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Comparison of GC and DSC monitoring the adulteration of camellia oil with selected vegetable oils

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Abstract This paper compared the potential application of gas chromatograph (GC) and differential scanning calorimetry (DSC) to verify adulteration of camellia oil (CMO) with sesame oil (SSO), sunflower oil (SFO), peanut oil (PNO), corn oil (CO) and canola oil (CNO) which are cheaper oils mixed as adulterants with CMO. DSC offers unique thermal profiling for each oil. A combination of analysis of FAs and fingerprint were applied for GC to detect the adulteration. According to a similarity calculation (with a standard below 0.9989) of included angle, the detection limit of sesame oil, sunflower oil and corn oil was 10 %, peanut oil 20 %, and rapeseed oil 30 %; for DSC, similarly CMOs had the unique fingerprint according to their DSC peak shape and thermodynamic parameters, and an adulteration contents of 5 % could be detected qualitatively. Satisfactory results were achieved from stepwise multiple linear regression analysis (SMLR) for the data of T_{on}, T_{off}, T_{peak}, $\triangle H$ and peak height (H) of DSC to quantitatively predict the other five oils adulteration in CMO with R^2 to 0.999. The average error obtained from the error analysis corresponding to SMLR was 1.2620 %. The preliminary results presented in this study suggest that DSC analysis is an attractive tool in detecting SSO, SFO, PNO, CO and CNO adulteration in CMO.

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Introduction

Camellia oil is also known as oil-tea camellia seed oil, tea tree oil or tea seed oil. It is a kind of edible vegetable oil squeezed or extracted from the seed of camellia (Camellia oleifera Abel). Its main producing areas are located in Hunan, Jiangxi, Guangxi, Zhejiang and other southern provinces of China [1]. Camellia oil is one of the four major woody oil plants in the world. As its many similarities with olive oil in physical and chemical constants, it is generally referred as "eastern olive oil" and "the king of cooking oil." Meanwhile, because of the high nutritional value (rich in vitamins A, B, E and other essential fatty acids, especially oleic acid which is 74–87 % of its fatty acid compositions [2]), the consumption of camellia oil has been associated with health benefits, such as a reduced risk of high blood pressure, coronary heart disease, atherosclerosis and also other diseases [3]. A special example is extending lifespan in a longevity village of Bama in Hechi city, Guangxi province, China, where camellia oil locally represents the main source of dietary fats. Therefore, camellia oil is usually called as the "longevity oil" (confirmed by National medical center of America) and "beauty oil" [4].

Food adulteration is a longtime problem in food trade and industry. Almost all foodstuffs that have high intrinsic commercial values face the quality problems. The price of camellia oil is generally 3–5 times more expensive than canola oil in edible oil market in China, but in Japan, it is higher than olive oil. Therefore, based on the high economic benefit of camellia oil, some unscrupulous traders have been mixing the cheap vegetable oils or non-edible

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oils with the camellia oil to seek high profits, which violate the rights and interests of consumers. Nowadays, Chinese government has taken many measurements to vindicate consumer rights. With regard to authentication of pure camellia oil, GB/T5539-2008 [5] and GB 11765-2003 [6] are specifically chosen as the qualitative and quantitative methods, respectively. However, the researches on adulteration methods of camellia oil are very few. The method of GC/GC-MS was adopted by Yan et al. [7] and Chen et al. [8], respectively, to differentiate camellia oil through testing fatty acid compositions and contents. Li et al. [9] and Zhang et al. [10] combined near-infrared spectroscopy (NIR) with pattern recognition techniques and PLS separately to discriminate camellia oil with good results. The basic physical and chemical testing methods unavoidably have artificial errors and may involve some highly toxic and corrosive chemical reagents. For GC methods, sample pretreatment is time consuming and tedious, and professional experiments are required to operate. NIR is a rapid online method which needs a combination with chemometrics. When studying oils, the feature information of them is not easy to extract by the NIR detector due to their complexities; in chemometrics analysis, selection of variables is difficult.

In the world of inspecting edible oils adulteration, many new methods have been introduced. These examples would be Raman spectroscopy [11–15], near-infrared spectroscopy (NIR) [16, 17], nuclear magnetic resonance (NMR) [18–21], electronic nose technique [22–24] and differential scanning calorimetry (DSC) method [25, 26].

DSC is a thermo-analytical technique which promises to offer a sensitive, rapid and reproducible fingerprint method for the identification of edible oils and fats [27]. Recently, DSC has been widely employed for its several advantages, no chemical treatment and hazardous manipulation practices required. As different edible oils show different contents and ratios of the chemical compositions (FA and TAG), the thermal properties of cooling and heating curves in DSC are closely associated with them. Many reported researches indicated the applicability of DSC for discriminating the authenticity of edible oils, especially for olive oil [28–35]. These publications presented that DSC method is a valuable tool with a broad prospect.

Nowadays, a combination of GC and fingerprint is widely used in many fields with satisfactory results. However, DSC application on camellia oil has not been reported in the literature. The objective of this preliminary work was through the comparison of GC combined with fingerprint with DSC combined with stepwise multiple linear regression analysis (SMLR) methods to evaluate the compromising use of DSC to detect adulteration of camellia oil with selected vegetables qualitatively and quantitatively.

Materials and methods

Sampling

Camellia oil (CMO) was mainly gathered from Hechi, Guangxi, produced by semi-refining. Sesame oil (SSO), sunflower oil (SFO), peanut oil (PNO), corn oil (CO) and canola oil (CNO) were purchased from a local supermarket. One sample of each oil was analyzed.

Preparation of blends

Camellia oil was separately mixed with SSO, SFO, PNO, CO and CNO in the following ratios (mass of CMO to adulterant: 95:5, 90:10, 80:20, 70:30 and 60:40, w/w). Each blend was prepared in triplicate. Samples were stored in dark bottles without headspace at room temperature before analysis.

Reagents, solvents and standards

All solvents used were of analytical or high-performance liquid chromatography (HPLC) grade. The standard mixture of FA methyl esters (GLC 463) was supplied by Supelco (America).

Acid value and peroxide value

Acid value and peroxide value were determined only on pure oils, according to the GBT5009.37-2003 [36] and GB/5538-2005 [37] (Official methods, China), respectively. Three replicates were analyzed per sample.

Fatty acid compositional analysis

Fatty acid methyl esters were prepared according to the method of GBT17376-2008 [38] by dissolving oil sample (60 mg) with isooctane (4.0 mL) and potassium hydroxide methanol solution (2 mol L^{-1} 0.2 mL) followed by subsequent analysis using a gas chromatograph (Agilent 7890A, America) fitted with a flame ionization detector. A polar capillary column Qmegawax250 (30 m × 0.25 mm × 0.25 μm) was used. The initial column temperature was 80 °C (kept for 2 min), then increased to 220 °C at a rate of 10 °C min^{-1} and kept for 14 min at 220 °C. The temperature of the injector and detector was maintained, respectively, at 250 and 260. Standard fatty acid methyl esters were used as authentic samples, and peak identification was done by comparing relative retention times.

Thermal analysis by DSC

DSC-200PC (from Germany NETZSCH company) equipped with thermal analysis data station was used to perform DSC analysis. Nitrogen (99.99 % purity) was used as the purge gas
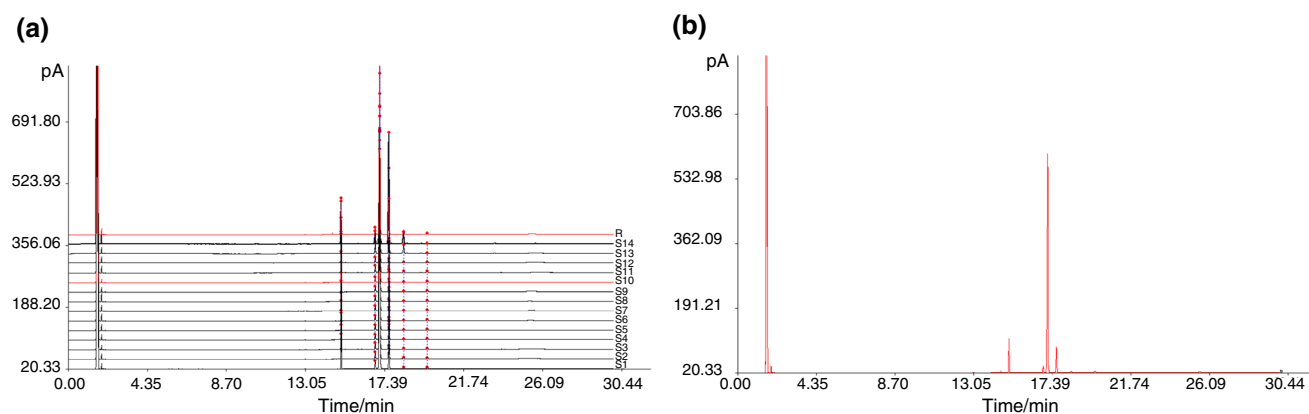
Fig. 1 **a** The superposed chart of the main fatty acid fingerprint of 14 kinds of pure camellia oil, S1–S14 represent the 14 kinds of camellia oil respectively. **b** The fingerprint of the main fatty acid of 14 kinds of pure camellia oil

at a flow rate of 50 mL min^{-1}. Indium (melting temperature 156.6 °C, $\Delta H_f = 28.45$ J g^{-1}) and n-dodecane (melting temperature -9.65 °C, $\Delta H_f = 216.73$ J g^{-1}) were used to calibrate the instrument. Samples of oil (8–10 mg) were weighed into aluminum pans and then hermetically sealed. An empty covered pan was used as a reference. The reference used was an empty covered aluminum pan of the same size as used in the samples. The following temperature program was used to obtain the cooling and melting profiles: 30 °C isotherm for 3 min, cooled at 2 °C min^{-1} to -80 °C and held for 3 min. The same sample was then heated from -80 to 30 °C at the same rate. The scanning rate was programmed at 2 °C min^{-1} to reduce the lag in output response from the DSC instrument as well as to preserve the minor peaks and to reduce the peak smoothing tendencies, which can occur at a high scanning rate. The software (Version 3.9A, TA Instruments) was used. 3 replicates were analyzed per sample.

Statistical analysis

Means and standard deviations (SD) were calculated with SPSS (version 19.0, SPSS) statistical software. SPSS was used to perform one-way analysis of variance and Tukey's honest significant difference test at a 95 % confidence level ($p < 0.05$) to identify differences among groups. DSC data were also further evaluated by the stepwise multiple linear regression model using SPSS.

Results and discussion

Chemical indices

Acid value is a sign of free fatty acid content and the index of rancidity in fat, whose value is based on the raw material, processing technology, shipping method and the suitable conditions and so on. Peroxide value is also used to

judge the quality and degree of metamorphism in oils. All the samples were tested according to GBT5009.37-2003 and GB/5538-2005. Meanwhile, their results were all within the standard limits which suggest the oils keep a good quality albeit the peroxide value of corn oil (CO) was a little higher.

FAs composition

Different oil or fat has different characteristic FA profiles which can be used as the method to determine the purity of oils, albeit some similarities of FAs in different oils. The results of FAs compositions would not be discussed in this report as many literatures have illustrated them. Through research and analysis, fingerprinting technology is adopted and the level of oleic acid can be regarded as an index of fraud mixing of the other five oil samples in CMO which has higher levels of oleic acid.

Fingerprinting technology is a sensitive and accurate detection method as the supplement for the food traceability system to keep products from adulteration, it refers to the spectrum or image with specificity and representative characteristic generated by certain analytic tools; GC has relatively higher separation efficiency than most high-performance liquid chromatography (HPLC) detectors. The GC fingerprint of the same vegetable oil under certain experimental conditions is basically stable, and therefore, it has a good repeatability, when measured a kind of oil mixing with other oils, the fingerprints of the oil would change owing to the differences of the fatty acid composition and content. According to that, GC fingerprint can be a method to detect oil counterfeit. In this study, with the method to verify the effectiveness of determining the adulteration quantity in camellia oil samples, we observed that a fingerprint similarity greater than 0.9989 of the 15 kinds of camellia oil is presented in Fig. 1a. Based on that, a parameter lower than 0.9989 can estimate the
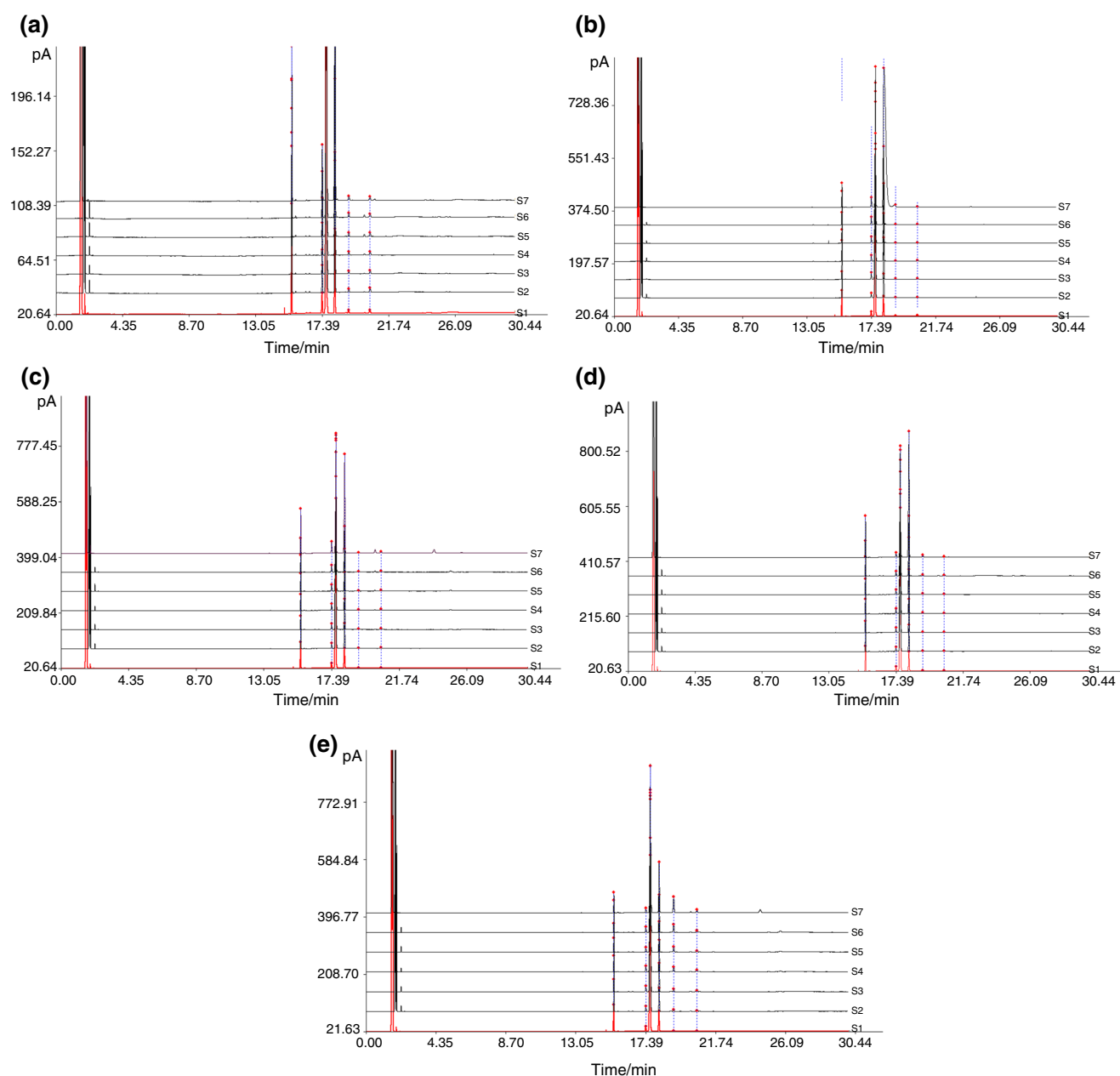
Fig. 2 Superposed chart of GC fingerprint of Camellia oil blended with different proportion of SSO, SFO, PNO, CO and CNO **a**, **b**, **c**, **d** and **e** represent SSO, SFO, PNO, CO, and CNO respectively, S1–S7 represent 7 kinds of camellia oil respectively

adulteration in contrast to the 15 kinds of camellia oil. Figure 1b shows the six common peaks as a comparison in these camellia oils. Through comparison, the GC fingerprint of camellia oil mixed with the other vegetable oils, respectively (mass of CMO to adulterant: 95:5, 90:10, 80:20, 70:30 and 60:40, w/w), changed regularly as the addition increased as shown in Fig. 2. According to the similarity calculation (with a standard below 0.9989) of included angle, the detection limit of sesame oil, sunflower oil and corn oil was 10 %, peanut oil 20 %, and rapeseed oil 30 % (Table 1). It must be mentioned that the analysis

of FAs combining GC fingerprint in our study produced relatively satisfactory results with regard to the levels of adulteration, whereas the method might be inadequate to detect the lower adulteration percentage.

Thermal analysis of camellia oil by DSC(DSC analysis of cooling and melting curves)

DSC is characterized by representing the crystallization and melting phase transition. This is an especially suitable technique for detecting vegetable oils. As shown in

Table 1 Similarity between the GC fingerprint of the samples of Camellia oil blended with different proportion of SSO, SFO, PNO, CO and CNO

	Adul/%	Similarity		Adul/%	Similarity
SSO	0	1	PNO	0	1
	5	0.9997		5	0.9998
	10	0.9987		10	0.9992
	20	0.994		20	0.996
	30	0.9843		30	0.9905
	40	0.9722		40	0.9808
	100	0.7282		100	0.8024
SFO	0	1	CO	0	1
	5	0.9993		5	0.9992
	10	0.9975		10	0.9972
	20	0.9876		20	0.9891
	30	0.9691		30	0.9728
	40	0.943		40	0.9457
	100	0.5245		100	0.5397
CNO	0	1			
	5	0.9999			
	10	0.9998			
	20	0.9989			
	30	0.9974			
	40	0.9951			
	100	0.9478			

Fig. 3, all the 14 camellia oil samples (CMO) exhibited their single defined events onsetting at −35.0 °C in the cooling and −14.6 °C in the heating curve. Whereas the endothermic event carried with a small shoulder peak which was at around −4 °C. All of them presented similar peak shape and thermodynamic parameters whose RSD % were in a range of 10 and 5 % respectively, especially the

onset temperature of peaks, RSD % were −1.52 % and −2.13 % respectively. Based on that, we can speculate that the similar cooling and heating curves may be used as "fingerprint" of CMO and their peaks as the "fingerprint peak." Considering the differences in growing condition, cultivar type, maturity and origin of CMO, and also unsteady condition of different DSC instruments, the subtle shifts of peak can happen. However, this would be in a limited range and we might as well conclude the unchangeable similarity of different CMO in a certain condition. The "fingerprint" of CMO can be studied further.

Thermal analysis of mixed oil by DSC

Cooling curve

Crystallization is commonly used to characterize the thermal behavior of oil samples as a physical event which requires the release of thermal enthalpy. DSC cooling curves obtained for CMO, SSO, SFO, PNO, CO, CNO and their mixtures (5–40 % SSO, SFO, PNO, CO, and CNO in CMO, respectively) are presented in Fig. 4. The other vegetable oils addition to CMO altered the overall line-shape of the exothermic peak which showed significant differences in comparison with pure CMO, and its peak height of crystallization event decreased upon addition of the other five vegetable oils. The inevitable co-crystallization happened in only one exothermic peak among all the six vegetable oil samples because of the wide variety of TAG that are mostly unsaturated cooling in their uniquely exothermic region.

Different contents of saturated or unsaturated TAG and FA lead to different endothermic and exothermic peaks. In
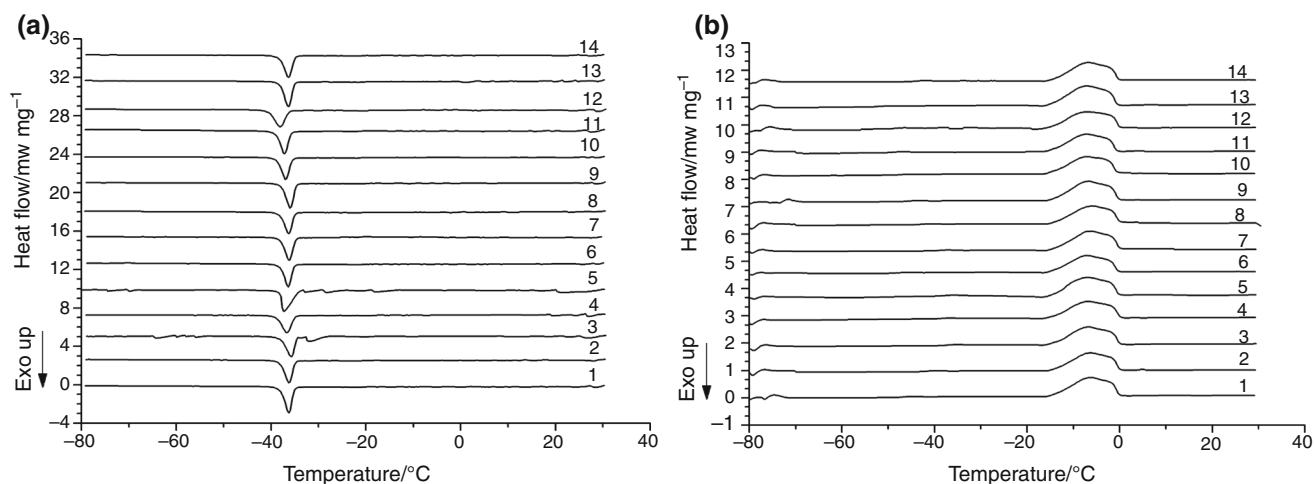
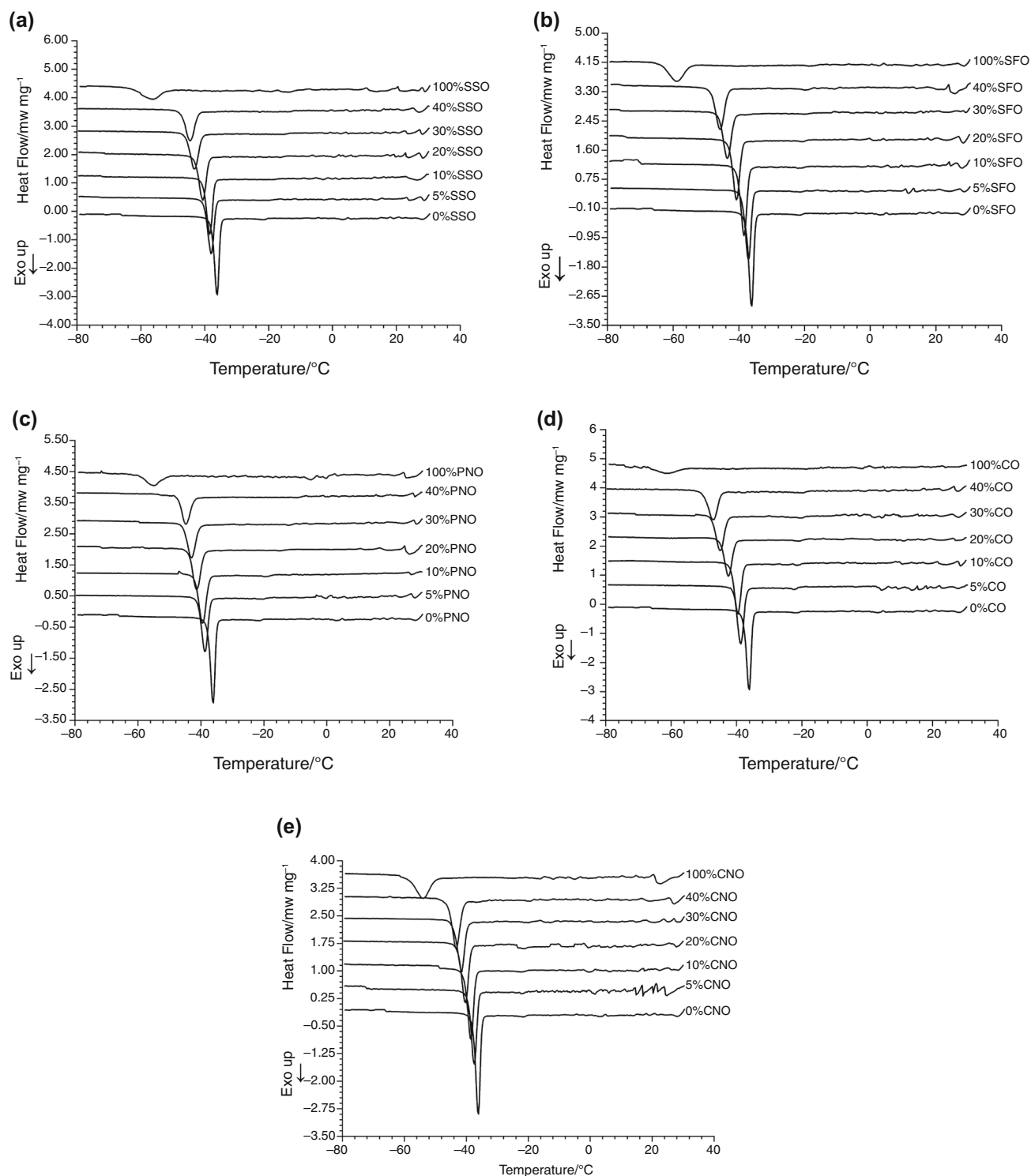**Fig. 3** DSC cooling curve of 14 kinds of CMO

Fig. 4 DSC cooling curve of CMO (camellia oil) adulterated with SSO (sesame oil), SFO (sunflower oil), PNO (peanut oil), CO (corn oil) and CNO (canola oil) in **a**, **b**, **c**, **d**, and **e** respectively

contrast, the taller and sharper crystallization peak which developed over a narrower temperature range resulted from a more compactly associated TAG chains which attributed to a highly cooperative phase transition in CMO. This was possibly associated with the much higher TUTAG and

MUFA contents (e.g., OOO and oleic acid) in CMO. The thermal behavior of oils correlates well with their FA composition (reported above by this paper) according to Fasina et al. [39]. As for SSO, SFO, PNO, CO and CNO, a much lower T_{on} of about -62.05, -64.05, -59.10,

Table 2 DSC data obtained from the cooling curves of the samples of CMO blended with SSO, SFO, PNO, CO and CNO

	Adul/%	T_{onset}/°C	T_{peak}/°C	T_{offs}/°C	ΔH/J g^{-1}	H/mW mg^{-1}
SSO	0	-35.10 ± 0.47^e	-36.54 ± 0.55^f	-38.30 ± 0.55^f	-137.05 ± 54.55^a	2.38 ± 0.29^d
	5	$-36.35 \pm 0.07^{d,e}$	-37.85 ± 0.21^e	-40.00 ± 0.28^e	-143.50 ± 6.65^a	2.03 ± 0.17^d
	10	$-36.95 \pm 0.07^{c,d}$	-38.50 ± 0.14^e	-40.55 ± 0.07^e	-135.75 ± 2.47^a	$1.96 \pm 0.03^{c,d}$
	20	-38.60 ± 0.14^c	-40.45 ± 0.35^d	-42.90 ± 0.14^d	-125.75 ± 2.19^a	$1.52 \pm 0.03^{b,c}$
	30	-40.55 ± 0.35^b	-42.85 ± 0.49^c	-45.55 ± 0.49^c	-119.65 ± 5.30^a	1.23 ± 0.04^b
	40	-41.70 ± 0.42^b	-44.25 ± 0.35^b	-47.00 ± 0.42^b	-110.75 ± 1.63^a	1.07 ± 0.00^b
	100	-49.55 ± 0.45^a	-57.00 ± 0.85^a	-62.05 ± 0.92^a	-83.35 ± 2.05^a	0.40 ± 0.01^a
SFO	0	-35.10 ± 0.47^g	-36.54 ± 0.55^f	-38.30 ± 0.55^f	-137.05 ± 54.55^a	2.38 ± 0.29^d
	5	-35.95 ± 0.35^f	$-37.5 \pm 0.57^{e,f}$	-39.55 ± 0.78^e	-128.00 ± 1.27^b	$1.84 \pm 0.21^{b,c}$
	10	-36.90 ± 0.14^e	-38.45 ± 0.07^e	-40.55 ± 0.07^e	-142.95 ± 0.78^a	$2.08 \pm 0.08^{c,d}$
	20	-38.75 ± 0.07^d	-40.60 ± 0.14^d	-42.80 ± 0.14^d	-135.50 ± 6.93^a	$1.71 \pm 0.05^{b,c}$
	30	-41.00 ± 0.28^c	-43.15 ± 0.49^c	-45.60 ± 0.71^c	-127.15 ± 5.59^a	1.41 ± 0.08^b
	40	-42.95 ± 0.07^b	-45.10 ± 0.14^b	-47.65 ± 0.21^b	-125.25 ± 1.17^a	1.39 ± 0.00^b
	100	-54.25 ± 0.07^a	-58.90 ± 0.14^a	-64.05 ± 0.21^a	-121.20 ± 9.05^a	0.57 ± 0.02^a
PNO	0	-35.10 ± 0.47^e	-36.54 ± 0.55^f	-38.30 ± 0.55^g	-137.05 ± 54.55^a	2.38 ± 0.29^f
	5	-36.60 ± 0.57^d	-38.25 ± 0.64^e	-40.35 ± 0.78^f	-125.70 ± 8.91^a	1.76 ± 0.03^d
	10	-37.40 ± 0.14^d	-39.55 ± 0.07^d	-41.95 ± 0.07^e	-139.25 ± 4.60^a	$1.59 \pm 0.04^{c,d}$
	20	-38.95 ± 0.07^c	-41.30 ± 0.00^c	-43.85 ± 0.07^d	-126.25 ± 0.64^a	$1.32 \pm 0.02^{b,c,d}$
	30	-39.90 ± 0.85^c	-43.50 ± 0.71^b	-45.65 ± 0.07^c	-107.55 ± 2.05^a	$1.13 \pm 0.04^{b,c}$
	40	-41.50 ± 0.71^b	-44.35 ± 0.49^b	-47.10 ± 0.14^b	-96.45 ± 4.88^a	0.95 ± 0.05^b
	100	-49.05 ± 3.04^a	-53.30 ± 2.12^a	-59.10 ± 0.85^a	-71.30 ± 3.11^a	0.35 ± 0.01^a
CO	0	-35.10 ± 0.47^g	-36.54 ± 0.55^g	-38.30 ± 0.55^g	-137.05 ± 54.55^a	2.38 ± 0.29^e
	5	-36.90 ± 0.14^f	-38.55 ± 0.21^f	-40.50 ± 0.28^f	-140.55 ± 4.60^b	$1.99 \pm 0.08^{d,e}$
	10	-37.85 ± 0.21^e	-39.75 ± 0.35^e	-42.10 ± 0.57^e	-129.50 ± 5.51^a	$1.59 \pm 0.21^{c,d}$
	20	-40.35 ± 0.07^d	-42.60 ± 0.14^d	-45.00 ± 0.14^d	-115.80 ± 2.26^a	$1.27 \pm 0.03^{b,c}$
	30	-42.85 ± 0.21^c	-45.10 ± 0.14^c	-47.80 ± 0.28^c	-113.15 ± 3.61^a	$1.16 \pm 0.08^{b,c}$
	40	-45.85 ± 0.49^b	-47.90 ± 0.56^b	-51.05 ± 0.49^b	-92.75 ± 2.47^a	0.87 ± 0.00^b
	100	-55.45 ± 0.35^a	-61.25 ± 0.07^a	-66.95 ± 0.63^a	-52.80 ± 13.58^a	0.24 ± 0.06^a
CNO	0	-35.10 ± 0.47^f	-36.54 ± 0.55^f	-38.30 ± 0.55^f	-137.05 ± 54.55^a	2.38 ± 0.29^d
	5	-35.80 ± 0.28^f	-37.25 ± 0.21^f	-39.15 ± 0.35^f	-138.30 ± 11.17^a	2.12 ± 0.22^d
	10	-36.75 ± 0.21^e	-38.40 ± 0.28^e	-40.40 ± 0.28^e	-138.55 ± 0.78^a	$1.96 \pm 0.10^{c,d}$
	20	-38.50 ± 0.14^d	-40.50 ± 0.28^d	-42.80 ± 0.14^d	-132.30 ± 1.13^a	$1.58 \pm 0.04^{b,c}$
	30	-39.65 ± 0.07^c	-41.65 ± 0.21^c	-44.10 ± 0.14^c	-127.30 ± 4.53^a	1.39 ± 0.03^b
	40	-40.90 ± 0.14^b	-43.40 ± 0.14^b	-46.00 ± 0.14^b	-131.30 ± 9.05^a	1.32 ± 0.05^b
	100	-49.20 ± 0.99^a	-53.25 ± 0.92^a	-58.80 ± 0.28^a	-95.15 ± 0.49^a	0.59 ± 0.01^a

The same letters in same column means no significant difference among them under the significance level of $P < 0.05$, and vice versa

-66.95, -58.80 °C, respectively, and also the shorter, broader peaks might be related with their higher contents of PUFA (especially linoleic acid and linolenic acid).

The other vegetable oils addition to CMO changed its chemical composition, allowing TAG crystallization during cooling. It is assumed that ΔH (the enthalpy taken from the measurement of the area under the peaks), H (peak height), T_{onset} and T_{peak} lessoned, the range of the transition increased with the ever-growing adulteration in CMO as a whole. Table 2 lists their respective T_{onset} (Temperature of curves start), T_{offs} (Temperature of curves end), T_{peak} (Temperature of curves at the peak) H and ΔH (J g^{-1}) through data processing, and we can conclude that a significant difference existed in T_{onset} and T_{peak} when their addition to 5 % except CNO which increased to 10 %. Otherwise, ΔH (enthalpy) rises in the adulteration of 5 % of SSO, CO, CNO and 10 % of SFO, PNO. This can be explained by the possibility that some of the unsaturated TAG joined the saturated TAG to increase their cooling enthalpy.
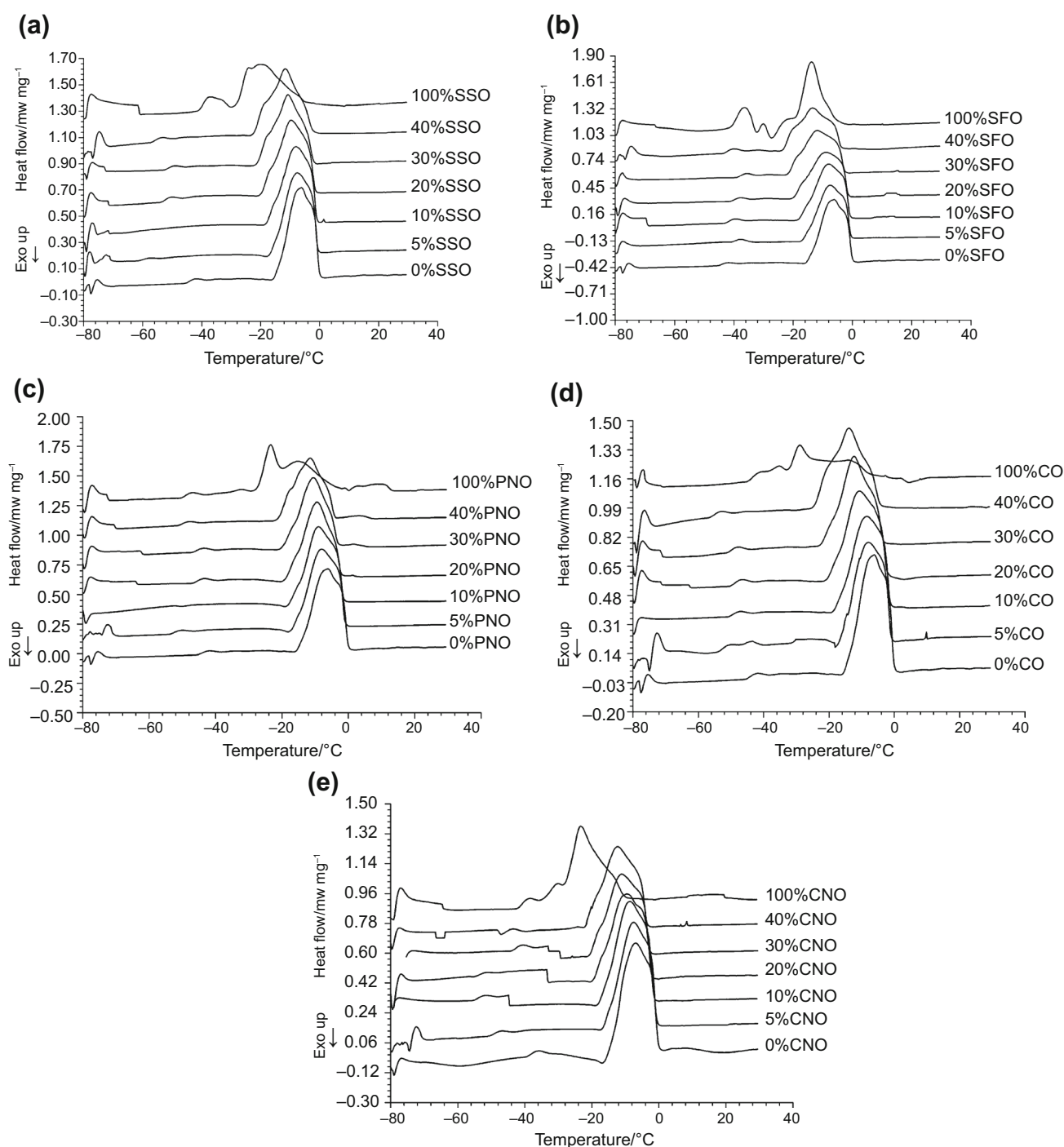
Fig. 5 DSC heating curve of CMO adulterated with SSO (sesame oil), SFO (sunflower oil), PNO (peanut oil), CO (corn oil) and CNO (canola oil) in **a**, **b**, **c**, **d**, and **e** respectively

Heating curve

DSC heating curves obtained for CMO, SSO, SFO, PNO, CO, CNO and their admixtures (5–40 %) are shown in Fig. 5. CMO displayed a well-defined endothermic event peaking at −6.65 °C, with a less distinct shoulder peak embedded at a higher temperature (−2 °C). The major

endothermic peak may be ascribed to the melting of the most unsaturated fraction of TAG (e.g., OOO) and the minor shoulder peak to less unsaturated TAG in CMO. Polymorphism phenomenon which could be associated with the solid-to-solid transformation happened in all the other five oil samples before the melting onset. Besides these peaks mentioned above, SSO and PNO showed two

Table 3 DSC data obtained from the heating curves of the samples of CMO blended with SSO, SFO, PNO, CO and CNO

	Adul/%	T_{onset}/°C	T_{peak}/°C	T_{offs}/°C	ΔH/J g^{-1}	H/mW mg^{-1}
SSO	0	-14.73 ± 0.41^b	-6.65 ± 0.54^e	-4.63 ± 0.51^e	143.58 ± 10.19^e	0.73 ± 0.30^a
	5	-13.80 ± 0.14^c	-7.65 ± 0.07^d	-5.70 ± 0.00^d	92.75 ± 0.49^d	0.48 ± 0.04^a
	10	-13.90 ± 0.14^c	-8.05 ± 0.21^d	$-5.20 \pm 0.28^{d,e}$	72.85 ± 1.20^c	0.37 ± 0.02^a
	20	-13.85 ± 0.07^c	-9.55 ± 0.07^c	-7.50 ± 0.28^c	39.65 ± 0.21^b	0.25 ± 0.01^a
	30	-13.80 ± 0.00^b	-10.80 ± 0.14^b	$-8.30 \pm 0.00^{b,c}$	19.10 ± 1.13^a	0.17 ± 0.01^a
	40	-14.70 ± 0.14^b	-11.65 ± 0.07^b	$-9.10 \pm 0.14^{b,c}$	18.45 ± 1.48^a	0.16 ± 0.01^a
	100	-27.80 ± 0.14^a	-24.10 ± 0.14^a	-23.20 ± 0.00^a	$30.35 \pm 0.49^{a,b}$	0.28 ± 0.01^a
SFO	0	-14.73 ± 0.41^c	-6.65 ± 0.54^f	-4.63 ± 0.51^e	143.58 ± 10.19^e	0.73 ± 0.30^b
	5	-13.55 ± 0.49^d	$-7.55 \pm 0.07^{e,f}$	$-5.20 \pm 0.28^{d,e}$	76.45 ± 9.97^d	$0.41 \pm 0.04^{a,b}$
	10	-13.60 ± 0.28^d	-7.80 ± 0.28^e	$-4.80 \pm 0.00^{d,e}$	$68.85 \pm 6.29^{c,d}$	$0.36 \pm 0.02^{a,b}$
	20	-15.10 ± 0.14^c	-8.95 ± 0.07^d	-6.70 ± 0.00^d	$50.95 \pm 2.23^{b,c}$	$0.26 \pm 0.01^{a,b}$
	30	-17.00 ± 0.14^b	-12.10 ± 0.42^c	-9.15 ± 0.35^c	47.75 ± 3.32^b	$0.26 \pm 0.03^{a,b}$
	40	-16.70 ± 0.00^b	-13.50 ± 0.14^b	-11.05 ± 0.21^b	17.25 ± 1.48^a	0.14 ± 0.00^a
	100	-24.70 ± 2.55^a	-26.95 ± 0.21^a	-23.00 ± 4.94^a	$33.35 \pm 3.32^{a,b}$	$0.22 \pm 0.02^{a,b}$
PNO	0	-14.73 ± 0.41^c	-6.65 ± 0.54^f	-4.63 ± 0.51^e	143.58 ± 10.19^c	0.73 ± 0.30^a
	5	-13.25 ± 0.35^d	-8.10 ± 0.28^e	-5.45 ± 0.21^e	69.60 ± 7.07^b	0.40 ± 0.02^a
	10	-13.65 ± 0.35^d	$-8.95 \pm 0.21^{d,e}$	-7.05 ± 0.35^d	69.05 ± 6.01^b	0.43 ± 0.03^a
	20	-14.60 ± 0.00^c	-9.35 ± 0.07^d	$-6.80 \pm 0.00^{c,d}$	70.30 ± 1.27^b	0.41 ± 0.00^a
	30	-15.30 ± 0.00^c	-10.50 ± 0.00^c	-7.90 ± 0.00^c	$56.55 \pm 0.35^{a,b}$	0.34 ± 0.01^a
	40	-16.40 ± 0.28^b	-11.45 ± 0.07^b	-9.00 ± 0.28^b	42.35 ± 6.29^b	0.27 ± 0.04^a
	100	-27.05 ± 0.07^a	-23.30 ± 0.28^a	-21.15 ± 0.07^a	$52.30 \pm 1.56^{a,b}$	0.36 ± 0.03^a
CO	0	-14.73 ± 0.41^e	-6.65 ± 0.54^f	-4.63 ± 0.51^e	143.58 ± 10.19^e	0.73 ± 0.30^a
	5	$-13.95 \pm 0.35^{e,f}$	-8.20 ± 0.42^e	-5.30 ± 0.85^d	81.90 ± 13.01^d	0.43 ± 0.04^b
	10	-13.45 ± 1.06^f	-8.90 ± 0.71^e	-6.65 ± 1.91^c	$65.95 \pm 7.42^{c,d}$	0.39 ± 0.07^a
	20	-15.95 ± 0.35^d	-10.75 ± 0.07^d	-7.90 ± 0.28^c	$53.35 \pm 0.07^{b,c}$	0.30 ± 0.01^a
	30	-17.15 ± 0.21^c	-12.30 ± 0.00^c	-9.60 ± 0.57^b	$50.05 \pm 1.20^{b,c}$	0.30 ± 0.02^a
	40	-18.10 ± 0.00^b	-13.55 ± 0.21^b	-10.50 ± 0.28^b	$38.60 \pm 3.11^{a,b}$	0.25 ± 0.01^a
	100	-32.15 ± 0.21^a	-29.15 ± 0.21^a	-26.90 ± 0.57^a	23.30 ± 4.80^a	0.18 ± 0.06^a
CNO	0	-14.73 ± 0.41^c	-6.65 ± 0.54^f	-4.63 ± 0.51^e	143.58 ± 10.19^d	0.73 ± 0.30^a
	5	-13.35 ± 0.35^d	-7.40 ± 0.14^f	$-4.90 \pm 0.28^{d,e}$	78.80 ± 13.15^c	0.42 ± 0.07^a
	10	-14.55 ± 0.07^c	-8.35 ± 0.35^e	-5.80 ± 0.70^d	91.10 ± 9.90^c	0.46 ± 0.03^a
	20	-14.95 ± 0.48^c	-9.75 ± 0.35^d	-7.30 ± 0.28^c	54.10 ± 8.49^b	0.29 ± 0.03^a
	30	-15.80 ± 0.00^b	-10.95 ± 0.21^c	-8.60 ± 0.71^b	$42.95 \pm 3.18^{a,b}$	0.26 ± 0.01^a
	40	-16.50 ± 0.14^b	-12.30 ± 0.14^b	-9.45 ± 0.21^b	32.05 ± 2.47^a	0.21 ± 0.01^a
	100	-27.45 ± 0.07^a	-23.15 ± 0.21^a	-20.55 ± 0.49^a	55.00 ± 1.84^b	0.33 ± 0.01^a

The same letters in same column means no significant difference among them under the significance level of $P < 0.05$, and vice versa

overlapping peaks which were assumed to be the melting peaks of all the TAG in this wide endotherm region. The peaks at the lower temperature may be related with the highly unsaturated TAG, especially LLL, LLO and LLO, LOO, respectively. And the first distinguishably peak in PNO might be connected to LOO. Similarly, for SFO and CNO, each of them shows a well-defined endothermic event peaking at -13.8, -23.1 °C, with a minor shoulder peak at -8, -8.1 °C, respectively. The prominent and shoulder peaks correspond to the highly and less unsaturated TAGs. The endothermic events in CO were smaller, flatter and less distinct than in other oils that might result from higher values of POV, PAV and free acidity, whose molecules adsorbed in the crystal lattice of the TAG might form mixed crystal, leading to the lower phase transition enthalpy. All the other oil samples presented the completely different lineshape from CMO.

Tan et al. [40, 41] reported that the inseparable shoulder peak which may melt over the same temperature range arrives from the complex mature of TAG, and the smaller or shoulder peak corresponds to differing type of TAG. It is hypothesized that the shoulder peak of CMO is

Table 4 SMLR analysis of DSC cooling thermal properties in the CMO adulterations

Adulation sample	Step	Regression equation	R^2	P
SSO	1	$\%SSO = -180.17 - 4.927\,T_{peak}$	0.999	<0.0001
SFO	1	$\%SFO = -161.875 - 4.454\,T_{peak}$	0.999	<0.0001
	2	$\%SFO = -170.082 - 2.364\,T_{peak} - 2.41T_{on}$	0.999	<0.0001
PNO	1	$\%PNO = -193.12 - 4.928\,T_{off}$	0.990	<0.0001
CO	1	$\%CO = -136.897 - 3.511\,T_{off}$	0.996	<0.0001
	2	$\%CO = -171.134 - 4.022\,T_{off} + 7.377H$	0.999	<0.0001
CNO	1	$\%CNO = -221.16 - 6.021\,T_{peak}$	0.998	<0.0001

Table 5 Error analysis of the regression equations obtained by SMLR

Adulation sample	Step	Regression equation	Measured value/%	Predictive value/%	Error/%	Average error/%
SSO	1	$\%SSO = -180.17 - 4.927\,Tpeak$	39.8576	37.6034	2.2542	1.2620
			20.5471	17.8954	2.6517	
SFO	1	$\%SFO = -161.875 - 4.454\,T_{peak}$	10.0443	9.6040	0.4403	
			41.0474	41.6728	−0.6254	
	2	$\%SFO = -170.082 - 2.364T - 2.41T_{on}$	10.0443	10.1020	−0.0577	
			41.0474	42.0648	−1.0174	
PNO	1	$\%PNO = -193.12 - 4.928\,T_{off}$	5.7705	6.4640	−0.6935	
			9.9367	13.3632	−3.4265	
CO	1	$\%CO = -136.897 - 3.511\,T_{off}$	6.2648	6.1050	0.1598	
			40.0485	39.9902	0.0583	
	2	$\%CO = -171.134 - 4.022\,T_{off} + 7.377H$	6.2648	4.5963	1.6685	
			40.0485	41.1107	−1.0622	
CNO	1	$\%CNO = -221.16 - 6.021\,T_{peak}$	20.5811	23.8947	−3.3136	
			30.7571	30.5178	0.2393	

due to the complex mature of TAG because of its higher contents of OOO. The other oils might be on account of the different types of TAG. Along with adulteration, the shoulder peak belonging to CMO disappeared, the total heating event significantly shifted toward lower temperature, and the heating enthalpy decreased, which is owing to increased highly unsaturated TAGs. According to Table 3, when SSO, SFO, PNO and CO is adulterated to 5 % and CNO to 10 %, T_{onset}, T_{peak} and ΔH changed significantly. The more compactly associated TAG chains formed a more ordered crystal structure which needs higher energy to melt, leading to the increasing heating enthalpy.

Different melting profiles may be observed because of different experimental conditions and/or DSC instrumentation and/or nature of the samples. In a controlled condition, the misbranding of CMO by other five vegetable oils can be detected from DSC melting data. The limit of detection (LOD) for all these five oils adulteration with CMO was 5 % by the synthesis in characterizing DSC curves and overall thermal properties.

Quantitative analysis by SMLR

Through the quantitative analysis of their DSC thermal properties in the cooling events, the accurate adulteration percentage of SSO, SFO, PNO, CO and CNO in CMO can be estimated. Adopting the method of stepwise multiple linear regression analysis (SMLR), the data of Tonset, Toffs, Tpeak, ΔH and peak height (H) were collected as independent predictors to analyze the relevance among them. We obtained the regression models as given in Table 4. The coefficient of determination (R^2) was calculated to be 0.999 that was a very good correlation.

In order to test the feasibility of these polynomials, we adopted the error analysis method for validation. Ten kinds of CMO samples adulterated with the other five oils were chosen to test their accuracy. As a result from Table 5, the range of error is between −3.4265 and 2.6517 % and the average error 1.2620 % which was relatively small to be accepted. Therefore, the quantitative prediction models established by SMLR combining DSC profiles could be acted as the method to determine the specific adulteration contents in CMO.

Conclusions

This work showed the comparison of GC and DSC to detect the adulteration of CMO with selected vegetable soils (SSO, SFO, PNO, CO and CNO). DSC had a more satisfactory result, and the cooling and heating curves of DSC combining the use of stepwise multiple linear regression (SMLR) analysis could be an effective method to detect CMO adulterated with selected vegetable soils qualitatively and quantitatively with the lower limit of detection to 5 % and higher coefficient of determination (R^2) to 0.999. Meanwhile, the average error that arrived from the error analysis corresponding to SMLR was 1.2620 %. The result from FA analysis which was operated by GC and fingerprint was lower than the method of DSC in the qualitative and quantitative analysis and are restricted by the complicated pretreatment and instrument operation procedures. DSC offers a simple, sensitive and rapid method for quality control of oils by this passage.

Although the precision and feasibility of the results obtained above were proven by more samples in this study, they should be confirmed further by a larger number of samples considering the variation of chemical composition of oils from different cultivars, geographical origins, agronomical practices, processing technologies and harvesting periods. Moreover, a further evaluation should be made using X-ray diffraction or other techniques that could gather the structural information to help determine the specific DSC peak which are contributed by specific TAG or FA, thus gaining more accurate detection information about oils.

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