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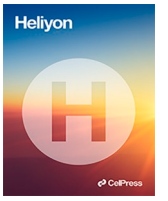

Research article

Combination of fingerprint and chemometric analytical approaches to identify the geographical origin of Qinghai-Tibet plateau rapeseed oil

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ABSTRACT

Verification of the geographical origin of rapeseed oil is essential to protect consumers from fraudulent products. A prospective study was conducted on 45 samples from three rapeseed oil-producing areas in Qinghai Province, which were analyzed by GC-FID and GC-MS. To assess the accuracy of the prediction of origin, classification models were developed using PCA, OPLS-DA, and LDA. It was found that multivariate analysis combined with PCA separate 96% of the samples, and the correct sample discrimination rate based on the OPLS-DA model was over 98%. The predictive index of the model was $Q^2 = 0.841$, indicating that the model had good predictive ability. The LDA results showed highly accurate classification (100%) and cross-validation (100%) rates for the rapeseed oil samples, demonstrating that the model had strong predictive capacity. These findings will serve as a foundation for the implementation and advancement of origin traceability using the combination of fatty acid, phytosterol and tocopherol fingerprints.

1. Introduction

Rapeseed is considered the most significant oil crop after soybean and is cultivated throughout the world [1]. According to the Food and Agriculture Organization (2020), over 6.9 million hectares of rapeseed were planted in China, with a total output of 14 million tons, accounting for 20% of the world's supply [2]. Qinghai Province is located in the Qinghai-Tibet Plateau, with its unique plateau geography and suitable climate contribute to the production of high-quality rapeseed oil with low erucic acid and glucosinolate concentrations. Due to its high oil content and unique fatty acid structure, rapeseed oil is regarded as one of the healthiest edible oils [1]. Rapeseed oil is rich in monounsaturated fatty acids (MUFA, 68.6%) and polyunsaturated fatty acids (PUFA) that are readily digested and absorbed by the human body [3,4]. The major fatty acid in the oil is oleic acid (63.7%), followed by linoleic acid (17.4%) and -linolenic acid (6.8%). A variety of health benefits have been described for rapeseed oil, including the reduction of blood cholesterol and low-density lipoprotein (LDL) levels without affecting the levels of high-density lipoprotein (HDL). The incidence of colon cancer and coronary heart disease is less in people with high MUFA consumption [5].

Rapeseed oil contains a variety of bioactive substances in addition to fatty acids, including phytosterols (α-sitosterol and β-sitosterol), tocopherols, carotene, and phenolic compounds (sinapic acid and sinapine). The majority of the unsaponifiable matter in edible oil is made up of phytosterol, which is also a naturally occurring active component. A previous study has shown that rapeseed oil is a

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good source of phytosterols (700.1 mg/100 g), superior to both flaxseed oil (283.5 mg/100 g) and olive oil (80.2 mg/100 g) [6]. Tocopherol is a natural antioxidant that prevents lipid oxidation by modulating the self-oxidation of free radical chains [7]. In addition to lowering serum cholesterol, rapeseed oil also has antioxidant, antitumor, and immune-stimulatory activities. The shelf life of the oil may be increased by phytosterol, which also exhibits significant antioxidant activity [8].

Nowadays, the presence of inferior and fake products has become increasingly common, which violates the legitimate rights and interests of organizations and clients [9]. As a result, consumers are becoming increasingly more conscious of the importance of the quality and safety of oil products [10]. Compared to other items, high-quality oil products with a known geographical origin cost more and bring in a larger financial benefit for the producers [11], leading to an increased demand for accurate identification, certification, and traceability of oil products to ensure both quality and safety. The chemical composition and contents of rapeseed oil, including fatty acids, tocopherols, and volatile components, vary widely due to numerous factors. This variability mostly depends on the soil, climate, rapeseed cultivar, agronomic factors (irrigation, fertilization), cultivation (harvesting, ripeness), pretreatment methods, and extraction techniques [12].

Fortunately, methods and techniques for determining the composition of oils have become more sophisticated and refined. These methods include GC and high-performance liquid chromatography (HPLC), GC-MS, DNA technology, and isotope ratio mass spectrometry (IRMS), as well as infrared spectroscopy (IR) and atomic absorption spectroscopy (AAS). All these methods have been shown to be able to analyze different components of edible oil in previous studies [13]. GC and GC-MS are standardized techniques for the identification and quantification of fatty acids, volatiles, and phytosterols [14]. HPLC is beneficial for the identification and quantification of carotenoids, tocopherols, and polyphenols, while fatty acids and volatile substances can also be evaluated using IR [15,16]. The use of specific indicators for edible oils from different geographical regions could offer alternatives for the traceability of oil products [17]. These suggested traceability systems are generally separated into information coding and food analysis techniques. In contrast to the physical and biochemical analytical methods described above that are typically used in food analysis, the information-coding techniques include the use of bar codes and radio frequency identification techniques [18]. The accurate identification of the geographical origins of edible oils is generally difficult when using a single methodology or procedure. Different instrumental analytical techniques provide a large number of data variables, which not only offer the opportunity to mine useful chemical information from the original datasets, but also mean that it is difficult to interpret useful chemical information through univariate analysis [19]. Particularly for complex classification tasks such as the differentiation between edible oils from diverse biological or geographical sources, the analysis needs to be comprehensively examined using multivariate analysis to improve the accuracy of the classification [20].

Chemometrics is an interdisciplinary field that combines statistical, mathematical, and computer science techniques for the extraction of information from the chemical system through mathematical models [21]. With the development of related science and technology, the use of multivariate statistical analysis of the original information using chemometrics has become widely used. This includes various methods, such as cluster analysis (HC), principal component analysis (PCA), linear discriminant analysis (LDA), orthogonal partial least squares (OPLS), and support vector machine models (SVM) [22]. Beatriz et al. [23] found that GC-MS fingerprints combined with multivariate statistical methods such as partial least squares discriminant analysis (PLS-DA) and cluster analysis, were able to validate the geographical origins of extra-virgin olive oils and other olive oils. Besides, previous tudy have shown that the determination of phenolic compounds and phytosterols in extra-virgin olive oil from different countries based on liquid chromatography, combined with the PLS-DA model, can also be used to identify extra-virgin olive oils from Tunisia and Italy [24]. The

Table 1
Information of 45 rapeseed samples.

NO.	Variety	Origin	Date	NO.	Variety	Origin	Date
QH-1	Qingza 1	Haidong	2022.09	QH-24	Qingza 10	Haibei	2022.08
QH-2	Qingza 2	Haidong	2022.09	QH-25	Qingza 12	Haidong	2022.10
QH-3	Qingza 2	Xining	2022.10	QH-26	Qingza 15	Haidong	2022.10
QH-4	Qingza 2	Haidong	2022.09	QH-27	Qingza 18	Xining	2022.12
QH-5	Qingza 2	Haidong	2022.09	QH-28	Haiyou 1	Haidong	2022.09
QH-6	Qingza 2	Haidong	2022.09	QH-29	Haiyou 1	Haidong	2022.09
QH-7	Qingza 3	Xining	2022.10	QH-30	Lanhaiyou 3	Haidong	2023.03
QH-8	Qingza 3	Xining	2022.10	QH-31	Lanhaiyou 3	Xining	2023.03
QH-9	Qingza 4	Haidong	2022.08	QH-32	Beiyou 2	Haibei	2023.03
QH-10	Qingza 5	Haidong	2022.08	QH-33	Beiyou 2	Haibei	2023.03
QH-11	Qingza 5	Xining	2022.10	QH-34	Beiyou 2	Haibei	2023.03
QH-12	Qingza 5	Haibei	2022.10	QH-35	Heyou 5	Haidong	2022.10
QH-13	Qingza 5	Haidong	2022.09	QH-36	Qingyou 14	Haidong	2022.10
QH-14	Qingza 5	Haidong	2022.09	QH-37	Qingyou 14	Xining	2022.10
QH-15	Qingza 6	Haidong	2022.09	QH-38	Qingyou 21	Haibei	2022.09
QH-16	Qingza 7	Haidong	2022.09	QH-39	Qingyou 21	Haibei	2022.09
QH-17	Qingza 7	Haidong	2022.12	QH-40	Aoluo	Xining	2022.10
QH-18	Qingza 7	Xining	2022.09	QH-41	Qingza 19	Xining	2022.11
QH-19	Qingza 7	Xining	2022.10	QH-42	Ganyouza 701	Haidong	2022.09
QH-20	Qingza 7	Haidong	2022.09	QH-43	Xiao 1	Haibei	2022.10
QH-21	Qingza 9	Haidong	2022.12	QH-44	Xiao 1	Haidong	2022.10
QH-22	Qingza 9	Xining	2022.10	QH-45	Qingza 19	Xining	2022.10
QH-23	Qingza 9	Xining	2022.10				

use of comprehensive analytical data facilitates the identification of misclassifications [25]. The most significant chemical features associated with a specific sample may be assessed both qualitatively and quantitatively through the application of multivariate metrological analysis in food quality control and food source identification [26]. Therefore, the use of the multivariate analysis of physicochemical and rheological data is ideal for the tracing of edible oil origins.

At present, the analysis of rapeseed oil focuses essentially on the screening different marker components and substance changes. There is thus a need for the further development of techniques for measuring marker components and their relation to the origin of the oil. Thus, the goal of the current study was to evaluate whether the fatty acid GC fingerprints and phytosterol and tocopherol GC-MS fingerprints in rapeseed oil can be used to trace the origin of the oil. Therefore, the fatty acids, phytosterols, and tocopherols in rapeseed oil were first analyzed, followed by the identification of chemical markers by the fingerprints. Subsequently, similarity evaluation (SE), PCA, OPLS-DA, and LDA were used to establish qualitative and quantitative models to trace the origin of rapeseed oil from different sources.

2. Materials and methods

2.1. Materials

Forty-five rapeseed samples were collected from different areas of Qinghai Province (City Xining, Haidong, and Prefecture Haibei). The sampled area covered most of the rape-planting areas in Qinghai Province, the sample details are shown in Table 1 and Fig. 1. The oil was extracted from the samples using an Xz-z505w horizontal oil screw press (Guangzhou Xuzhong Food Machinery Company, China), the 45 pure rapeseed oil samples were prepared for stoichiometric analysis and stored at 4 °C before analysis.

Methanol (HPLC grade), potassium hydroxide (analytical grade), n-heptane (HPLC grade), and anhydrous sodium sulfate (analytical grade) were obtained from Yuhe NewMat (Shandong, China). Six fatty acid methyl ester (FAME) standards, including undecanoic acid (purity 97.0%), stearic acid (purity 97.0%), palmitic acid (purity 97.0%), oleic acid (purity 97.0%), linoleic acid (purity 97.0%), and linolenic acid (purity 97.0%) were obtained from Sigma-Aldrich (St Louis, MO, USA). Squalene (purity 98%) α-tocopherol (purity 97%) γ-tocopherol (purity 98%), rapeseed sterol (purity 98%), and β-sitosterol (purity: 98%) were obtained from Desite Company (Sichuan, China).

2.2. Analytical methods

2.2.1. Fatty acid composition

The oil samples (100 ± 0.01 mg) were accurately weighed into conical flasks with stoppers for the separation of FAMEs. Added 40

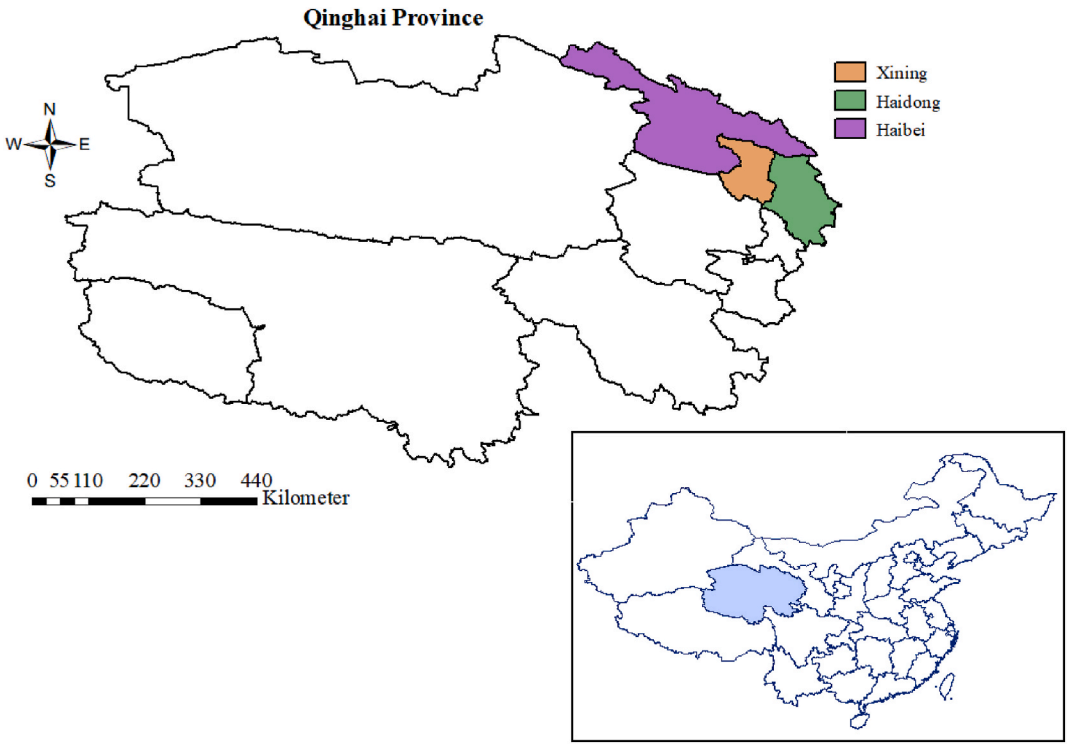

Fig. 1. The geographical location of rapeseed samples.

mL of methanol and 1 mL of KOH-methanol solution (1 mol/L) to each oil samples, followed by the addition of 0.5 mL of the internal standard solution, and mixed well. A heating magnetic stirrer set to 50 °C was used for condensation and reflux for 65 min. After the reaction, the flask was cooled to room temperature, and the solution was poured into a separating funnel. Separate liquid extraction was carried out, 10 mL of n-heptane was added, followed by 10 mL of distilled water, to the liquid separation funnel, and after full oscillation, and static stratification, the bottom layer was collected. A further 10 mL n-heptane was then added to the water layer for secondary extraction, and two collections of the extracted ester layer were made. Finally, the bottom layer was pooled with 10 mL of distilled water. After separation of the ester layer, anhydrous sodium sulfate was added for dehydration and drying. The filtrate was filtered and collected in a 25 mL brown volumetric flask for the quantitative analysis of FAMEs in rapeseed oil by the internal standard method.

Gas chromatographic analyses were performed on a Shimadzu GC 2030 gas chromatograph (Shimadzu, Japan) equipped with a flame ionization detector and a Wonda Cap WAX fused silica capillary column (60 m × 0.25 mm × 0.25 μm). In all experiments, high-purity nitrogen was used as the carrier gas, the inlet and detector temperatures were kept constant at 250 °C, and the constant flow rate was 1 mL/min. The injection volume was 1 μL and the split ratio was 46:1. The column temperature were set as follows: 100 °C maintained for 13 min, increasing with a rate of 10 °C/min to 180 °C for 6 min, followed by increasing at 1 °C/min to 200 °C for 20 min, and at 4 °C/min to 230 °C for 10.5 min.

2.2.2. Phytosterol and tocopherol composition

Oil samples (2.0 ± 0.0001 g) were accurately weighed into 10 mL conical flasks. The internal standard (0.5 mL) was then added to each flask, and the volume was made up with n-heptane. The solution was placed in a water bath (60 °C) for 2 min, ultrasonicated for 2 min, and vortexed for 6 min to fully dissolve the sample.

Gas chromatographic analyses were performed on a Shimadzu GC 2030 gas chromatograph equipped with a flame ionization detector and a Wonda Cap WAX fused silica capillary column (30 m × 0.32 mm × 0.50 μm). The temperatures used were 60 °C maintained for 1 min, followed by an increase at a rate of 40 °C/min to 300 °C over 15 min. The flow rate of the high-purity helium (99.999%) was 1.0 mL/min, the split ratio was 15:1, and the temperature at the injection port was 300 °C. The mass spectrum conditions were: electronic energy, 70 EV; transmission line 280 °C; ion source temperature, 230 °C; filament emission current, 200 μA; quality scanning range m/z 35–350 amu.

2.3. Data processing

2.3.1. Profiling approach

The fatty acid, phytosterol, and tocopherol compositions were calculated and analyzed by one-way analysis of variance (ANOVA). The relative retention times and chromatographic peak areas were compared to determine the characteristic compounds. A total of five fatty acids, three phytosterols, and two tocopherols were found to be geographical identifiers of rapeseed oil provenance. Univariate and multivariate data were analyzed by low-level fusion.

2.3.2. Fingerprinting approach

The similarity evaluation method used Chinese medicinal fingerprinting to confirm the fingerprint profiles of the established standards. The vector angle cosine technique was used to determine the matching degree between each sample and the standard fingerprint. Each chromatographic fingerprint is regarded as a set of values of peak height corresponding to the retention time. This set of values can be regarded as a vector in the multidimensional space, so that the similarity between the two fingerprints can be converted into the similarity between the two vectors in the multidimensional space, and the value of cosθ is calculated to quantitatively characterize. If cosθ is closer to 1, the two vectors are more similar. This was done to evaluate the test sample's reliability, quality, and stability in comparison with the standards.

2.3.3. Chemometrics

All experiments were performed in triplicate, and data were presented as mean ± standard deviation, whereas SPSS 26.0 (IBM Corp., Armonk, NY, USA) was used to perform one-way ANOVA and LDA. SIMCA14.1 (Umetrics AB, Umea, Sweden) was used for the PCA and OPLS-DA analysis. To assess if variations in the average compound values in the rapeseed oil samples were associated with specific geographical regions, one-way ANOVA followed by a post hoc least significant difference (LSD) test ($P < 0.05$) was used. After preliminary data analysis, PCA was used to analyze the chromatographic data, using score and loading plots to evaluate the clustering trends of several PCA models between sample groups. An OPLS-DA classification model was established to validate the geographical origin of the 45 samples from three different origins. OPLS-DA is a supervised identification method that is used to determine the most significant association between the data and each category [23]. The prediction ability (Q^2 value) and the proportion of correctly classified data were used to assess the model's effectiveness. LDA was also used to refine the classification and differentiation of the samples. In addition, In this study, the receiver operating characteristic curve (ROC) were used to measure the performance of the model more objectively.

3. Results and discussion

3.1. Composition and contents of fatty acids in rapeseed oil

The fatty acid profile is an essential index for the characterization of rapeseed oil. Different rapeseed oils were examined by GC to determine the concentrations of five key fatty acids, namely, palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) (Fig. 2). Oleic acid, which may be present at concentrations up to 58.82 g/100 g and accounts for 68% of the total fatty acid content, was found to make up the bulk of the fatty acid content in the rapeseed oil samples. Besides oleic acid, the samples had significant levels of linoleic acid and linolenic acid. A previous study has shown that oleic acid is successively desaturated to form linoleic acid and linolenic acid [27]. Accordingly, the contents of linoleic and linolenic acids were somewhat lower than that of oleic acid, with average concentrations of 18.52 g/100 g and 10.13 g/100 g, respectively. The average concentration of palmitic acid was 3.37 g/100 g. The overall fatty acid composition of the rapeseed oils found in the present study was comparable with previous reports [5,28]. For further characterization of the rapeseed oil, several indicators related to fatty acids were determined (Table 2). Compared with the measurement of a single fatty acid, it is significantly more sensitive to use the relative ratios of oleic, palmitic, stearic, and linoleic acids in a specific oil sample as a certification tool [29]. The levels of oleic, linolenic, and linoleic acids in rapeseed oils varied significantly according to the three areas of origin. Similar to the individual fatty acid compositions, these indices differed significantly among the various samples. This indicated that the fatty acid composition and distribution are highly dependent on both the oil variety and its source.

Furthermore, there were marked variations in the different values in relation to geographical origin, with most of these variations showing statistical significance. The oleic acid and steric acid contents were observed to be particularly important in distinguishing between oils of different origins. Although oleic acid usually contributes the most to the total fatty acid content, marked variations were seen in the oleic acid contents of oils from different producing areas. The highest oleic acid content among the 45 rapeseed oils was QH-25 (Qingza 9), which differed significantly from the oleic acid content of QH-23 (Qingza 9) from a different production area, demonstrating that rapeseed oil's fatty acid content varies in different regions where the same variety is produced. A previous study on camellia oil concluded that differences between these samples may be influenced by different species, growing areas, climate, and preprocessing techniques [30]. This provides theoretical support for the selection of the origin of rapeseed cultivation and for subsequent studies on their potential application for the classification and quality assessment of rapeseed oil based on its components.

3.2. Composition and contents of phytosterols and tocopherols in rapeseed oil

Phytosterols make up a large component of the unsaponifiable ingredients in edible oils and are useful in the characterization of rapeseed oils [31]. Tocopherols play an important role in reducing lipid oxidation. They have both antioxidant and nutritional value and are documented to improve the overall quality of the oil [32]. The data obtained from the analysis of the phytosterol and tocopherol contents in rapeseed oil samples based on GC-MS are shown in Table 3, demonstrating the wide variation in the composition of rapeseed oil. As expected, five chemical compounds were found in all the rapeseed oil samples. In terms of the phytosterol content, the main compounds detected in the oil were β-sitosterol, campesterol, and brassicasterol. The β-sitosterol contents were significantly higher than those of other phytosterols in all samples, ranging from 75.67 to 190.07 mg/100 g, and accounting for 37–58% of the three types of phytosterols. The average concentration of campesterol in the rapeseed oil was 80.91 mg/100 g, accounting for 30%. Brassicasterol is a unique phytosterol in rapeseed oil, where it was found to have the lowest concentrations of the three phytosterols, with contents ranging from 26.84 to 98.92 mg/100g, accounting for 15–28%. Two tocopherols were included, namely, γ-tocopherol and α-tocopherol. γ-tocopherol (62.60–170.51 mg/100 g oil; 66–82%) was the tocopherol component with the highest concentration, followed by α-tocopherol (13.06–55.49 mg/100 g oil; 18–34%), which was consistent with the findings of

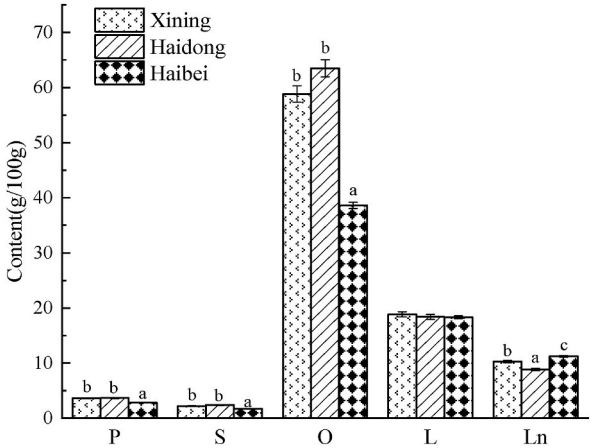

Fig. 2. Fatty acid profiles of rapeseed oils (P-palmitic acid, S-stearic acid, O-oleic acid, L-linoleic acid, Ln-linolenic acid).

Table 2
Calculation and analysis of the primary fatty acid indices in rapeseed oil.

Area	SFA	UFA	P/S	O/L	O/P	L/S	O/Ln
Xining	5.81 ± 0.19^{b}	87.97 ± 1.92^{b}	1.65 ± 0.01^{b}	3.12 ± 0.03^{b}	26.74 ± 0.21^{b}	8.57 ± 0.06^{b}	5.72 ± 0.00^{b}
Haidong	6.05 ± 0.17^{b}	90.84 ± 2.19^{b}	1.53 ± 0.01^{a}	3.45 ± 0.03^{c}	26.57 ± 0.19^{b}	7.70 ± 0.05^{a}	7.18 ± 0.06^{c}
Haibei	4.56 ± 0.06^{a}	68.20 ± 0.97^{a}	1.63 ± 0.02^{b}	2.11 ± 0.02^{a}	22.32 ± 0.02^{a}	10.60 ± 0.01^{c}	3.43 ± 0.03^{a}

Note: P-palmitic acid, S-stearic acid, O-oleic acid, L-linoleic acid, Ln-linolenic acid. Different lowercase letters indicate significant differences in the fatty acid composition of rapeseed oil among different regions ($p < 0.05$).

Table 3
Phytosterol and tocopherol contents in rapeseed oils from different regions (mg/100 g).

Area	α-tocopherol	γ-tocopoerol	brassicasterol	campesterol	β-sitosterol
Xining	35.26 ± 1.23^{ab}	97.84 ± 1.78^{a}	52.53 ± 1.22^{a}	77.35 ± 1.70	124.28 ± 2.62
Haidong	39.54 ± 1.35^{b}	98.35 ± 1.88^{a}	57.94 ± 1.33^{b}	83.07 ± 1.61	129.77 ± 2.02
Haibei	30.35 ± 1.28^{a}	107.76 ± 1.21^{b}	52.81 ± 1.02^{a}	82.31 ± 1.85	131.24 ± 2.46

Note: Different lowercase letters indicate significant differences in the composition of phytosterols and tocopherols in rapeseed oil between different regions ($p < 0.05$).

Moreau's study [33].

According to a recent analysis, variations in the tocopherol contents of rapeseed oils may be influenced by the planting region, seed cultivar, and seed maturity [34]. Additionally, it has been demonstrated that the tocopherol content of rapeseed oil rises with increasing latitude of the rapeseed-growing zone [35]. The variability of the tocopherol content of rapeseed oil is significantly influenced by the interaction between the cultivar and the environment. Samples from the Haidong area were found to have the highest average levels of both phytosterols and tocopherols, with sample QH-35 having the highest contents of α-tocopherol (190.07 mg/100 g) and γ-tocopherol (170.51 mg/100 g). Meanwhile, the average levels of phytosterols and tocopherols in Xining were lower than those in oils from the other two regions. This may be due to the influence of altitude and heat, as well as planting areas, as differences in temperature and altitude were associated with marked differences in their content [36,37]. Both the phytosterol and tocopherol contents of rapeseed oil were heritable and had the potential to distinguish between different geographical origins.

3.3. Similarity evaluation

The similarity of fingerprints indicates an overall correlation. Calculation of the similarity between oil samples can provide a more systematic evaluation of the oil samples. The fatty acid, phytosterol, and tocopherol composition of 45 Qinghai rapeseed oil samples were analyzed by GC and GC-MS. To obtain the original gas chromatogram, the channel definition format (AIA) data of the sample chromatograms were imported into the chromatographic fingerprint system used in similarity evaluations in traditional Chinese medicine (2004A edition) (Fig. 3a and b). The chromatograms of the 45 samples were automatically matched by multi-point correction, and the standard fingerprints of rapeseed oil fatty acids, phytosterols, and tocopherols were acquired (Fig. 3c and d). According to the Pharmacopoeia Commission, an oil can be considered to fulfill the similarity evaluation requirement if there is a similarity of more than 90%. The 45 batches of rapeseed oil samples from Qinghai showed good consistency in their fatty acid, phytosterol, and tocopherol compositions, according to the similarity calculation by the angle cosine method, which revealed that the similarity of the fingerprint profiles of the 45 batches of rapeseed oil samples were over 96%. Therefore, the standard fingerprint profile could be used to express comprehensive information on the fatty acid, phytosterol, and tocopherol profiles of Qinghai rapeseed oils.

3.4. Verification of origin traceability of rapeseed oil by PCA

Principal Component Analysis (PCA) was used as an unsupervised method for exploratory analysis, using multivariate data analysis techniques to reduce the number of raw variables [38]. Forty-five samples (subjects) from three different regions of Qinghai Province were submitted to PCA with different univariate and multivariate combined data matrices. This showed that the composition of rapeseed oil had no relation to geographical origin and it was, therefore, retained for further analysis. In the univariate analysis using fatty acids as an indicator, the PCA score plot for the first two PCs of the fatty acid profiles (67.8% of the explained variance, Fig. 4a), did not show a clear separation between Xining and Haidong while showing separation of Haibei samples. For the phytosterol and tocopherol fingerprints, the PCA score plot (Fig. 4b) yielded an unsatisfactory result for classification; in comparison with the fatty acid compositions, there were fewer phytosterol tocopherols with notable geographical variations. These findings indicated that identifying the provenance of rapeseed oils using these two characteristics individually is limited. Nevertheless, it provided a broad overview of the ability of the fatty acid profiles, phytosterol, and tocopherol fingerprints to define rapeseed oils from various origins. The analysis of the loadings for each trait revealed that PC1 was highly positively correlated with oleic acid and α-tocopherol and negatively correlated with γ-tocopherol and linolenic acid, while PC2 was highly positively correlated with linoleic acid and negatively correlated with β-sitosterol. Each principal component had elements that were highly correlated with it, which indicated that the principal

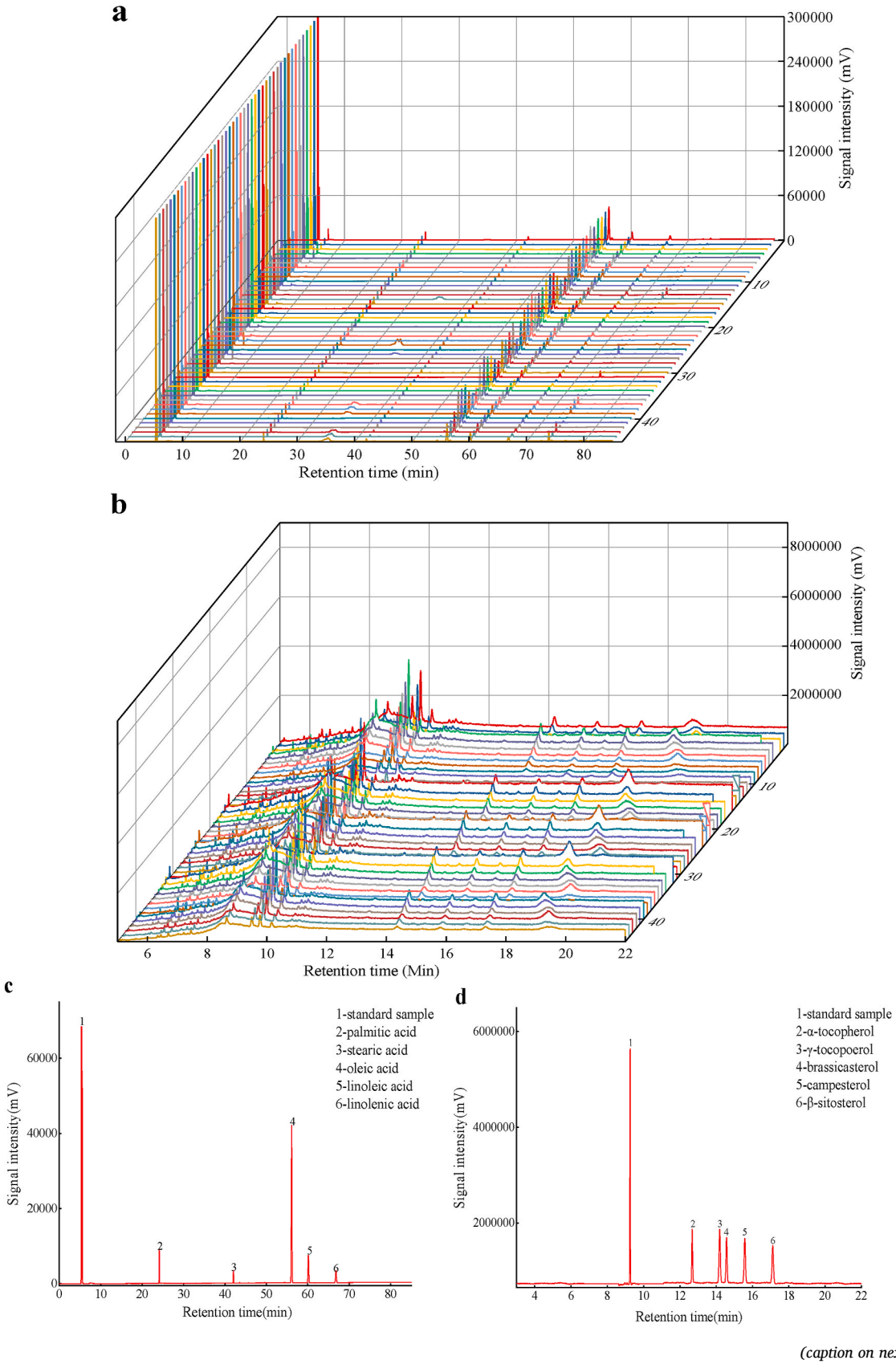

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Fig. 3. Original GC-FID chromatogram chromatograms (a), original GC-MS chromatograms (b), standard GC-FID chromatograms (c), and standard GC-MS chromatograms (d) for 45 rapeseed oil fatty acid, phytosterol, and tocopherol profiles.

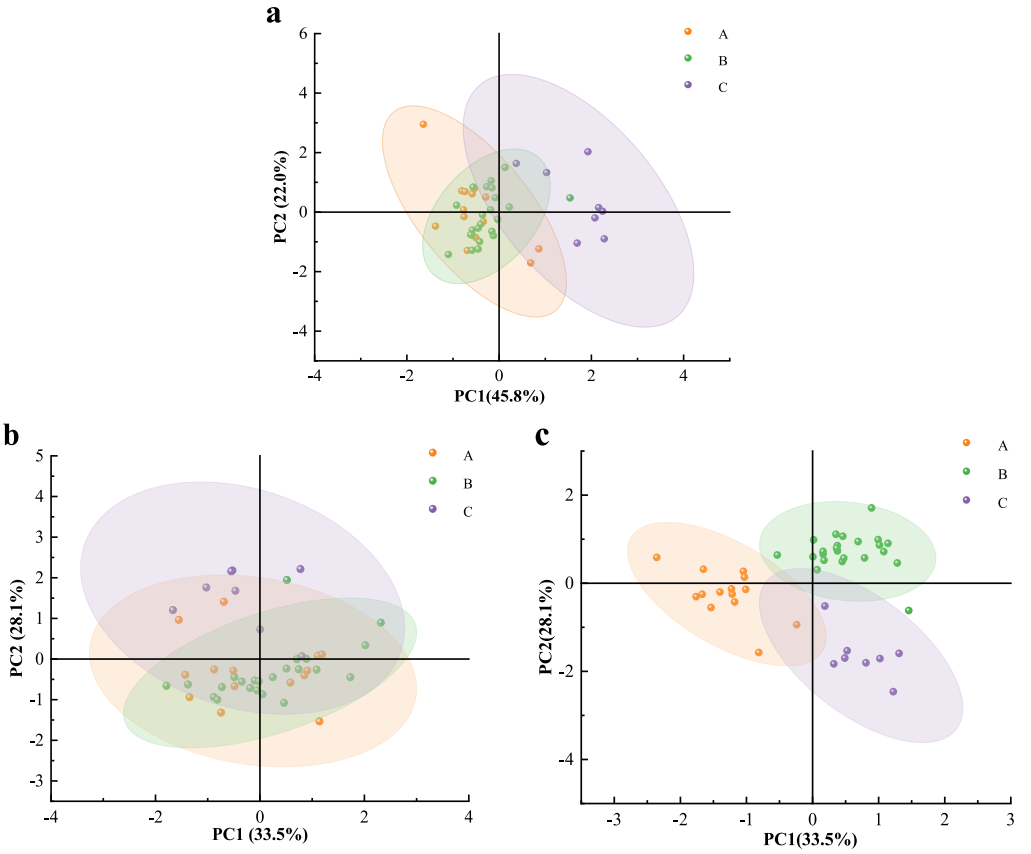

Fig. 4. PCA score diagram of the bioactive components of rapeseed oil samples. (a-fatty acid; b-phytosterol tocopherol; c-fatty acid and phytosterol tocopherol).

component can reflect information on the components that were strongly associated with it. The PCA score plot (61.6% of the explained variance, Fig. 4c) showed that the rapeseed oils from various origins have noticeable variance, which may be attributed to the Haidong samples having the highest concentrations of γ-tocopherol and the lowest concentrations of oleic acid, with this information contained in PC1. However, some samples from Xining City showed significant overlap with samples from the other two cities, which can be explained by the fact that Xining City is adjacent to both Haidong City and Haibei Prefecture.

Overall, the PCA demonstrated a natural grouping of the data according to the production region, although some groups appeared to overlap in the score plots. It confirmed that there were some variations in the concentrations of components in the rapeseed oils from different geographical origins. To create a hierarchy that can provide greater distinction, supervised approaches should be applied.

3.5. Verification of origin traceability of rapeseed oil by OPLS-DA

Multivariate techniques based on profiling and fingerprinting methods allow for a better exploration of differences between samples from different regions [23]. No outliers were found when using the profiling approaches after data pre-treatment and PCA investigation. Therefore, an OPLS-DA classification model using all the samples was created for the data. In this study, all of the oil samples came from established sources, and the methods used to identify sources were validated and accredited [39]. Typically, test samples were compared to established sample databases for analysis and classification, and their geographic origin was investigated. A total of 45 rapeseed oil samples from the Qinghai region were sorted into three categories which essentially captured the essence of each location.

The modeling analysis first conducted using univariate analysis of fatty acids showed that the score plot (Fig. 5a) outlined by OPLS-DA indicated an overlap between multiple samples from Xining and Haidong City, indicating that the modeling was unsatisfactory. This may have been due to the similarity in fatty acid contents between the two regions, which was consistent with the PCA results. Furthermore, the score plot of phytosterol and tocopherol (Fig. 5b) showed that samples from Haidong City and Haibei City showed

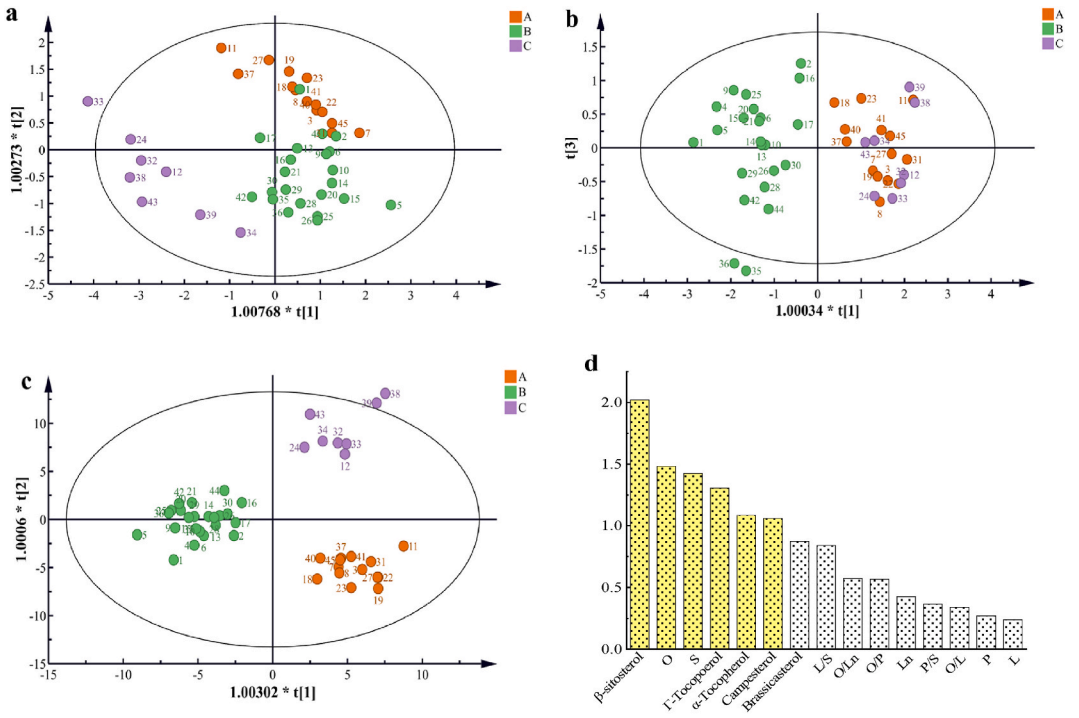

Fig. 5. The OPLS-DA score plot and VIP values of the model of the bioactive components of rapeseed oil samples (a-fatty acid; b-phytosterol tocopherol; c-fatty acids and phytosterol tocopherols; d-VIP value).

significant overlap, attributed to the insignificant difference in the content of plant sterols and tocopherols between Xining and Haibei regions, and the lower content compared to Haidong region, this also indicating unsatisfactory classification. Based on the univariate analysis, we then amalgamated the data and the score plot (Fig. 5c), resulting in a clear distinction between samples from different origins. R^2X and R^2Y were the independent and dependent variables, respectively, of the model, and their indices were 0.871 and 0.89, respectively. The model parameters were found to be very robust, specifically, the goodness-of-prediction ($Q^2 = 0.841$). The model had a cumulative R^2 and Q^2 higher than 0.5. The experimental model was good and did not over-fit, as per the inspection criterion. The Variable Importance in Projection (VIP) score of the markers of variation generated by fitting the OPLS-DA model analysis can show the importance of the factors in the model [35]. The differential components from different oil sources were examined by VIP using the

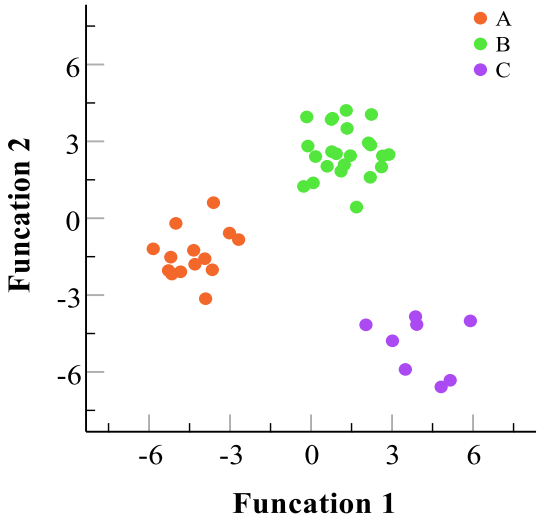

Fig. 6. LDA model diagram of fatty acid, phytosterol, and tocopherol contents of rapeseed oil samples.

OPLS-DA results as a basis (Fig. 5d), with six variables, namely, β-sitosterol, oleic acid, stearic acid, γ-tocopherol, α-tocopherol and campesterol showing a major contribution to the sample discrimination (VIP values greater than 1.00 were considered as differential metabolites) according to geographical origin, which can be applied as characteristic indicators for tracing the origin of rapeseed oil. Of these, β-sitosterol and oleic acid had the highest weight values in distinguishing rapeseed oil from different origins, which is consistent with the findings of other studies [40]. The combined analysis of the six characteristic variables showed that the classes received nearly all of the samples in the appropriate order, with minor differences in distance between individual samples from Xining and Haidong cities, which may be due to geographical similarities between the two producing areas. It is worth noting that due to the limited sample size, we should hold an objective attitude for subsequent verification [39].

3.6. Verification of origin traceability of rapeseed oil by LDA

To maximize separation between known provenances, the supervised technique known as linear discriminant analysis (LDA) introduces a new linear axis. To examine the effectiveness of the selected characteristic indicators, the data were then analyzed by LDA to confirm the classification of the rapeseed oil samples from the three areas using the combined 45 (objects) × 6 (variables include stearic acid, oleic acid, α-tocopherol, γ-tocopherol, campesterol, and β-sitosterol) data matrix. Three Fisher's discriminant functions that accounted for 100% of the variance were built. The functions of the correlation between the predictor variables and the discriminant functions are shown below; the coefficients of variables indicated that discriminant functions 1 and 2 (f_1 and f_2) accounted for 53% and 47% of the between-group variation, respectively. The first discriminant function (f_1) explained 53% of the variance, according to the variable coefficients, showing positive relationships with α-tocopherol, γ-tocopherol, campesterol, stearic acid, and oleic acid and a negative association with β-sitosterol. The second discriminant function (f_2) was positively correlated with α-tocopherol, brassicasterol, β-sitosterol, stearic acid, and oleic acid, and was negatively associated with γ-tocopherol. Fig. 6 shows that there was satisfactory separation between samples from the three producing regions. Particularly well-clustered samples were observed from Xining, Haidong, and Haibei.

Fisher's discriminant functions were as follows:

Y_{Xining} = 5.785 α-Tocopherol+8.817 γ-Tocopoerol+14.111 Campesterol-0.450 β-sitosterol+2.491 stearic acid-4.126 oleic acid-1236.487.

$Y_{Haidong}$ = 7.440 α-Tocopherol+9.056 γ-Tocopoerol+15.168 Campesterol-0.440 β-sitosterol+3.714 stearic acid-4.053 oleic acid-1447.971.

Y_{Haibei} = 5.527 α-Tocopherol+10.102 γ-Tocopoerol+15.661 Campesterol-0.656 β-sitosterol+4.268 stearic acid-4.191 oleic acid-1530.899.

To further evaluate the predictive ability, the generated model was validated through leave-one-out cross-validation. As shown in Table 4, the predictive ability of the origin and cross-validation (percentage of the training set correctly classified) was 100% and 100%. The ability to successfully separate samples from various places demonstrated that there was greater variation in the chemical properties between different origins than between different varieties [41]. The ROC curve is a comprehensive index reflecting the continuous change of sensitivity and specificity. Generally, the area under the ROC curve AUC is used as the evaluation index of the model, the maximum value is 1, and the performance of the classifier is proportional to the AUC value. The area under the ROC curve can better reflect the generalization force of the model. The closer the area under the curve is, the better the generalization power of the model is. The classification accuracy and AUC of the three classification models shown in Table 5, the AUC values of PCA, OPLS-DA, and LDA models are 0.804, 0.958, and 0.984 respectively, the performance of the origin model is good, the identification rate of origin is higher than 85%, and the correct rate of origin identification is high. Although the prediction performance of LDA is similar to that of PLS-DA, the AUC (0.9911) of LDA is slightly higher than that of PLS-DA (0.9837) in the subsequent evaluation of model performance, indicating that LDA has better performance and generalization ability in rapeseed oil origin classification. A previous study showed that models created from chemical composition data are not the most accurate in predicting geographical origin [42]. The chemical composition of samples can vary depending on how they were extracted. To create accurate models with strong predictive power, the collection of samples under the same conditions is strongly advised.

This study confirmed that the combination of fatty acids(stearic acid, oleic acid), phytosterols(campesterol, β-sitosterol), and tocopherols(α-tocopherol, γ-tocopherol) can provide a precise method for tracing the origin of rapeseed oil. This is likely due to the

Table 4
Classification and validation of LDA model of rapeseed oil from three regions.

		Origin	Predicted group membership			
			Xining	Haidong	Haibei	Total
Original	Count	Xining	14	0	0	14
		Haidong	0	23	0	23
		Haibei	0	0	8	8
	%		100	100	100	100
Cross-validated		Xining	14	0	0	14
		Haidong	0	23	0	23
		Haibei	0	0	8	8
	%		100	100	100	100

Table 5
Classification accuracies and areas under ROC curve(AUC) of different classification models.

Model	Training set/%	Prediction set/%	AUC
PCA	93.33	85.83	0.804
OPLS-DA	100	90	0.958
LDA	100	97.78	0.984

significant influence of the environment on the bioactive ingredients in rapeseed oil. However, the effects of the environment on the individual components differed. Compared to Haibe, the amounts of γ-tocopherol, campesterol, and β-sitosterol were much lower in Xining. The concentrations of these components appeared to be more significantly influenced by the environment than variety. A previous study also demonstrated that the environment has a major impact on variations in the stearic acid contents of rapeseed oil. However, there were differences in the contents of palmitic acid, linoleic acid, and linolenic acid in different varieties of rapeseed oil from the same origin. It is speculated that the influence of the specific variety may be more significant than that of the environment, or that there may be synergy between the two.

Temperature, precipitation, and sunshine, as the main environmental factors, affect the active ingredients in rapeseed oil. Apart from the regional junction, the annual sunshine and rainfall in Xining were far lower than in the other two regions, and some studies have suggested that a colder climate during seed growth results in a higher unsaturated fatty acid content compared with those grown under warmer conditions. In contrast, the climate of Haidong is more suitable for growing high-quality rapeseed. Overall, the LDA algorithm supported the hypothesis that specific features of oils can be used for the accurate discrimination of rapeseed oil samples. The methodological approach, multivariate model, and results of this study provide helpful information for identifying oils in industrial settings, especially in the application of fingerprinting to rapeseed oil identification.

4. Conclusion

In this study, a stepwise methodology comprising PCA, OPLS-DA, and LDA was developed to trace the origin of rapeseed oil using fatty acid, phytosterol, and tocopherol profiles with GC and GC-MS analysis.These results show that there are differences between the main components and trace components in all rapeseed oils from three different regions. OPLS-DA further shows that the regional characteristics of rapeseed oil from different areas are obvious, and the model can effectively distinguish and identify rapeseed oil without over-fitting. The accuracy of LDA was applied to the identification and prediction of rapeseed oil from three producing areas, and the discriminant accuracy was 100% and 95.56%, respectively. Stearic acid, oleic acid, α-tocopherol, γ-tocopherol, campesterol, and β-sitosterol can be used as discriminant markers of geographical sources of Lactobacillus tantrum, indicating that multivariate analysis can be used as an accurate and promising tool for tracing the origin of rapeseed oil. The pertinent findings of this study provide a feasible and efficient method for determining the geographical source of rapeseed oil and creating an identification database. However, the dataset requires expansion to explore these relationships in greater depth and perform an in-depth study using DNA extraction from rapeseed oils to identify their geographical origins. Thus, combined with multivariate analysis, will provide more accurate data for tracing the origin of rapeseed oil.

Data availability

All data generated or analyzed during this study are included in this published article.

CRediT authorship contribution statement

Ziqin Ye: Writing – original draft, Methodology, Formal analysis, Data curation. **Jinying Wang:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Shengrui Gan:** Methodology, Formal analysis. **Guoxin Dong:** Methodology, Formal analysis. **Furong Yang:** Methodology, Formal analysis.

Declaration of competing interest

The authors declare they have no conflicts of interest.

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