

Chemotaxonomic variation of volatile components in *Zanthoxylum bungeanum* peel and effects of climate on volatile components

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Abstract

Background

Zanthoxylum bungeanum Maxim. is widely distributed in China, and the aroma of *Z. bungeanum* peel is mainly determined by volatile components. In this study, the characteristics and correlation of volatile components of *Z. bungeanum* peels in different regions and their correlation with climate factors were analyzed.

Results

The results showed that 126 compounds were detected in *Z. bungeanum*. Among the 27 compounds with odor characteristics, the one with highest content was Linalool, and the average relative content was 21.664%. The volatile oil of *Z. bungeanum* mainly presents a spicy, floral, citrus and mint aroma. The classification results were geographically continuous, with the ZB10 collection site in Shaanxi showing significant differences in altitude compared to other groups. Temperature, average annual precipitation, and wind speed played an important role in the accumulation of volatile components.

Conclusions

This study is helpful to improve the quality of *Z. bungeanum*, enrich the influence of climate factors on the accumulation of volatile substances, and promote agricultural practices in regions with similar climatic conditions.

1 Introduction

Zanthoxylum bungeanum is one of the most important traditional condiments in China, of which the main edible and medicinal components are *Zanthoxylum bungeanum* peels^[1]. Due to its low environmental requirements and strong ecological adaptability, *Zanthoxylum bungeanum* is widely cultivated throughout the country^[2]. *Zanthoxylum bungeanum* is widely cultivated in different growing environments, and some varieties may overlap in the same origin. In general, the composition of the volatile oil will be diverse due to differences between different varieties, changes in the growing environment, maturity and picking time, and storage extraction methods^[3–5]. Volatile oil combined with chemometrics as a biological strategy is used to identify the species and origin of certain plants^[6–7]. A comprehensive comparative study on the volatile oil of *Zanthoxylum bungeanum* peel from different origins is necessary.

Zanthoxylum bungeanum is mainly planted in Sichuan, Yunnan, Guizhou, Chongqing, Shaanxi, Gansu, and other regions of China. The harvest season of *Zanthoxylum bungeanum* is from June to August every year. Due to its unique flavor, *Zanthoxylum bungeanum* is widely regarded as an indispensable seasoning and is widely used in food processing in China. *Zanthoxylum bungeanum* is rich in bioactive compounds^[8], including alkaloids^[9], volatile oils^[10], amides^[11] and phenols^[12].

Zanthoxylum bungeanum is known for its distinctive odors^[13], which are mainly determined by the volatile components in the peel^[14–15]. Volatile oils are synthesized by defense- and reproduction-related organs in aromatic plants^[16], and consist of complex mixtures of a dozen to several hundred substances of varying concentrations of composition^[17–18]. Two or three of these are the main components at concentrations greater than 30%, while the others are present only at trace levels^[19]. Among them, the most common components are monoterpenes, sesquiterpenes, and their oxygen-containing derivatives, but some other trace components also play an indispensable role.

Headspace solid phase microextraction and gas chromatography-olfactory mass spectrometry (HS-SPME-GC-O-MS) are two methods for the analysis and identification of volatile compounds^[20–22]. These volatile compounds, in general, include terpene-hydrocarbons (e.g., d-limonene, α -pinene, β -myrcene, γ -terpinolene, α -thujene, and α -cubebene), alcohols (e.g., β -

terpineol, linalool, and citronellol), aldehydes (e.g., octanal, nonanal, citronellal, decanal, and geranial), ketones (e.g., cyclohexanone, nootkatone, pulegone, verbenone, and (-)-carvone), oxides (e.g., caryophyllene oxide, (Z)-limonene oxide, and (E)-limonene oxide), esters (e.g., neryl acetate and geranyl acetate), and others (e.g., toluene and ethylbenzene)^[23]. In the volatile oils identified in this study, d-Limonene, Linalool, Geranyl Acetat, α -Pinene, α -Phellandren, and (Z)-3, 7-Dimethyl-2, 6-Octadien-1-OL compounds appear. These compounds are responsible for the fragrance of peppercorns^[24]. The difference in characteristic aroma substances of *Zanthoxylum bungeanum* from different producing areas was analyzed by combining qualitative and quantitative analysis. In addition to aroma sources, volatile substances are also the main indicators reflecting the essential quality of *Zanthoxylum bungeanum*. *Zanthoxylum bungeanum* essential oil has anti-tumor, anti-inflammation, anti-itching, and other pharmacological activities, showing its value and potential in many aspects^[25–27]. In addition to being widely used in spices, cooking, and antioxidant fields, *Zanthoxylum bungeanum* pepper extract has demonstrated a variety of benefits, including antibacterial, antiviral, peeling, weeding, medicinal transdermal, and lipid-lowering effects. *Zanthoxylum bungeanum* plays an important role in food, cosmetics, pharmaceutical, and agricultural fields and has a wide range of application prospects^[28–36]. In addition, *Zanthoxylum bungeanum* not only protects soil, maintains water, increases farmers' income, and improves livelihoods, but also plays a key role in important projects such as "returning farmland to forest" and the transformation of rural industrial structures, demonstrating its important potential for sustainable development and rural revitalization.

The formation of plant secondary metabolites is related to plant growth and development^[37–38], and is also strongly regulated by environmental factors (including precipitation, temperature, humidity, soil, etc.)^[39]. The accumulation of active substances in plants is affected by many factors, including plant characteristics, growth stage, seasonal changes, light intensity, altitude, climate conditions, and soil environment. Studies have shown that the physiological and ecological changes and genetic background of plants can affect the quality and quantity of secondary metabolites and then affect their biological activities^[40–41]. Altitude, precipitation, and soil texture are the main factors affecting the composition of *Zanthoxylum bungeanum*^[42]. The altitude directly affects the temperature, precipitation, sunshine hours, and humidity, which affect the growth and development of plants and the accumulation of secondary metabolites^[43–45]. In high-altitude areas, latitude and longitude will directly affect the temperature and precipitation and then indirectly affect the growth environment of medicinal plants. Therefore, latitude and longitude play a key role in these regions and have an important influence on the growth of medicinal plants^[46]. The production and accumulation of secondary metabolites in plants are influenced by many aspects of climate conditions, as these metabolites can help plants cope with climate stress and provide adaptive advantages. Therefore, in the process of plant growth and development, in addition to genetic factors, the type, content, and proportion of secondary metabolites may also be regulated by a variety of climatic factors^[37, 47]. In recent years, diverse climatic and soil conditions have had a significant impact on the growth and quality of food and medicinal plants, including *Ferula assa-foetida*, *Brassica oleracea*, *Vaccinium myrtillus*, and *Curcuma longa*. Research on the impact of different geographical locations on the content of secondary metabolites has been reported, such as *Eucommia ulmoides* and *Sinopodophyllum hexandrum*^[48–51]. The types and contents of volatile components of *Zanthoxylum bungeanum* were different in different habitats and showed different morphological characteristics under different climatic conditions. Therefore, it is of great significance to study the influence of climatic factors on the accumulation of volatile substances in *Zanthoxylum bungeanum* peel for identification and directional application of *Zanthoxylum bungeanum* peel.

In the present study, 10 skin samples of *Zanthoxylum bungeanum* Maxim. were collected from different regions of China, and the corresponding climatic data were collected. The content and characteristics of volatile oil in *Z. bungeanum* peel were described by combining ultra-high-performance liquid chromatography and mass spectrometry with multivariate statistics (multivariate statistical method using hierarchical cluster analysis, principal component analysis, correlation analysis, and path analysis), and the correlation between volatile oil compounds and climate factors was explained. These results provided a better understanding of the effects of climate factors on the plant components (quantity and quality) of *Z. bungeanum* peel, revealed the regional differences of volatile oil substances in the natural distribution area of *Z. bungeanum* peel, clarified the key environmental factors affecting the accumulation of volatile oil substances in *Z. bungeanum* peel, and

provided a theoretical and practical basis for quality evaluation, quality classification, and product source traceability of *Z. bungeanum* peel.

2 Materials and methods

2.1 Materials

Zanthoxylum bungeanum Maxim. samples were collected through the local forestry bureau or zanthoxylum planting company. *Z. bungeanum* (Fig. 1) was collected at 10 sites at different altitudes (457-2450m) in 3 provinces in China from July to September 2022. The collected *Z. bungeanum* fruits were deseeded and dried to obtain the dried *Z. bungeanum* peel (moisture content less than 10.5%) with a sampling volume of 5-10kg.. After crushing the dried peel, pass 60 mesh sieve and store in the refrigerator at -20°C for future use.All the specimens were authenticated by Professor Xu Danping of China West Normal University and stored in the School of Life Sciences, China West Normal University.

The origin information of *Z. bungeanum* samples is shown in Table 1.

Table 1
Sample source information of *Z. bungeanum*.

NO	Species	Origin (Province, city /State, County/District)	Longitude(°)	Latitude(°)	Elevation(m)	Tree-age(year)	Collection number
ZB1	<i>Zanthoxylum bungeanum</i> Maxim	Sichuan, Liangshan, Yanyuan	101.6	27.4	2450	8	SCYY-ZB-20220719.1
ZB2	<i>Zanthoxylum bungeanum</i> Maxim	Sichuan, Ya 'an, Hanyuan	102.2	29.4	996	8	SCHY-ZB-20220725.1
ZB3	<i>Zanthoxylum bungeanum</i> Maxim	Sichuan, Ya 'an, Hanyuan	102.7	29.3	990	8	SCHY-ZB-20220814.2
ZB4	<i>Zanthoxylum bungeanum</i> Maxim	Sichuan, Liangshan, Jinyang	103.3	27.7	2050	9	SCJY-ZB-20220803.1
ZB5	<i>Zanthoxylum bungeanum</i> Maxim	Sichuan, Aba, Maoxian County	103.9	31.7	1640	10	SCMX-ZB-20220816.1
ZB6	<i>Zanthoxylum bungeanum</i> Maxim	Gansu, Longnan, Wudu	104.8	33.4	1048	10	GSWD-ZB-20220825.1
ZB7	<i>Zanthoxylum bungeanum</i> Maxim	Gansu, Longnan, Wudu	104.8	33.3	1048	10	GSWD-ZB-20220825.2
ZB8	<i>Zanthoxylum bungeanum</i> Maxim	Gansu, Longnan, Wudu	104.8	33.3	1048	10	GSWD-ZB-20220826.3
ZB9	<i>Zanthoxylum bungeanum</i> Maxim	Gansu, Longnan, Wudu	104.8	33.4	1048	10	GSWD-ZB-20220826.4
ZB10	<i>Zanthoxylum bungeanum</i> Maxim	Shaanxi, Weinan, Hancheng	110.4	35.5	457	10	SXHC-ZB-20220910.1-2

2.2 Sample preparations

The volatile oil was extracted by the HS-SPME method from the dried and crushed *Z. bungeanum* peels. The powdered sample of 1.5g was transferred into a 10 ml headspace bottle, equilibrated at 80°C for 30 minutes, and extracted by a solid-phase micro-extraction needle (100 µL PDMS fiber, SUPELCO, USA). After extraction, HS-SPME-GC-O-MS analysis was performed by desorption at the inlet for 5 minutes. All experiments were repeated three times.

2.3 GC/MS conditions

Take an appropriate amount of volatile oil and dilute it 40 times with methanol, pass a 0.22µm filter membrane, and take 1 mL into an automatic sampling bottle. The injection volume is 1 µL. The column was an HP-5MS elastic quartz capillary column (30 m×0.25 mm, 0.25 µm). Elastic quartz capillary column. The heating procedure is that the column temperature is 50 °C (reserved for 1 minute), and it is raised to 75 °C at 1 minute. Hold it for 1 minute and then rise to 120 °C at 6 °C/min. Hold it for 1 minute, and then rise to 135°C at 1 minute. For 1 minute, the temperature rises to 200 °C at 15 °C/min and maintains it for 5 minutes^[52]. Helium is used as the carrier gas, and the flow rate is 1.0 mL/min; the purge flow rate of the spacer is 3 mL/min; the pressure is 7.6522 psi; and the inlet temperature is 250 °C.

The ion source is an electron impact (EI) ionization source with an ion source temperature of 230°C, a quadrupole temperature of 150°C (maximum 200°C), electron energy of 70 eV, an interface temperature of 280°C, and a mass scanning range of 50 to 550 amu.

2.4 Statistical Analysis

In this study, the combination of *Z. bungeanum* and climate factors is analyzed. The data on average annual temperature (XAMT), average maximum temperature (XAMAT), average annual minimum temperature (XAMIT), annual relative humidity (XRH), average wind speed (XMW), maximum wind speed (XMAW), extreme wind speed (XEW), annual sunshine duration (XASD), and average annual precipitation (XAAP) in the sampling area are obtained from the Meteorological Bureau provided. Climate factors are listed in Table S1. According to the relative content of the main flavor substances, cluster and principal component analyses were performed on *Z. bungeanum* from different origins. Origin software (Origin 2021) was used for statistics and calculation, and hierarchical cluster analysis, principal component analysis, and correlation analysis charts were generated. SPSS 24.0 software was used to calculate hierarchical cluster analysis, correlation analysis, regression analysis, and path analysis (IBM SPSS Statistics 27). All samples were processed three times.

3 Results

3.1 Quantitative study of volatile components in *Z. bungeanum* peel

The volatile components of 10 *Z. bungeanum* populations were determined by gas chromatography-mass spectrometry (GC-MS), and the results showed that a total of 126 volatile components were detected, as shown in Table S2. The contents and types of olefins, alcohols, and esters are the main factors affecting the difference in volatile components. The most kinds of terpenes were detected, with a total of 63 kinds, followed by alcohols (30) and esters (15). The compounds with the highest average relative content were terpenes, followed by alcohols and esters. The alcohols in volatile oil were mainly terpenoids, and the most important terpene was linalool, with an average relative content of 23.13%.

The compounds with relatively high average relative content in *Z. bungeanum* were d-Limonene (24.71%) and Linalool (23.13%). The types of compounds that were most abundant varied depending on the sample. The relative content of d-Limonene was close to the relative content of Linalool in all samples except ZB3 and ZB6. While the relative content of linalool in ZB3 and ZB6 was 2.3 and 3.1 times that of d-limonene, respectively, The main volatile components of *Z. bungeanum* from Hancheng, Shaanxi Province (ZB10) were significantly different from other samples, with the highest relative content of limonene (15.95%).

The 10 common components (and average relative content) of *Z. bungeanum* from different main producing areas were d-limonene (24.71%), linalool (23.13%), terpinen-4-ol (3.79%), trans- β -ocimene (2.57%), terpinolen (1.28%), terpinyl acetate (1.11%), germacrene D (1.03%), alloocimene (0.86%), (Z)-3,7-dimethyl-2,6-octadien-1-ol (0.44%), and γ -elemene (0.29%). A total of seven shared compounds had a relative content greater than 1%.

Figure 2 shows the significant differences in the content of different substances in the 10 samples. Figure 2(A) shows that ZB8 has the highest content of esters (14.77%), followed by ZB5 (14.03%), and ZB7 (12.91%). As can be seen from Fig. 2(B), only ZB1, ZB4, ZB5, ZB7, ZB8, and ZB9 exist in ethers, and the contents are all below 0.2%. In ketones (Fig. 2(C)), the highest content of ZB10 was 1.13%, and the other contents except ZB9 are between 0.04% and 0.7%. It can be seen from Fig. 2(D) that the contribution rate of terpenes is the highest among the volatile components of peel, among which ZB1 and ZB10 have the highest content, up to 72.93% and 78.10%, followed by ZB2 (69.37%), ZB4 (66.83%), ZB9 (60.27%), and ZB3 (39.91%), which have the lowest content. The content of alcohols in ZB6 is 56.55%, followed by ZB3 (48.11%).

3.2 Analysis of common volatile characteristic components of *Z. bungeanum* peel

The fragrance and quality of *Z. bungeanum* peel are mainly determined by the content and composition of volatile oil. In the study, the odor of volatile oil was determined by GC-MS. Of all the volatile oils detected, 27 identify odor signatures, as detailed in Table 3. Terpenes were the most common, with 11, followed by 8 alcohols, 5 lipids, 2 ketones, and 1 aldehyde.

Among the 27 volatile substances, 18 aroma substances were identified by GC-O, indicating that not all volatile substances have an aroma-forming effect. The increase in the content of volatile substances such as terpinen-4-ol and linalyl acetate may not contribute to the formation of aroma. On the contrary, low-content subcomponents such as α -Pinene, α -Phellandren, and (Z)-3, 7-dimethyl-2, 6-Octadien-1-OL contribute to the aroma. D-Limonene and Linalool not only have odor characteristics but also have the highest relative content of all *Z. bungeanum*, which is speculated to be an important compound affecting the fragrance of *Z. bungeanum*.

Using Linalool ROAV_{stan} = 100, the relative odor activity ROAV values of each compound were obtained according to the odor threshold of each substance. According to the odor threshold and relative content of the compounds listed in Schedule S3, the ROAV values of various compounds are obtained in Table 2 below. The greater the ROAV value, the greater the contribution to the overall flavor of the sample. Groups with ROAV values above 1 were classified as key flavor compounds of the sample. Compounds with ROAV values of 0.1-1 have an important modification effect on the overall flavor of the sample. The ROAV values of linalool, geranyl acetat, d-limonene, β -pinene, and limonene are all greater than 1, which are the key flavor substances of zanthoxylum. In addition, there are 12 main flavor substances, including α -Copaene, Copaene, Caryophyllene, α -Terpineol, (R)-3, 7-dimethyl-6-octenal, Terpinolen, and L- α -Terpineol. The main fragrances of the volatile oil of *Z. bungeanum* are occidental, floral, citrus, and mint. In this study, the content of key aroma substances such as limonene and linalool in *Z. bungeanum* in the northwest and southwest regions was higher, so the pepper in this region showed a stronger citrus aroma.

Table 2
The ROAV value of volatile components in *Z. bungeanum*

NO.	Compound name	ROAV	Odor characteristic
1	Linalool	100.00	Sweet, floral, kale and lavender scent
2	Geranyl acetat	7.99	Aromas of rose, bergamot and lavender
3	d-Limonene	3.95	Fresh citrus, mint flavor
4	β -Pinene	2.08	Resinous and rosin aromas
5	Limonene	1.02	Turpentine, lemon
6	α -Copaene	0.71	With pine, turpentine aroma
7	Copaene	0.65	With pine aroma
8	Caryophyllene	0.33	Light lilac scent
9	α -Terpineol	0.25	Rich floral notes, typical of cloves
10	(R)-3,7-Dimethyl-6-octenal	0.24	Strong, fresh herbaceous citrus notes
11	Terpinolen	0.20	Smell of lemon
12	L- α -Terpineol	0.13	Clove

3.3 HCA and PCA analysis

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used to analyze *Z. bungeanum*, and 12 common volatile characteristics (Linalool, Geranyl Acetat, d-Limonene, β -Pinene, Limonene, α -Copaene, Copaene, Caryophyllene, α -Terpineol, (R)-3,7-Dimethyl-6-octenal, Terpinolen, and L- α -Terpineol) compounds with ROAV values greater than 0.1 are selected for correlation analysis, as shown in Fig. 3. HCA was used to group the samples, and Pearson correlation was used as the measurement standard. The Z-score method was used to standardize the relevant variables, and the cluster graph was obtained.

The results of HCA are shown in Fig. 4. When the distance coefficient is 0.4, 10 *Z. bungeanum* samples can be divided into two groups. When the distance coefficient is 0.15, 10 *Z. bungeanum* samples can be divided into 3 groups. Samples ZB1, ZB2, ZB4, ZB5, ZB7, ZB8, and ZB9 are grouped together; samples ZB10 are grouped separately; and ZB3 and ZB6 are grouped together. ZB10 is collected in Shaanxi Province at the lowest altitude and has a big difference from other groups. The flavor substance associated with ZB10 is limonene. ZB5, ZB7, ZB8, and ZB9 belong to the same group at an altitude of 1000–2000 m, and ZB1 and ZB4 belong to the same group at an altitude of 2000 m or more in Sichuan. These results show that the relative content of characteristic aroma substances is closely related to the growth site. The influence of climate factors on secondary metabolites is comprehensive because each class of secondary metabolites has geographical continuity.

In the principal component analysis (Fig. 5), two principal components were constructed, and the interpretation rates of PC1 and PC2 were 31.9% and 25.7%, respectively. As can be seen from the 3D scoring diagram of PCA (Fig. 6), there is a tendency that the tested samples are separated into relatively independent groups, and 10 samples can also be divided into 2 groups, which is roughly consistent with HCA.

Consistent with the results of cluster analysis, the distance between sample ZB10 and other samples on the main component dispersion plot is relatively large. This indicates that the flavor of sample Z10 from Hancheng, Shaanxi Province, is obviously different from other samples. The flavor compound that distinguishes ZB10 from other samples is limonene; ZB3 and ZB6 are close to each other in the principal component score chart and far from other samples. Caryophyllene is the flavor substance closely associated with these two samples.

3.4 Correlation analysis between climate factors and volatile components of *Z. bungeanum*

3.4.1 Correlation analysis

The production and accumulation of volatile oil in *Z. bungeanum* peel from different producing areas were regulated by climate factors. The results of correlation analysis show that there are different degrees of correlation between effective components and climate factors (Fig. 7 and Table S4). Dividing all climate factors into two categories and looking at the relationship between them at the top of the heat map, XAMT, XAMAT, XASD, and XMW are included in one cluster, and XAMIT, XAAP, and XRH are included in one cluster. In addition to terpinolen, β -Pinene, Limonene, d-Limonene, Caryophyllene, α -Copaene, and Copaene were positively correlated with XAMAT, XAMIT, and XAMT, indicating that high temperatures are conducive to the formation of terpene. Linalool, L- α -Terpineol, and α -Terpineol were negatively correlated with XAMT, XAMIT, and XAMAT, suggesting that high temperatures and temperature fluctuations are not conducive to the formation of alcohols. β -Pinene, α -Copaene, Linalool, L- α -Terpineol, and YGE were negatively correlated with XASD. Limonene, Copaene, and (R)-3, 7-dimethyl-6-octenal were significantly positively correlated with XMW. Linalool, Geranyl Acetat, and L- α -Terpineol were positively correlated with XAAP and XRH and negatively correlated with XAMT, suggesting that low temperatures and sufficient precipitation were conducive to the accumulation of Linalool, Geranyl Acetat, and L- α -Terpineol. β -Pinene, d-Limonene, and α -Copaene were significantly positively correlated with XAAP and XRH, indicating that sufficient precipitation was conducive to the accumulation of β -Pinene, d-Limonene, and α -Copaene.

3.4.2 Path analysis

The direct and indirect effects of climate factors on volatile components were calculated by path analysis (PA), and the relationship between climate factors and compounds was revealed. The contents of 12 common characteristics of volatile compounds were selected as independent variables, and climate factors were selected as dependent variables. The specific process is conducted as follows: First, the climate factors and volatile components in *Z. bungeanum* peels were analyzed by stepwise regression analysis using SPSS statistical software. Then, according to the regression analysis, the dominant climate factors of each compound were screened out, and finally, the direct path coefficients and indirect path coefficients were calculated.

XMW was significantly positively correlated with Copaene and (R)-3,7-dimethyl-6-octenal ($P < 0.001$). XMW is a key factor in limonene (1.071), copaene (0.886), and (R)-3, 7-dimethyl-6-octenal (1.071). XAMT had positive direct and indirect effects on limonene and (R)-3,7-dimethyl-6-octenal, but negative direct and indirect effects on geranyl acetat. The direct effect of XAMIT on Terpinolen (-0.695) was negative ($P < 0.05$), and the direct effect of XAAP on α -Copaene (0.644) was positive ($P < 0.05$). The positive correlation coefficient of XMW to Limonene was the largest (0.988), indicating that XMW was the main reason affecting Limonene. The direct effects of XASD and XAAP on limonene and (R)-3,7-dimethyl-6-octenal are negative, and the indirect effects are positive. XAAP is a key factor affecting α -Copaene and has a positive direct effect (0.644). XAMT is a key factor influencing geranyl acetat with a negative direct effect (-0.632). In conclusion, path analysis explains the relative importance of each climatic factor to volatile components, making multivariate statistical analysis more reasonable. The results showed that temperature, rainfall data, and average wind speed had significant effects on the contents of single volatile oils and total volatile oils.

Table 3
Path analysis between climate factors and volatile component of 6 *Z. bungeanum* peels.

Item	Factors	Correlation	Direct Path	Indirect Path coefficient						Signifi- cance level
		Coefficients	Coefficients							P- value
Limonene				Total	XAMT	XAMAT	XASD	XMW	XAAP	
	XAMT	0.527	0.035	0.038		0.021	0.005	0.020	-0.008	0.527
	XAMAT	0.398	-0.173	-0.25	-0.106		0.015	-0.090	-0.069	0.398
	XASD	0.368	-0.070	0.005	-0.010	0.006		-0.026	0.035	0.368
	XMW	0.988	1.071	1.146	0.600	0.557	0.401		-0.412	0.988
	XAAP	-0.490	-0.035	0.024	0.008	-0.014	0.017	0.013		-0.490
Terpinolen				Total	XAMIT					
	XAMIT	-0.695	-0.695							0.013
Geranyl acetat				Total	XAMT					
	XAMT	-0.632	-0.632							0.050
α - Copaene				Total	XAAP					
	XAAP	0.644	0.644							0.022
Copaene				Total	XMW					
	XMW	0.886	0.886							< 0.001
(R)-3,7- Dimethyl- 6-octenal				Total	XAMT	XAMAT	XASD	XMW	XAAP	
	XAMT	0.527	0.035	0.038		0.021	0.005	0.020	-0.008	0.059
	XAMAT	0.398	-0.173	-0.25	-0.106		0.015	-0.090	-0.069	0.127
	XASD	0.368	-0.070	0.005	-0.010	0.006		-0.026	0.035	0.148
	XMW	0.988	1.071	1.146	0.600	0.557	0.401		-0.412	< 0.001
	XAAP	-0.490	-0.035	0.024	0.008	-0.014	0.017	0.013		0.075

4 Discussion

The production and accumulation of secondary metabolites are affected by many factors, including internal factors such as genetic inheritance, tree age, and season, as well as external ecological conditions such as light, temperature, and precipitation. The same plants with different provenances have differences in the same environment, and these factors jointly affect the synthesis and accumulation of secondary metabolites in plants^[53]. Different environmental conditions in different producing areas lead to different levels of active ingredients in plants. In 10 natural habitat samples of *Z. bungeanum*, significant differences in volatile matter contents were found. 126 kinds of compounds were detected in *Z. bungeanum*, mainly terpenes (terpenes and terpene alcohols). Terpenoids are mainly secondary metabolites of plants and play an important role in the aroma production of plants^[54]. From the perspective of individual compounds, the compounds with the highest average relative content in *Z. bungeanum* were linalool and d-limonene. The contribution rate of terpenes in

volatile components of *Z. bungeanum* peel was the highest in ZB1 (72.93%) and ZB10 (78.10%). The relative content of alcohol in the *Z. bungeanum* sample was the highest in ZB6 (56.55%). ZB8 (14.77%) is the highest among esters.

Among the 27 common volatile substances, d-Limonene presented fresh citrus and mint notes; Linalool presented sweet floral notes reminiscent of kale and lavender; and Geranyl Acetat presented rose, bergamot, and lavender notes. The volatile oil of *Z. bungeanum* is mainly fragrant, floral, citrus, and mint. The main flavor substances in *Z. bungeanum* were linalool, d-limonene, geranyl acetat, 1-caryophyllene, α -copaene, These substances may play an important role in the composition of the distinctive flavor of *Z. bungeanum*^[55].

In addition, due to the different growing environments, the volatile substance content of the same variety is very different. For example, ZB1, ZB7, and ZB10 belong to the same variety of *Z. bungeanum*, but the climate factors in their growth environment are different, resulting in significant differences in volatile component content, indicating that the difference in volatile component content may be caused by climate factors. The flavor of *Z. bungeanum* samples from Hancheng City, Weinan City, and Shaanxi Province is obviously different from other *Z. bungeanum* samples, which may be related to variety, environmental factors, and human factors^[56].

The results of PCA and HCA analyses showed that there are significant differences in volatile substances in different habitats. β -pinene, limonene, and linalool are potential key compounds for the identification of *Z. bungeanum* from different origins. They can be used as a mark of different origins and can be used for the quality evaluation of *Z. bungeanum* peel.

Climatic factors, including temperature, precipitation, relative humidity, wind speed, and annual sunshine duration, may affect the production and accumulation of plant secondary metabolites^[57]. Research by Olha Mykhailenko and her team shows that the duration of sunlight has a significant positive effect on the accumulation of phenolic compounds in iris flowers^[58]. It was found that temperature, water vapor pressure, and other parameters showed a significant negative correlation with flavonoid content in the iris, while wind speed showed a significant positive correlation with flavonoid content^[59].

In this study, the relationship between 12 common characteristic volatile substances and climate factors is different. The higher the temperature, the higher the levels of β -Pinene, Limonene, d-Limonene, Caryophyllene, alpha-copaene, and Copaene. Low temperatures and small temperature fluctuations are conducive to the formation of Linalool, L- α -Terpineol, and α -Terpineol. Low temperatures and sufficient precipitation are conducive to the accumulation of linalool, geranyl acetat, and L-alpha-terpineol. Sufficient precipitation is conducive to the accumulation of β -Pinene, d-Limonene, and α -Copaene. In the same environment, d-Limonene, α -Terpineol, L- α -Terpineol, Linalool, Caryophyllene, Terpinolen, α -Phellandren, and Geranyl Acetat were more susceptible to environmental stress. The contents of β -pinene and limonene were less affected by climatic factors. Therefore, we can study the regulatory effect of volatile substances in *Z. bungeanum* peels by regulating climate conditions and further explore the mechanism of synthesis and accumulation of volatile oil in *Z. bungeanum* peels cultured under different terrain conditions by different ecological factors. Its expression profile is worth studying. In addition, molecular biology technology was used to evaluate the relationship between ecological factors and reproductive and nutritional factors, so as to improve the quality of *Z. bungeanum* peel. Therefore, we can explore the regulatory effect of volatile substances in *Z. bungeanum* peel by changing the climate factors. In conclusion, this study provides new valuable insights into the ecological response behind the mechanism of volatile oil accumulation in *Z. bungeanum* peel.

5 Conclusion

In summary, the aromatic substances and aroma characteristics of 10 kinds of *Z. bungeanum* from different origins were analyzed and identified by the HS-SPME-GC-O-MS method. The contents of volatile oil compounds of wild *Z. bungeanum* were significantly different in different regions, among which terpenes were the most abundant, followed by alcohols and esters. The compounds with relatively high average relative content in *Z. bungeanum* were d-Limonene (24.71%) and Linalool (23.13%). In addition, among the 27 common volatile signature substances, the key volatile substances d-Limonene and Linalool are important compounds that affect the fragrance of *Z. bungeanum*, so the *Z. bungeanum* in the region shows a

stronger citrus aroma. Through the correlation analysis and path analysis of volatile components and ecological factors, it was found that temperature, rainfall data, and average wind speed were the main environmental factors affecting the accumulation of volatile oil compounds. This study not only provides a basis for identifying high-quality *Z. bungeanum* resources through the characteristics of volatile substances, but also provides detailed information and valuable reference value for the accumulation of volatile substances under climatic conditions.

Declarations

Acknowledgements

Not applicable.

Author contribution

Conceptualization, Zhihang Zhuo; methodology, Yuhang Wu and Danping Xu; software, Danping Xu and Yuhang Wu; formal analysis, Yuhang Wu and Zhihang Zhuo; investigation, Qian Qianqian; data curation, Qian Qianqian; writing-original draft preparation, Yuhang Wu; writing-review and editing, Danping Xu and Zhihang Zhuo; supervision, Zhihang Zhuo.

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Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Ethics declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no conflict of interest

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Figures

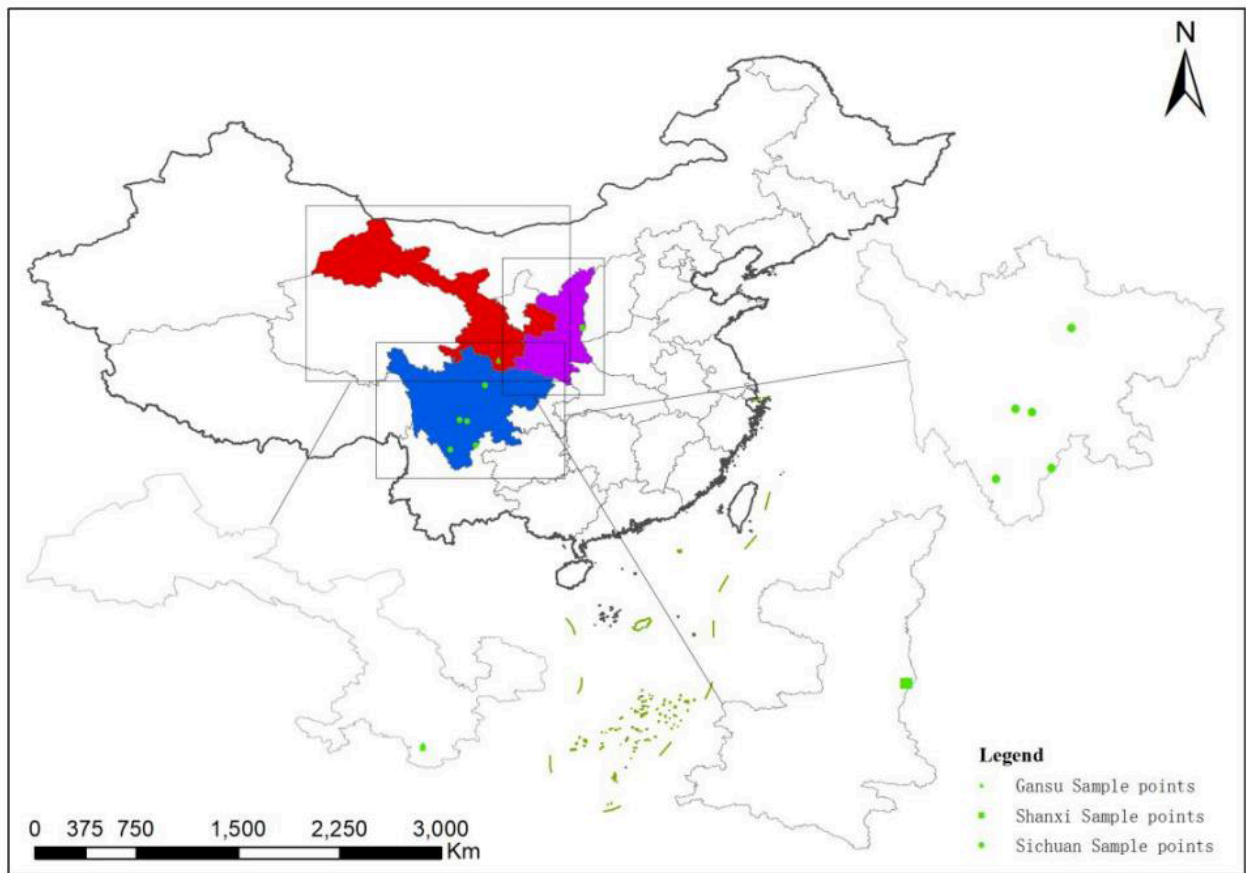


Figure 1

Map of samples collection sites.

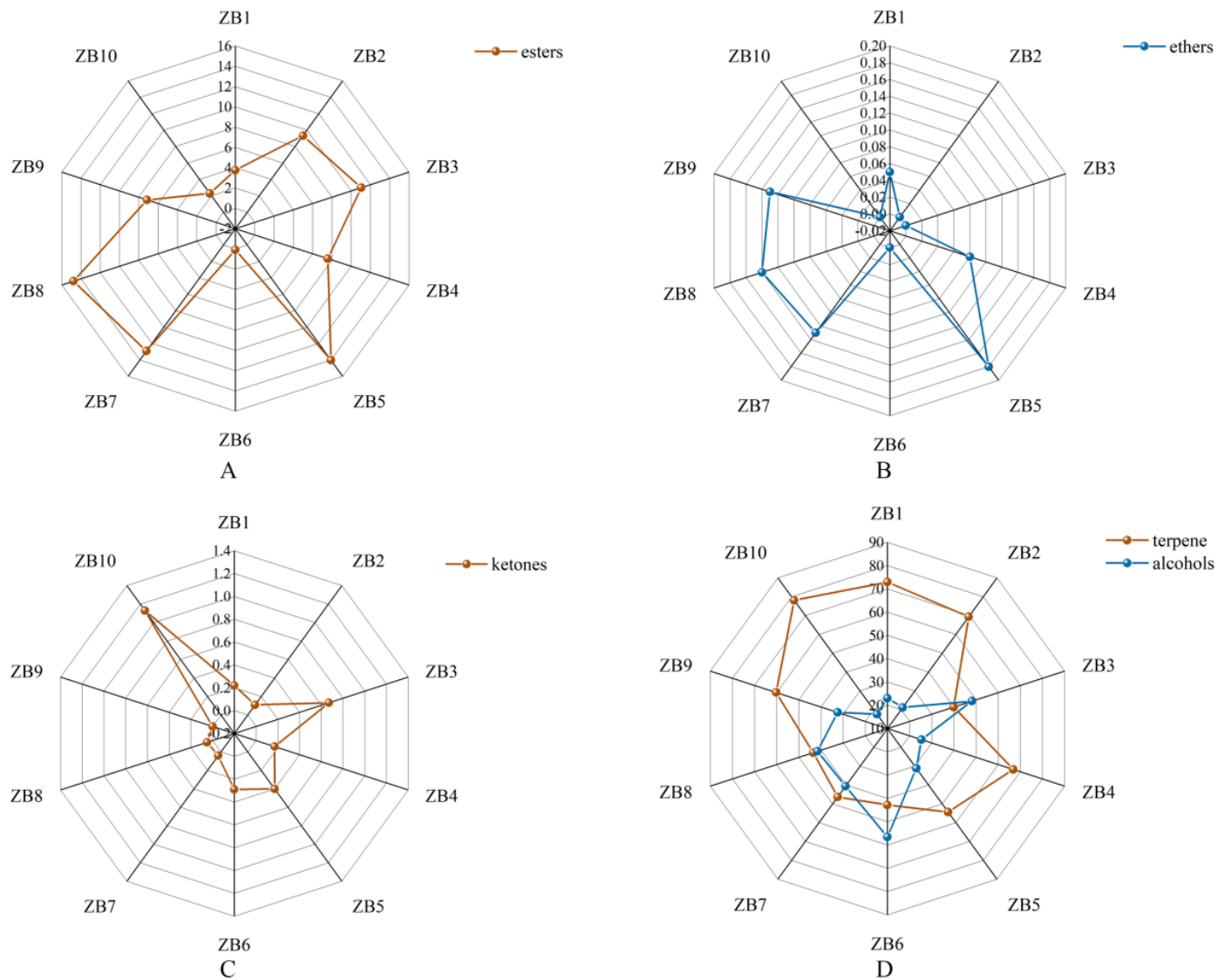


Figure 2

Distribution of volatile component content composition in samples from different area. A, esters; B, ethers; C, ketones; D, terpene and alcohols.

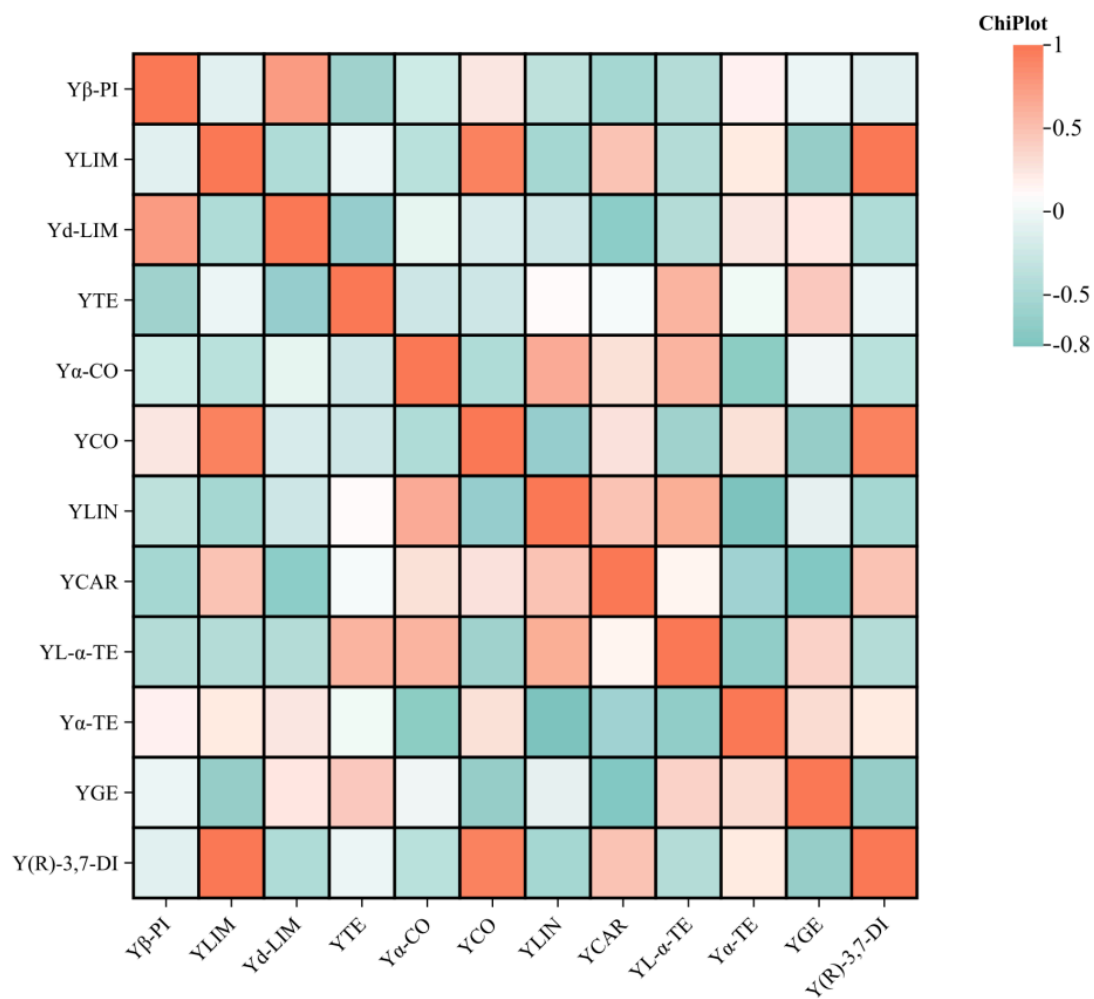


Figure 3

The relative content of common volatile components in *Z. bungeanum* samples.

Yβ-PI, β-Pinene; YCO, Copaene; YLIM, Limonene; Yd-LIM, d-Limonene; YTE, Terpinolen; YCAR, Caryophyllene; YLIN, Linalool; YL-α-TE, L-α-Terpineol; Yα-TE, α-Terpineol; YGE, Geranyl acetat; Y(R)-3,7-DI, (R)-3,7-Dimethyl-6-octenal; Yα-CO, α-Copaene.

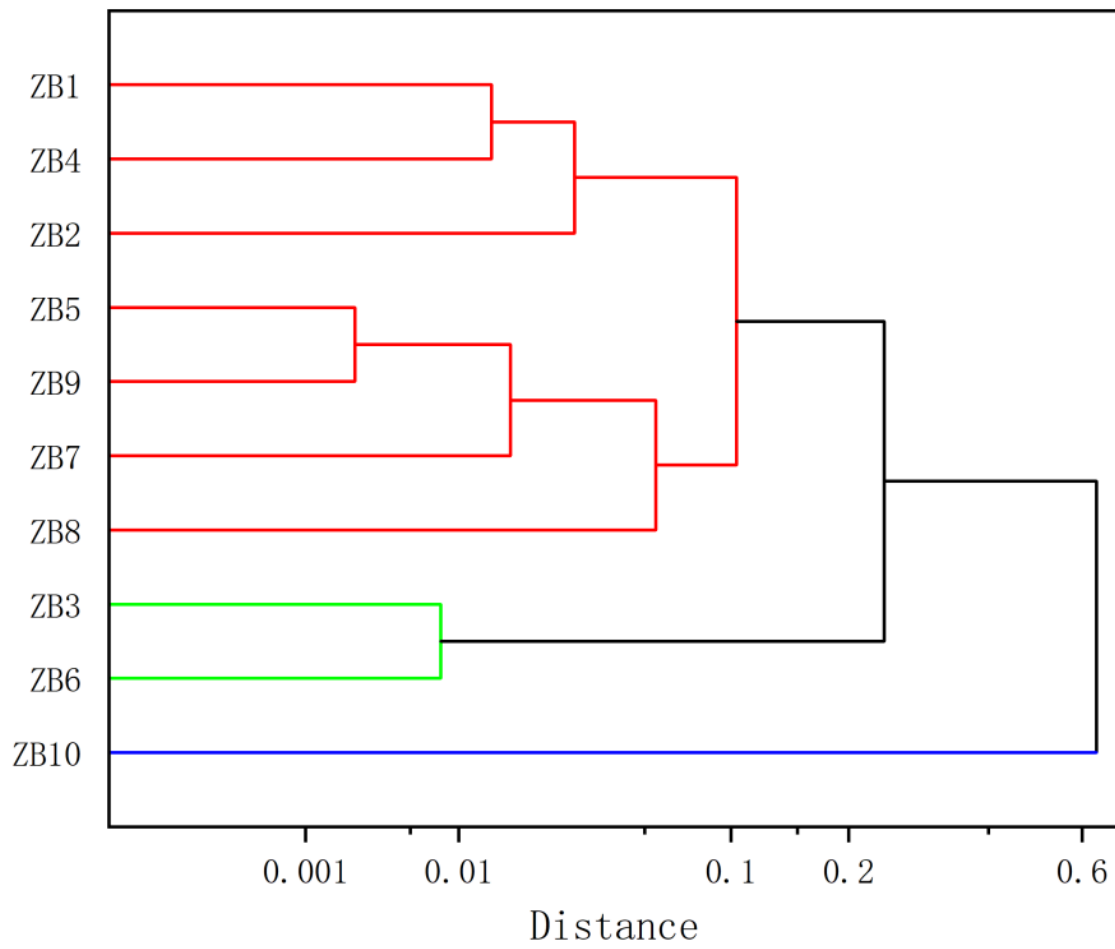


Figure 4

Dendrograms resulting from hierarchical clustering analysis of *Z. bungeanum* from different locations.

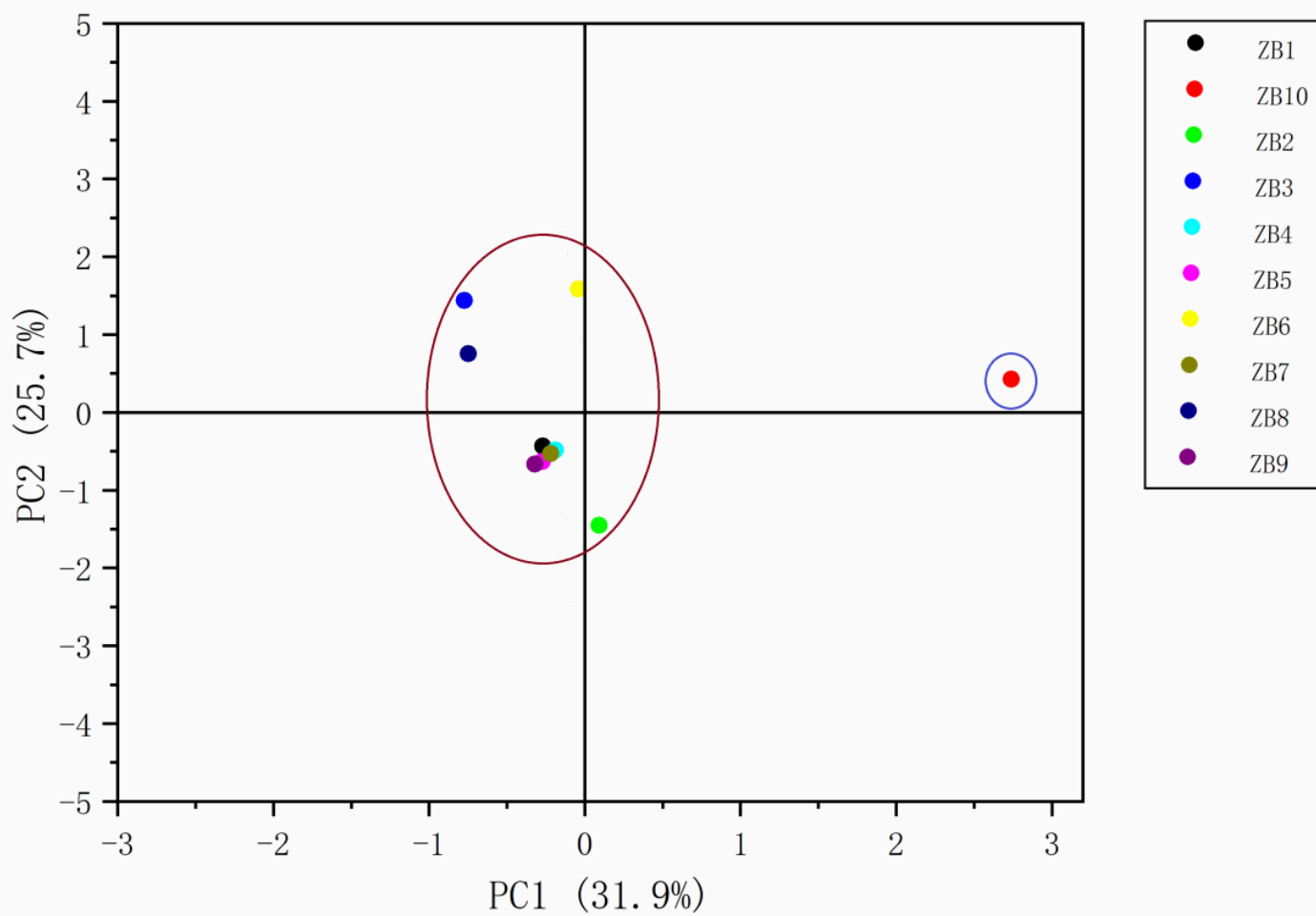


Figure 5

2-D scores plot of the PCA of 10 samples

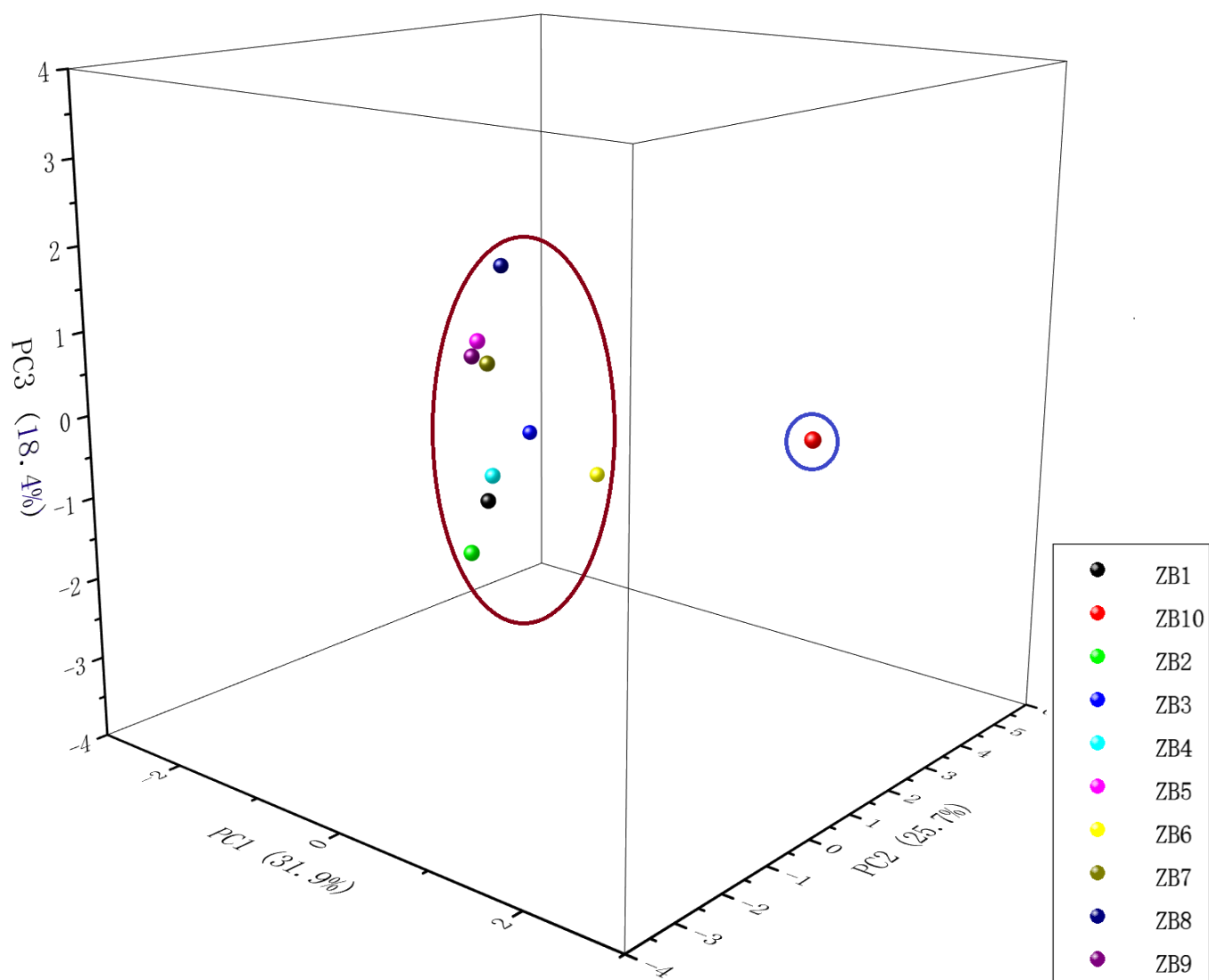


Figure 6

loading values of PCA of all 10 common characteristic volatile components on 3-D map.

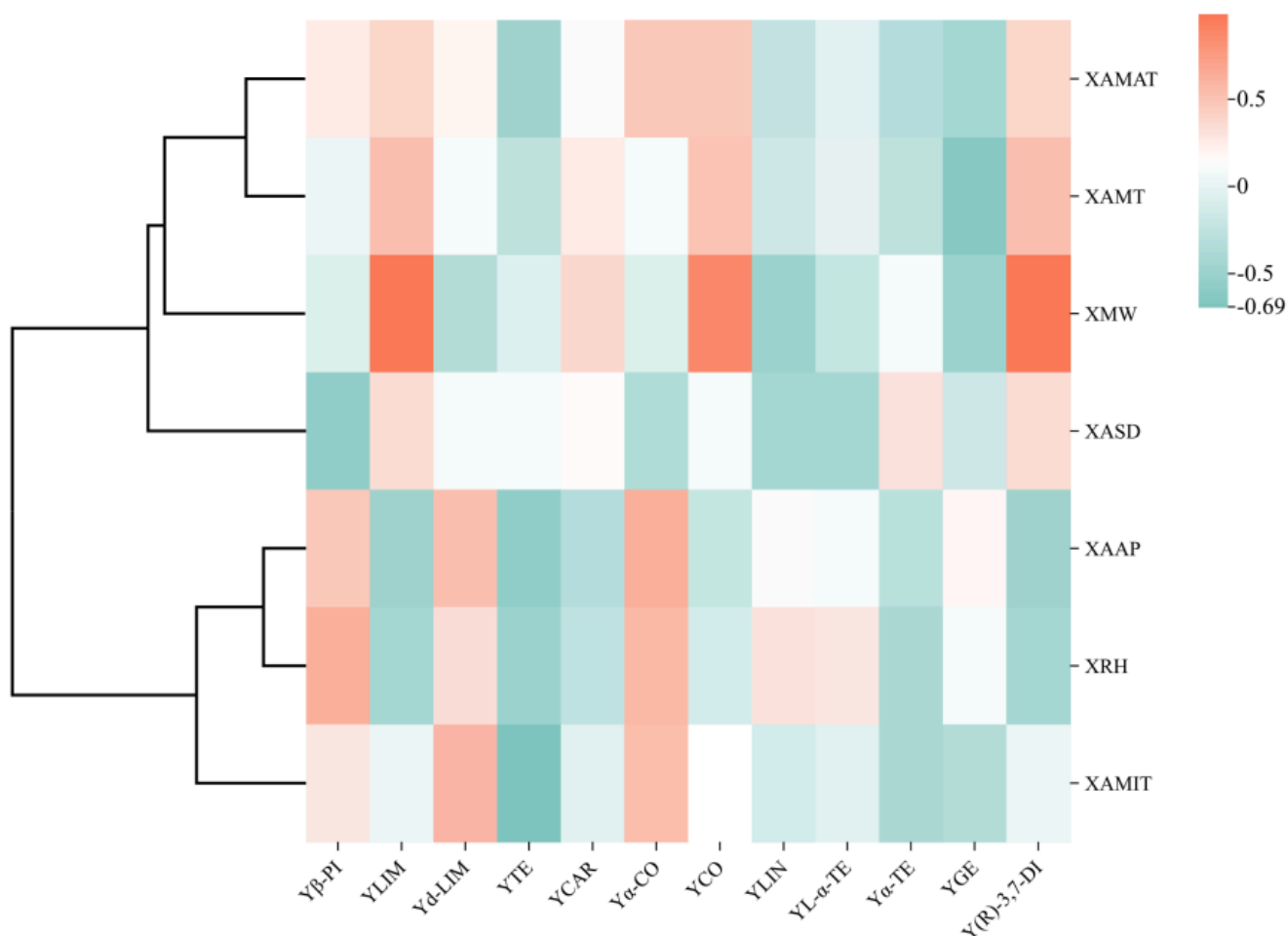


Figure 7

Correlation analysis results of environmental factors and volatile components of *Z. bungeanum* peels.

XMW(m/s), wind speed; XASD(h), Annual sunshine duration; XAMIT($^{\circ}$ C), minimum temperature; XAMT($^{\circ}$ C), average temperature; XAAP(mm), Rainfall data; XRH(%), medial humidity; XAMAT($^{\circ}$ C), highest temperature; Yβ-PI, β-Pinene; YCO, Copaene; YLIM, Limonene; Yd-LIM, d-Limonene; YTE, Terpinolen; YCAR, Caryophyllene; YLIN, Linalool; YL-α-TE, L-α-Terpineol; Yα-TE, α-Terpineol; YGE, Geranyl acetat; Y(R)-3,7-DI, (R)-3,7-Dimethyl-6-octenal; Yα-CO, α-Copaene.

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