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Comparison and Analysis of Fatty Acids, Sterols, and Tocopherols in Eight Vegetable Oils

Changmo Li, Yunping Yao, Guozhong Zhao, Wen Cheng, Huilin Liu, Chunyang Liu, Zhen Shi, Yao Chen, and Shuo Wang*

Key Laboratory of Food Nutrition and Safety, Ministry of Education of China, Tianjin University of Science and Technology, Tianjin, 300457, China

ABSTRACT: The similarities and differences of eight vegetable oils produced in China were investigated in terms of their fatty acid, sterol, and tocopherol compositions and subsequent data processing by hierarchical clustering analysis and principal component analysis. The lipid profiles, acquired by analytical techniques tailored to each lipid class, revealed great similarities among the fatty acid profiles of corn and sesame oil as well as few differences in their sterol profiles. It turns out that not only was there great similarity between the fatty acid profiles of corn oil and sesame oil but also there were not too many differences for the sterol profiles. Sunflower and tea-seed oil showed similar sterol compositions, while the tea-seed oil tocopherol was very similar to palm oil. The results demonstrated that the use of only one of these profiles was unreliable for indentifying oil origin and authenticity. In contrast, the use of the sterol or tocopherol profile together with the fatty acid profile more accurately discriminates these oils.

KEYWORDS: fatty acids, sterols, tocopherols, vegetable oils, authentication

INTRODUCTION

The issue of authenticity is becoming increasingly important in vegetable oils. Adulteration is generally motivated by maximizing benefit by replacing an expensive with a cheaper vegetable oil. [1] The nature and quantitative distribution of oil's components are characteristic of any lipid source, mainly composed of triacylglycerols (TAGs), diacylglycerols (DGs), free fatty acid (FFAs), and other minor components.

In the literature TAGs and fatty acids have received the most attention, due to the TAGs being the most important group of compounds which are in chemical terms trihydric alcohols esterified with fatty acids (FAs).[2] Mainly composed of triglycerides, an oil's characteristic fatty acid composition, which can serve as an oil's fingerprint, not only is useful for identifying its biological origin[2−4] but also can be utilized for detecting adulteration.[5] More recently, TAG fingerprint has also been investigated.[2,6,7] Identification of adulteration by FA and TAG composition analysis creates the risk of mislabeling oil due to the very similar fatty acid and triacylglycerol composition in some oils. The wide range in adulterants and adulterated oils makes such compositional analyses unsuitable for this purpose.[6,8,9] The minor unsaponifiable components of vegetable oils, which include various hydrocarbons, triterpenoids, carotenoids, tocopherols, and phytosterols, have been widely used by food analysts since the proportions of these trace compounds can provide a useful "fingerprint",[10,11] although content and composition of these components in each kind of oil can vary due to environmental conditions, fruit or seed quality, oil extraction system, and refining process.[12] Al-Ismail et al. have employed sterol profiling of olive oil to detect adulteration with some plant oils,[13] and reversed-phase high-performance liquid chromatography determination of tocopherols and tocotrienols has been employed to detect olive oil adulteration.[14] Different classes of chemical compounds were investigated toward the potential of unambiguous discrimination between manipulated and genuine vegetable oils.

Fingerprint analysis technology is greatly improved by exploring chromatographic data sets with chemometric techniques, such as principal component analysis (PCA) and hierarchical clustering analysis (HCA). These approaches for processing chromatographic data have been shown to be efficient tools for classifying and searching for oil sample similarities and could be useful for routine quality control of oils.[7,15,16]

Previous research has paid more attention to high consumption oils, but few studies focused on minor oils (tea-seed, sesame).[5,17] The main objective of the present work was to establish for the first time the fatty acid, sterol, and tocopherol profiles of eight principal vegetable oils produced in China. These profiles were then subjected to chemometric techniques to reveal their similarities and differences, which could then be used to control the purity and establish the authenticity of these oils.

MATERIALS AND METHODS

Sampling and Reagents. Samples of refined vegetable oils were kindly provided by the manufacturers and guaranteed regarding botanical origin and quality grade. The vegetable oils comprised soybean oil (SO), peanut oil (PE), corn oil (CO), sunflower oil (SU), rapeseed oil (RA), tea-seed oil (TE), sesame oil (SE), and palm oil (PA). Each kind of vegetable oil was composed of four samples which were produced from four different batches. Samples were stored at 4 °C and protected from light prior to analysis.

A 37-component fatty acid methyl ester (FAME) mix was purchased from Sigma-Aldrich (Bellefonte, PA). Plant Sterol Mixture (β-sitosterol 53%, stigmasterol 7%, campesterol 26%, brassicasterol 13%) was purchased from Matreya LLC Co. (Swedish). Standards of α-, β-, γ-,

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Table 1. Relative Fatty Acid, Sterol, and Tocopherol Composition of Vegetable Oils[a]

compd	soybean	peanut	corn	sunflower	sesame	rapeseed	tea-seed	palm
				Fatty Acid[b] (%)				
C12:0	nd[c]	nd	nd	nd	nd	nd	nd	0.19 a ± 0.02
C14:0	nd	nd	nd	nd	nd	nd	nd	1.10 a ± 0.07
C16:0	11.00 c ± 0.33	11.62 c ± 0.13	13.20 b ± 0.23	6.41 e ± 0.13	9.51 d ± 0.88	4.44 f ± 0.02	8.89 d ± 0.19	46.38 a ± 3.02
C16:1	nd	nd	nd	nd	nd	0.23 ± 0.01	nd	nd
C18:0	4.30 c ± 0.02	3.61 d ± 0.19	1.87 f ± 0.06	4.36 c ± 0.04	5.71 a ± 0.2	1.93 f ± 0.07	2.43 e ± 0.32	4.65 b ± 0.37
C18:1	22.27 b ± 0.14	39.63 b ± 1.48	31.12 b ± 0.95	22.97 b ± 0.20	38.52 b ± 0.99	60.92 a ± 0.45	77.57 a ± 0.37	38.08 b ± 2.55
C18:2	54.52 b ± 0.14	38.34 e ± 1.77	52.49 c ± 1.24	64.77 a ± 0.10	44.85 d ± 0.71	20.72 f ± 0.33	10.77 g ± 0.24	9.33 h ± 0.72
C20:0	0.37 d ± 0.03	1.58 a ± 0.05	0.42 c ± 0.01	0.29 e ± 0.00	0.63 b ± 0.02	0.63 b ± 0.04	nd	0.38 cd ± 0.01
C18:3n6	0.68 a ± 0.19	nd	nd	nd	nd	0.37 b ± 0.13	nd	nd
C20:1	nd	1.06 a ± 0.04	nd	0.25 c ± 0.03	nd	nd	0.74 b ± 1.00	nd
C18:3n3	6.44 b ± 0.67	nd	0.89 c ± 0.02	nd	0.63 cd ± 0.16	9.88 a ± 0.66	nd	0.28 de ± 0.00
C22:0	0.43 c ± 0.04	2.81 a ± 0.08	nd	0.74 b ± 0.01	0.15 e ± 0.01	0.37 d ± 0.01	nd	nd
C24:0	nd	1.34 a ± 0.04	nd	0.22 b ± 0.01	nd	0.17 c ± 0.00	nd	nd
C24:1	nd	nd	nd	nd	nd	0.18 ± 0.01	nd	nd
				Sterol[d] (%)				
brassicasterol	nd	nd	nd	nd	nd	7.66 ± 0.25	nd	nd
campesterol	28.07 c ± 1.07	21.4 d ± 0.34	32.29 b ± 0.99	14.35 e ± 0.93	27.53 c ± 0.35	51.19 a ± 0.42	14.69 e ± 0.20	31.91 b ± 0.5
stigmasterol	32.65 a ± 0.90	17.48 c ± 0.89	9.99 e ± 0.52	16.19 c ± 0.31	13.28 d ± 0.60	1.03 f ± 0.17	21.45 b ± 0.86	21.54 b ± 0.86
β-sitosterol	39.91 g ± 1.65	61.11 c ± 0.97	57.42 e ± 1.22	69.46 a ± 0.70	59.19 d ± 0.95	40.12 g ± 0.57	63.86 b ± 1.02	46.55 f ± 0.93
				Tocopherol[e] (%)				
α-tocopherol	7.87 e ± 1.68	54.13 c ± 2.2	23.15 d ± 1.79	90.1 b ± 0.59	nd	23.3 d ± 1.44	95.22 a ± 0.68	88.15 b ± 1.57
β-tocopherol	1.59 d ± 0.12	1.88 d ± 0.12	2.19 c ± 0.61	3.87 b ± 0.29	nd	11.91 a ± 0.89	nd	nd
γ-tocopherol	62.15 c ± 2.03	40.08 d ± 1.78	69.48 b ± 2.28	5.98 f ± 0.23	100 a	60.99 c ± 2.08	4.76 f ± 0.65	11.85 e ± 1.56
δ-tocopherol	28.39 a ± 1.6	3.91 c ± 0.74	5.18 b ± 0.89	nd	nd	3.8 c ± 0.73	nd	nd

[a] Each oil was composed of four samples of four different batches. Row means containing a common letter (a−h) are not significantly ($p < 0.05$) different. Values given are the means of four samples ± standard deviation. [b] The total fatty acid measured was normalized to 100%. [c] Not detected. [d] The total sterol measured was normalized to 100%. [e] The total tocopherol measured was normalized to 100%.

and δ-tocopherol were purchased from Tama Biochemical Co. (LTD, Japan).

Distilled water was produced by a Water Pro water system (Labconco Corp, Kansas City, MO, USA). All reagents were purchased from KRS Fine Chemical Co., Ltd. (Tianjin, China) and were analytical or HPLC grade.

Sample Preparation. *Analysis of Fatty Acid Composition.* We accurately weighed 20 mg of oils to a sealable tube, and 4 mL of 2% concentrated sulfuric acid/methanol (v/v) was added. The tube was placed in an 80 °C water bath for 2 h, and then 2 mL each of distilled water and hexane was added after the tube cooled in cold water. For extraction, the mixture was vortexed for 2 min, the hexane phase removed and dried over anhydrous sodium sulfate, and 1 μL of the resulting FAME solution analyzed by gas chromatography (GC).

GC was performed by an HP-88 capillary column (100 m, 0.25 mm i.d., and 0.2 μm film thickness, Agilent Corp., Palo Alto, CA, USA) mounted in an Agilent 6820 gas chromatograph (Agilent Corp. USA) equipped with a flame ionization detector (FID) and the injector and detector at 230 and 250 °C respectively. Nitrogen carrier gas at 1 mL min^{-1} was split in a 1:23 ratio. The oven temperature was held at 120 °C for 4 min, then programmed to 175 at 10 °C min^{-1} and held for 6 min, then programmed to 210 at 5 °C min^{-1} and held for 5 min, then programmed to 230 at 4 °C min^{-1}, and held for 30 min at 230 °C. FAMEs were identified by retention time comparison with that of the corresponding standards.

Analysis of Sterols. 100 mg of oil was placed in a sealable tube with 2 mL of 2 M KOH in ethanol, sealed, heated at 85 °C for 1 h, and cooled in cold water, and 2 mL of distilled water and 5 mL of hexane were added. The unsaponifiable matter was extracted three times with hexane, and the combined hexane fractions were washed 2−4 times with 10% ethanol/water (v/v) until the washing solution was neutral. The hexane phase was then dried with anhydrous sodium sulfate, the residue after evaporation dissolved in 5 mL of hexane, and 1 μL of product analyzed by GC−MS.

Sterol samples were analyzed by a Shimadzu GC-MS QP-2010 (Shimadzu Corp., Kyoto, Japan) equipped with a DB-5 MS capillary column (30 m; 0.25 mm i.d., 0.52 μm film thickness; Agilent Corp.).The carrier gas was helium with a flow rate of 1 mL min^{-1}; split ratio was 1:5. Analyses were performed under the following temperature program: oven temperature from 150 to 300 °C at a rate of 10 °C min^{-1} and held for 10 min at 300 °C. Ion source temperature of the instrument was 200 °C, transfer line of 220 °C, and solvent delay was 18 min. Scan time and mass range were 1 s and 50−500 (m/z), respectively. Sterols were identified by comparing their mass spectra with those of the corresponding standards.

Analysis of Tocopherols. Tocopherol analysis was carried out following the AOCS Official Method Ce-8-89. 0.5 g of oil was placed in a 5 mL volumetric flask and dissolved with hexane and filtered through a 0.45 μm PTFE membrane filter. 20 μL of the filtrate was injected into an Agilent 1200 series HPLC system (Agilent Corp.) equipped with a Phenomenex Luna Sil column (250 mm, 4.6 mm i.d., and 5 μm particle size; Phenomenex, Inc., Torrance, CA) and mobile phase of *n*-hexane/isopropyl alcohol (99/1, v/v) at 1.0 mL min^{-1} and 40 °C column temperature. The mobile phase was previously degassed by sonication for 10 min. Fluorescence detection of all peaks was performed at an excitation wavelength of 290 nm and an emission wavelength of 330 nm.

Statistical Analyses. All sample preparation and instrumental analyses were performed in triplicate. HCA was applied to classify the oils according to their chemical composition. PCA was used to identify the main factors controlling composition and distribution of the analyzed components. All peak areas were made by area normalization, and values expressed as percentages and sample results were expressed as mean ± standard deviation ($m \pm$ SD). ANOVA, PCA, and HCA used Statistical Analyzed Software (Version 9.0, SAS Institute, Inc., Cary, NC, USA).

RESULTS AND DISCUSSION

Method Repeatability and Instrument Precision. The method reproducibility was obtained by five independently prepared samples (soybean oil). The % relative standard deviation (RSD) for all components after normalization was found to be ≤5%. The instrument precision was assessed by six repetitive injections of the same sample solution, and the sample stability was investigated by analyzing the same sample solution at 0, 4, 8, 24, 48, and 72 h ($n = 6$). The relative standard deviation of peak areas and retention time of six replicate runs for these components was ≤4%.

Fatty Acid Profiles from Eight Vegetable Oils. The normalized chromatographic percentages of the lauric (C12:0), myristic (C14:0), palmitic (C16:0), palmitoleic (C16:1), stearic (C18:0), oleic (18:1), linoleic (18:2), arachidic (C20:0), γ-linolenic (18:3n6), *cis*-11-eicosenoic (C20:1), linolenic (C18:3n3), behenic (C22:0), lignoceric (C24:0), and nervonate (C24:1) acids in the eight oils are shown in Table 1. The percentage distributions of each fatty acid for these oils were clearly different, allowing oil kind identification and detection of adulteration by peak area and height comparisons.[18] The experimental fatty acid contents obtained here were in good agreement with those of the Codex Alimentarius standard.[19] Rapeseed, tea-seed, and palm oils were clearly distinguished by their fatty acid profiles due to their far greater oleic acid content than in the other oils.

HCA is a computerized tool for examining large sets of data for common characteristics, and, over the years, a multitude of algorithms for this purpose have been developed.[20] The clustering observed by HCA reveals chemical similarities and differences not detectable by simple visual data inspection.[21] To determine the best similarity between the fatty acid profiles of these samples, HCA of fatty acid profile data from 32 samples from four batches was performed using SAS to determine their relative similarities (Figure 1).

In comparing Table 1 with Figure 1, HCA revealed a clear clustering tendency of samples containing the same fatty acids, with the tree structure of the hierarchical cluster analysis, divided into two levels (Figure 1). When a 50−60 average distance threshold was chosen, SO, CO, SU, PE, and SE were grouped in cluster 1, and PA, RA, and TE in cluster 2, the latter showing similar fatty acid compositions, but in RA the linolenic acid concentration (9.88 ± 0.66%) was about ten times higher than in TE. In addition, PA was unique in having a high palmitic acid concentration (46.38 ± 3.02%). At the second level, the initial two groups were split into four. The SE and PE group had a similar content of C18:1 and C18:2 in a ratio of approximately 1:1, while the SU, CO, and SO group was characterized by similar C18:2 and C18:1 content at approximately 2:1,with the exception that the C18:3 content in SO and CO was higher than in SU.

HCA created a rough framework for these oils, but the fitting error[22] should also be considered. Further PCA analysis of the samples was used to confirm the oils' similarities and differences using groups directly correlated by chemical composition.

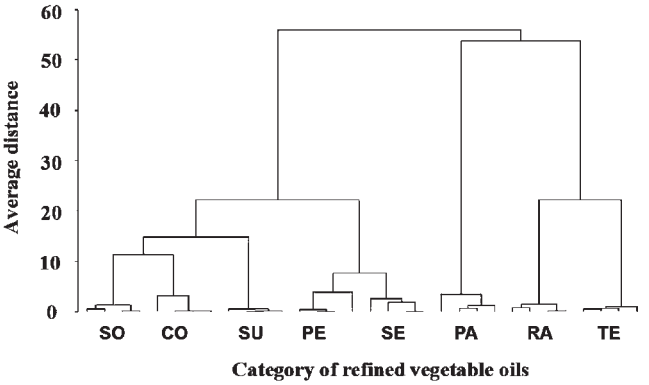

Figure 1. Cluster analyses of eight vegetable oils using the collected fatty acid data. Each kind of oil was composed of four samples of four different batches. Sample codes: SO, soybean oil; CO, corn oil; PE, peanut oil; SU, sunflower oil; RA, rapeseed oil; TE, tea-seed oil; PA, palm oil; SE, sesame oil.

Table 2. Eigenvalues of the Correlation Matrix

	component 1	component 2	component 3	component 4
eigenvalue	4.17199045	3.94966867	2.65638820	1.86418256
percentage of total variance (%)	29.80	28.21	18.97	13.32

PCA was applied to the complete set of values corresponding to fatty acids in the eight vegetable oils. Four principal components accounted for 90.30% of the total variance, and were considered significant based on eigenvalues >1 (Table 2).

Interpretation of the PCA results is usually carried out by visualization of the component scores and loadings. Figure 2 and Figure 3 show the PCA loading and score plots respectively of the first three principal components. A loading plot for the plane PC1−PC2 and the plane PC1−PC3 (Figure 2) revealed that four variables (C12:0, C14:0, C16:0, and C18:0) with two variables (C16:1 and C24:1) had an inverse correlation on PC1, three variables (C20:1, C22:0, and C24:0) had positive loading values on PC2, and one variable (C18:2) had negative loading values on PC3.

Three dimensional PCA score plots of the data showed that the eight oils were clearly divided into seven groups, with CO and SE mistakenly classified as a single group. It simply means that the fatty acid composition of corn and sesame oils cannot be differentiated. This conclusion is consistent with literature,[23] indicating that similarity and differences of oil samples cannot be interpreted and assessed sufficiently though the analysis of fatty acid profiles.

Sterol Profiles from Eight Vegetable Oils. Sterols, which constitute a major portion of the unsaponifiable material in these oils, are found in all fats and oils, their composition is characteristic of each vegetable oil, and it can be considered as a fingerprint.[24]

The four major sterols, campesterol, brassicasterol, β-sitosterol, and stigmasterol, known to constitute more than 95% of the total sterols in oils,[25] were assessed after sample saponification of the eight oils (Table 1). The resulting profiles showed marked variations in the RA sterol content in comparison with the other oils. Brassicasterol was a characteristic RA component not found in other oils, while stigmasterol content was higher in the other oils than in RA.

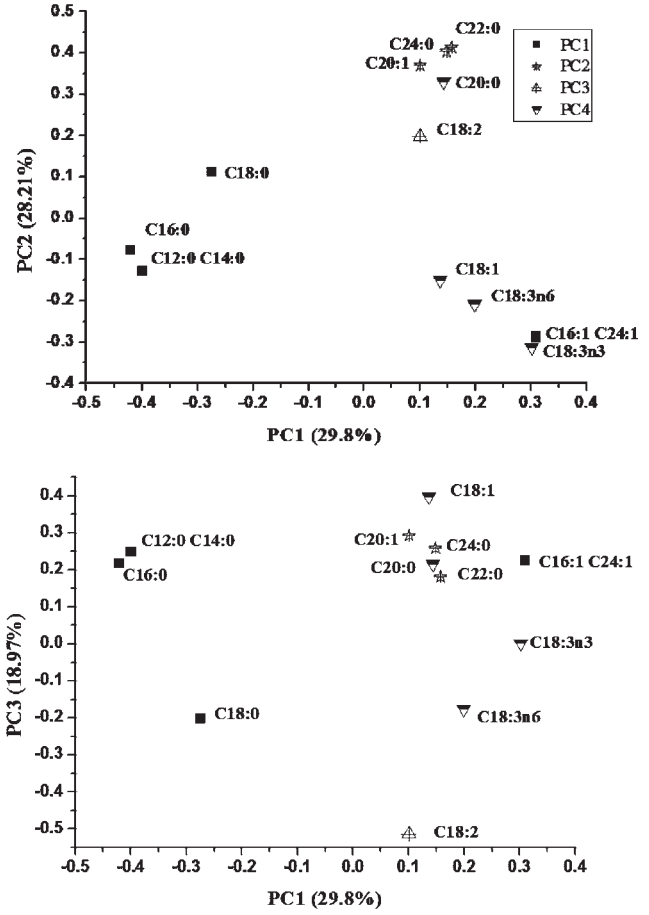

Figure 2. Loading plots obtained from the PCA of data about fatty acid compositions, in the PC1−PC2 and PC1−PC3 planes. PC1 contains C12:0, C14:0, C16:0, C18:0, C16:1, and C24:1; PC2 contains C20:1, C22:0, and C24:0; PC3 contains C18:2; PC4 contains C18:1, C20:0, C18:6, and C18:3.

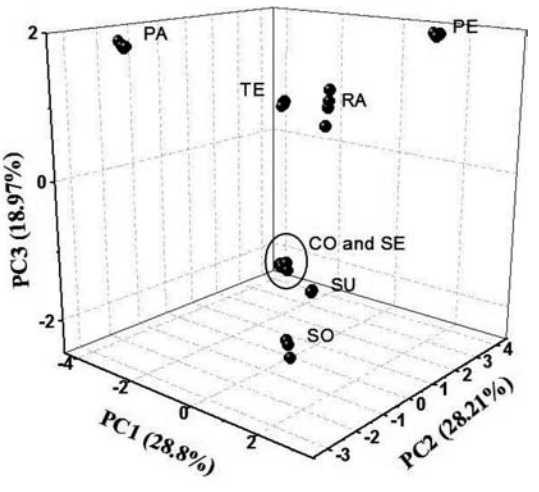

Figure 3. Score plot of PCA of the first three principal components of fatty acid composition data of eight vegetable oils; each kind of oil was composed of four samples of four different batches. Sample codes: SO, soybean oil; CO, corn oil; PE, peanut oil; SU, sunflower oil; RA, rapeseed oil; TE, tea-seed oil; PA, palm oil; SE, sesame oil.

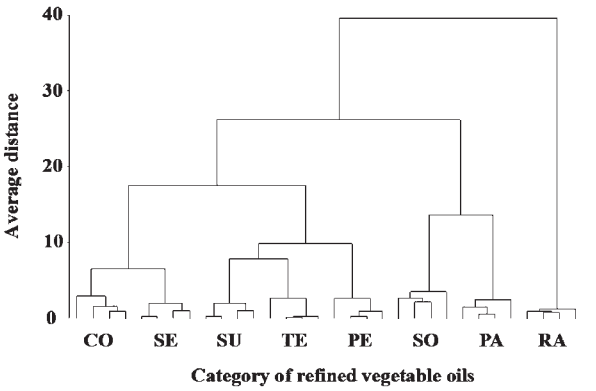

Figure 4. Cluster analyses of eight vegetable oils using the collected sterol data. Each kind of oil was composed of four samples of four different batches. Sample codes: SO, soybean oil; CO, corn oil; PE, peanut oil; SU, sunflower oil; RA, rapeseed oil; TE, tea-seed oil; PA, palm oil; SE, sesame oil.

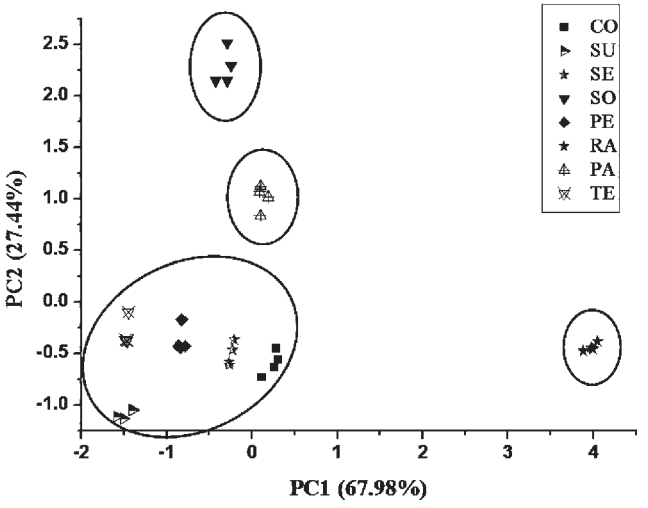

Figure 5. Score plot of PCA of sterol composition data of eight vegetable oils; each kind of oil was composed of four samples of four different batches. Sample codes: SO, soybean oil; CO, corn oil; PE, peanut oil; SU, sunflower oil; RA, rapeseed oil; TE, tea-seed oil; PA, palm oil; SE, sesame oil.

The dendrogram produced by the HCA corresponding to sterol data is given in Figure 4 and showed that, at a rescaled distance of 20−30, the samples were distributed into three major clusters: the first group consists of the RA; the second group is composed of the SO and PA in which the ratio of campesterol/β-sitosterol was approximately 3:4; while the third group includes the remaining samples. In this group, it was found that these oils were rich in β-sitosterol, which constituted more than 50%. At a rescaled distance of 10−20, the third group was distributed into two clusters: one group consists of CO and SE in which the ratios of campesterol/stigmasterol/β-sitosterol were approximately 3:1:6, while the other group includes SU, TE, and PE. This group is characterzed by the contents of campesterol and stigmasterol that account for less than 25%.

The sterol PCA results showed that two principal components are enough to explain 95.42% of the data variance. The score plots in Figure 5 show that all samples are classified into four

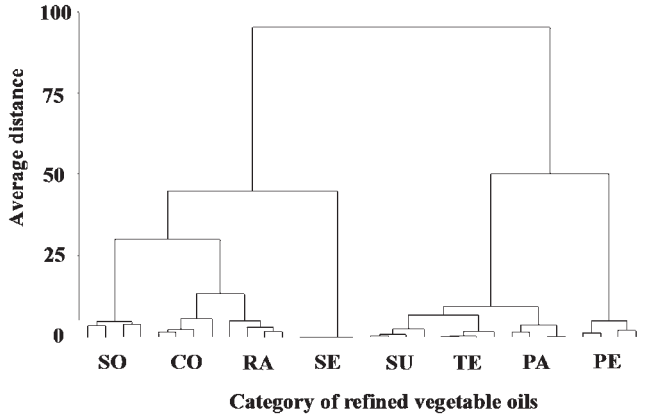

Figure 6. Cluster analyses of eight vegetable oils using the collected tocopherol data. Each kind of oil was composed of four samples of four different batches. Sample codes: SO, soybean oil; CO, corn oil; PE, peanut oil; SU, sunflower oil; RA, rapeseed oil; TE, tea-seed oil; PA, palm oil; SE, sesame oil.

major categories. These results provide a classification pattern similar to that obtained by HCA analysis, constituting a strong foundation for the assessment and control of oil samples. It is worth mentioning that oils in a cluster of similar fatty acid profiles, such as SO, CO, and SU, showed obvious differences in their sterol profiles and oils in a cluster of similar sterols profiles, such as SU, TE, and PE, showed obvious differences in their fatty acid profiles. Thus, the sterol profiles of oils with similar fatty acid profiles can be used to distinguished them very well. However, similar proportions of sterols were observed in samples CO and SE, revealing the need of new methods to assess the authenticity of new oils.

Tocopherol Profiles from Eight Vegetable Oils. Another minor oil component, the tocopherols are very interesting due to their antioxidant properties,[26] but these same properties yield them liable to losses during oil processing. However, even with this expected decrease in total tocopherol content, the relative compositions of tocopherols in SO are constant during processing.[27] Several authors have suggested the utilization of tocopherols as tracers for the identification and differentiation of vegetable oils.[14,28−30] The tocopherol isomer proportions for the eight oils revealed considerable differences among the relative proportions in CO and SE (Table 1), with CO rich in α-tocopherol (23.15 $\pm$ 1.79%), while SE had none. This indicated that, unlike the sterols of these two oils, α-tocopherol could be used as a marker compound for SE adulterated with CO.

The HCA tree structure showed the oils divided into two groups: one characterized by high γ-tocopherol content and the other by a high α-tocopherol (Figure 6). After an appropriate distance of 25 was chosen for sample differentiation, the initial two groups were split into five: SO had a higher percentage of β-tocopherol and γ-tocopherol compared with the other oils; CO and RA had similar α-tocopherol composition, but RA β-tocopherol was about five times that of CO; PE was principally α-tocopherol and γ-tocopherol at 54.13% and 40.08%, respectively; SU, TE, and PA had the shorter distance between them in their cluster, attributable to their similar α-tocopherol compositions and varying most in β-tocopherol content; and SE, which was all γ-tocopherol. The significant differences in the SU, TE, and PA group might be used to detect SU addition to TE and PA, but, unfortunately, the low β-tocopherol of TE and PA lack utility in detecting SU adulteration with TE or PA.

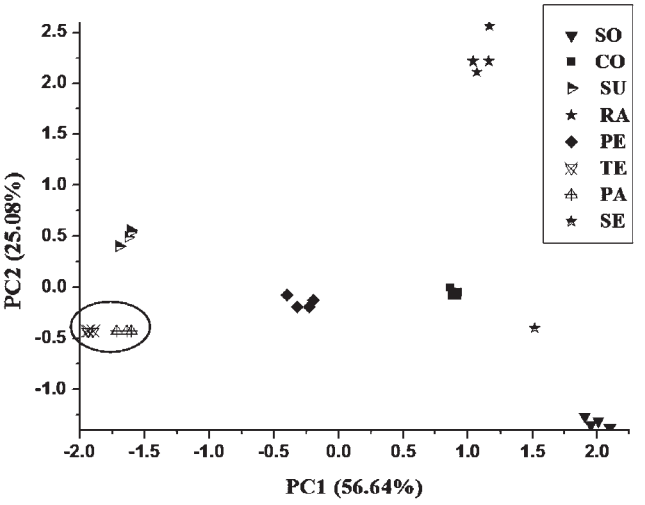

Figure 7. Score plot of PCA of tocopherol composition data of eight vegetable oils; each kind of oil was composed of four samples of four different batches. Sample codes: SO, soybean oil; CO, corn oil; PE, peanut oil; SU, sunflower oil; RA, rapeseed oil; TE, tea-seed oil; PA, palm oil; SE, sesame oil.

The PCA score plot clearly separated the eight oils into the above classifications according to their tocopherol compositions (Figure 7). Nevertheless, it was difficult to distinguish between PA and TE based on their very similar tocopherol content, but the composition of fatty acid was significantly differed. When the various differences observed here are taken together, these results indicated that the combination of fatty acid and tocopherol profiles could be used to accurately distinguish between and establish the authenticity of the eight vegetable oils.

The results of this study illustrated that the use of sterol or tocopherol profiles in conjunction with fatty acid profiles could offer an advantage in oil analysis and identification, as oil matching based on overall major lipid class profiles alone can be ambiguous when analyzing oils produced from multiple raw materials. HCA and PCA results obtained here were identical and provided a strong foundation for quality control and evaluation of oil samples.

AUTHOR INFORMATION

Corresponding Author

*Tel: (86 22) 60601456. Fax: (86 22) 60601332. E-mail: s.wang@tust.edu.cn.

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