=== **ARTICLES** ===

Differential Scanning Calorimetry as a Method for Controlling the Authenticity of Wild Milk Thistle Oil

O. B. Rudakov[a], *, I. A. Saranov[b], **, Sh. A. Balaeva[c], A. Sh. Ramazanov[c], and Ya. O. Rudakov[d]

[a] Voronezh State Technical University, Voronezh, 394006 Russia
[b] Voronezh State University of Engineering Technology, Voronezh, 394036 Russia
[c] Dagestan State University, Makhachkala, Dagestan, 367000 Russia
[d] Voronezh State University, Voronezh, 394018 Russia
*e-mail: robi57@mail.ru
**e-mail: mr.saranov@mail.ru

Abstract—Thermophysical properties of wild milk thistle (*Silybum marianum*) oil from different regions of Dagestan were studied by differential scanning calorimetry (DSC). Characteristic heat effects were determined for a series of oil samples, namely, temperatures of the maxima of endothermic peaks on DSC thermograms in five ranges: T_1 from -37.6 to -31.1°C, T_2 from -27.6 to -23.8°C, T_3 from -19.9 to -14.4°C, T_4 from -13.5 to -4.2°C, and T_5 from -4.7 to -1.2°C and the areas of these peaks. The maximum at T_1 was attributed to the fraction of triunsaturated triacylglycerols (UUU; U means unsaturated), which have the lowest T_{mp}. The most pronounced maxima at T_2 and T_3 were formed by a mixture of triunsaturated (UUU) and diunsaturated, monosaturated triacylglycerol (UUS, S means saturated) fractions. The maxima at T_4 and T_5 were formed upon the melting of fractions of monounsaturated and trisaturated triacylglycerols (USS and SSS). Phenotypic factors, that is, a set of conditions for the growth of raw materials (altitude, humus content in the soil, amount of precipitation, and a number of sunny days throughout the year) affect the positions of the maxima of endothermic peaks and their areas. It was demonstrated that DSC can help to control the authenticity of milk thistle oil and its origin.

Milk thistle (*Silybum marianum* (L.) Gaertn) is a raw material source of valuable biologically active substances such as flavonolignans, flavonoids, fatty oil, proteins, carbohydrates, and micro- and macroelements [1–5]. Medicines based on milk thistle oil are used to treat wounds, pressure ulcers, and inflammatory processes [3]. Milk thistle oil is a valuable biologically active dietary supplement. The most valuable are dietary supplements isolated from wild-growing raw materials. The quality of such dietary supplements must be controlled since they are often falsified or diluted with inexpensive oils, which are an order of magnitude cheaper than genuine dietary supplements.

Differential scanning calorimetry (DSC) is one of the effective methods for controlling the quality and authenticity of vegetable oils and animal fats [6–14]. In [6, 7], the thermophysical properties of seven typical vegetable oils, liquid at room temperature, were studied by DSC. The endothermic peaks and their areas in the DSC melting thermograms were compared with the fatty acid and triglyceride compositions determined by chromatographic methods, and significant correlations between the thermal effects and the chemical composition of oils were found. To interpret the crystallization and melting curves of vegetable oils and edible fats (17 varieties), chromatographic data on the fatty acid and triglyceride composition of the fats under consideration were also used as confirmatory methods [8]. Crystallization curves are commonly used to study oils and fats by DSC, although they are less reproducible than melting curves [7, 9, 11]. The so-called "fast" DSC with a 10–20 K/min temperature gradient is used [10, 12]. At such heating rates, the peaks characterizing thermal effects are separated worse, partially or entirely merge, which worsen the information content of thermograms, while a decrease in the heating rate increases the duration of thermal analysis. In this regard, a heating or cooling rate of 5 K/min is most often recommended for the DSC of vegetable oils [7].

The high sensitivity of DSC to the composition of the fat phase is advantageous for the quality control and identification of the latter. The method does not require much time, reagents, solvents, or additional

Table 1. Characteristics of the growing conditions of wild milk thistle in Dagestan

Characteristics	District (settlement)				
	Kaitag (Madzhalis)	Magaramkent (Kuisun)	Suleyman-Stalsky (Gerekhanovo)	Levashinsky (Kutisha)	Kulinsky (Khosrekh)
Altitude, m above the sea level (H)	408	532	480	1593	2150
Soil type	Alluvial meadow	Brown forest	Mountain meadow	Mountain chestnut	Mountain meadow
Humus content in soil (G)	3.6–6.0	3.6–6.0	4–5	5–8	5–8
Average annual temperature in 2019, °C	11.5	14.6	15.3	13.0	11.6
Temperature amplitude in 2019, °C	36	46	45	41	37
Total precipitation in 2019, mm (D)	460	258	278	448	671
Number of sunny days in 2019 (Q)	157	101	107	116	113

laboratory equipment. The characteristic profile of DSC thermograms can be used to check the authenticity of the oil sample and the geographical origin and variety of the oil plant from which it was obtained [13]. In [7], we proposed an algorithm for identifying vegetable oils using control charts that visualize digital information containing several parameters of thermograms.

The aim of this work was to study the thermophysical properties of wild milk thistle oil from various regions of Dagestan, to determine the relationship of characteristic thermal effects observed in DSC melting thermograms with the origin of plant raw materials, and to test the use of the obtained data to verify the authenticity of milk thistle oil.

EXPERIMENTAL

Samples of milk thistle oil were obtained under laboratory conditions at the Dagestan State University by supercritical carbon dioxide fluid extraction [4]. Before obtaining oil, the fruits were dried in a drying cabinet at 50°C and ground in an LM-201 laboratory mill to a fraction of 0.1–1.0 mm; the yield of the fraction was 99.0 ± 0.3%. Oil was obtained using an SFE 1000M1-2-FMC 50 laboratory extraction system model (Waters, United States). A sample of crushed milk thistle fruits (40 g) was placed in a 200-mL autoclave and treated with carbon dioxide at a pressure of 400 bar at 40°C and a flow rate of 50 g/min for 60 min. Table 1 presents information on oil samples from milk thistle raw materials obtained in different regions of Dagestan.

The iodine number (NI) of the samples of milk thistle oil was determined by the standard procedure [15]. Thermal analysis was performed using an STA 449 F3 Jupiter® device for synchronous thermal analysis (NETZSCH, Germany). Weighed portions of oils of 15–22 mg were collected for analysis. An aluminum crucible with a weighed portion, covered with an aluminum lid, was placed into the instrument and weighed. Then, the temperature of the sample was increased to 60°C at a rate of 5 K/min to melt the sample entirely and remove the "thermal history." Thermophysical properties were measured in the temperature range from −150 to +20°C; the heating rate was 5 K/min. The system was cooled with liquid nitrogen at a cooling rate of 1 K/min to exclude recrystallization (cold crystallization). Measurements were carried out under helium; 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. To increase the information content of the DSC thermograms, we used the software separation of the superposition of the peaks of thermal effects nonoverlapping each other in the NETZSCH Peak Separation program according to the Gauss algorithm. The fatty acid residues in triacylglycerols (TAG) are denoted as follows (Table 2): B, behenic; E, eicosenic; L, linoleic; O, oleic; P, palmitic; S, stearic. For example, L_2O denotes a triacylglycerol formed by two linoleic and one oleic acid radicals.

RESULTS AND DISCUSSION

Triacylglycerols of milk thistle oil contain in total from 75 to 90% of unsaturated fatty acids (mainly linoleic and oleic), 5–20% of saturated fatty acids (palmitic, stearic, arachinic, and behenic), and a certain amount (up to 5% in total) of minor unsaturated and saturated fatty acids (Table 2) [1–7].

According to the data of [1−7] and the primary sources cited in them, we carried out a correlation analysis and found significant correlations between the ratios of some fatty acids caused by the effect of genotypic and phenotypic factors. Thus, with an increase in the proportion of palmitic acid (C16:0) in the milk thistle oil, the proportion of linoleic acid (C18:2) decreases asymmetrically: $W(\text{C18:2}) = 104 - 7W(\text{C16:0})$, $R = 0.59$, $n = 15$. In this case, the proportion of stearic acid increases symbatically: $W(\text{C18:0}) = 1.7W(\text{C16:0}) - 9.0$, $R = 0.62$, $n = 15$. Similarly, the proportion of arachidic acid increases symbatically with an increase in the proportion of stearic acid: $W(\text{C20:0}) = 0.7W(\text{C18:0}) - 1.4$, $R = 0.82$. In other words, with a symbate increase in the proportion of saturated fatty acids in milk thistle oil, the concentration of the main unsaturated acid, linoleic acid (C18:2), decreases. There are significant correlations between the position of the endothermic maxima in the DSC melting curves, their area, and the concentration of main fatty acids in vegetable oils [6]. Thus, the identified trends should naturally affect the thermophysical properties of the fat phase of milk thistle grown under different conditions, since the phase transitions of TAGs with different ratios of saturated and unsaturated fatty acids appear at different temperatures [6, 7].

Fatty acids characteristic of milk thistle oil form approximately 20 different TAGs, without considering the position of fatty acid residues in the structure of the molecule. In chemical technology, they are subdivided into four fractions according to the degree of unsaturation: (1) triunsaturated TAGs that contain three residues of unsaturated fatty acids (UUU), (2) diunsaturated, monounsaturated TAGs (UUS), (3) monounsaturated, disaturated TAGs (USS), and (4) trisaturated TAGs (SSS). For example, the fruits of milk thistle cultivated in the Lipetsk region contain approximately 60% of TAGs of the UUU type and only 3% of TAGs of the SSS type in oil (Table 3) [7].

Triacylglycerols formed predominantly by unsaturated fatty acids (UUU, UUS) have melting points below zero degrees Celsius, while TAGS of the SSS type have melting points at positive temperatures [7]. Because of the mutual solubility of TAGs due to the presence of eutectics and various phase transitions, the DSC curves of melting of fats (TAG mixtures) have several maxima and extrema that are unique for various fats. For the melting curves of milk thistle oil, five characteristic endothermic maxima can be distinguished (Fig. 1), which reflect the integral properties of the fractions, in which TAGs have similar thermophysical properties, rather than individual TAGs. To determine T_i of weakly expressed thermal effects, the so-called "shoulders" on the main peaks, the second derivatives of the DSC curves were used (Fig. 1h).

Table 2. Composition of fatty acids in milk thistle oil [1−7]

Fatty acid	W, %
Palmitic (C16:0)	8−11
Stearic (C18:0)	3−11
Oleic (C18:1)	21−33
Linoleic (C18:2)	35−57
Linolenic (C18:3)	0−6
Arachinic (C20:0)	0−7
Eicosenoic (C20:1)	0−2
Behenic (C22:0)	0−4

Table 3. Composition of triacylglycerols in a sample of milk thistle cultivated in the Lipetsk region, Russia [7]

TAG fraction	Fraction concentration, %	TAG	TAG concentration, %
UUU	59.1	L_3	15.6
		L_2O	20.5
		O_3	8.1
		LO_2	11.6
		L_2E	1.6
		O_2E	1.7
UUS	33.9	L_2P	8.4
		L_2S	7.1
		LOP	6.7
		LOS	5.8
		O_2P	1.7
		O_2S	2.0
		LOB	2.2
USS	4.2	S_2O	0.9
		LPB	0.6
		LP_2	1.8
		OPS	0.9
SSS	2.8	P_3	1.6
		PS_2	1.2

Table 4 shows the values of thermophysical characteristics of the studied samples—T_i and areas S_i, determined by computer separation of overlapping peaks.

Liquid vegetable oils containing >60% of UUU and >17% of UUS, for example, olive oil, have the most pronounced endothermic peak in the DSC melting curves in the range from −42 to +6°C, on the shoulders of which at least two or three more peaks appear on the left and right [6−8]. The main thermal effects in the studied samples of milk thistle oil were observed in a narrower temperature range.
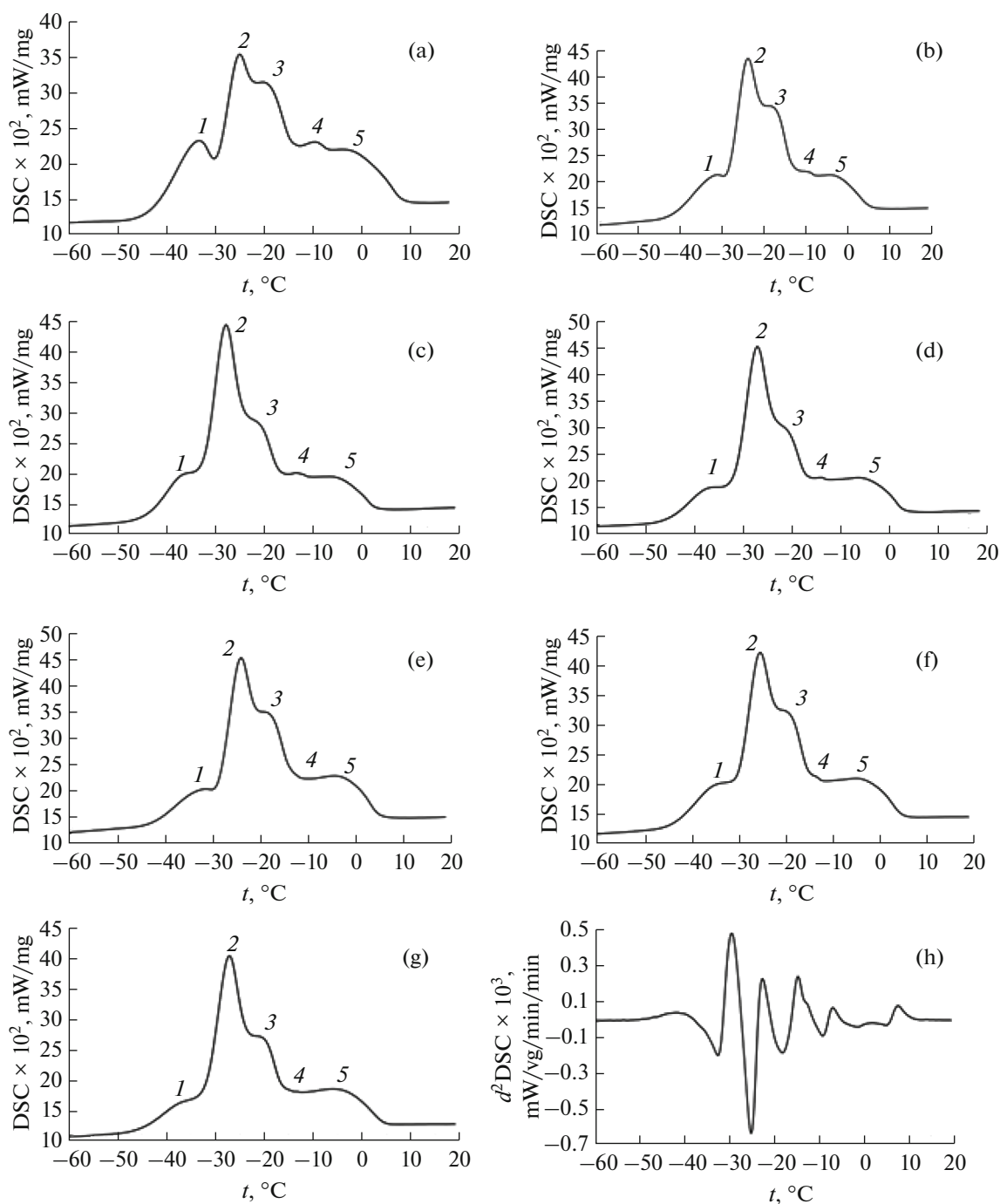
Fig. 1. DSC melting profiles of milk thistle oils: (a) Kulinsky district; (b) Levashinsky district; (c) Suleyman-Stalsky district; (d) Kaitag district; (e) Magaramet district; (f) a mixture of oils from all regions of Dagestan; (g) Biokor (Penza, Russia); (h) the DSC second derivative, Kulinsky district; (*1–5*) endothermic maxima.

Maximum at T_1. The maximum of the peak at T_1 varies slightly from −37.6 to −31.1°C (Table 4). This peak can be attributed, first of all, to the TAG fraction of the UUU type with the lowest melting points; in particular, it is formed due to the presence of L_3 [7].

Maximum at T_2. The second peak with a maximum at T_2 from −27.6 to −23.8°C has the largest area. It is formed by a mixture of TAG fractions of the UUU and UUS types, which contain residues of linoleic acid (L_3, L_2O, LOP), while an increase in the proportion of TAGs of the LOP and LOS type, as shown in [7], leads to a shift of the peak maximum to the higher temperature region due to the inclusion of palmitic, stearic, and other saturated fatty acids in the TAG composition.

Table 4. Maxima of endothermic peaks T_i, their areas S_i, and iodine number NI for milk thistle oil samples

Origin of milk thistle oil	T_1	T_2	T_3	T_4	T_5	S_1	S_2	S_3	S_4	S_5	NI
Kulinsky district, Dagestan	−32.4	−25.0	−18.3	−8.9	−1.2	23.3	15.8	29.7	15.6	15.6	112
Levashinsky district, Dagestan	−31.5	−24.1	−16.4	−9.3	−3.0	20.6	26	33.0	5.3	15.1	110
Suleyman-Stalsky district, Dagestan	−37.0	−27.6	−19.9	−13.1	−4.4	18.6	34.3	23.8	12.2	11.1	116
Kaitag district, Dagestan	−37.2	−26.7	−19.6	−13.5	−4.7	16.7	36.3	16.1	21.8	9.1	113
Magaramet district, Dagestan	−31.1	−23.8	−16.6	−12.1	−2.6	15.3	29.4	26.3	20.5	8.5	108
Mixture of samples from all regions of Dagestan	−35.3	−25.2	−18.2	−13.1	−3.6	19.4	30.2	23.1	19.1	8.1	111
Biokor, Penza	−37.6	−27.1	−19.3	−13.2	−3.6	18.2	33.9	21.4	18.2	8.3	109

The **maximum at T_3** shifts from −19.9 to −14.4°C; it is formed by a mixture containing mainly TAGs of UUS with an admixture of UUU and USS. An increase in the proportion of oleic, palmitic, and stearic acids and the total USS triacylglycerols shifts the peak maximum to higher temperatures [7].

Maximum at T_4. This indistinct peak is most likely formed by TAG fractions of the USS type.

The **maximum at T_5** from −4.7 to −1.2°C is due to the presence of a mixture of USS and SSS TAGs. This peak is located in the region of temperatures below zero, which means that due to the small amount of SSS TAGs containing palmitic, stearic, arachidic, and behenic acids, there is no peak characterizing the "pure" SSS fraction in the thermograms of the studied milk thistle oils.

Table 5 summarizes the results of a correlation analysis of oil samples obtained from wild milk thistle from various regions of Dagestan, differing in climatic conditions (Table 1) [16].

A study of the wild milk thistle of one region made it possible to exclude genotypic differences and evaluate how phenotypic factors affect the DSC curves. The samples of milk thistle oil were characterized not only by significant (the absolute value of the pair correlation coefficient of $|R| > 0.50$) but also by close correlations ($|R| \geq 0.80$) both between the temperatures of the maxima of the T_i peaks or the S_i values and between them and individual climatic conditions, that is, altitude above sea level (H), the average humus content in the soil (G), the number of sunny days (Q), and precipitation (D) per year (Table 5). For example, with an increase in altitude, all T_i values increased, which indicated a decrease in the degree of unsaturation of TAGs in this raw material. This was also indicated by the asymptotic correlations between T_i and the iodine number NI. The more significant the observed shift of
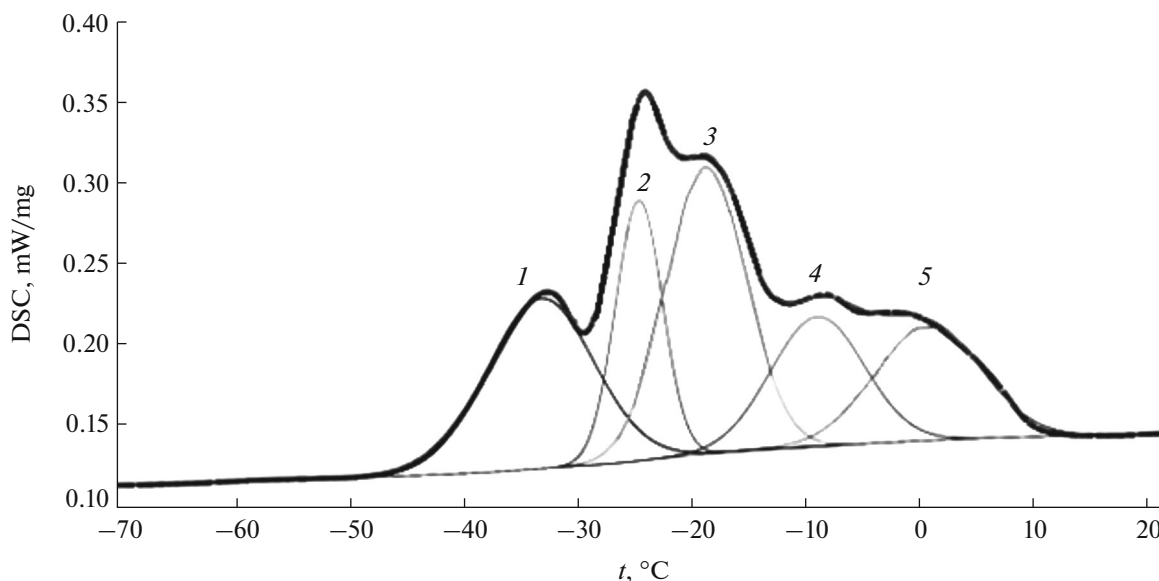

Fig. 2. DSC melting profile of milk thistle (Kulinsky district) with software-separated peaks; (*1−5*) endothermic maxima.

Table 5. Significant linear correlations between the temperature maxima and areas of endothermic peaks (T_i, S_i) in the DSC melting curves of wild milk thistle oil under varying growing conditions, Dagestan

X/Y	$Y = aX + b$	R	X/Y	$Y = aX + b$	R
T_1/T_2	$Y = 0.5X - 8.4$ (1)	0.93	T_5/H	$Y = 450X + 2580$ (24)	0.74
T_1/T_3	$Y = 0.5X - 1.6$ (2)	0.92	T_5/NI	$Y = 108.1 - 1.1X$ (25)	−0.51
T_1/T_4	$Y = 0.6X + 7.2$ (3)	0.75	T_5/G	$Y = 0.5X + 7.0$ (26)	0.71
T_1/T_5	$Y = 0.4X + 9.6$ (4)	0.81	S_1/S_2	$Y = 68.6 - 2.1X$ (27)	−0.78
T_1/H	$Y = 170X + 6770$ (5)	0.58	S_1/S_3	$Y = 1.2X + 1.2$ (28)	0.59
T_1/G	$Y = 0.2X + 12.0$ (6)	0.60	S_1/S_4	$Y = 38.3 - 1.2X$ (29)	−0.54
T_1/Q	$Y = 19.6 - 4.1X$ (7)	−0.57	S_1/S_5	$Y = 1.0X - 8.0$ (30)	0.80
T_1/NI	$Y = 84.2 - 0.8X$ (8)	−0.81	S_2/S_3	$Y = 42.7 - 0.6X$ (31)	−0.76
T_2/T_3	$Y = 1.0X + 5.9$ (9)	0.96	S_2/S_5	$Y = 21.4 - 0.4X$ (32)	−0.77
T_2/T_4	$Y = 0.8X + 8.6$ (10)	0.58	S_2/H	$Y = 5814 - 94X$ (33)	−0.88
T_2/T_5	$Y = 0.6X + 11.9$ (11)	0.69	S_2/G	$Y = 8.3 - 0.1X$ (34)	−0.84
T_2/H	$Y = 270X + 7910$ (12)	0.51	S_2/D	$Y = 845 - 15X$ (35)	−0.72
T_2/G	$Y = 0.3X + 13.9$ (13)	0.56	S_3/S_4	$Y = 35.2 - 0.8X$ (36)	−0.75
T_2/NI	$Y = 67.0 - 1.8X$ (14)	−0.95	S_3/S_5	$Y = 0.4X - 0.3$ (37)	0.76
T_3/T_4	$Y = 0.8X + 2.5$ (15)	0.56	S_3/H	$Y = 106X - 1578$ (38)	0.79
T_3/T_5	$Y = 0.5X + 5.7$ (16)	0.56	S_3/G	$Y = 0.1X + 2.5$ (39)	0.75
T_3/G	$Y = 0.3X + 11.0$ (17)	0.51	S_3/Q	$Y = 2.3X + 177.8$ (40)	0.67
T_3/NI	$Y = 80.7 - 1.7X$ (18)	−0.91	S_4/S_5	$Y = 17.6 - 0.4X$ (41)	−0.75
T_4/T_5	$Y = 0.5X + 2.8$ (19)	0.82	S_4/H	$Y = 2277 - 74X$ (42)	−0.59
T_4/H	$Y = 354X + 5240$ (20)	0.92	S_4/G	$Y = 6.6 - 0.1X$ (43)	−0.54
T_4/D	$Y = 46X + 960$ (21)	0.63	S_5/H	$Y = 199X - 1122$ (44)	0.85
T_5/D	$Y = 60X + 630$ (22)	0.54	S_5/G	$Y = 0.2X + 3.0$ (45)	0.81
T_5/Q	$Y = 93 - 8X$ (23)	−0.52	S_5/D	$Y = 28X + 105$ (46)	0.63

$Y = aX + b$ ($n = 6$, $P = 0.95$); H is the altitude above the sea level; G is the average humus content in the soil, %; Q is the number of sunny days in a year; D is the total amount of precipitation per year; NI is the iodine number.

T_i towards positive temperatures in the DSC curves, the lower the iodine number of the oil sample. A similar trend for T_i was observed with an increase in the humus content in the soil. At the same time, the areas S_i of these peaks behave differently. For example, the S_2 peak area decreased, while the S_3 and S_5 areas increased with T_i shifting to a more positive region, which indicated an increase in the proportion of TAGs with a smaller number of double bonds. The T_4 and T_5 values, caused by the USS and SSS TAGs, grew symbatically in oil with an increase in precipitation. At the same time, the sunnier days in the zone of milk thistle growth, the lower values of T_1 and T_5 were observed in the melting curves, which indicated an increase in the degree of unsaturation of TAGs, while the area S_3 of the peak increased noticeably, which meant that the content of the TAGs of the UUU and UUS type in oil increased. A total of 46 correlations were found:

(1)−(46). Thus, checking the samples of milk thistle oil from Dagestan by correlations (1)−(46) made it possible to find the conditions for the maturation of this plant raw material and, with a high degree of probability, the place of growth.

An analysis of a series of samples of genuine oil of wild-growing milk thistle determined the ranges of variation of its thermophysical parameters (T_i, S_i). Let us demonstrate the capabilities of the DSC method in controlling the authenticity of milk thistle oil by comparing the data for Dagestan wild plants with a sample of oil we isolated from milk thistle fruits purchased from a pharmacy chain (Biokor, Russia) (Table 4) and two samples of milk thistle oil purchased in "VkusVill" chain store. We specially added 10% of sunflower or corn oils to each of these samples, as in [7]. For visualization and data analysis, we constructed control charts (CC) with normalized T_i and S_i parameters in
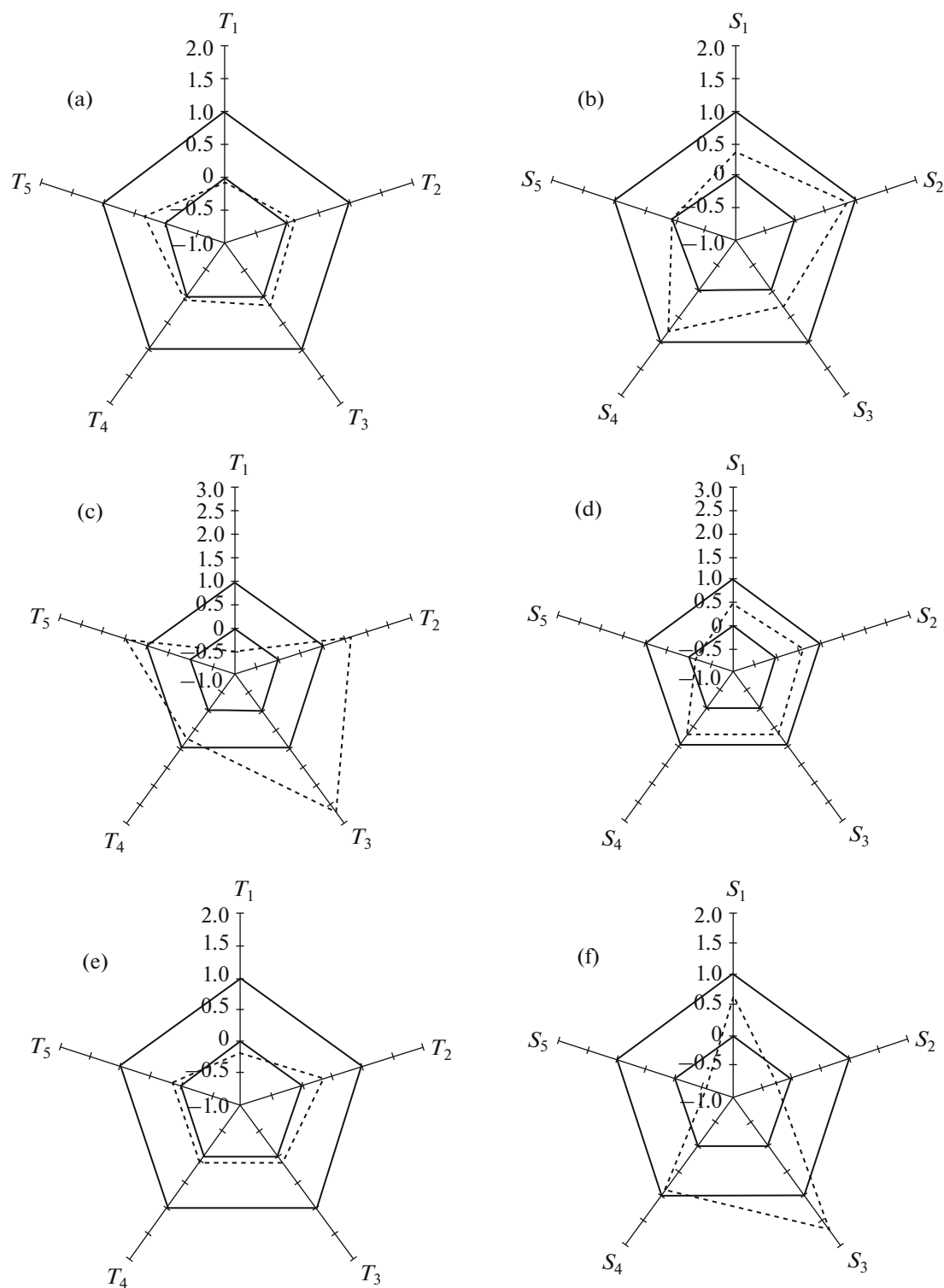
Fig. 3. Control charts for milk thistle oil: normalized values of T_i and S_i for (a, b) a Biokor sample and a sample of the VkusVill trading chain with the addition of (c, d) sunflower oil (9 : 1) and (e, f) corn oil (9 : 1).

the form of petal diagrams mm (Fig. 3) [17] and highlighted the established range of permissible values from 0 to 1 (solid lines) and control data (dashed lines). We used the equation

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

where X_f is the found normalized value of T_i or S_i, X_{max} and X_{min} are the maximum and minimum values of

these parameters in the sample from Table 4 for Dagestan wild milk thistle.

Milk thistle oil from the raw materials of the Biokor company only for one indicator (T_1) slightly exceeded the limits of the permissible corridor, typical for the sample from the Dagestan region; in terms of thermophysical characteristics, it was the closest to the oil obtained from the milk thistle of the Suleyman-Stalsky district (Fig. 3a).

In milk thistle oil with the addition of sunflower oil, the values of T_1, T_2, T_3, and T_5 did not fall into the range of permissible values from 0 to 1 in terms of temperature at the peak maximum, as well as the area S_5 was below the norm (Fig. 3). This means that the proportion of TAGs of the UUU and UUS types was overestimated compared to the milk thistle oil, and the proportion of SSS was underestimated. In the sample with corn oil, the T_1 value was underestimated, the S_3 area was noticeably overestimated, and the S_5 area was underestimated. This indicates a change in the composition of UUU, in particular, an increase in the proportion of L_3 [7], and UUS and a decrease in the proportion of SSS in artificially prepared counterfeit products. Constructing control charts in the form of normalized lobe diagrams in the MS Excel shell and loading experimental data into them is a convenient algorithm for identifying the authenticity of vegetable oils according to DSC data.

CONCLUSIONS

Thus, we obtained and characterized a sample of data on the thermophysical parameters of wild milk thistle oil from different regions of Dagestan using the DSC method, determined the range of variation of these indicators, and proposed an algorithm for proving the authenticity of milk thistle oil, based on thermal analysis data. The studies confirmed the fact that the phase transitions of vegetable oil correlate with particular fractional compositions of triacylglycerols, which vary with changes in phenotypic factors in rather wide ranges, but according to the genotype and natural patterns of maturation of plant materials rather than randomly. The found correlations between the thermal effects in the samples of milk thistle oil and the climatic conditions of the growth of raw materials can be helpful from the point of view of thermal analysis and the chemistry of plant raw materials, biochemistry, and pharmacognosy.

FUNDING

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