Hindawi
Journal of Food Quality
Volume 2019, Article ID 7525201, 7 pages
https://doi.org/10.1155/2019/7525201

Research Article

Origin Identification of the Sauce-Flavor Chinese Baijiu by Organic Acids, Trace Elements, and the Stable Carbon Isotope Ratio

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Received 3 April 2019; Revised 24 June 2019; Accepted 14 July 2019; Published 1 August 2019

Academic Editor: Jesús Lozano

Sauce-flavor baijiu is a popular Chinese baijiu. To avoid adulteration and market cheating, this study aims to develop a new, reliable, and accurate traceability system for characterization of the geographical origins. Totally, 100 samples collected from seven regions in Guizhou Province of China are analyzed, involving 13 trace elements, 5 organic acids, and stable carbon isotope composition of acetic acid. Based on these data, a geographical classification model is established. The origin accuracy is found to reach as high as 83%, thus providing a useful technique for authentication of the sauce-flavor baijiu and contributing to the healthy development of the baijiu industry in China.

1. Introduction

Sauce-flavor baijiu (Chinese baijiu) is recognized as the most popular alcohol beverage in China. It has been produced primarily in Guizhou Province in southwest China. The history of its local production traces back over 1000 years, and it plays a critical role nowadays in the Chinese baijiu industry [1]. In 2017, the sales of the Guizhou production rose to 90.2 billion (RMB) with a profit up to 43.0 billion (RMB), accounting for 35% of the total profits of the baijiu industry in China [2]. As an iconic sauce-flavor baijiu of Guizhou province, Moutai-Jiu's sales revenue reaches as high as 75 billion in 2018 [3]. The sauce-flavor baijiu is reputable for its complicated volatilities and wonderful flavors. All of these derive from the certain ingredients (sorghum, wheat, and so on), local water, climate, soil, and local "daqu" (yeast), as well as from the special process of solid fermentation, which has typical local characters [1]. Motivated by the high price of the baijiu, there were quite a few market cheating scandals occurring, such as adulteration, counterfeit, and fraudulent sauce-flavor baijiu (Sohu/business, 2018). To address these problems, the State Administration for Market Regulation and Department of Agriculture issued the geographical indications (GIs) policy directed at the industry of sauce-flavor baijiu [4]. As revealed by studies, the volatile compounds of baijius have the potential to assist in tracing the geographical origin. Despite this, it remains difficult to distinguish the baijius from the same aroma type produced in the surrounding regions [5]. Similarly, trace elements can be applied to differentiate the baijius between Shandong, Guizhou, or Sichuan provinces. Despite this, they are unable to make distinction between the baijius produced in Guizhou and that produced in Sichuan due to geographic proximity [6]. Since the distilleries are located close to each other to compete for favorite resources and the baijius are produced by applying the same technique, the aroma compounds are quite similar. Therefore, it is necessary to introduce combined traceability by using multiple markers. Stable carbon isotope ratio has already been used to trace grape wine [7, 8]. Never before, however, was it tried in the sauce-flavor baijiu. In this study, volatile compounds, trace elements, and stable carbon isotope ratios are combined with an aim to establish the traceability of the sauce-flavor baijius produced in Guizhou Province. In conjunction with multivariate statistics, the most effective indicators to the origins are explored, and the mathematical model that is capable of predicting the geographical region of the sauce-flavor baijius is constructed.

2. Materials and Methods

2.1. Sauce-Flavor Baijiu Samples. A total of 100 samples were collected from seven regions in Guizhou Province, namely, Bijie (7 baijiu samples), Zunyi (7 baijiu samples), Tongren (18 baijiu samples), Qiandongnan (18 baijiu samples), Qiannan (17 baijiu samples), Qianxinan (16 baijiu samples), and Anshun (17 baijiu samples) (Figure 1). All of them were collected under different brands but produced in the same year, 2016, with the same technique, namely, the daqu sauce-flavor fermentation. The number of baijiu producers varied from region to region, and the sample number was different. This, however, made no impact on the representativeness of the samples. All of them were sourced from the local sauce-flavor baijiu factory. The samples were stored in a baijiu cabinet at 17°C prior to analysis. For baijiu, its brand and producer information were not indicated as required by a previous agreement reached with the baijiu maker, which prohibited any information in relation to the brand and producer from being disclosed on any research reports and publications.

2.2. Reagents and Solutions. All the chemicals used were of analytical grade unless stated otherwise. Deionized water (18.2 MΩ/cm) was prepared by using the Milli-Q system (Millipore, Bedford, MA). Nitric acid, phosphoric acid, methanol, and anhydrous ethanol were purchased from Merck & Co. Inc. (New Jersey, USA). Formic acid, acetic acid, lactic acid, butyric acid, caproic acid, and propionic acid were sourced from Sigma-Aldrich. The standard metal solution (22 metal elements, 1000 μg/mL) was supplied by the National Center for Analysis and Testing of Nonferrous Metals and Electronic Materials (Beijing, China).

2.3. Measurement of Carbon Isotope Ratios. The $^{13}C/^{12}C$ abundance ratio was expressed as $\delta^{13}C$ values calibrated against the international standard Vienna Pee Dee Belemnite (VPDB), which is calculated as follows:

$$\delta^{13}C_{\text{sample}}\,(‰) = \left[\left(\frac{R_s}{R_{st}}\right) - 1\right] \times 1000, \qquad (1)$$

where R_s represents the ratio of $^{13}C/^{12}C$ in the sample and R_{st} denotes the ratio of the standard. The result is in the form of a relative δ (‰) against the standard.

The determination of $\delta^{13}C_{AA}$ (AA, acetic acid) was performed by using the referenced method [9]. The baijiu samples were directly injected into EA/LC-IRMS (Delta V Advantage, Thermo Fisher, USA), before analyses were conducted in triplicate.

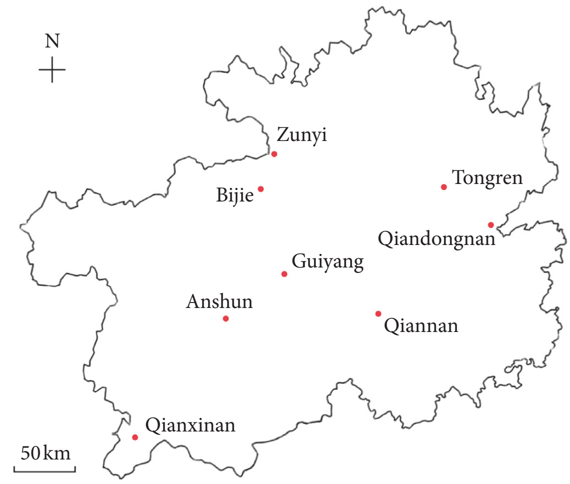

Figure 1: The geographical origin map of sauce-flavor baijiu (Chinese baijiu) samples from Guizhou Province.

2.4. Measurement of Lactic Acid. The measurement of lactic acid was performed by HPLC (Agilent 1260, Agilent, USA) using the method discussed in [10]. In brief, the baijiu sample was directly introduced into the HPLC-DAD (Agilent 1260, Agilent, USA) with the Eclipse XDB-C18 column (250 mm × 4.6 mm, 5 μm) and a column temperature of 30°C. The analyses were carried out in triplicate.

2.5. Measurement of Propanoic Acid, Acetic Acid, Butyric Acid, and Hexanoic Acid. The determination of these 4 organic acids was conducted based on the method discussed in [11]. In brief, the baijiu sample was injected directly into GC-FID (Agilent 7890B, Agilent, USA) with the Agilent WAX column (30 m × 0.32 mm × 0.25 μm). The analyses were conducted in triplicate.

2.6. Measurement of Elements. The determination of the trace metal elements was carried out by using the standard methods [6]. In brief, 25 mL baijiu sample was evaporated to be alcohol-free using a water bath, before being diluted to 25 mL again by 1% nitric acid solution. This solution was subjected to analysis by ICP-MS (ICAP Qc-UltiMate 3000, Thermo Fisher, USA) for Ba, Cr, Cu, Li, Mn, and Zn as well as by ICP-OES (iCAP 6300MFC, Thermo Fisher, USA) for Al, Ca, Fe, K, Mg, Na, and Sr. All of the analyses were conducted in triplicate.

2.7. Statistical Analysis Method. Multivariate analysis was performed by using the R-Project Version 3.5.1 software (https://www.r-project.org/) [12]. These analyses involved PCA (principal components analysis), PLS-DA (partial least squares discriminant analysis).

Normally, PCA analysis is intended to convert a set of observations made of potentially correlated variables into a set of values of linearly uncorrected variables [13]. PLS-DA is regarded as a versatile algorithm used for predictive and descriptive modeling, as well as for the discriminative variable selection [14]. Over the most recent two decades, PLS-DA has achieved a huge success in modeling high-dimensional datasets for a range of different purposes, such as product authentication in food analysis [15].

3. Results and Discussion

3.1. Carbon Isotope Composition. δ^{13}C values of acetic acid in the baijius of the 7 regions are listed in Table 1, which reveals that it varied from -19.05 ± 1.70 to -13.17 ± 1.62. The one-way ANOVA analysis was conducted to discriminate between the regions. The results demonstrated significant variations among those regions. For example, Bijie is notably different from other areas. Zunyi differs from Qiannan. Anshun is distinct from Tongren. These results indicated clearly that the stable carbon isotope ratios can be taken as an effective geographical marker. Up to now, there has yet to be any relevant studies where δ^{13}C of acetic acid is used as marker for the origin of Chinese baijiu. Andreas RoBmann [16] reported on using δ^{13}C of ethanol in wine as the original marker for grape wine. The stable isotope ratios of ethanol in wine reflects the geographical information of the wine-producing area; in the same way, acetic acid of sauce-flavor baijiu was produced from material sorghum during fermentation, which also indicates the characteristic of original information, so δ^{13}C of acetic acid is used in tracing the geographical region of sauce-flavor baijiu.

3.2. Analysis of Organic Acids. Organic acids are known as essential volatiles compounds, playing a crucial role in the sensory evaluation of sauce-flavor baijiu [17, 18]. The organic acids are derived from fermentation of the raw material (local sorghum). A variety of microorganisms such as *Saccharomyces cerevisiae* play a significant role in the production process. Different environments tend to suit the habitation by different microorganisms that produce different organic acids in the baijiu [19]. As indicated by the prior studies, volatiles compounds can be taken as the markers of geographical origins for baijiu [5, 20]. The six organic acids represent the major flavor components for sauce-flavor baijiu. Due to this, the precursor of esters and the typical representative organic acids are relatively high in sauce-flavor baijiu. Five organic acids of sauce-flavor baijiu were determined by GC-FID/HPLC-DAD. Tables 2 and 3 illustrate the five organic acids of linear range, linear equation, detection limit, and results. The range of lactic acid, acetic acid, propanoic acid, butyric acid, and hexanoic acid obtained from seven different origins (Bijie, Zunyi, Qiandongnan, Qiannan, Tongren, Anshun, and Qianxinan) in Guizhou Province are found to be from 510.99 ± 64.97 to 1024 ± 209.34, from 0.93 ± 0.09 to 1.90 ± 0.42, from 0.09 ± 0.03 to 0.36 ± 0.58, from 0.07 ± 0.05 to 0.21 ± 0.07, and from 0.04 ± 0.03 to 0.21 ± 0.01 mg/L, respectively. There is a noticeable variation spotted between the seven regions, which suggests that those acids can be identified as an ideal marker of geographical origins.

3.3. Analysis of Elements. The elements of sauce-flavor baijiu are derived from the raw material (local sorghum) and the locally available water (river or well). After the fermentation process, those alcohol/water liquids are distilled for multiple times. Under the steam current, those elements are transferred into sauce-flavor baijiu, which is clearly indicative of the geographical information. Meanwhile, the elements can be identified as the indicators of geographical origin for baijiu (Chinese baijius) [6]. In this work, a total of 13 elements (Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Sr, and Zn) are identified by ICP-OES/MS. Tables 4 and 5 show the 13 elements for their linear range, correlation coefficient, detection limit, and results. It can be seen clearly that the contents of Al, Ca, K, and Na are significantly higher as compared to others, especial for Ca, the maximum content of which reaches 7.29 ± 1.44 mg/L (Qiandongnan city). Meanwhile, the results demonstrate that every single element has a notable difference among the seven different regions. Thus, elements can be identified as the marker of the geographical regions for sauce-flavor baijiu originating from Guizhou Province of China.

There remains plenty of data that need to be taken into consideration for analysis in this work. The multivariate statistics will be further applied to the exploration of the main contributors for determining geographical origins.

3.4. Multivariate Analysis of Nineteen Parameters

3.4.1. PCA Results. Being one of the multivariate analysis techniques, PCA (principal component analysis) is frequently conducted as a dimension-reduction tool to reduce a large set of variables to a small set that remains capable of containing most of the information in the large set. Considering this, PCA was employed for the transformation of largely correlated variables of this work into smaller uncorrected variables [15]. In this work, totally 100 sauce-flavor baijiu samples were collected from seven different geographical locations in Guizhou Province (Figure 1 shows the map), and the possible indicators were tested, including five organic acids (important volatile compounds of baijiu), thirteen elements, and stable carbon isotope ratio of acetic acid of sauce-flavor baijiu. The above 19 parameters were analyzed for their contributions in tracing the geographical region of sauce-flavor baijiu, which is based on the principle of PCA; that is, the more the value of cumulation means, the more significant the variance is. Table 6 indicates the cumulative contribution rate of the principal component analysis of 19 variances, respectively. Normally, for the sake of constructing a PCA model, the contributions made by parameters need to exceed 75%, which will be deemed sufficient [15]. Therefore, it can be seen that the 10 variances (Al, Li, Ca, Cu, hexanoic acid, Fe, $\delta^{13}C_{\text{acetic acid}}$, Zn, lactic acid, and acetic acid) top down are major contributors in this model, with their accumulative contributions being up to 76.63% in this PCA model. The biggest contributor is made up of 6 elements (Al, Li, Ca, Cu, Fe, and Zn) with 52.43% contributions. The second one includes 3 organic acids (hexanoic acid, lactic acid, and acetic acid) with 16.77% contributions. The last one is comprised of carbon stable isotope ratio with 7.42% contributions in this model. When compared to other studies [5, 20], only volatile compounds

Table 1: The mean ± standard error value of the carbon stable isotope of acetic acid of sauce-flavor baijiu from seven different origins (unit: ‰).

Isotope (‰)	Region						
	Bijie ($n = 7$)	Zunyi ($n = 7$)	Qiandnan ($n = 18$)	Qiannan ($n = 17$)	Tongren ($n = 18$)	Anshun ($n = 17$)	Qianxnan ($n = 16$)
$\delta^{13}C_{acetic\ acid}$	-15.37 ± 1.23^a	-7.64 ± 1.92^b	-17.75 ± 1.06^b	-19.05 ± 1.70^c	-13.17 ± 1.62^d	-16.74 ± 1.30^b	-13.23 ± 0.97^d

^{a,b,c,d}Means in the same row with different superscript letters are statistically significantly different according to one-way ANOVA ($p < 0.05$); these values indicate $\delta^{13}C_{acetic\ acid}$ values that are responsible for sauce-flavor baijiu from different regions.

Table 2: The mean ± standard error value content of five organic acids of sauce-flavor baijiu from seven different origins (unit: mg/L).

Content of organic acids (g/L)	Region						
	Bijie ($n = 7$)	Zunyi ($n = 7$)	Qiandnan ($n = 18$)	Qiannan ($n = 17$)	Tongren ($n = 18$)	Anshun ($n = 17$)	Qianxnan ($n = 16$)
Lactic acid	0.51 ± 0.65^a	0.95 ± 0.26^b	1.01 ± 0.21^b	1.02 ± 0.09^b	$0.79 \pm 0.09^{b,c}$	0.91 ± 0.11^b	0.84 ± 0.16^b
Acetic acid	1.51 ± 0.15^a	1.16 ± 0.18^a	$0.93 \pm 0.09^{a,b}$	$1.70 \pm 0.53^{a,c}$	1.84 ± 0.35^c	1.90 ± 0.42^c	1.60 ± 0.41^a
Propanoic acid	0.17 ± 0.02^a	0.09 ± 0.04^b	0.36 ± 0.58^a	$0.13 \pm 0.07^{a,b}$	0.23 ± 0.03^c	0.09 ± 0.03^b	$0.34 \pm 0.45^{b,c}$
Butyric acid	0.07 ± 0.05^a	0.08 ± 0.02^a	0.15 ± 0.08^b	0.21 ± 0.07^c	$0.10 \pm 0.03^{a,d}$	0.15 ± 0.09^e	0.08 ± 0.03^a
Hexanoic acid	0.05 ± 0.01^a	0.04 ± 0.03^a	0.21 ± 0.11^b	0.15 ± 0.03^c	0.07 ± 0.03^d	0.11 ± 0.05^d	0.09 ± 0.04^d

^{a,b,c,d}Means in the same row with different superscript letters are statistically significantly different according to one-way ANOVA ($p < 0.05$); these values indicate those organic acids that are responsible for sauce-flavor baijiu from different regions.

Table 3: The mean ± standard error value content of thirteen elements of sauce-flavor baijiu from seven different origins (unit: mg/L).

Content of elements (mg/L)	Region						
	Bijie ($n = 7$)	Zunyi ($n = 7$)	Qiandnan ($n = 18$)	Qiannan ($n = 17$)	Tongren ($n = 18$)	Anshun ($n = 17$)	Qianxnan ($n = 16$)
Al	0.67 ± 0.18^a	0.54 ± 0.52^a	2.25 ± 0.16^b	0.56 ± 0.2^a	1.60 ± 0.14^c	1.24 ± 0.25^d	2.92 ± 0.07^e
Ba	0.02 ± 0.01^a	0.002 ± 0.001^a	$0.003 \pm 0.001^{a,b}$	$0.002 \pm 0.001^{a,c}$	$0.002 \pm 0.00^{a,d}$	$0.002 \pm 0.00^{a,d}$	$0.003 \pm 0.00^{a,e}$
Ca	3.04 ± 0.43^a	3.32 ± 1.17^a	$7.29 \pm 1.44^{b,f}$	1.94 ± 0.86^c	6.27 ± 0.66^d	4.33 ± 0.45^e	$6.75 \pm 0.04^{d,f}$
Cr	0.01 ± 0.005^a	0.02 ± 0.01^a	$0.02 \pm 0.02^{a,b}$	0.002 ± 0.003^c	0.0005 ± 0.0001^c	$0.02 \pm 0.003^{a,d}$	$0.02 \pm 0.001^{a,e}$
Cu	$0.009 \pm 0.006^{a,c}$	$0.03 \pm 0.02^{b,c}$	0.03 ± 0.03^b	0.008 ± 0.008^c	0.02 ± 0.001^c	$0.02 \pm 0.007^{b,c}$	0.39 ± 0.0004^d
Fe	0.36 ± 0.07^a	0.43 ± 0.43^a	1.23 ± 0.41^b	0.58 ± 0.31^a	0.45 ± 0.43^a	0.25 ± 0.16^a	0.92 ± 0.005^c
K	1.02 ± 0.49^a	1.60 ± 1.12^a	0.90 ± 0.69^b	$1.31 \pm 1.15^{a,b}$	1.94 ± 0.07^c	2.38 ± 0.80^c	$0.81 \pm 0.02^{b,d}$
Li	0.008 ± 0.003^a	0.005 ± 0.003^b	0.002 ± 0.002^b	$0.001 \pm 0.001^{b,c}$	0.02 ± 0.002^d	0.015 ± 0.006^e	0.017 ± 0.001^f
Mg	$0.77 \pm 0.22^{a,e}$	$0.58 \pm 0.30^{a,e}$	1.34 ± 0.40^b	$0.58 \pm 0.31^{a,c}$	1.22 ± 0.05^d	1.19 ± 0.02^d	$0.57 \pm 0.39^{e,c}$
Mn	0.025 ± 0.006^a	0.13 ± 0.13^a	0.14 ± 0.09^a	0.26 ± 0.26^b	0.07 ± 0.007^c	0.06 ± 0.007^c	$0.071 \pm 0.001^{a,c}$
Na	3.09 ± 1.65^a	3.37 ± 2.85^a	4.70 ± 2.08^b	3.71 ± 1.65^a	6.06 ± 0.59^c	6.50 ± 0.008^c	$3.95 \pm 0.04^{a,b,d}$
Sr	0.03 ± 0.03^a	3.37 ± 2.86^a	0.03 ± 0.02^a	0.34 ± 0.77^b	0.20 ± 0.00^c	0.02 ± 0.004^c	$0.016 \pm 0.002^{c,a}$
Zn	0.02 ± 0.008^a	3.37 ± 2.87^a	0.27 ± 0.33^b	0.05 ± 0.03^c	0.04 ± 0.008^c	0.10 ± 0.08^c	$0.29 \pm 0.007^{b,d}$

^{a,b,c,d}Means in the same row with different superscript letters are statistically significantly different according to one-way ANOVA ($p < 0.05$); these values indicate those elements that are responsible for Sauce-flavor baijiu from different regions.

were used to identify the origin of baijiu, which was based on the different aroma types of baijiu produced in different regions. However, for the only one aroma type, the sauce-flavor baijiu (Chinese baijius) requires more different types of parameters, like elements, acids, and stable isotopes. As we know that the elements are mainly derived from the locally obtained raw materials including water, both are able to indicate geographical information on the area of production. It is possible that a tiny fraction of the elements are derived from the containers of baijius, which is discounted in this study. Therefore, further study will be performed to evaluate the effect of elements from containers. For acids and stable isotopes, both are obtained from raw materials, which only reflect the geographical information of the raw materials. Therefore, the contributions are lower than elements.

3.4.2. PLS-DA Model. PLS-DA (partial least squares discriminant analysis) is a linear classification method that combines the properties shown by partial least square regression with the discrimination power of a classification technique [21], which was widely applied to the classification of food and beverages, just like honey and grape wine [22]. In accordance with Section 3.4.1, the data matrix (10 geographical indicators and 100 sauce-flavor baijiu samples from 7 different regions of Guizhou Province) was employed to conduct EigenMS normalization, the results of which were saved as normadata_res.csv. Then PLS-DA was performed by using the R-Project Version 3.5.1 software, with the results shown in Figure 2, which reveals that Qianxinan, Qiandongnan, Tongren, and Qiannan are noticeably separated, despite Qianxinan being close to Qiannan, Qiannan

Table 4: Nineteen parameters of variables on two principle components of principal component analysis from seven different origins.

Parameters	PC1	PC2	Euclidean distance	Contribution (%)
Al	21.25	0.06	21.25	12.35
Li	3.94	17.23	17.68	10.28
Ca	16.29	0.01	16.29	9.47
Cu	13.33	0.16	13.33	7.75
Hexanoic acid	0.03	13.32	13.32	7.74
Fe	6.89	10.85	12.85	7.47
$^{13}\delta C_{\text{acetic acid}}$	7.37	10.43	12.77	7.42
Zn	8.33	2.77	8.78	5.11
Lactic acid	0.20	8.05	8.06	4.68
Acetic acid	1.64	7.29	7.48	4.35
Cr	6.85	2.76	7.38	4.29
Mn	2.03	6.33	6.65	3.86
Butyric acid	3.40	5.14	6.17	3.59
K	3.38	5.13	6.14	3.57
Ba	0.55	4.76	4.79	2.79
Na	0.04	4.07	4.07	2.36
Propanoic acid	2.66	0.36	2.69	1.56
Sr	1.67	0.85	1.88	1.09
Mg	0.16	0.41	0.44	0.25

Table 5: Nineteen classification results by PLS-DA for seven different origins.

	Bijie	Zunyi	Qiandnan	Qiannan	Tongren	Anshun	Qianxnan	Accurate rate (%)
Bijie	6	0	0	0	0	1	0	85.71
Zunyi	2	3	0	2	0	0	0	42.86
Qiandnan	0	0	17	0	1	0	0	94.44
Qiannan	0	2	0	15	0	0	0	88.24
Tongren	0	0	0	0	18	0	0	100.00
Anshun	3	1	0	0	1	12	0	70.59
Qianxnan	0	0	0	0	0	0	16	100.00

Table 6: Nineteen parameters of variables on two principle components of principal component analysis from seven different origins.

Parameters	PC1	PC2	Euclidean distance	Contribution (%)
Al	21.25	0.06	21.25	12.35
Li	3.94	17.23	17.68	10.28
Ca	16.29	0.01	16.29	9.47
Cu	13.33	0.16	13.33	7.75
Hexanoic acid	0.03	13.32	13.32	7.74
Fe	6.89	10.85	12.85	7.47
$^{13}\delta C_{\text{acetic acid}}$	7.37	10.43	12.77	7.42
Zn	8.33	2.77	8.78	5.11
Lactic acid	0.20	8.05	8.06	4.68
Acetic acid	1.64	7.29	7.48	4.35
Cr	6.85	2.76	7.38	4.29
Mn	2.03	6.33	6.65	3.86
Butyric acid	3.40	5.14	6.17	3.59
K	3.38	5.13	6.14	3.57
Ba	0.55	4.76	4.79	2.79
Na	0.04	4.07	4.07	2.36
Propanoic acid	2.66	0.36	2.69	1.56
Sr	1.67	0.85	1.88	1.09
Mg	0.16	0.41	0.44	0.25

being close to Qiandongnan, and Qiandongnan being close to Tongren (Figure 1). Those sauce-flavor baijiu samples collected from 4 cities above can be distinguished. There is some crossover among Bijie, Anshun, and Zunyi, for which the samples collected from them cannot be significantly separated. Table 7 presents the classification results, from which it can be seen that Zunyi has the lowest accuracy rate (42.86%), which contributes samples, two of which are divided into Bijie and two of which are divided into Qiannan. This is speculated to be due to the limited number of samples, which makes it unlikely to provide sufficient geographical information. Besides, it is possibly attributed to those seven samples being collected from three different baijiu plants. More possibly, Zunyi is adjacent to Bijie and Qiannan separately. There are four areas of production as follows: Qiandongnan, Qiannan, Bijie, and Anshun. Some of them are mistaken for other regions. For instance, Qiandongnan involves one sample that was misidentified as Tongren. Qiannan involves two samples that were mistaken for Zunyi. Bijie involves one sample that was misidentified as Anshun. Anshun involves tree samples that were mistaken for Bijie, one sample misidentified as Zunyi and one sample mistaken for Tongren, all of which were wrong separation. This is possibly due to those areas of production covering

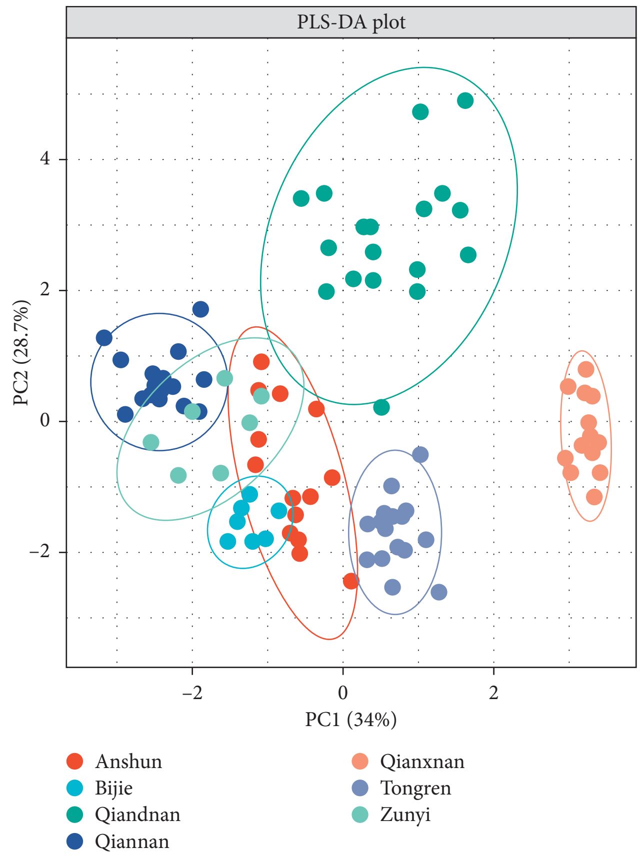

Figure 2: PLS-DA identification model of seven different geographical origin of sauce-flavor baijiu (Chinese baijius) from Guizhou Province.

Table 7: Nineteen classification results by PLS-DA for seven different origins.

	Bijie	Zunyi	Qiandnan	Qiannan	Tongren	Anshun	Qianxnan	Accurate rate (%)
Bijie	6	0	0	0	0	1	0	85.71
Zunyi	2	3	0	2	0	0	0	42.86
Qiandnan	0	0	17	0	1	0	0	94.44
Qiannan	0	2	0	15	0	0	0	88.24
Tongren	0	0	0	0	18	0	0	100.00
Anshun	3	1	0	0	1	12	0	70.59
Qianxnan	0	0	0	0	0	0	16	100.00

some adjacent regions. The last two regions are Tongren and Qianxinan, which show the highest discriminating precision rate, which reached up to 100%. According to Table 7, it can be found out that the discriminating precision rate of the whole PLS-DA model is 87%. Based on that, combined elements, stable isotope ratio, and organic acids were effective in achieving geographical origin identification for sauce-flavor baijiu (Chinese baijiu).

4. Conclusion

In this study, an innovative approach is proposed for the purpose of identifying the geographical origin for sauce-flavor baijiu. It took organic acid, stable isotope ratio, and elements as the geographical indicator and combined with multivariate analysis (PCA and PLS-DA). In our work, the contents of elements (Al, Li, Ca, Cu, Fe, and Zn) and organic acids (hexanoic acid, lactic acid, and acetic acid) were identified as the first and second important geographical markers of sauce-flavor baijiu, respectively, and the third important one is δ^{13}C acetic acid of sauce-flavor baijiu. $^{13}\delta C_{\text{acetic acid}}$ of sauce-flavor baijiu. In the meantime, the accuracy rate of the PLS-DA model for identification geographical was shown to be 87%. In summary, the method devised in this study can be employed as a technical tool to determine the geographical origins of sauce-flavor baijiu sourced from Guizhou Province of China.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors have declared no conflicts of interest regarding the publication of this article.

Acknowledgments

The research project was supported by the Planning Research project of Science and Technology of Guizhou Province (Qian KHZC [2017]2549).

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