Food Chemistry 430 (2024) 137000

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analysis of differences in the accumulation of tea compounds under various processing techniques, geographical origins, and harvesting seasons

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ARTICLE INFO

Keywords:
Six categories of Chinese tea
Fermentation degree
Geographical origins
Harvesting seasons
Biochemical properties

ABSTRACT

The processing techniques, geographical origins, and harvesting seasons have a significant impact on tea compound accumulation, leading to different flavor characteristics and consumer preferences for tea. Herein, six categories of tea involving 1329 samples revealed the distribution characteristics via compound accumulation, as well as the impact of production regions and harvesting seasons on flavor chemicals. With the increasing fermentation degree, the average content of tea polyphenols, catechins, and theanine in dark tea decreased by 57.78%, 94.64%, and 98.57% compared to green tea, respectively. The compounds in tea fluctuate with the geographical origins and seasons, with theanine and free amino acids being more accumulated in the Jiangnan tea region in spring tea, while total polyphenols and catechins were more abundant in Southwest China's tea region in summer and autumn tea. This study comprehensively understands the accumulation characteristics of tea compounds corresponding to processing techniques and the geographical origins of Chinese tea.

1. Introduction

Tea plants (*Camellia sinensis*) originated in the southwestern region of China and have a long history of tea cultivation and consumption, from the Shen Nong period to Tang Dynasty to the 21st century over 5000 years (Zhou et al., 2023). At present, China is the country with the largest tea production and the most diverse categories around the world. As of 2022, China's tea plantation area and tea production have exceeded 3.27 million hectare and 3.1 million tons, respectively (Li, 2022). Nowadays, tea is an important cash crop and one of three major non-alcoholic beverages in the world.

Tea, containing rich bioactive compounds, such as tea polyphenols, catechins, amino acids, and caffeine, is highly favored by people for its glamorous flavor and tremendous health benefits (Deng et al., 2023). Epidemiological studies showed that regular consumption of teas had significant health benefits for the human body, including anti-oxidant, anti-inflammatory, anti-bacterial, anti-obesity, and anti-cancer (Shang et al., 2021; Xu et al., 2020; Xu et al., 2021). The accumulation and efficacy of compounds in different tea leaves are related to multiple factors, such as processing technology, geographical origin, and harvesting season, which lays the foundation for distinguishing tea samples.

Generally, traditional Chinese tea is divided into six categories based on processing technology and quality characteristics according to the international standard 'ISO 20715:2023 Tea — Classification of tea types,' including unfermented green tea, lightly fermented white tea and yellow tea, semi-fermented oolong tea, fully fermented black tea, and post- or microbially fermented dark tea (Deng et al., 2023; Zhang et al., 2013). The key production processes and fermentation degree of diverse categories of tea are shown in Table 1. Under humid and oxygen conditions, polyphenol oxidase in tea could be oxidized tea polyphenols into corresponding oxidation products, producing various tea with different flavors and qualities (Xu et al., 2019). Fermentation has a dynamic impact on the accumulation of tea compounds, which could be distinguished from different tea samples based on the changes in compounds.

In addition to processing technology, the production region also has an obvious impact on the substance accumulation of tea. Ma et al. (Ma et al., 2022) found that white tea from Xinyang, Yunnan, and Fuding production regions could be completely divided based on compound divergence, implying the feasibility of tea classification by production

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https://doi.org/10.1016/j.foodchem.2023.137000
Received 25 April 2023; Received in revised form 18 July 2023; Accepted 23 July 2023
Available online 28 July 2023
0308-8146/

Table 1
Information of six tea categories.

Tea categories	Producing origins and numbers of tea samples	Main manufacturing processes and functions	Fermentation degree
Green tea	Yunnan (194), Guizhou (88), Sichuan (141), Chongqing (198), Zhejiang (431), Hunan (19), Jiangxi (13), Anhui (7), Jiangsu (3), Hubei (6), Guangxi (5), Fujian (19), Hainan (11), Shanxi-1 (7), Shandong (2), Shanxi-2 (2)	Withering, fixing, rolling, drying. Fixing is the key process for maintaining the quality of green tea and preventing tea polyphenols from being oxidized by enzymes.	0–5%
White tea	Shandong (2), Fujian (22), Yunnan (8), Chongqing (1), Hubei (1), Zhejiang (3)	Withering, drying. Withering is the key process, volatilizing green grass gas and emitting a sweet and mellow withering fragrance.	0–10%
Yellow tea	Shandong (1), Zhejiang (16), Anhui (1), Sichuan (9)	Fixing, rolling, yellowing, drying. The technology of yellowing is the critical process to produce yellow tea, in which tea polyphenols are oxidized to a certain extent, and the taste becomes mellow.	10–20%
Oolong tea	Guangdong (10), Fujian (26), Sichuan (2)	Withering, fine manipulation, fixing, rolling, drying. Fine manipulation is the key process of oolong tea production, destroying the leaf margin cells, producing colored substances, rising aromatic compounds, and forming green leaves and red edges.	30–60%
Black tea	Fujian (7), Shandong (4), Sichuan (18), Yunnan (6), Jiangxi (1), Guizhou (5), Guangxi (2), Hunan (2), Zhejiang (8), Hubei (5), Shanxi-1 (1), Guangdong (3)	Withering, rolling, fermentation, drying. Fermentation is the core process of black tea production, in which polyphenols are oxidized under enzymatic action, and tea turns from green to red, producing aromatic substances.	80–90%
Dark tea	Yunnan (18)	Fixing, rolling, pile-fermentation, drying. Pile-fermentation is the main process of dark tea processing, which decomposes and oxidizes the original organic compounds in tea to form new compounds under the action of damp heat, microorganisms, and enzymes.	85–100%

region. Researchers found that fluorescence spectroscopy could be used to identify and differentiate black tea produced in distinct tea gardens (Seetohul et al., 2013), indicating the accumulation of substances in tea samples are different. The accumulation differences of compounds in tea samples from diverse origins have laid the foundation for the development of characteristic tea.

Besides, the harvesting seasons exerts a significant impact on the tea quality (Xiao et al., 2023). There are vast differences in the metabolic profiles of early and late spring tea leaves like flavonoids, flavonols, and amino acids (Zeng et al., 2020), resulting in that huge discrepancies in the taste and suitability of tea at different stages. Another study analyzed green teas harvested in early, middle, and late spring at low altitudes, which of results showed that the concentration of amino acids gradually decreased, while the concentration of carbohydrates, flavonol, and their glycosides significantly increased in the late spring season (Liu et al., 2016). Hence, researching the accumulation of compounds in tea samples under different harvesting seasons is of great benefit for the in-depth utilization of tea resources.

In this study, a total of 1329 tea samples from different provinces, categories, and seasons in China were collected. The content of the main active biochemical components in tea samples, including total polyphenols, total catechins, total amino acids, theanine, and caffeine, were detected. The multivariate statistical analysis was used to reveal the reasons for the differential accumulation of compounds in different tea samples. This work contributes to a deeper and more comprehensive understanding of the accumulation characteristics of basic chemical substances in the six major tea categories in China and provides basic data for traceability analysis of tea production areas and harvesting periods.

2. Materials and methods

2.1. Source of tea samples

A total of 1329 tea samples were collected from the main tea-producing provinces of China, including Yunnan, Guizhou, Sichuan, and Chongqing in the Southwest Tea Area, Zhejiang, Hunan, Jiangxi, Anhui, Jiangsu, and Hubei in the Jiangnan Tea Area, Guangdong, Guangxi, Fujian, and Hainan in the South China Tea Area, Shanxi, Shandong, and Shanxi in the Jiangbei Tea Area (Table 1). Tea categories included green tea (1146), white tea (37), yellow tea (27), oolong tea (39), black tea (62), and dark tea (18). The harvesting seasons of tea samples included spring, summer, and autumn, namely spring tea, summer tea, and autumn tea, respectively.

2.2. Chemicals and standards

The chemical gallic acid (PubChem CID: 370), catechins EC (PubChem CID: 72276) and EGCG (PubChem CID: 65064), L-theanine (PubChem CID: 439378), ninhydrin (PubChem CID: 10236), and 1 mol/L Folin − Ciocalteu (FC) reagent were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Caffeine (PubChem CID: 2519) was purchased from Sichuan Vicki Biotechnology Co., Ltd. (Chengdu, China). Na_2EDTA (PubChem CID: 8759), $SnCl_2 \cdot 2H_2O$ (PubChem CID: 61436), Na_2HPO_4 (PubChem CID: 24203), KH_2PO_4 (PubChem CID: 24506), $C_4H_{10}O_8Pb_3$ (PubChem CID: 5284406), HCl (PubChem CID: 313), H_2SO_4 (PubChem CID: 1118), and Na_2CO_3 (PubChem CID: 10340) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The grade of the reagent was GR grade. High-performance liquid chromatography grade acetic acid (PubChem CID: 176), acetonitrile (PubChem CID: 6342), and methanol (PubChem CID: 887) were purchased from TEDIA Co, Ltd. (Fairfield, OH, USA). Deionized water used in the experiment was obtained from the Milli-Q direct 8 pure water instruments (France).

2.3. Detection of biochemical indicators in tea samples

Weighed 0.2 g (accurate to 0.001 g) of milled tea sample to a 10 mL centrifuge tube, and added 5 mL of 70% methanol–water (V/V) solution preheated at 70 ℃. After mixing, the samples were immediately transferred to a 70 ℃ water bath, extracted for 10 min, stirred every 5 min, cooled to room temperature after extraction, centrifuged for 10 min at 3500 rpm/min, and then the supernatants were transferred into a 10 mL volumetric flask. The residue was extracted with 5 mL of 70% methanol–water (V/V) again and repeated the above operation. Both extraction solutions were combined to a constant volume 10 mL, and shocked well, and then passed 0.45 μm organic filter membrane. The content of total polyphenol in the filtrate solution was measured via the Folin − Ciocalteu method as described by Fu et al. (Fu et al., 2022). The content of total catechins in the filtrate solution was qualitatively measured by the method of Jiang et al. (Jiang et al., 2017).

The content of total amino acids in different tea samples was determined as the method of GB/T8314-2013 (Hangzhou tea research institute, 2013b) by ultraviolet–visible spectrophotometry (PerkinElmer precisely, Lambda 25, America).

The content of total theanine in tea samples was tested by HPLC (Waters Alliance 2695, 2489-UV/Visible Detector, America) as the method of GB/T 23193–2017 (Hangzhou tea research institute, 2017).

The content of caffeine was determined according to the ultraviolet–visible spectrophotometry (PerkinElmer precisely, Lambda 25, America) method in the GB/T 8312–2013 (Hangzhou tea research institute, 2013a).

The detection methods of total amino acids, total theanine, and total caffeine are shown in Supplementary Document 1. Three biological repeated tests were conducted on each tea sample and the average percentage value was analyzed.

2.4. Statistical analysis

The data was counted using Microsoft Excel 2019, and significance was determined using SPSS, version 22 with a one-way analysis of variance and the least significant difference (LSD) test (mean ± standard deviation). Metabolic analysis was performed using SIMCA 14.1 software (Umetrics AB, Umea, Sweden), in which data were analyzed in the unit variance (UV) mode for the principal component analysis (PCA). The box plot was drawn by Prism 8.0 software, and the phenolic ammonia ratio represents the ratio of total polyphenols to total amino acids. The final group diagram was completed using Adobe Photoshop 2020 software.

3. Results and discussion

3.1. Application of multivariate statistical analysis in tea classification and identification

The multivariate statistical method was advantageous to analyze samples with a large amount of data, and could intuitively display the clustering and difference of samples. Here, the multivariate statistical method was used to analyze the distribution of six tea categories and explore the reasons for the differences between different tea categories. The results showed that two principal components were in the unsupervised PCA model, and the cumulative variances R2X and Q2 for data interpretation were 70.6% and 0.306, respectively (Fig. 1**A**). The contribution degree of the compounds from the high to the low was total catechins, total polyphenols, theanine, free amino acid, and caffeine, respectively (Fig. 1**B**). The distribution and aggregation of six major tea categories under UV, Par, and Ctr modes were compared and found that the aggregation degree of tea samples under UV analysis mode was better than Par and Ctr modes (**Fig S1**). Therefore, the UV analysis mode was selected for the PCA in the study. The distribution of tea on the PCA model showed that tea from left to right was dark tea, black tea, oolong tea, yellow tea, white tea, and green tea, respectively (Fig. 1**C**). Correspondingly, the compounds from left to right were caffeine, free amino acid, theanine, total polyphenols, and total catechins, respectively (Fig. 1**D**).

The above results showed that the six tea categories could be basically distinguished by multivariate statistical method, which was conducive to the subsequent analysis of the accumulation of the

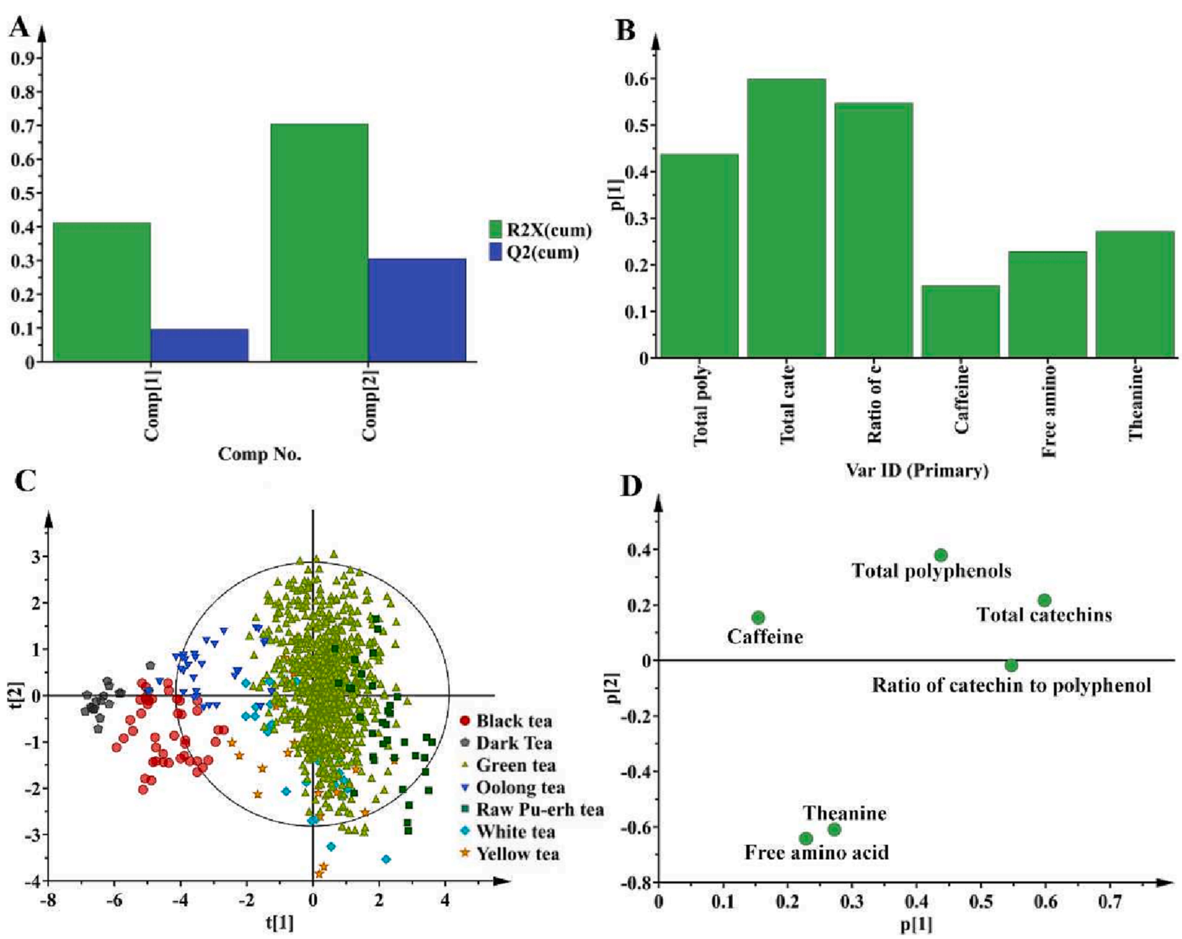

Fig. 1. Multivariate statistical analysis of different categories of tea samples. A, Summary of fit plot of PCA based on cross-validation. B, Contribution of different compounds to tea classification. C, PCA score scatters plot based on t1 versus t2. D, PCA loading scatter plot based on p1 versus p2.

compounds in different tea samples. The composition or metabolism of compounds in *Camellia sinensis* varies by numerous factors, such as manufacturing processes, geographical origin, variety, climate, harvesting seasons, and cultivation management (Shi et al., 2022), which are prerequisites for distinguishing different tea samples. The differential accumulation of compounds is one of the rich taste sources of tea.

3.2. The contribution of the biochemical substances to distinguish six tea categories

The accumulation of substances in different categories of tea is closely related to processing techniques, tea plant varieties, harvesting seasons, and geographical origins. So far, numbers of studies have been reported on harvesting tea leaves grown under the same conditions to produce various tea categories and analyzing the differences in substance accumulation. However, big data analysis on the impact of tea categories, harvesting time, and production environment on tea chemical composition is rarely reported. Big data analysis is conducive to revealing the impact of tea categories, geographical origins, and harvesting seasons on tea quality from a macro perspective, and mining the key factors affecting tea flavor characteristics. According to the differential accumulation of compounds in tea samples, the comprehensive economic benefits of tea could be improved by adopting appropriate technology to produce corresponding tea products.

To explore the differences among the six tea categories from different regions, the contents of total polyphenols, total catechins, free amino acids, theanine, and caffeine in all tea samples were determined, respectively. The results showed that the percentage of total polyphenols gradually decreased and significant differences among diverse tea categories, of which from raw Pu-erh tea (green tea production technology), green tea, white tea, yellow tea, oolong tea, black tea to dark tea were 22.45%, 20.19%, 18.78%, 17.69%, 15.40%, 13.48%, and

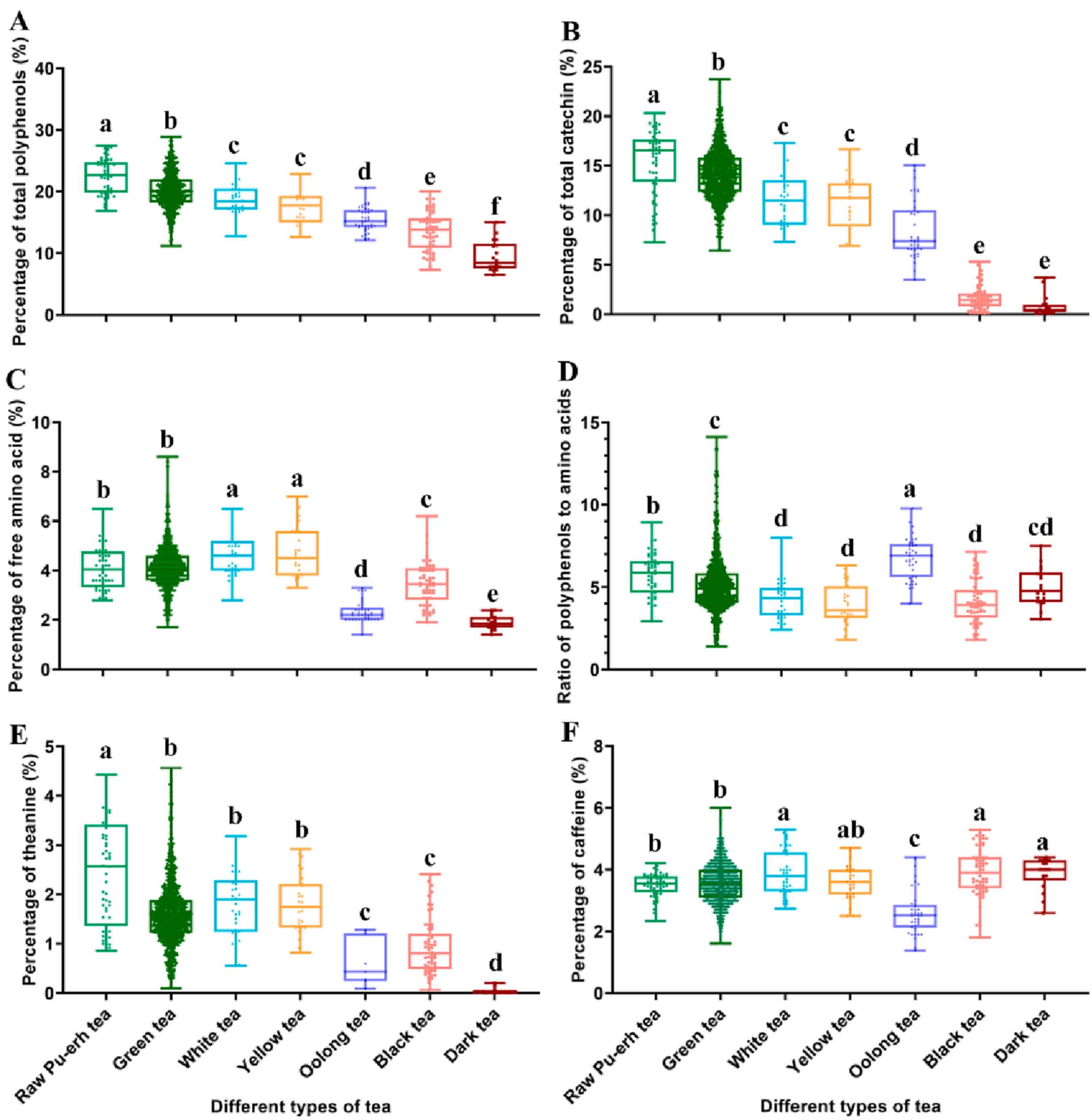

Fig. 2. Percentage of biochemical indicators in six categories of tea. A-F, Percentage of total polyphenols, total catechin, free amino acid, ratio of polyphenols to amino acids, theanine and caffeine. Data are presented as mean ± standard deviation. Significant differences among various tea samples are calculated using one-way ANOVA (LSD test) in SPSS 22.0. The different letters are indicated significant differences.

9.48%, respectively (Fig. 2**A**). The divergence in processing technology formed different categories of tea, and the degree of fermentation was the key factor to distinguishing (Jolvis Pou, 2016). With the increasing fermentation of tea, the average content of total polyphenols in green tea was 2.37 times that of dark tea, indicating that the fermentation process had a great impact on the total tea polyphenols. During the fermentation process, polyphenol oxidase could be converted polyphenols into compounds such as theaflavins and epigallocatechin dimer quinones, and the pyrogallol structure was more easily to be oxidized than the catechol and monophenol structures in B-ring (Tanaka, 2003). The polyphenols in tea are mainly catechin EGCG (with a pyrogallol structure), which leads to a significant decrease in the total polyphenol content in the tea sample after fermentation.

Catechins were the main polyphenol in tea leaves and the accumulation pattern was consistent with total polyphenols. The average percentage of total catechins in raw Pu-erh tea (15.48%) was 18.65 times that of dark tea (Fig. 2**B**). In this study, the total catechins in unfermented green tea accounted for about 70% of the total polyphenols, and the ratio significantly decreased with the increase of fermentation degree. In comparison, the decreasing rate of total polyphenols was far lower than that of total catechins, indicating that the fermentation degree had a greater impact on catechins. The catechins were easy to be oxidized during fermentation to produce polyphenol oxidation polymerization products, and the degree of oxidation was one of the important bases for dividing the six tea categories (Long et al., 2023). The conversion of polyphenols was an important factor affecting the rich taste and taste of tea soup.

Compared with total polyphenols and total catechins, the accumulation of total free amino acids in different tea samples was not completely consistent with the fermentation degree. The percentage of total free amino acids in raw Pu-erh tea, green tea, white tea, yellow tea, oolong tea, black tea, and dark tea was 4.09%, 4.17%, 4.61%, 4.71%, 2.33%, 3.49%, and 1.91% respectively (Fig. 2**C**), indicating that the fermentation degree was not the only factor affecting the content of free amino acids. The percentage of free amino acids in white tea and yellow tea had no difference but was significantly higher than in other tea categories, leading to a low phenolic ammonia ratio (Fig. 2**D**). Withering was the key process of white tea manufacturing, in which the technology could significantly increase the total amount of free amino acids (Jabeen et al., 2019; Wang et al., 2019). White tea did not undergo high temperature and rolling during the withering process, so the cells of tea leaves were relatively complete and the endogenous enzyme activity was mild, which was conducive to the formation and accumulation of amino acids. In comparison, black tea, oolong tea, and dark tea were processed with a high cell damage rate and violent oxidation of compounds, resulting in more decomposition and transformation of amino acids and less retention (Qi et al., 2021).

Secondly, the heating and roasting of black tea, oolong tea, and dark tea dehydrated amino acids and pectin into aromatic substances on the one hand, and amino acids formed glycosamine compounds via the Maillard reaction on the other hand (van Boekel, 2006). At the same time, many kinds of amino acids in tea were oxidized deamination and decarboxylation by o-quinone, the oxidation product of catechin, to form corresponding aromatic aldehydes, leading to amino acids in black tea, oolong tea, and dark tea were significantly reduced (Chen et al., 2019; Dai et al., 2017). The technology of yellowing is the critical process to produce yellow tea, and the tea leaves contain high water content in this procedure. The strong damp heat conditions during this process promote the hydrolysis and pyrolysis of the weak side chains in the protein structure, thus generating free amino acids and increasing the total amount of amino acids. Additionally, tea plant varieties and harvesting seasons are also important factors affecting amino acids content. In this study, the effect of processing techniques on the accumulation of amino acids in six major tea categories was mainly discussed, so we did not expound on the differences in amino acid accumulation between tea plant varieties and harvesting seasons. Theanine, accounting for about 50–70% of total free amino acids, plays an important role in the quality of tea, which could improve the fresh taste of tea soup and inhibit the bitter taste of tea soup. The change rule of theanine was similar to that of total polyphenols (Fig. 2**E**).

Caffeine was an important flavor and physiological characteristic component of tea, and was one of the main components that determine the quality of tea (Ning et al., 2016). The caffeine content was mainly influenced by the variety and geographical environment and then were processing techniques. There was no significant difference among white tea, yellow tea, black tea, and dark tea but was significantly higher than that in green tea and oolong tea (Fig. 2**F**), which was consistent with previous research results (Ning et al., 2017). When the temperature exceeds 100 ℃, caffeine was released crystalline water and began to sublimate, and the rate of sublimation depended on the temperature and time (Vuong & Roach, 2014). Generally, the roasting temperature of oolong tea was higher than the temperature at which caffeine begins to sublimate, resulting in a low content of caffeine in oolong tea. The divergence in biochemical composition content in tea caused by different processing techniques was the key to quantitatively identifying the six major categories of tea.

3.3. Regional and differential analysis of biochemical indicators in green tea

Green tea is the most widely distributed and highest-yielding tea among six categories of tea. The key processing step of green tea is the inactivation of enzyme activity by heating, preventing the oxidation of polyphenols in fresh leaves, reducing material loss, and basically reflecting the accumulation of substances in tea plants. There are noticeable differences in the processing techniques for fixing green tea in various regions, resulting in unique biochemical component in tea and forming special flavors and tastes. At present, there have been reports on identifying diverse green teas in the same region based on the differential accumulation of tea compounds (Liu et al., 2022; Wang et al., 2021), but the research on the differences of compound accumulation in green tea from dissimilar tea regions was relatively little. Here, to explore the influence of regions on the accumulation of tea compounds, the biochemical parameters of green tea in different areas were analyzed (Fig. 3). The green tea samples collected from different provinces in China were divided into four tea regions, including Southwest Tea Area, Jiangnan Tea Area, South China Tea Area, and Jiangbei Tea Area.

The average percentage values of total polyphenols (total catechins) in the Southwest Tea Area, Jiangnan Tea Area, South China Tea Area, and Jiangbei Tea Area were 21.03% (14.85%), 19.07% (13.34%), 21.68% (14.77%), and 21.41% (15.75%) respectively, indicating that the accumulation of polyphenols in different tea area was diversity (Fig. 3**A, B**). The contents of total polyphenols and total catechins in the Jiangnan Tea Area were significantly lower than those in the other three tea areas, while there was no significant difference in the content of total polyphenols and total catechins between different provinces in the same tea area.

Similarly, the average percentage values of total free amino acid (theanine) in the Southwest Tea Area, Jiangnan Tea Area, South China Tea Area, and Jiangbei Tea Area were 4.02% (1.52%), 4.39% (1.74%), 3.66% (1.47%), and 4.14% (1.68%), respectively (Fig. 3**C, D**). The contents of free amino acids and theanine in the Jiangnan Tea Area were significantly higher than those in the other three tea regions. Combined with the content of tea polyphenols, the accumulation patterns of amino acids and polyphenols may be opposite, which was consistent with Lin's conclusion that under nitrogen deficiency, the amino acid content in tea leaves decreases while the total flavonoids and polyphenols content increases (Lin et al., 2023). In addition, the coefficient variation of theanine in the South Tea Area, Jiangnan Tea Area, South China Tea Area, and Jiangbei Tea Area were 39.88%, 40.14%, 56.95%, and 45.84% respectively (Fig. 3**D**), indicating that theanine was significant

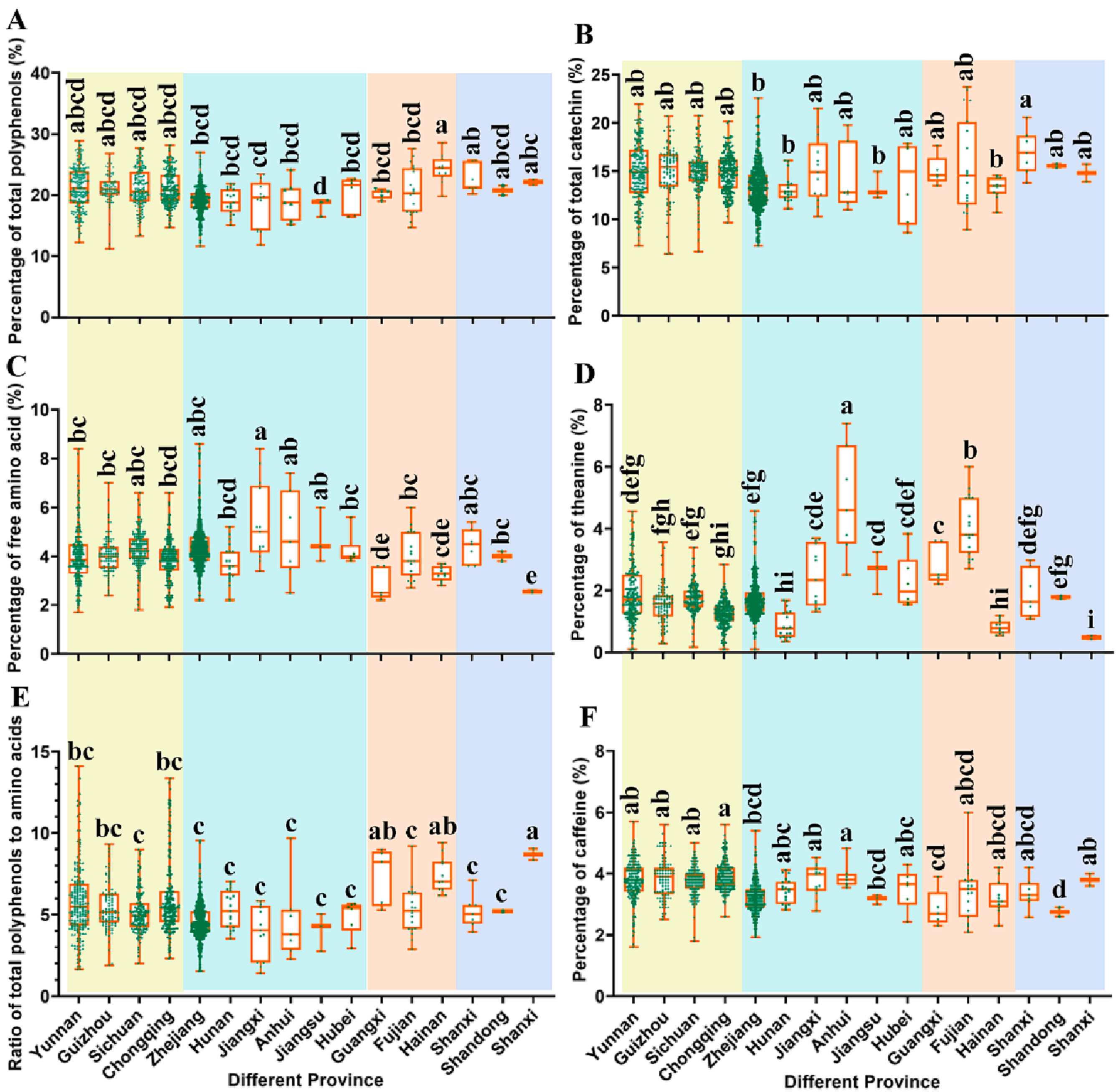

Fig. 3. Percentage of green tea biochemical indicators in different provinces. A-F, Percentage of total polyphenols, total catechin, free amino acid, theanine, ratio of polyphenols to amino acids, and caffeine. Data are presented as mean ± standard deviation. Significant differences among various tea samples are calculated using one-way ANOVA (LSD test) in SPSS 22.0. The different letters are indicated significant differences. The four areas from left to right represent Southwest Tea Area, Jiangnan Tea Area, South China Tea Area, and Jiangbei Tea Area, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

divergence in different provinces of the same tea area, and the diversity was broader and richer.

Generally speaking, polyphenols play essential roles in imparting bitterness and astringency taste, while most amino acids are related to umami (Zhuang et al., 2020). The phenolic ammonia ratio in tea is an important indicator to determine the taste of tea (Zhang et al., 2020). Green tea usually has an obvious bitter and astringent taste when the phenolic ammonia ratio exceeds 8 (Zhang et al., 2013). The phenolic ammonia ratio in South Tea Area, Jiangnan Tea Area, South China Tea Area, and Jiangbei Tea Area were 5.65, 4.56, 6.26, and 5.49, respectively (Fig. 3**E**). The phenolic ammonia ratio in the Southwest Tea Area and South China Tea Area was no significant difference but it was significantly higher than that in Jiangnan Tea Area. This is one of the reasons why the taste of tea in the Jiangnan Tea Area is generally weak but the umami. In addition, the phenolic ammonia ratio in the Southwest Tea Area (especially in Yunnan province) varied from 1.63 to 14.12, reflecting the rich characteristics of tea planting resources in Yunnan province (Fig. 3**E**).

The average percentage values of caffeine in the Southwest Tea Area (3.84%) were prominently high than Jiangnan Tea Area (3.24%), South China Tea Area (3.27%), and Jiangbei Tea Area (3.43%) (Fig. 3**F**), speculating that the caffeine content in large-leaf tea varieties was higher than that of small-leaf tea varieties. Generally, the content of caffeine in tea plants was 2–4%. The content of caffeine in the Southwest

Tea Area was 1.6%-5.7%, of which 201 and 4 tea samples were more than 4% and less than 2%, respectively. The rich tea plant resources in the Southwest Tea Area provided the possibility to screen specific high-caffeine tea and low-caffeine tea.

The concentrations of tea polyphenols, catechins, and phenolic ammonia ratio in the Southwest Tea Area and the South China Tea Area were generally higher than in the Jiangnan and Jiangbei Tea Area, while the free amino acids and theanine in tea plants were more accumulated in the Jiangnan Tea Area.

3.4. Analysis of differential accumulation of green tea substances at different harvest seasons in Yunnan province

Green tea in China can typically be separated into spring tea, summer tea, and autumn tea according to the harvest and production seasons, which refer to tea processed before late May, between early June and early July, and after mid-July, respectively (Xu et al., 2012). Affected by growth conditions, autumn tea accounts for only a small portion compared to spring tea and summer tea. The chemical composition and bioactive components of green tea produced in different seasons undergo dramatic changes (Wang et al., 2022), which can be used to identify tea samples from different harvest seasons.

The results of **Section 3.3** showed that the accumulation of tea compounds in Yunnan province had a large variation coefficient. Therefore, to explore the effect of different seasons on the compounds in tea samples, the PCA model was employed to analyze the distribution of tea samples in Yunnan province. The results showed that three principal components were in the unsupervised PCA model, and the cumulative variances R2X and Q2 for data interpretation were 91.16% and 0.612, respectively (Fig. 4**A**), illustrating that the model had a high degree of interpretation and accuracy. The analysis showed that the substances from left to right were free amino acid, theanine, caffeine, total catechin, and total polyphenol (Fig. 4**B**), and free amino acids and theanine, as well as total catechins and total polyphenols, had a high polymerization degree, respectively.

Furthermore, the cluster distribution of tea samples in different detection months and seasons showed that the distribution of tea samples in different months and seasons was highly consistent. The corresponding months of spring tea, summer tea, and autumn tea were March to May, June to July, and after August, respectively (Fig. 4**C, D**). Combined with the results of Fig. 4**B**, the accumulation of free amino acids and theanine in spring tea was enhanced, and the content of total catechins and total polyphenols in summer and autumn tea samples increased, which was similar to the results of Li et al (Li & Zhang, 2022). Previous studies have shown that spring tea typically contained higher levels of amino acids and moderate levels of catechins (resulting in a rich, mellow, and light flavor taste), whereas summer tea commonly had higher levels of catechins and lower levels of amino acids (yielding a

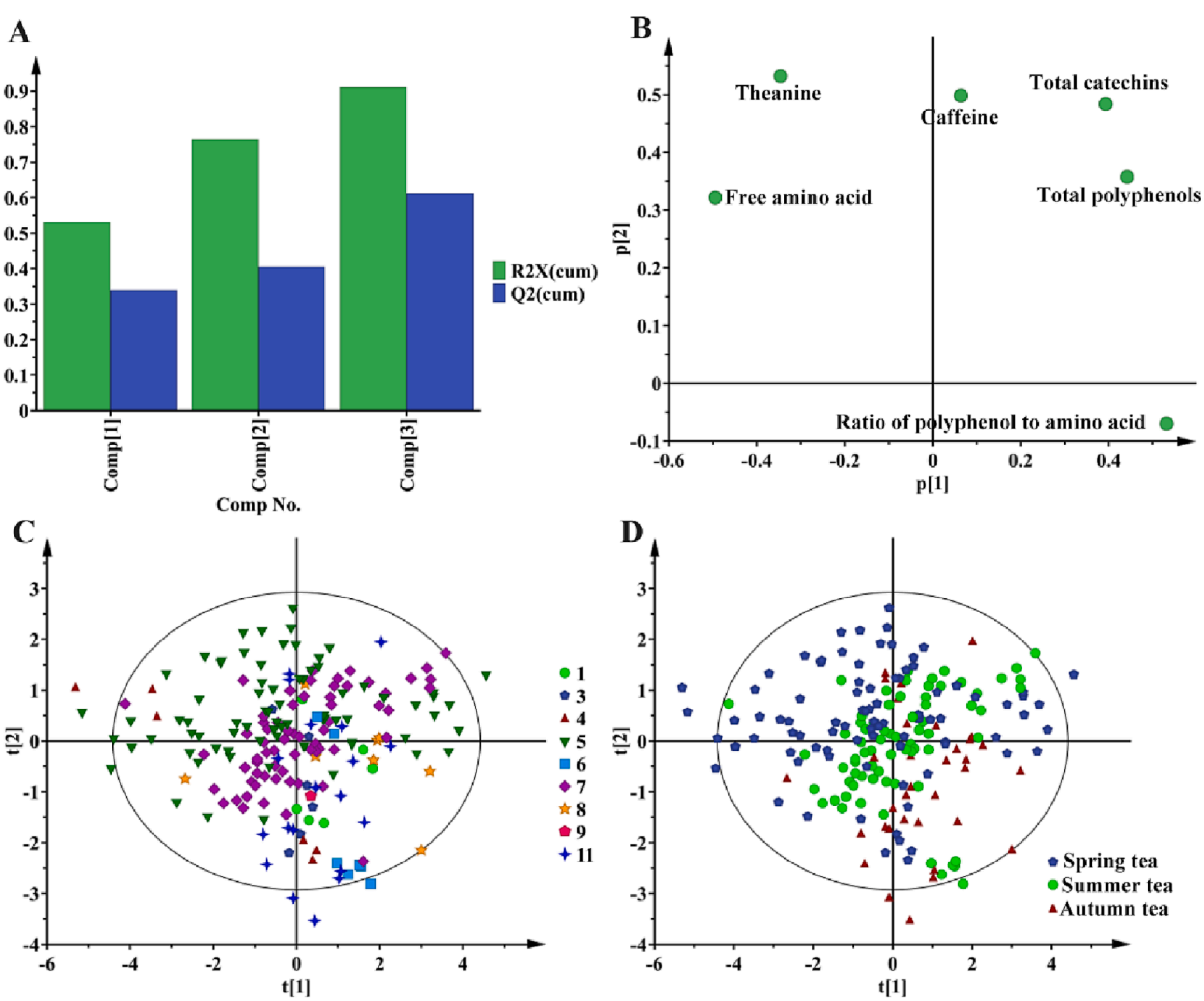

Fig. 4. Multivariate statistical analysis of the green tea samples in Yunnan province. A, Summary of the fit plot of PCA based on cross-validation. B, PCA loading scatters plot based on p1 versus p2. C, D, PCA score scatter plot based on t1 versus t2 at different months, season, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

more astringent taste) (Xu et al., 2012). This result showed that the accumulation of compounds in tea samples had temporal regularity, and tea samples in different seasons could be distinguished via the discrepancy of substances. Additionally, combined with the results of Fig. 3, it could be explained why spring green tea tastes umami and a litter bitter while summer and autumn green tea tastes bitter and astringent but not umami. According to the volatility of the accumulation of compounds in tea samples at different times, the comprehensive economic benefits of tea could be improved by using appropriate technology to produce corresponding tea products.

4. Conclusions

In summary, six categories of Chinese tea manufactured by different techniques were obviously different, and the contribution of compounds to distinguish various tea from high to low were total catechins, total polyphenols, theanine, free amino acids, and caffeine, respectively. The compound accumulation, including total polyphenols, total catechins, and theanine, decreased with the increase of tea fermentation degree. The differential accumulation of tea compounds caused by processing techniques was crucial for discriminating various tea samples. The accumulation of compounds in green tea was related to geographical origins. The contents of tea polyphenols and catechins in the Southwest Tea Area and the South China Tea Area were generally higher than in the Jiangnan and Jiangbei Tea Area, while the free amino acids and theanine were more accumulated in the Jiangnan Tea Area. Finally, spring tea amassed high levels of amino acids and moderate levels of catechins compounds, while summer and autumn tea had the opposite rule of compound accumulation compared with spring tea, which could be used to distinguish tea in different seasons.

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.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2022YFF0606800), Innovative Program of Chinese Academy of Agricultural Sciences (Y2022QC24, CAAS-ASTIP-2021-TRI), Modern Agro-Industry Technology Research System (CARS-19).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2023.137000.

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