm, 1.8 μm, Waters Corporation, USA), mobile phase A was 0.1% (v/v) formic acid–water, mobile phase B was 0.1% (v/v) formic acid-acetonitrile, flow rate was 0.4 mL/min and column temperature 50 °C. The mobile phase linear gradient was as follows: 0 min, 95% A; 0.5 min, 95% A; 18 min, 60% A; 20 min, 10% A; 20.9 min, 10% A; 21 min, 95% A; 25 min, 95% A. The injection volume was 3 μL.

Mass spectrometry conditions: (1) Ionization parameters: heated electrospray ionization source, spray voltage 4.0 kV (ESI positive ion mode) and −3.5 kV (ESI negative ion mode), sheath gas 45 arb, auxiliary gas 10 arb, heater temperature 350℃, capillary temperature 320℃. (2) Full scan parameter: scan range was 100–1000 m/z. ESI positive and negative ionization switching mode. The mass spectrometry resolution was 35,000 FWHM (full width at half-maximum peak height), automatic gain control threshold was 3E6, and ion implantation time was 15 ms. (3) Full scan and data-dependent MS^2 (full scan-ddMS^2) parameters: the resolutions of primary and secondary MS were set at 70,000 and 17,500 FWHM, respectively, and the parameters of primary MS were the same as above. The main parameters of the secondary mass spectrum are as follows: automatic gain control threshold 1E5, normalized collision energy 30 ± 15%, TopN 7, isolation window 1.0 Da, dynamic exclusion 4 s.

2.5. Data processing and analysis

Each data point was repeated three times, and the results were expressed as the average of the three replicates. Student's t test was performed using Excel (Microsoft Corp., Redmond, WA, USA). A bar chart was generated by Origin 8.0 (Origin Lab Inc., Northampton, MA, USA). Principal component analysis (PCA), Venn analysis and heatmap clustering analysis were performed using the R packages ggbiplot, ggVennDiagram and pheatmap, respectively.

3. Results and discussion

3.1. Comparison of volatile metabolites in HAGT and HCDGTs

The unique aroma characteristics of different green teas are produced by the comprehensive manifestation of different volatile metabolites. After matching and screening, 515 volatile compounds in green tea samples were identified in this study (Table S1), including 97 alcohols, 94 alkanes, 78 alkenes, 79 ketones, 50 esters, 44 aldehydes, 36 heterocycles and 37 other compounds. Based on the content of volatile metabolites, an unsupervised principal component analysis (PCA) was used to describe the variety of volatile compound profiles in green tea samples (Fig. 2A). Green tea samples were clearly divided into five groups according to hot-air drying and heat-conduction drying treatments (principal components 1 and 2 explained 38.3% and 20.6%, respectively), indicating that different drying processes caused significant differences in aroma characteristics ($p < 0.05$). As shown in Fig. 2B, there were 296 common volatile compounds among the five groups, indicating that they shared the same overall aroma characteristics of green tea. The overall trend of volatile substance quantity was RFGT (430) > FFGT (417) > CarFGT (411) > CalFGT (406) > HAGT (402), which showed that heat-conduction drying can improve the number of volatile metabolites in green tea compared with hot-air drying, and roller-frying could produce the most abundant volatile metabolites among them. In the heat-conduction drying patterns, tea leaf cells were broken under constant friction to patterns, leading to an increase in the spill of volatile compounds and their precursors, promoting the formation of more volatile metabolites (Wang et al., 2022). Under the same conditions, the tea leaves obtained the largest movement track in the roller-frying pattern which might produce the largest number of volatile metabolites (Fig. 1). However, the tea leaves were in a static state during hot-air drying, so the cell breakage rate was lower than that of HCDGTs. Besides, thermal reaction time of the tea leaves in drying also have a significant impact on the formation and conversion of volatile compounds.

To describe the changes in overall volatile metabolites under different drying patterns, a heatmap was generated based on the content of seven volatile metabolite categories in Fig. 2C. The heatmap showed that there was no consistent difference between HAGT and HCDGTs. Aldehydes and heterocycles showed higher levels in RFGT, while alcohol and ester contents were higher in CalFGT. Alkanes, alkenes and ketones were abundant in both CalFGT and RFGT. In contrast, FFGT and CarFGT showed lower contents of volatile metabolites. The overall variation trend of these volatile components was CalFGT > RFGT > HAGT > CarFGT > FFGT, which decreased gradually with the shortening of drying time. The results suggested that the total content of the main volatile components of green tea was determined by drying time, probably because the tea leaves were slowly heated during the drying process to prolong the drying time, which made the nonenzymatic degradation and oxidation more able to fully produce more volatile

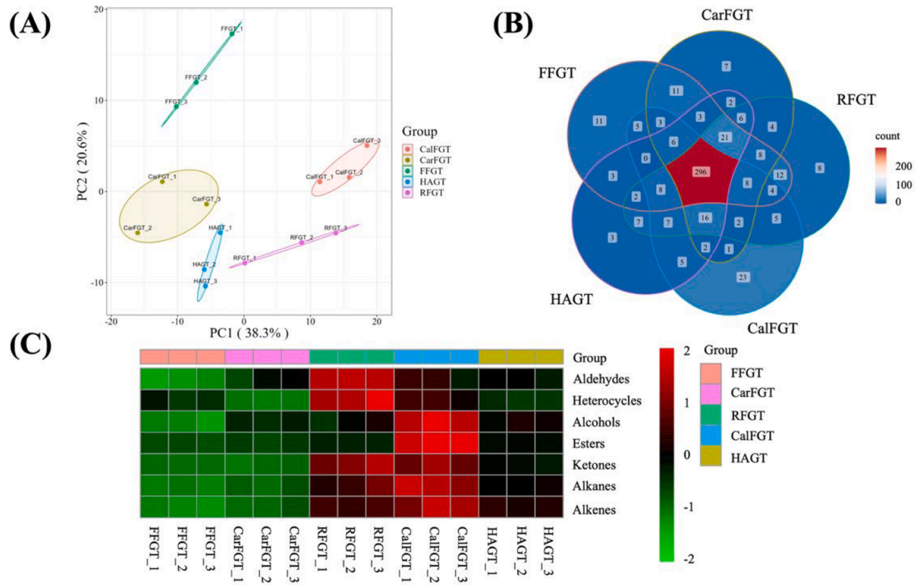

Fig. 2. Volatile metabolites in hot-air drying green tea and four types of heat-conduction drying green teas. HAGT, hot-air drying green tea; RFGT, roller-frying green tea; CalFGT, caldron-frying green tea; CarFGT, carding-frying green tea; FFGT, flat-frying green tea. (A), PCA score. (B), Venn diagram. (C), heat map of volatile compound categories. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compound contents (Feng et al., 2019).

As far as we know, there are only a few key aroma odorants that play an important role in the formation of tea aroma (Shi et al., 2021). Chestnut-like aroma is an important characteristic aroma of high-quality green tea. The key odorants contributing to chestnut-like aromas have been systematically researched and reported (Zhu et al., 2018; Yin et al., 2019). Thirteen chestnut-like key odorants were identified in this study, including (E, E)-3,5-octadien-2-one; (E)-2-octenal; benzaldehyde; butanal, 3-methyl-; benzeneacetaldehyde; furan, 2-pentyl-; linalool; nonanal; geraniol; 5,9-undecadien-2-one, 6,10-dimethyl-; (E)-4,8-dimethylnona-1,3,7-triene; *cis*-3-hexenyl *cis*-3-hexenoate and octanal (Fig. 3A). Interestingly, CalFGT had the most chestnut-like aromas, 10 of

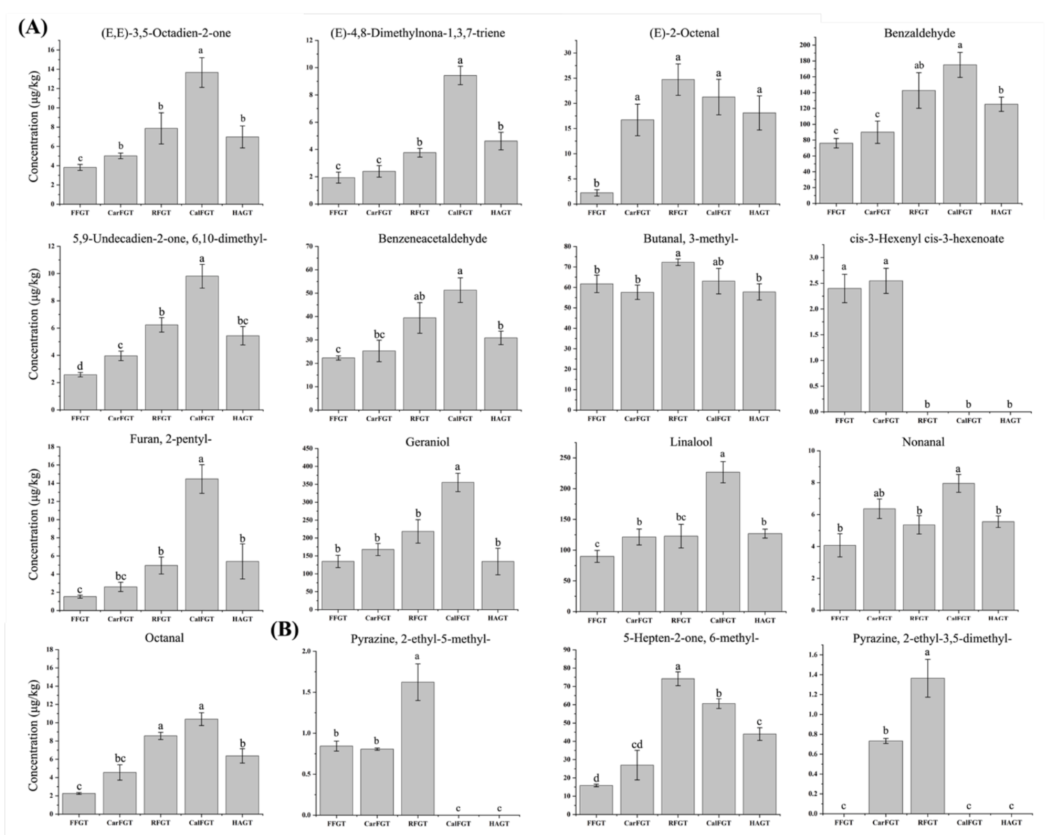

Fig. 3. Key volatile compounds of chestnut-like aroma (A) and caramel-like aroma (B) in hot-air drying green tea and four types of heat-conduction drying green teas. HAGT, hot-air drying green tea; RFGT, roller-frying green tea; CalFGT, caldron-frying green tea; CarFGT, carding-frying green tea; FFGT, flat-frying green tea.

which showed the highest concentration, and 6 of which were significantly higher than those of the other groups ($p < 0.05$). The results showed that it was more beneficial to produce a chestnut-like aroma by using caldron-frying than hot air-drying and the other three heat-conduction drying patterns. On the other hand, 3 caramel-like key odorants were observed among tea samples, including 5-hepten-2-one, 6-methyl-; pyrazine, 2-ethyl-3,5-dimethyl- and pyrazine, 2-ethyl-5-methyl- (Fig. 3B) (B.Y. Wang et al., 2022; J. Wang et al., 2022). We found that all the caramel-like key odorants from RFGT were significantly higher than those from the other groups ($p < 0.05$), while pyrazine, 2-ethyl-3,5-dimethyl- and pyrazine, 2-ethyl-5-methyl- were not found in CalFGT and HAGT. The results indicated that roller-frying was preferred to produce green tea with a caramel-like aroma compared to other treatments.

It is clear that most chestnut-like key odorants presented a similar increasing trend in HCDGTs, which was CalFGT > RFGT > CarFGT > FFGT. Chestnut-like green tea contains more volatile compounds with high boiling points (Wang, Zhu, Zhang, Shi, Lin & Lv, 2021). We suggest that prolonging the drying time may be beneficial to improve the chestnut-like aroma of green tea in the heat-conduction drying process. Pyrazine is generated by the reaction of sugars and amino acids under high-temperature conditions in a process called the Maillard reaction. Pyrazine has been reported to play an important role in the characteristic caramel-like flavor of green tea due to its strong odor (Sasaki et al., 2017). In this study, FRGT possessed the highest contents of pyrazine compounds; however, these compounds were not found in HAGT and CarFGT. We can infer that heating time and motion state both have important influences on the Maillard reaction. For instance, although CalFGT has suffered the longest heating time, the bead-like shape made it harder to heat internally. Therefore, we suggest that different drying patterns may affect the generation of crucial volatile components in green tea through different mechanical dynamics.

3.2. Comparation of nonvolatile metabolites in HAGT and HCDGTs

The variation in volatile metabolites commonly accompanied by changes in nonvolatile compounds. In this research, a nontargeted metabolomics technique was used to identify and quantitatively detect green tea metabolites with deep coverage. After data collation, 204 compounds of tea samples were identified, including 51 amino acids, 36 flavonol glycosides, 23 catechins, 16 phenolic acids, 11 organic acids, 11 carbohydrates, 10 nucleotides, 7 flavonols, 3 theaflavins, 3 thearubigins, 2 alkaloids, and 31 other compounds (Table S2). Orthogonal partial least squares-discriminant analysis (OPLS-DA) models were used to explain the differences between hot-air drying and heat-conduction drying on nonvolatile profiles. As shown in Fig. 4, the results showed that the models were robust and had strong forecasting ability. Each sample was clearly separated into two groups, which demonstrated that the

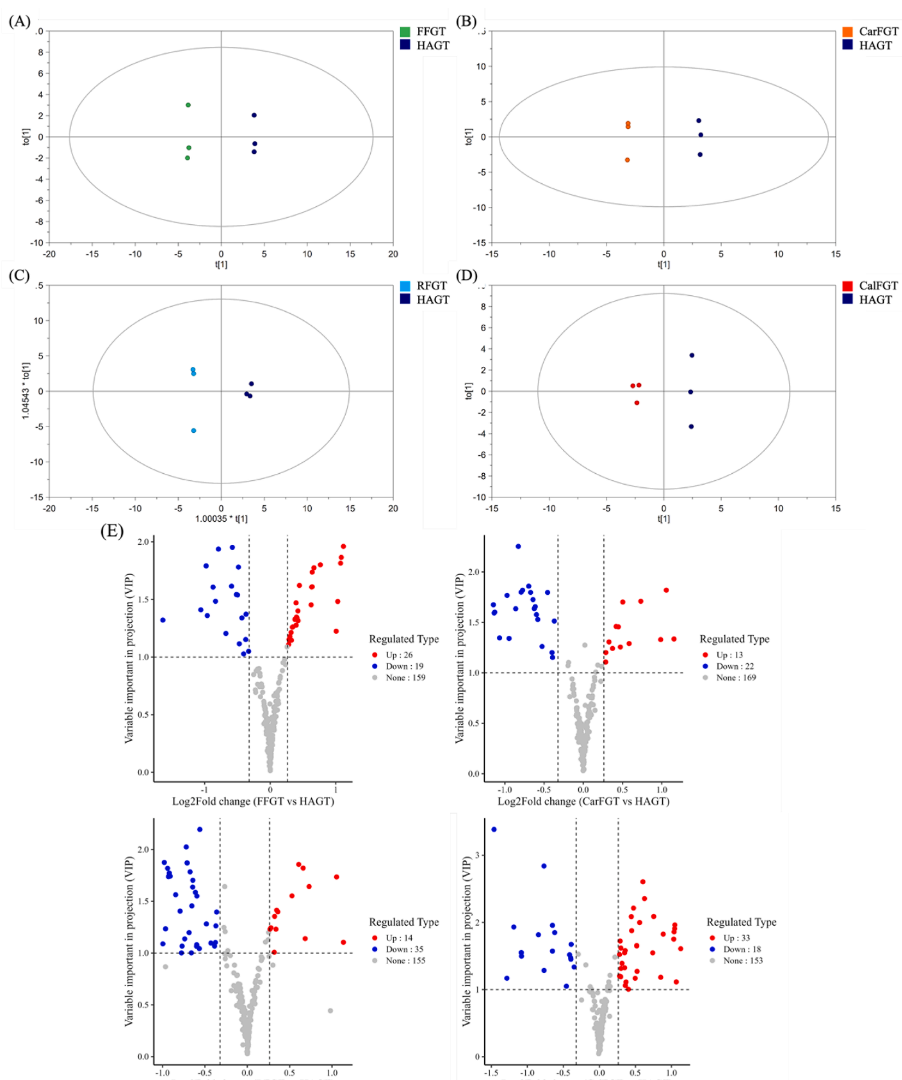

Fig. 4. The OPLS-DA score plot and volcano plot of nonvolatile metabolites in hot-air drying green tea compared with four types of heat-conduction drying green teas, respectively. (A), $R^2Y = 1$, $Q^2 = 0.979$, intercepts of $Q^2 = -0.199$; (B), $R^2Y = 1$, $Q^2 = 0.925$, intercepts of $Q^2 = -0.039$; (C), $R^2Y = 0.997$, $Q^2 = 0.946$, intercepts of $Q^2 = -0.047$; (D), $R^2Y = 0.996$, $Q^2 = 0.873$, intercepts of $Q^2 = -0.107$. HAGT, hot-air drying green tea; RFGT, roller-frying green tea; CalFGT, caldron-frying green tea; CarFGT, carding-frying green tea; FFGT, flat-frying green tea.HAGT, hot-air drying green tea. RFGT, roller-frying green tea; CalFGT, caldron-frying green tea; CarFGT, carding-frying green tea; FFGT, flat-frying green tea. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

nonvolatile metabolite contents between HAGT and HCDGTs were different. Afterward, the differential metabolites of HAGT relative to HCDGTs were analyzed by variable importance in the project (VIP) ≥ 1 and fold change ≥ 1.2 or ≤ 0.8. The volcano plots showed great variations between HAGT and HCDGTs (Fig. 4). There were 78 differential metabolites determined in HCDGTs compared to HAGT, among which FFGT, CarFGT, RFGT, and CalFGT were 45 (26 up, 19 down), 35 (13 up, 22 down), 49 (14 up, 35 down), and 51 (33 up, 18 down), respectively. The results demonstrated that great disparities in chemical reactions occurred in nonvolatile metabolites in green tea during hot-air drying and heat-conduction drying processes. Specifically, Table S3 shows that flavonol glycosides had the greatest differential number, 20 of which were upregulated or downregulated between HAGT and HCDGTs, followed by amino acids, catechins, phenolic acids, flavonols and carbohydrates. However, the results showed that the differential nonvolatile metabolites between each HCDGT and HAGT were distinct. For instance, 9 amino acids were upregulated in CalFGT, but only 6 in FFGT, 5 in CarFGT, and 3 in RFGT were upregulated. The results demonstrated that each heat-conduction drying pattern had a different influence on the nonvolatile metabolite content of green tea during the drying process, which might be related to the different dynamic principal exerted by each heat-conduction drying pattern.

Student's *t* test was further performed for the 78 differential metabolites, and a total of 51 compounds showed significant differences ($p < 0.05$), including 14 flavonol glycosides, 10 catechins, 9 phenolic acids, 8 amino acids, 7 flavonols and 3 sugars (Table S4). The results indicated that hot-air drying and heat-conduction drying had significant differences in flavor metabolites, such as flavonol glycosides, catechins, phenolic acids, amino acids, flavonols and sugars, which contribute greatly to the taste of tea infusion.

3.2.1. Amino acids and sugars

It has been reported that approximately 1–4% of amino acids are found in dry tea leaves (Zhao et al., 2013). As shown in Fig. 5, eight amino acids showed significant changes between HAGT and HCDGTs, including guanidinobutanoic acid, L-leucine, trimethyl-L-lysine, L-tryptophan, *N*-acetyl-L-phenylalanine, *N*-acetyl tryptophan and glutathione. Seven of them were significantly upregulated in CalFGT, and five amino acids were upregulated in FFGT, while there were fewer changes in CarFGT and RFGT ($p < 0.05$). Overall, the amino acids in CalFGT and FFGT were found to be apparently higher than those in HAGT. The changes in amino acids might be attributed to the degradation of proteins during the drying process (Chen, Shi, Mu, Chen, Dai & Lin, 2020). Our research presented a high level of glutathione in HAGT, which indicated that heat-conduction drying has a better effect on facilitating protein degradation and producing more amino acids than hot-air drying. In addition, many amino acids are important precursors involved in the formation of volatile compounds (Wang et al., 2019), and the amino acid derivatives found to be upregulated in HCDGTs compared with HAGT, including trimethyl-L-lysine, *N*-acetyl-L-phenylalanine and *N*-acetyl tryptophan, indicated that there was a dramatic conversion of amino acids in heat-conduction drying. The formation and conversion rate of amino acids may be related to the dynamic heating mode of tea leaves under different drying patterns.

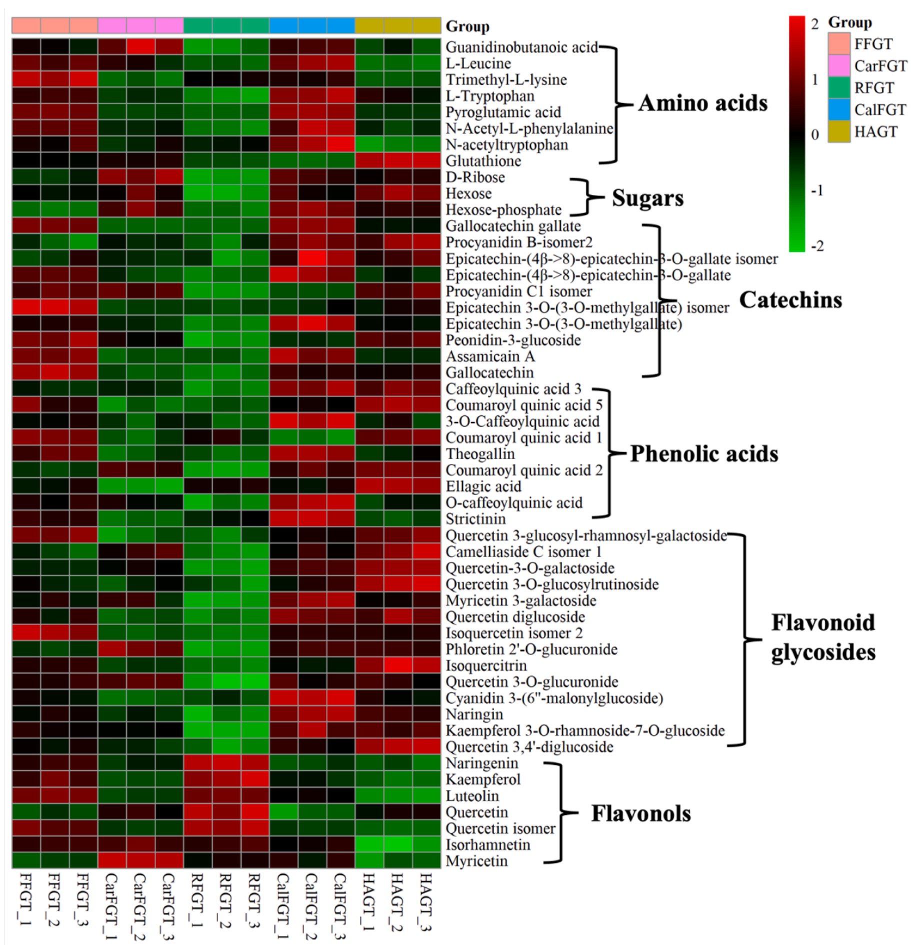

Fig. 5. Heat map of significantly different nonvolatile metabolites in hot-air drying green tea compared to four types of heat-conduction drying green teas. HAGT, hot-air drying green tea; RFGT, roller-frying green tea; CalFGT, caldron-frying green tea; CarFGT, carding-frying green tea; FFGT, flat-frying green tea. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Sugars are important metabolites for improving the sweet taste of green tea. As shown in Fig. 5, there was no consistent difference between HAGT and HCDGTs. All three sugars in RFGT were found to be significantly downregulated in HAGT, including D-ribose, hexose and hexose-phosphate ($p < 0.05$). The results showed that green-tea drying via roller-frying was not conducive to maintaining sugar. In addition to the contribution to taste, the combination of amino acids and sugars was also considered an important precursor to the formation of aroma compounds. For instance, amino acids generally react with sugars to generate typical roasted aroma products (e.g., pyrazines and their derivatives) (Liu, Zhao, Yan, Hu, Yang & Cai, 2015). Therefore, we speculated that a great portion of amino acids were involved in volatile compound generation during the roller-frying process.

3.2.2. Catechins and phenolic acids

Catechins are the main components of polyphenols in green tea, accounting for approximately 12–24% in dried tea leaves (Chen, Liu, Yang, Tu, Lin & Xu, 2021). As shown in Fig. 5, there was no consistent variation in catechins in HCDGTs compared to HAGT, while they were most apparently downregulated in RFGT. Gallocatechin gallate, procyanidin B-isomer 2, epicatechin-(4β->8)-epicatechin-3-O-gallate isomer, peonidin-3-glucoside and gallocatechin were significantly decreased in both RFGT and CarFGT, while procyanidin C1 isomer and epicatechin 3-O-(3-O-methylgallate) were decreased in RFGT compared with HAGT ($p < 0.05$). In addition, other catechins presented different changes during drying processes. In this study, roller-frying was more conducive to reducing dimer and monomer catechin contents during the drying process. It has been reported that catechins are prone to nonenzymatic oligomerization under high-temperature conditions, leading to the synthesis of high-molecular-weight polymers (Fan, Shi, Nie, Zhao, Ye & Liang, 2016). Furthermore, a reduction in catechins can reduce the phenol-amino ratio to alleviate the astringent taste of tea soup (Wan, 2003).

Phenolic acids are important constituents of polyphenols in tea, and their taste properties are sourness and astringency (Lisa & Allison, 2015). As shown in Fig. 5, phenolic acids had similar changes to catechins, which were most apparently downregulated in RFGT. Caffeoylquinic acid 3, coumaroyl quinic acid 5, coumaroyl quinic acid 1 and ellagic acid were significantly decreased in both RFGT and CarFGT, while theogallin, coumaroyl quinic acid 2 and O-caffeoylquinic acid were decreased in RFGT only compared with HAGT ($p < 0.05$). The results showed that roller-frying may facilitate a decrease in phenolic acids during the green tea drying process. Losses in phenolic acids by hot air-drying patterns have been reported (Wanyo, Siriamornpun, & Meeso, 2011), but roller-frying seemed to possess better function than hot air-drying. Differences in catechins and phenolic acids may be related to the dying time and the quantity of tea leaves in the drying patterns because they presented a decreasing trend of FFGT > CarFGT > RFGT and were even correlated with the shape of tea leaves because of the apparent increase in CalFGT compared with other heat-conduction patterns.

3.2.3. Flavonols

Flavonols and their glycosides accounted for approximately 3–4% of the weight of dried tea leaves. Flavonols are commonly conjugated with sugars to form flavonoid glycosides in tea (Dai et al., 2017). The overall flavonoid glycoside levels in HCDGTs were lower than those in HAGT, as presented in Fig. 5, and most of them in HCDGTs were significantly decreased ($p < 0.05$). In particular, quercetin-3-O-galactoside, isoquercitrin and quercetin 3,4′-diglucoside were consistently significantly decreased in HCDGTs compared with HAGT ($p < 0.05$). Furthermore, there were the lowest flavonoid glycosides in RFGT, 13 of which were significantly downregulated compared with HAGT, except for cyanidin 3-(6′'-malonylglucoside) ($p < 0.05$). Nine flavonoid glycosides in CarFGT, 7 in FFGT, and 5 in CalFGT were significantly downregulated compared with HAGT ($p < 0.05$). However, flavonols showed an apparent improvement in HCDGTs compared with HAGT. In particular, luteolin and isorhamnetin in HCDGTs were consistently significantly higher than those in HAGT ($p < 0.05$). In addition, RFGT had the greatest changes in that all 7 flavonols were significantly deregulated compared with HAGT ($p < 0.05$). The results indicated that heat-conduction drying patterns can increase the flavonol content and decrease the flavonoid glycoside content compared with hot air-drying patterns during the green tea drying process, and roller-frying had the best effect.

To the best of our knowledge, flavonoid glycosides contribute a green–yellow color to the green tea infusion (Wan, 2003). Thus, the color of tea infusions in Fig. 1 proved that RFGT contained the least flavonoid glycosides because of the great yellow–green color of the tea infusions. In addition, it was reported that flavonoid glycosides can be easily decomposed during the drying process (Dou, Lee, Tzen, & Lee, 2007). In our study, the flavonoid glycoside contents in HCDGTs were lower than those in HAGT, but the flavonol contents were increased. It was obvious that heat-conduction drying had a better function in promoting the degradation of flavonoid glycosides into flavonols and sugars than hot-air drying, as evidenced by the variation in several flavonols and their glycosides, such as quercetin and naringenin. Heat-conduction drying allowed the tea leaves to directly friction and collide with the heat source, leading to leaf tissue breakage and promoting bound flavonoid glycoside hydrolysis(Wang et al., 2022). FRGT presented the most effective conversion of flavonoid glycosides in HCDGTs. We suggest that physical changes caused by different forces combined with heat conduction could exert important effects on tea flavonols. That is, different heat-conduction patterns could cause distinctive shapes, cell breakage rates, and heating areas, resulting in different compositions in the components of green tea.

4. Conclusion

In conclusion, hot-air drying and heat-conduction drying patterns presented remarkable differences in volatile and nonvolatile metabolites (Fig. 6). For volatile compounds, this research indicated that heat-conduction drying patterns could produce much more abundant volatile compounds than hot-air drying. In addition, caldron-frying could promote chestnut-like aroma odorants, and roller-frying was preferred to generate caramel-like flavor compounds. In nonvolatile metabolites, hot-air drying could reduce the content of amino acids and flavonols but enhance the flavonoid glycosides. In addition, caldron-frying could enhance the amino acid content, while roller-frying had the greatest influence on reducing the catechin, sugar, phenolic acid and flavonoid glycoside content, but enhanced the content of flavonols. Because the above patterns are the most commonly used drying methods in tea processing factories, our results will provide a clear recommendation for the selection of drying equipment for green tea precision processing.

CRediT authorship contribution statement

Zheng Tu: Data curation, Formal analysis, Investigation, Writing – original draft. **YueYun Liu:** Writing – review & editing. **JiaZheng Lin:** Software, Writing – original draft. **HaoWei Lv:** Writing – original draft. **Wei Zhou:** Writing – review & editing. **XiaoFeng Zhou:** Writing – review & editing. **YuanFeng Qian:** Writing – review & editing. **Xu Zeng:** Resources, Writing – review & editing. **WeiZhong He:** Funding acquisition, Writing – review & editing. **Yang Ye:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

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

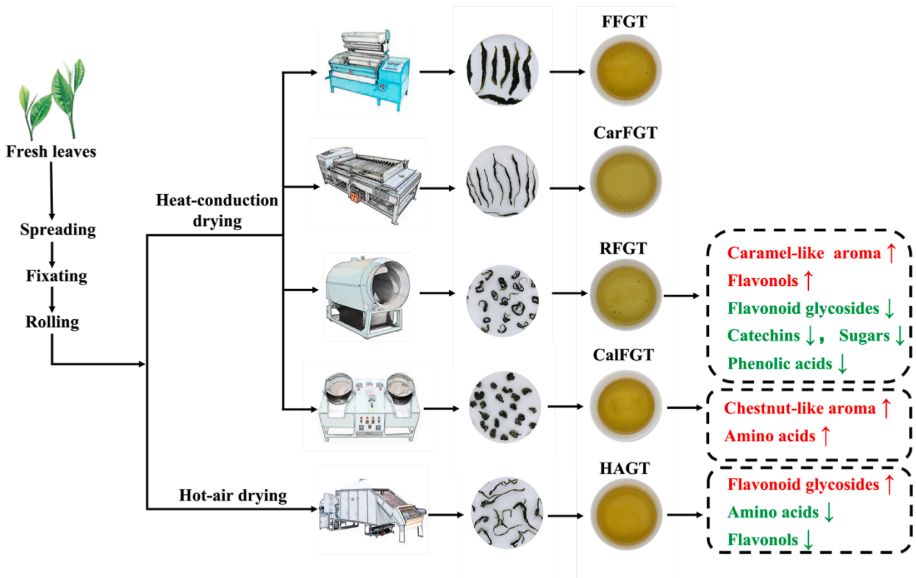

Fig. 6. Illustrators of variations on volatile and non-volatile metabolites in hot-air drying and four types of heat-conduction drying patterns. "↑" and "↓" represents the most and least abundance among five treatments, respectively. HAGT, hot-air drying green tea; RFGT, roller-frying green tea; CalFGT, caldron-frying green tea; CarFGT, carding-frying green tea; FFGT, flat-frying green tea. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the special funds for the earmarked fund for China Agriculture Research System (CARS-19).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2023.100767.

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