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ARTICLES

Differential Scanning Calorimetry as a Method for the Control of Vegetable Oils

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Abstract—Differential scanning calorimetry (**DSC**) was used to study the thermophysical properties of oils of amaranth, corn, flax, sunflower, rapeseed, milk thistle, camelina, and pumpkin seed, liquid at room temperature. The characteristic thermal effects of these oils (temperatures of the maxima of endothermic peaks and their areas in the DSC thermograms) were determined. Endothermic peaks of different intensities on the melting curves of liquid vegetable oils in the ranges from –40 to –15°C, from –25 to –8°C, from –19 to +6°C, and from –10 to +4 °C as identification factors are discussed. The coordinates of the maxima of these peaks on the abscissa axis (T_i) and their areas (S_i) significantly correlate with the concentrations of basic fatty acids and triacylglycerols (W_i, %), determined by reversed-phase HPLC. We demonstrated that the authenticity of vegetable oils could be effectively controlled by DSC.

Keywords: liquid vegetable oils, differential scanning calorimetry, melting curves, reversed-phase HPLC, triglyceride composition

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The thermophysical properties of solid fats, such as milk fat, cocoa butter, palm and coconut oil, as well as a whole range of milk fat and cocoa butter substitutes, have been studied by differential scanning calorimetry (**DSC**) in sufficient detail [1–4], because information on the melting and crystallization temperatures of fats is essential for the food technology and consumption. Milk fat and cocoa butter are rather expensive products; therefore, they are partially or completely replaced with artificial combined fats to reduce the cost of fat, oil, and confectionery products and optimize the technology. Thermal analysis was also used for liquid vegetable oils [5–7]. Tan and Cheman [1] presented the most detailed DSC study of the thermophysical properties of 17 edible fats, including typical vegetable oils. To interpret the crystallization and melting curves, gas–liquid chromatography (**GLC**) and HPLC (data on the fatty acid and triglyceride composition of fats) were used as confirmatory methods, the iodine number and the distribution of triunsaturated, diunsaturated, monounsaturated, and trisaturated triacylglycerol (**TAG**) fractions are also taken into account. The authors compared the DSC data for different vegetable oils; however, they performed no correlation analysis of the change in the temperatures of the maxima and their areas in the thermograms, depending on the chemical composition of vegetable oil [1]. Crystallization curves are commonly used to study vegetable oils by DSC; although they are less reproducible than melting curves [2, 4]. The so-called "fast" DSC with a temperature gradient of 10–20 deg/min is used [3, 5]. Upon rapid heating, the peaks characterizing the thermal effects merge, and the information content of the thermograms decreases; therefore, the standard heating or cooling rate is only 5 deg/min. Chromatographic data are often not given in DSC studies of vegetable oils to support the conclusions made; it was emphasized that DSC is a self-sufficient method for identifying fats that does not require a lot of time, reagents, solvents, sophisticated equipment, or highly qualified personnel. Demonstrating the high sensitivity of thermograms to changes in the fatty acid and triglyceride composition, the authors of the cited works did not discuss the variability of the chemical composition of vegetable oils caused by genotypic or phenotypic factors. Finally, no understandable and simple identification algorithm was proposed in [1–7], for example,

using control charts that visualize digital information containing several parameters of thermograms [8].

The goal of this work was to study the thermophysical properties of some liquid vegetable oils obtained from raw materials grown in Russia using DSC melting curves and control charts, taking into account the variability of the chemical composition, to verify the authenticity of these oils.

The test samples were sunflower, corn, rapeseed, and camelina oils as inexpensive varieties and amaranth, flaxseed, pumpkin seed, and milk thistle oils, which are mainly used as dietary supplements based on expensive natural vegetable oils and can be adulterated or diluted with inexpensive vegetable oils, which are10–20 times cheaper.

The priority methods for controlling the quality and authenticity of fats and oils are capillary gas–liquid chromatography of fatty acids (**FAs**) and reversed-phase HPLC of triacylglycerols contained in the fat phase [8–18]. Triacylglycerols of the considered liquid vegetable oils contain totally from 75 to 90% of unsaturated fatty acids (oleic, linoleic, and linolenic), 5–20% of saturated fatty acids (palmitic and stearic), and various amounts of minor saturated and/or unsaturated fatty acids [8, 9]. The componentwise identification of triacylglycerols in various plant materials by HPLC made it possible to obtain a large database of chromatographic data [8–18], which was used in this work to interpret chromatograms. We used the incremental approach developed by Deineka et al. [10–15] based on the idea of the additivity of contributions (increments) of functional groups to the adsorbate retention [15]. This approach does not make it possible to distinguish between positional isomers or individual triacylglycerols with similar chromatographic properties, but it has generally proved to be productive and in good agreement with the data of other works.

In contrast to the componentwise analysis by GLC and HPLC, the geometric parameters of **DSC** curves are used as identification parameters and analytical signals, namely, the extrema of melting or crystallization temperatures, areas of endo- and exothermic peaks, and their ratios [1–4]. The advantage of the DSC method is the simplicity of sample preparation and the high sensitivity of the thermophysical characteristics to the composition of the fat phase. For example, DSC of mixtures of milk fat and palm oil reveals 2–10% of the addition of the latter to milk fat [2–4]. Similar results were obtained in the DSC analysis of mixtures of olive oil with other cheaper vegetable oils [5, 6]. The characteristic profile of DSC thermograms can be used to check not only the authenticity of the oil sample but also the geographical origin and the variety of the oil plant from which it was obtained [6].

EXPERIMENTAL

Oil samples (reference samples) were produced under laboratory conditions at the Voronezh State University of Engineering Technology (VSUET) and Russkaya Oliva (Voronezh, Russia) by cold pressing using a screw press. Thermal analysis was performed using an STA 449 F3 Jupiter® device for synchronous thermal analysis (NETZSCH, Germany). Weighed portions of vegetable oil samples of 15–22 mg were collected for analysis. Thermophysical properties were measured in the temperature range from –150 to +20°C; the heating rate was 5 deg/min. The system was cooled with liquid nitrogen. Measurements were carried out in a helium atmosphere; the purge gas flow rate was 10 mL/min, and the protective gas flow rate was 10 mL/min. The temperature measurement accuracy was ±0.3°C.

The vegetable oil composition was analyzed by HPLC using a Shimadzu L20 chromatograph with a Shimadzu RID-10A refractometric detector (Japan). We used a Kromasil 100-5C18 column, 250 × 4.6 mm in size, at 35°C. An acetonitrile–acetone mixture (15 : 85, vol) was an eluent; the eluent flow rate was 0.8 mL/min. Triacylglycerols and fatty acids were identified using an incremental calculation [15].

To increase the information content of the thermograms obtained by DSC, we used the software separation of the superposition of peaks of thermal effects overlapping each other using the NETZSCH Peak Separation program according to the General algorithm.

Triacylglycerols were designated according to the generally accepted procedure: letters were used to indicate the type of fatty acid, indicating their number in a triacylglycerol using a subscript without differentiating the position of the radicals in the molecule. The letter designations of acids included in the studied vegetable oils are (A) arachidic, (B) behenic, (E) eicosenoic, (E") erucic, (L) linoleic, (L') linolenic, (O) oleic, (P) palmitic, and (S) stearic acids. For example, L_2O denotes a triacylglycerol formed by two linoleic and one oleic acid radicals.

RESULTS AND DISCUSSION

Figures 1 and 2 show DSC melting curves for the samples of vegetable oils and chromatograms of triacylglycerols. In the DSC melting thermograms of oils, one can distinguish from two to four characteristic endothermic maxima, which have different amplitudes and geometries and are located at different distances along the temperature axis. The peaks have different areas (S_i), which also carry identification features.

For a more accurate determination of T_i of weakly expressed thermal effects, the so-called "shoulders" in the main peaks, the second derivatives of the DSC curves were used (see the example in Fig. 2e). The

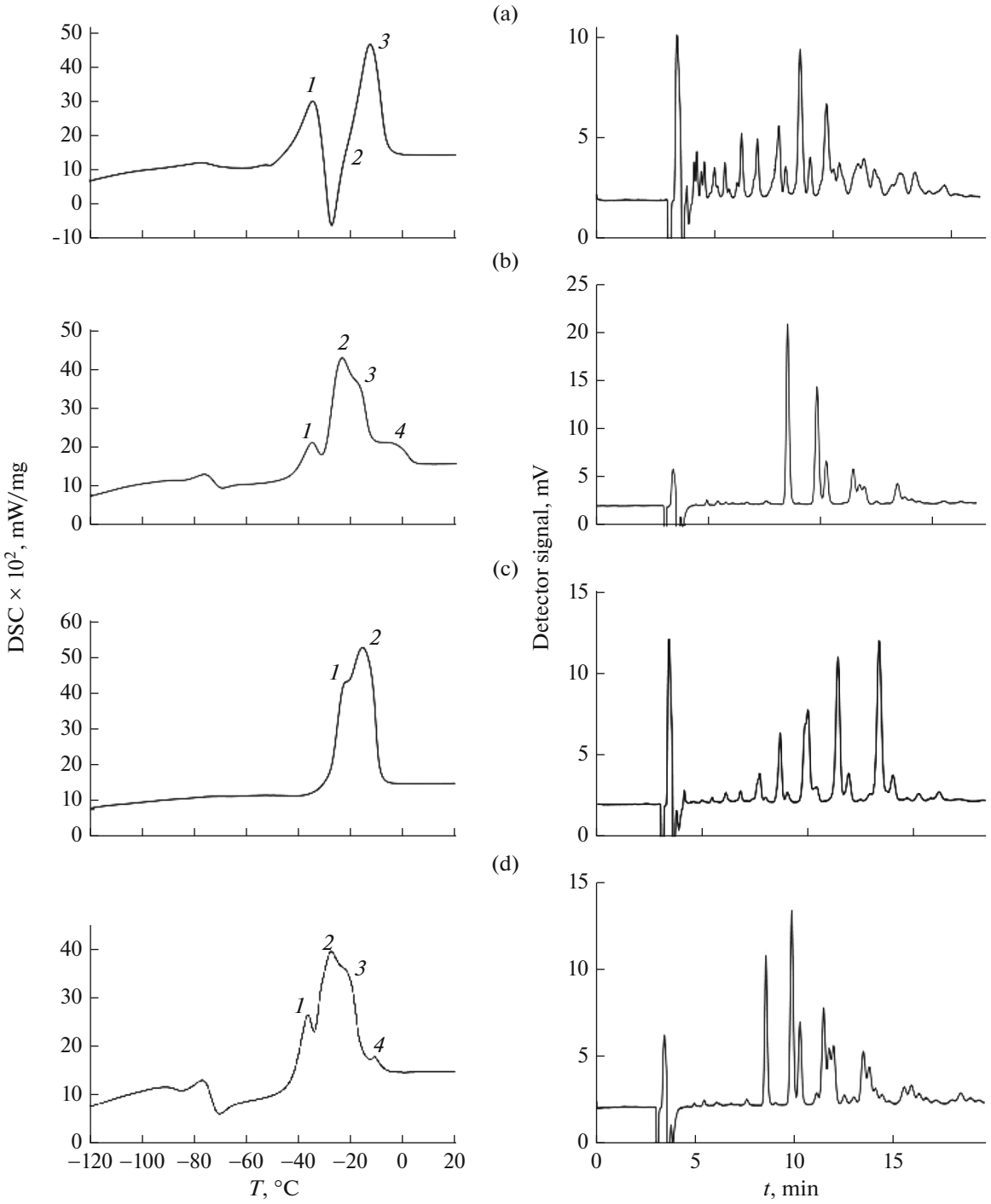

Fig. 1. DSC melting thermograms and HPLC chromatograms of (a) camelina, (b) milk thistle, (c) rapeseed, and (d) sunflower oils.

most intense peak or, rather, the superposition of unseparated peaks, in the DSC thermograms, which has an asymmetric shape, was located in the range from −30 to −20°C, and the end of melting occurred in the range from −10 to + 5°C. Because of the poor separation of the superposition of the peaks of the vegetable oil endothermic effects, they were programmatically divided into groups of two to four peaks, and the relative areas S_i(%) were calculated. Figure 3 shows examples of programmed peak separation in DSC melting thermograms.

The found values of thermophysical characteristics of the investigated samples of vegetable oils (T_i and S_i) are presented in Table 1. The results of the identifica-

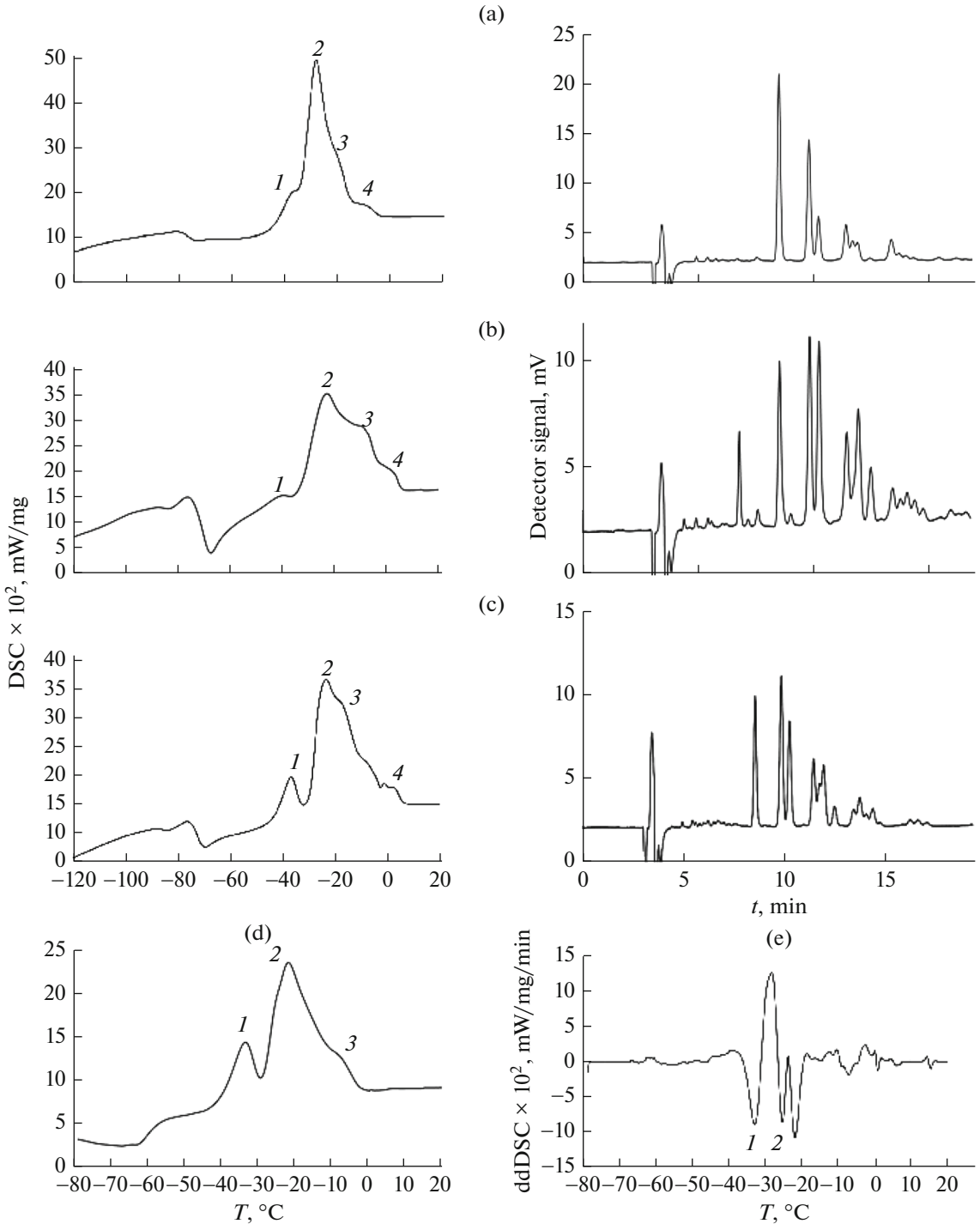

Fig. 2. DSC melting thermograms and HPLC chromatograms of (a) flax, (b) amaranth, (c) pumpkin seed, and (d) corn oils; (e) second derivative of the DSC melting curve of corn oil.

tion of triacylglycerols are given in Table 2, and the detected fatty acids are listed in Table 3. Tables 2 and 3 contain our data obtained for specific samples of vegetable oils, the thermophysical properties of which were determined in this work. This is an essential note, because the thermophysical properties of oils are sensitive to the chemical composition of fats, which can vary markedly even for vegetable oil of the same plant species, depending on the genotype and phenotype [8, 9]. The chromatographic data are in the typical ranges of fatty acid concentration, standardized or determined earlier for the considered species of vegetable

oil [8, 9]; there are no data on fatty acids the concentration of which is <1%. A detailed interpretation of the DSC curves is complicated by the presence of polymorphism, mutual solubility of various triacylglycerol fractions, and the eutectics formed. However, correlation analysis performed for the sample of vegetable oils showed that there are significant correlations between the chemical composition of vegetable oil and endothermic effects. Tan and Cheman [1] demonstrated that liquid food vegetable oil containing 61–81% of triunsaturated triacylglycerols (UUU) and 35–17% of diunsaturated and monounsaturated triacylglycerols (UUS), such as olive oil, canola oil, etc. have a pronounced endothermic peak in the range from −42 to + 6°C in the DSC melting curves, on the left and right shoulders of which at least two more peaks can be distinguished. We also observe the main thermal effects in the vegetable oils under study in the indicated temperature range; in our samples, the sum of triacylglycerols (UUU) is from 84 to 44% and triacylglycerols (UUS) is 16–40%. In addition to these triacylglycerols, vegetable oils contain several percent of monounsaturated and disaturated triacylglycerols (USS) and an insignificant or trace amount of trisaturated triacylglycerols (SSS), which have higher melting points than triacylglycerols (UUU) and (UUS) (Table 2).

The individual character of a combination of the maximum temperatures (T_i) and areas (S_i) in the DSC curves of vegetable oils ensures the use of these thermophysical parameters for qualitative identification.

Triglyceride composition of vegetable oils is ranked in Table 2 according to the value of the equivalent carbon number NEC, which, as a first approximation, predicts the range of melting and chromatographic behavior of triacylglycerols [18]. The lower the NEC value, the lower the melting point of triacylglycerol, and the shorter its retention time in reversed-phase HPLC. Table 4 shows the found significant linear correlations (1)–(32) between the thermophysical properties of vegetable oils and the chemical composition (pair correlation coefficients $R > 0.50$). The observed particular trends (1)–(32) cannot be considered representative for large databases on the properties of vegetable oils; however, the trends found made it possible to interpret the thermophysical properties of vegetable oils and help to verify their authenticity.

Maximum at T_1. The maximum of the peak at T_1 varies slightly from −39 to −33°C; its relative area S_1 also changes slightly depending on the type of vegetable oil in the range of 12–16% (Table 1), asymptotically decreasing with an increase in the sum of triacylglycerols (UUS) and symbatically increasing with an increase in the share of L_3 in oil (Table 4). Thus, this peak can be attributed primarily to the triacylglycerol fraction (UUU) with the lowest melting points and NEC ≤ 41.4.

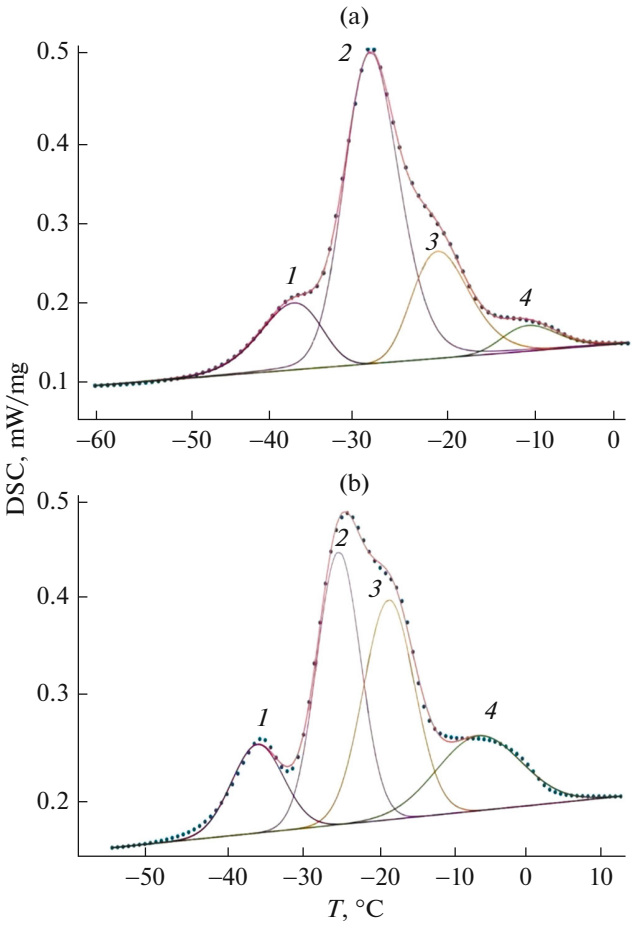

Fig. 3. DSC melting thermograms with computerized peak separation for (a) flaxseed oil and (b) milk thistle oil.

Maximum at T_2. The second peak with a maximum at T_2 from −28.5 to −21.5°C has the largest area S_2, which varies from 32 to 72%. It is formed by a mixture of triacylglycerol fractions (UUU) and (UUS). The S_2 area increases with an increase in the fraction of linoleic acid and triacylglycerols in the vegetable oil, in which the residue of this acid (L_3, L_2O, LOP) is present, while an increase in the LOP fraction leads to a shift of the peak maximum to the region of higher temperatures. An increase in the total amount of triacylglycerols (UUS) in general decreases the S_2 area due to the inclusion of stearic and other saturated fatty acids in the triacylglycerol composition. The NEC of these triacylglycerols is generally in the range of 41.6 to 45.6.

The **maximum at T_3** shifts from −19 to −6°C. Its area (S_3) for liquid vegetable oil can vary depending on the type of oil in the widest range, from 6 to 77.5%. It is formed by a mixture containing mainly triacylglycerols (UUS), but with an admixture of triacylglycerols (UUU) and (USS). An increase in the proportion of oleic, palmitic, and stearic acids and the amount of triacylglycerols (USS) shifts the peak maximum to

Table 1. Temperatures of maxima (T_i, °C) and areas of characteristic peaks (S_i, %) of the DSC melting curves of vegetable oils

Vegetable oil	T_1	T_2	T_3	T_4	S_1	S_2	S_3	S_4
Amaranth	−39.3*	−22.6	−6.3*	4.2*	12.1	55.0	29.4	3.5
Flax	−38.2*	−28.5	−19.1*	−7.4	14.1	60.2	21.0	4.8
Sunflower	−36.4	−27.4	−18.8*	−10.7	15.3	71.8	8.4	4.5
Rape	–	−23.0*	−15.4	–	–	22.5	77.5	–
Camelina	−34.6	−23.8*	−12.8	–	14.1	21.3	64.6	–
Pumpkin seed	−36.6	−23.1	−16.3*	3.8*	16.1	50.4	5.8	16.1
Corn	−33.2	−21.5	−7.0*	–	12.9	32.1	55.0	–
Milk thistle (VSUET), sample 1	−35.7	−24.9	−18.2*	−6.2*	13.5	35.2	33	18.4
Milk thistle (Russkaya Oliva), sample 2	−34.8	−21.7	−15.1*	−5.8*	11.9	40.5	28.5	21.0
Milk thistle (retail chain), sample 3	−38.3	−26.6	−20*	−3.7*	14.3	12.1	49.6	23.9
Milk thistle, sample 3 + sunflower (9 : 1)	−40.3	−21.4	−10.5*	0.4*	19.3	28.5	7.8	14.3
Milk thistle, sample 3 + corn (9 : 1)	−35.5	−28.1	−22.5*	−13.3*	7.8	3.6	64.4	24.2

* Temperature values are determined based on the second time derivative of DSC.

higher temperatures. The S_3 area grows symbatically with an increase in the proportion of oleic and palmitic acids (O_3, LP_2) in triacylglycerols and decreases asymbatically with an increase in the proportion of linoleic and linolenic acids. This melting region can be attributed to the triacylglycerol fraction, which is characterized by NEC values from 45.8 to 48.8.

Maximum at T_4. This peak is primarily formed by the triacylglycerol fractions (USS) and (SSS). If this peak is in the region of positive temperatures, then triacylglycerols (SSS), containing palmitic and stearic acids, prevail in it. The S_4 area grows symbatically with the sum of triacylglycerols (USS) and (SSS). The triacylglycerols forming this peak are characterized by NEC values from 48 to 52.

The real samples were considered using the example of milk thistle oil. An oil sample obtained in the laboratory (Voronezh State University of Engineering Technology) was used as a reference sample. Another sample obtained under our supervision was provided by Russkaya Oliva. The third sample was purchased in the retail network. The third sample was used to prepare two mixtures with 10% sunflower and corn oils. The results of determining the thermophysical characteristics are given in Table 1. To visualize and analyze the data, we plotted control charts (CC) with normalized parameters T_i and S_i in the form of diagrams, the normalized values of T_i and S_i are placed along the ordinate axis (Fig. 4),

$$X_n = (X - X_{min})/(X_{max} - X_{min}),$$

and the abscissa axis is the category axis, on which the monitored parameters are indicated. The natural composition of vegetable oil varies within a wide range, depending on genotypic and phenotypic factors [8, 9], which somewhat complicates the control of the authenticity of the product. Taking into account the typical scatter in the chemical composition of vegetable oils, which affects the shape of the DSC curves, we included a corridor of admissible values in the control charts, which was ±15% of the T_i and S_i values typical for the reference sample. In normalized form, the minimum acceptable value is 0, the maximum is 1, and a perfect match is 0.5. Only sample *2* falls into the corridor of permissible values from 0 to 1 (Fig. 4). In sample *3*, the values of T_4 and S_3 are noticeably below the corridor, and the value of S_2 is overestimated. The addition of sunflower oil to this sample leads to an underestimation of the T_3 value, leveling of S_2 to the norm, and a sharp decrease in T_4 with an overestimated S_1 value and an underestimated S_3 value. The addition of corn oil leads to an additional drop in the normalized values of T_4 and S_3 and an overestimation of the S_2 value relative to the permissible level. In the most general form, such changes in the DSC curves for sample *3* and its mixtures with sunflower and corn oils can be interpreted as an overestimated proportion of triacylglycerols (UUU) in them, compared to natural milk thistle oil, in particular, L_3, and an underestimated proportion of triacylglycerols (SSS). A comparison of the data obtained suggests that a sample of milk thistle oil purchased from a retail network contains an additive of about 5% of corn oil.

CONCLUSIONS

Thus, modern developments in the field of thermal analysis of vegetable oils by DSC demonstrate its wide capabilities in the identification and quality control of vegetable oils. The DSC method makes it possible to characterize the thermophysical properties of oil samples, which are essential in the technology of their production and use in the pharmaceutical, food, and technical industries. The studies confirm the fact that the fatty phase of each vegetable oil has its unique ratio

Table 2. Triglyceride composition of vegetable oil samples

Triglyceride	NEC*	Camelina	Flax	Rape	Sunflower	Amaranth	Pumpkin seed	Milk thistle	Corn
L''_3	35.4	4.6	22.6	1.2	0	0	0	0	0
L''_2L	37.4	4.5	11.4	1	0	0	0	0	0
$L''L_2$	39.4	3.1	3.7	3.8	0	0	0	0	3.7
L''_2O	39.4	4.9	13.9	7.7	0	0	0	0	1.9
L''_2P	39.6	3.0	7.0	0.6	0	0	0	0	0
L_3	41.4	3.3	1.5	1.4	33.0	12.0	14.2	15.6	30.7
L''LO	41.4	12.7	5.4	6.5	0	0	0	0	5.7
L''_2E	41.4	9.8	0	0	0	0	0	0	0
L''LP+L''_2S	41.6	4.1	8.5	1.2	0	0	0	0	0
L_2O	43.4	2.5	2	9.1	26	16.4	19.6	20.5	15
$L''O_2$	43.4	3.2	6.9	8.9	0	0	0	0	0
L''LE	43.4	4.9	0	0	0	0	0	0	0
L'LS + L_2P	43.6	4.2	0	1.2	0	0	0	0	0
L''OP	43.6	1.8	3.6	2	0	0	0	0	0
$L''P_2$	43.8	2.7	0	0	0	0	0	0	0
L_2P	43.6	0	0	0	9.8	15.8	14.3	8.4	0
LO_2	45.4	6.2	2.5	18.7	9.3	10.2	10.7	11.6	12
L_2E	45.4	3.9	0	0	0	0	0	1.6	0
L_2S	45.6	3.9	2.7	0	4.8	3.7	5.2	7.1	5.7
LOP	45.6	2.3	0	3.7	4.3	11.4	10.3	6.7	5.9
LOP + L''OS	45.6	0	4	0	0	0	0	0	0
LP_2	45.8	2.3	0.9	0	0.8	6.4	3.8	1.8	2
L''OE	45.4	2	0	0	0	0	0	0	0
L''OA	47.6	0	0	1.6	0	0	0	0	0
LPS	45.8	0	0	0	0	3.2	4.0	0	0
O_3	47.4	5.2	2.4	24.2	6.5	5	3.9	8.1	7.8
LOS	47.4	0	0	0	1.9	3.1	5.3	5.8	2.5
O_2P	47.6	1.5	1	3.9	2.0	4.0	2.6	1.7	2.6
P_3	48.0	0	0	0	0.9	1.3	1.3	1.6	0.3
OP2	48.8	0	0	0	0	2.1	1.2	0	2.8
LS_2	49.8	0	0	0	0	2.0	0	0	0
OPS	49.8	0	0	0	0	2.3	1.2	0.9	0.5
O_2E	49.4	0	0	1.5	0	0	0	1.7	0
O_2S	50.4	0	0	1.8	0.7	1.1	2.4	2.0	0.9
O_2E''	51.4	3.4	0	0	0	0	0	0	0
LOB	51.6	0	0	0	0	0	0	2.2	0
S_2O	51.8	0	0	0	0	0	0	0.9	0
LPB	51.8	0	0	0	0	0	0	0.6	0
PS_2	52.0	0	0	0	0	0	0	1.2	0
ΣTAG (UUU)		72.2	72.3	84.0	74.8	43.6	48.4	59.1	76.8
ΣTAG (UUS)		20.8	26.8	16	23.5	39.1	40.1	33.9	17.6
ΣTAG (USS)		7	0.9	0	0.8	16	10.2	4.1	5.3
ΣTAG (SSS)		0	0	0	0.9	1.3	1.3	2.9	0.3

* NEC = NC – 2.0ND – 0.2NAl, where NC is the total number of carbon atoms in fatty acid residues, ND is the total number of double bonds in the triacylglycerol structure, and NAl is the amount of unsaturated fatty acids in the molecule [18].

Table 3. Composition of fatty acids of the studied samples of vegetable oils (W, %)

Fatty acid	Amaranth	Flax	Sunflower	Corn	Rape	Milk thistle	Camelina	Pumpkin seed
Palmitic (C16:0)	17.9	8.3	6.5	12.3	4.4	9.7	9.0	13.3
Stearic (C18:0)	5.3	1.4	2.8	2.0	1.4	6.1	2.8	6.4
Oleic (C18:1)	25.2	18.7	23.3	27.8	58.6	28.3	20	27.7
Linoleic (C18:2)	49.1	16.9	66.4	54.1	20.1	50.4	21.6	52.6
α-Linolenic (C18:3)	1.3	54.6	–	1.9	11.6	–	32.3	–
Arachidic (C20:0)	–	–	–	–	–	1.7	1.3	–
Eicosenoic (C20:1)	–	–	–	–	–	1.0	11.1	–
Behenic (C22:0)	–	–	–	–	–	1.6	–	–

Table 4. Significant correlations between the thermophysical properties of vegetable oils and the concentration of fractions of triacylglycerols and individual fatty acids: $T_i = ax + b$ and $S_i = ax + b$ ($n = 8$, $P = 0.95$)

x/y	Trend	R	x/y	Trend	R
ΣTAG (UUU)/ΣTAG (UUS)	$y = -0.6x + 69.2$ (1)	–0.96	O_3/S_3	$y = 2.6x + 13.6$ (17)	0.71
ΣTAG (UUU)/ΣTAG (USS)	$y = -0.3x + 27.0$ (2)	–0.85	$L3 + L_2O/S_2$	$y = 0.6x + 31.2$ (18)	0.60
ΣTAG (UUS)/ΣTAG (USS)	$y = 0.4x - 5.3$ (3)	0.69	$L3 + L2O/S_3$	$y = -0.9x + 56.1$ (19)	–0.64
ΣTAG (UUS)/S_1	$y = -0.4x + 29.3$ (4)	–0.57	$LP_2 + O_3/S_3$	$y = 2.8x + 5.4$ (20)	0.69
ΣTAG (UUS)/S_2	$y = -2.0x + 89.9$ (5)	–0.66	P/T_3	$y = 0.9x - 26.6$ (21)	0.92
ΣTAG (UUU)/S_3	$y = 1.0x - 27.9$ (6)	0.53	P/T_4	$y = 1.0x - 18.4$ (22)	0.77
ΣTAG (USS)/T_3	$y = 0.7x - 17.4$ (7)	0.73	S/T_3	$y = 1.5x - 22.7$ (23)	0.69
ΣTAG (USS)/T_4	$y = 0.8x - 6.8$ (8)	0.76	S/T_4	$y = 1.7x - 14.6$ (24)	0.67
ΣTAG (USS,SSS)/T_3	$y = 0.5x - 17.1$ (9)	0.64	S/S_4	$y = 1.6x + 3.7$ (25)	0.53
ΣTAG (USS,SSS)/T_4	$y = 0.8x - 8.1$ (10)	0.83	O/T_3	$y = 0.7x - 32.9$ (26)	0.57
ΣTAG (SSS)/T_4	$y = 4.5x - 7.5$ (11)	0.69	O/S_3	$y = 1.2x - 0.7$ (27)	0.60
ΣTAG (SSS)/S_4	$y = 3.8x + 5.8$ (12)	0.58	O/S_4	$y = 1.4x - 24.2$ (28)	0.77
L_3/S_1	$y = 0.3x + 11.6$ (13)	0.58	L/S_2	$y = 0.6x + 22.9$ (29)	0.59
L_3/S_2	$y = 0.9x + 33.6$ (14)	0.63	L/S_3	$y = -1.0x + 72.1$ (30)	–0.59
L_3/S_3	$y = -1.6x + 52.5$ (15)	–0.65	L''/T_2	$y = -0.2x - 22.8$ (31)	–0.73
*LOP/T_2	$y = 0.5x - 26.6$ (16)	0.69	L''/T_3	$y = -0.2x - 8.2$ (32)	–0.90

* $n = 3$.

of thermophysical characteristics, which is interconnected with a certain fractional composition of triacylglycerols. The method for identifying vegetable oils by DSC melting thermograms is distinguished by the simplicity of sample preparation and good reproducibility, offers additional information on the origin of raw materials to those obtained using chromatographic methods, and can be an independent method for identifying and controlling the quality of the fat phase.

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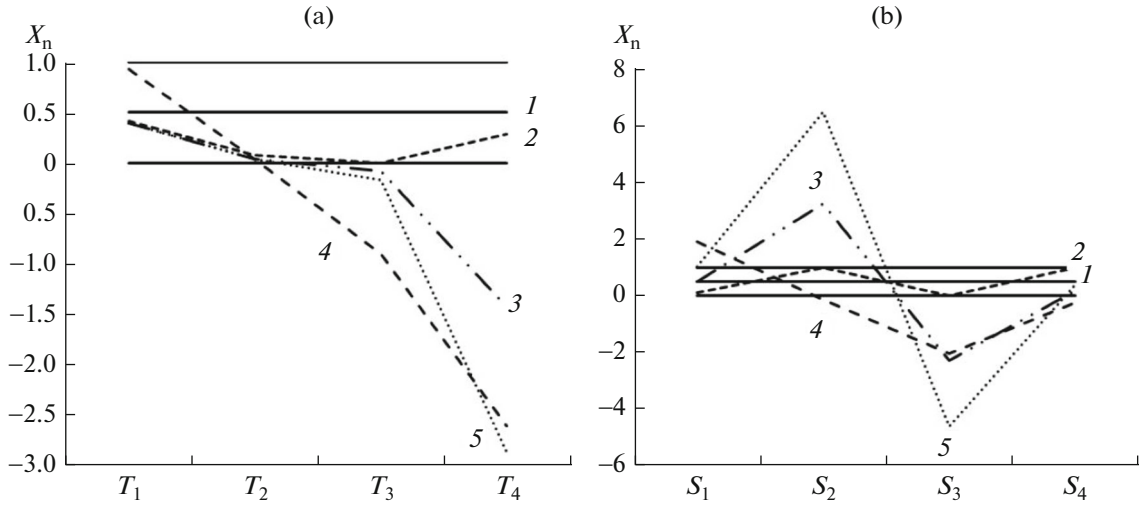

Fig. 4. Control charts for milk thistle oil: (*1*) normalized values of (a) T_i and (b) S_i, reference sample; (*2*) sample from Russkaya Oliva; (3) sample from the retail chain; (*4*) sample 3 with sunflower oil (9 : 1); and (*5*) sample 3 with corn oil (9 : 1).

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