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CRYSTALLISATION AND MELTING BEHAVIOUR OF FISH OIL MEASURED BY DSC

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Fish oil which is characterised by important amounts of poly-unsaturated ω-3 fatty acids attach increasing importance within functional foods. Recently attention is directed on physical methods that allow fast and relatively easy the identification and discrimination of oils. DSC measurements yield in information on thermal effects, characterised by changes in enthalpy and their temperature range such as melting and crystallisation. The aim of the investigation presented here was to take DSC curves in the temperature range +20 to –40°C on several fish oils and fish oil capsules to visualise the crystallisation and melting behaviour and to compare transition temperatures and enthalpies.

Keywords: *crystallisation, differential scanning calorimetry (DSC), fish oil, melting*

Introduction

Fish oil is derived from the tissues of oily fish and recommended for a healthy diet because it contains the ω-3 fatty acids, eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA). As result of long lasting and intensive research worldwide the following possible health benefits are ascribed to these poly-unsaturated fatty acids (PUFAs): lowering blood pressure, preventing sudden death by heart attack, regulating the symptoms of attention deficit hyper-activity disorder, improving fertility, preventing pre-mature birth, managing and overcoming depression, improving children's IQ, controlling and reducing inflammation and reducing the risk of asthma. Further-more, ω-3 fatty acids-rich fish oil acts as effective arthritic pain reliever and reduces the risk of cancer. There are recent studies that have suggested that fish oil may affect suicide risk. Other studies found that ω-3 exerts neuroprotective action in Parkinson's disease, may help protect the brain from cognitive problems associated with Alzhemimer's disease and suggest that ω-3 fatty acids could also help delay or prevent the onset of schizophrenia [1, 2].

Due to the benefits listed above, the US American Heart Association gave the following population recommendation [3]:

- Patients without documented coronary heart disease (CHD) eat a variety of (preferably fatty) fish at least twice a week; include oils and foods rich in alpha-linolenic acid (flaxseed, canola and soybean oils; flaxseed and walnuts).
- Patients with documented CHD consume about 1 g of EPA+DHA per day, preferably from fatty fish, EPA+DHA in capsule form could be consi-dered in consultation with the physician.
- Patients who need to lower triglycerides, 2 to 4 g of EPA+DHA per day provided as capsules under a physician's care.

Fish do not actually produce ω-3 fatty acids, but instead accumulate them from either consuming micro algae that produce these fatty acids, as is the case with prey fish like hering and sardines, or, as is the case with fatty predatory fish, by eating prey fish that have accumulated ω-3 fatty acids from micro algae.

Many people have turned to fish oil to get adequate ω-3 fatty acids. New fish oil products based on natural fish oil or their derivatives are constantly being introduced on the international market as health foods (capsules) or medicines. Most of the fish oil capsules on the market today are blends of natural fish oil and their derivatives. The quality of the fish oil products may vary significantly according to the quality of the raw material and how they have been produced or manufactured [4].

To check the quality of fish oil supplements, the International Fish Oil Standards program, a voluntary review process, was created at University of Guelph, Canada. The laboratory tests ω-3 and whole fish products for PCB, mercury, heavy metals, dioxin and furan and oxidation levels in accordance with existing national and international regulations. The ω-3 con-centration is tested and compared with the product

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label claim [5]. There has been a corresponding demand for analytical methods with the capacity to routinely monitor the nature and levels of ω-3 fatty acids in fish oil products in order to ensure their quality control and quality maintenance. Although gas chromatographic methods have previously been extensively employed for the purpose of determining the PUFAs in both fish and fish oils, these methods are labour intensive and time consuming and also involve a complex series of chemical manipulation stages. More recently, the analysis of PUFA components in marine oils has been augmented by the employment of high-resolution ^{1}H and ^{13}C NMR spectroscopy [2].

DSC has been used successfully in lipid chemistry in solving different tasks for long time [6, 7]. DSC has significant advantages compared to the classical chemical methods, including small sample size (<20 mg), minimal sample preparation, no use of chemical agents or solvents, short experimental times, and simplicity of operation [7]. Recently, numerous papers have been published on the characterisation and discrimination of vegetable oils by investigating their cooling and melting behaviour using DSC [8–17] as well as on the use of DSC for assessing the oxidative deterioration of vegetable oils [7, 18]. Despite their nutritional importance, only few papers have been found which deal with the melting and cooling behaviour of fish oil [19–21]. Therefore, the aim of the investigation presented here was to take DSC curves in the temperature range from +20 to –40°C on several fish oils and fish oil capsules to visualise the crystallisation and melting behaviour and to compare the transition temperatures and enthalpies.

Experimental

Materials

Fish oils were commercially processed samples. Commercial fish oils capsules were bought at different supermarkets, retail pharmacy and health food stores. Sample numbers and comments are given in Table 1.

DSC measurement

DSC measurements were performed using a power compensation device DSC 7 equipped with PerkinElmer Intra cooler II and Pyris software 3.81 (PerkinElmer, Überlingen, Germany) as described earlier [22]. Small amounts of fish oil (7–8 mg) were weighed (±0.1 mg) in 50 μL aluminium pans (B0143017) and covers (B0143003) were hermetically sealed into place. At least three samples were scanned with a scanning rate of 10°C min^{-1} with a sealed empty pan as reference in the temperature range from 50 to –40°C. The following temperature profiles were used for heating and cooling the samples with and without thermal pre-treatment: starting at 20°C→heating to 50°C with 10°C min^{-1}, keeping for 1 min at 50°C→cooling to 20°C with 10°C min^{-1} (thermal pre-treatment); keeping for

Table 1 Commercial fish oils and commercial fish oil capsule (details to species and PUFA content are derived from the label)

No.	Fish species and comments	Kind	EPA/%	DHA/%
1	Sardine, herring, anchovies, mackerel	Oil	18.0	12.6
2	Unknown	Oil	18.0	12.3
3	Unknown	Oil	19.8	12.8
4	Unknown	Oil	14.0	14.0
6	Cod liver	Oil	Unknown	Unknown
7	Unknown, marine oil, ω-3, natural	Oil	19.7	13.9
8	Unknown, lot 1490201	Oil	Unknown	Unknown
9	Unknown, lot 1589301	Oil	6.2	10.8
10	Marine fish	Capsule	14.0	10.0
11	Salmon	Capsule	Unknown	Unknown
12	Salmon	Capsule	18.0	12.0
13	Salmon	Capsule	18.0	12.0
14	Salmon and other fish	Capsule	12.0	10.0
15	Salmon	Capsule	18.0	12.0
16	Unknown	Capsule	36.0	Unknown
17	Krill	Capsule	15.0	9.0
18	Salmon	Capsule	Unknown	Unknown

1 min at 20°C, cooling to –40°C with 10°C min^{-1}, keeping for 1 min at –40°C, heating to 20°C with 10°C min^{-1} (crystallisation and melting).

Results are presented as average curves in the figures. The average curves are used to record the onset and transition temperatures (T_{ons} and T_{max}) and to calculate the transition enthalpy (ΔH) expressed as J g^{-1} of the sample material from the peak area.

Results and discussion

Fish oil

Scanning rate

Because DSC curves taken on vegetable oils were markedly influenced by the scanning rate during heating and cooling [9, 10] in size as well as in transition temperatures, at first this influence was investigated using fish oil sample 1. As to be seen (Fig. 1, Table 2) variations in the scanning rate from 1–20°C min^{-1} during cooling and heating caused also variations in DSC curves taken on fish oil. An increase in the scanning rate resulted in decreasing T_{max} and was accompanied by a comparable slight decrease in ΔH. Investigating the effects of cooling rate variation on DSC traces of vegetable oils it was found by Tan and Che Man [10] that increasing the cooling rate resulted in higher T_{ons} for the crystallisation transition. It was pointed out further that the exothermic T_{max} decreases as a function of the cooling rate [10]. When the wax appearance temperatures of vegetable oils were determined by DSC it was observed at a lower cooling rate (1–5°C min^{-1}) the signal-to-noise ratio was low and T_{ons} was hard to estimate [23]. In DSC analysis of vegetable oils the crystallisation exotherm shifted to lower temperature as the rate of cooling increased. Also the breadth of the exothermic peak, on cooling from the melt, increased with increasing cooling rate [12]. The endothermic transition of the melting curves appears to be less influenced by scanning rate compared to the crystallisation curves (Fig. 1, Table 2). T_{max} shifted to higher temperatures with increasing scanning rate. This shift is only marginal in the scanning range 1–10°C min^{-1} and becomes pronounced when rate increased to 20°C min^{-1}. The reduction in T_{max} is accompanied by a strong decrease in ΔH. For vegetable oils was found that melting transition temperature shifted to higher values with increasing rates of heating, as the breadth of the endothermic peak and the area under the melting peak also increased with increasing heating rate [9]. A shift of the offset temperature (T_{off}) toward higher values with increasing heating rates was observed and it was noted that oil samples with a higher degree of saturation requires more energy during the melting process [12]. Therefore, the behaviour of fish oil and vegetable oil regarding the influence of variation in scanning rate of DSC appears to be comparable during crystallisation as well as melting. Furthermore, Fig. 1 demonstrates perfectly the phase transitions, which a sample undergoes during heating and cooling in a differential scanning calorimeter. As a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat

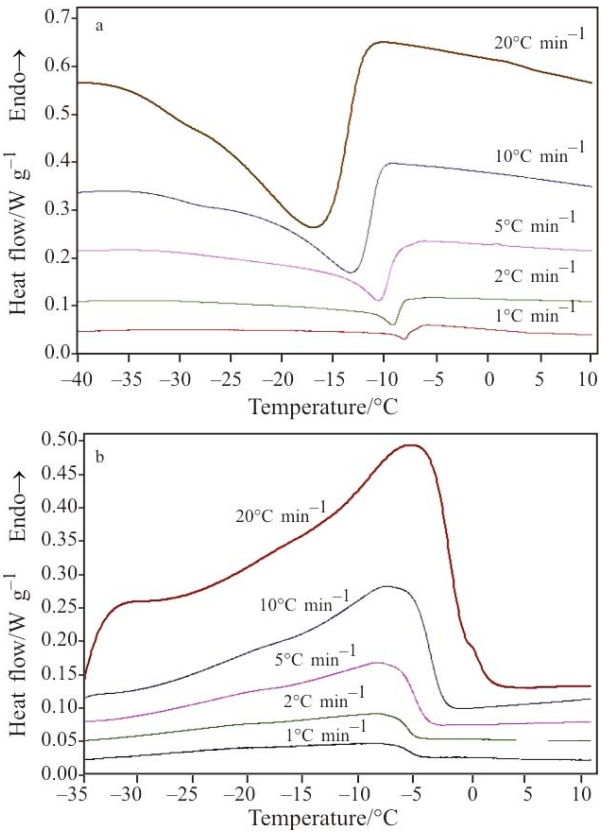

Fig. 1 DSC curves (a – cooling; b – melting) taken on fish oil No. 1 processed from sardine, herring, anchovies, mackerel (Table 1) as affected by different scanning rate

Table 2 Transition temperature and enthalpy during cooling and melting of fish oil No. 1 processed from sardine, herring, anchovies, mackerel as affected by the scanning rate

Scanning rate/ °C min^{-1}	Cooling		Melting	
	T_{max}/°C	ΔH/J g^{-1}	T_{max}/°C	ΔH/J g^{-1}
1	–8.27	–11.73	–8.07	23.73
2	–9.29	–12.65	–8.32	19.08
5	–10.64	–13.07	–8.25	16.57
10	–13.05	–13.13	–7.36	15.41
20	–16.78	–13.80	–4.88	13.00

Table 3 Transition temperature and enthalpy during cooling of untreated and thermally pre-treated commercial fish oils No. 1 processed from sardine, herring, anchovies, mackerel; Nos 2, 3 and 4 of unknown origin each (Table 1)

Sample	Untreated			Pre-treated		
	T_{ons}/°C	T_{max}/°C	ΔH/J g^{-1}	T_{ons}/°C	T_{max}/°C	ΔH/J g^{-1}
1	–10.36	–13.13	–12.749	–10.77	–13.40	–13.227
2	–8.82	–11.60	–12.792	–9.27	–11.37	–12.866
3	–9.74	–13.00	–14.700	–9.13	–12.63	–13.566
4	–6.84	–9.10	–6.563	–6.36	–9.20	–7.821

by the sample as it undergoes the endothermic from solid to liquid. Likewise, as the sample undergoes exothermic processes, such as crystallisation, less heat is required to raise the sample temperature.

Crystallisation

After investigating the influence of the scanning rate on DSC pattern taken on fish oil, different fish oils were investigated regarding their behaviour during crystallisation. The protocol of these trials included the direct cooling down of oil samples after they have been inserted in the DSC machine beside a thermal pre-treatment of samples to 50°C prior to cooling down using a scanning rate of 10°C, in general. Figure 2 demonstrates the DSC curves taken on samples 1–4. Respective values of T_{ons}, T_{max} and ΔH are shown in Table 3. Fish oil 1 and 3 appear to have comparable DSC traces while fish oil 4 deviates most. A possible reason for this different behaviour can be seen in the different contents on ω-3 PUFAs (Table 1). It can further be noted that thermal pre-treatment of fish oils did not have a marked influence on the DSC curves.

Therefore, Fig. 3 displays only the DSC curves taken on the untreated commercial fish oils 6–9 during crystallisation and for comparison DSC curves taken on untreated vegetable oils customary in the trade using same measuring conditions. As can be seen fish oils differ significantly in their DSC pattern. Sample 6 (cod liver oil) had the lowest T_{max} while that of sample 9 (fish oil, lot 1589301) was highest.

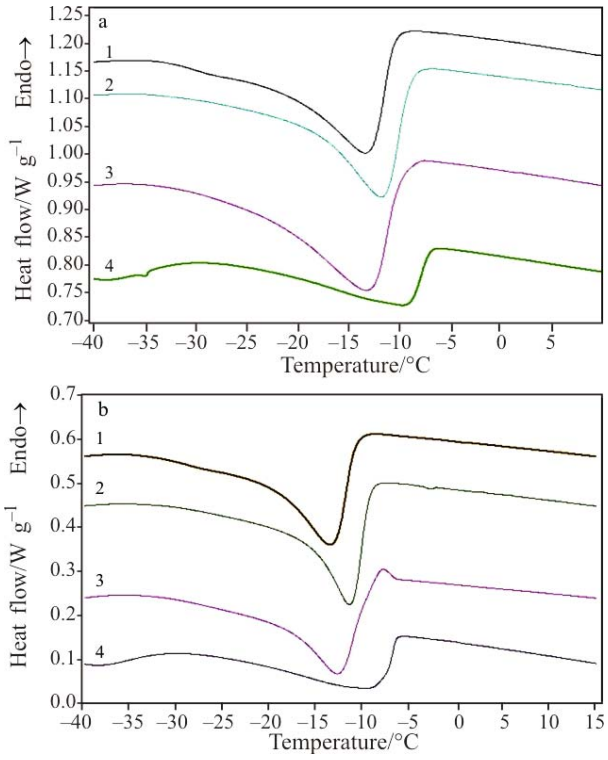

Fig. 2 DSC cooling curves taken on a – untreated and b – thermally pre-treated commercial fish oils, 1 – processed from sardine, herring, anchovies, mackerel; 2, 3 and 4 – of unknown origin each (Table 1)

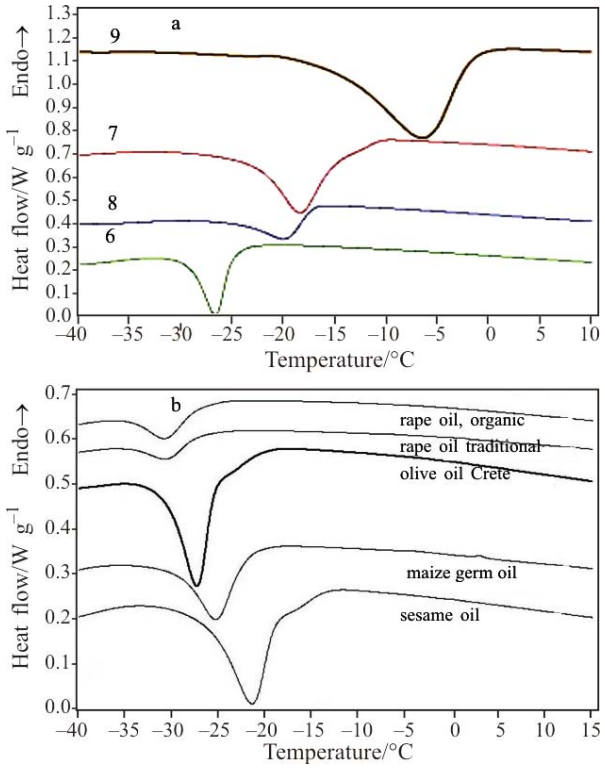

Fig. 3 DSC cooling curves taken on a – untreated commercial fish oils: 6 – processed from cod liver, 7, 8 and 9 – of unknown origin each and b – commercial vegetable oils as indicated in the figure

Table 4 Transition temperature and enthalpy during cooling of untreated commercial fish oils: No. 6 processed from cod liver, Nos 7, 8 and 9 of unknown origin each (a) and commercial vegetable oils as indicated in Fig. 3b

Vegetable oil	T_{max}/°C	ΔH/J g^{-1}	Fish oil	T_{max}/°C	ΔH/J g^{-1}
Rape oil, organic	–30.47	–1.572	6	–26.57	–4.769
Rape oil, traditional	–30.30	–1.067	7	–18.33	–11.934
Olive oil, Crete	–27.07	–6.420	8	–19.87	–4.049
Maize germ oil	–25.07	–4.463	9	–6.40	–19.277
Sezame oil	–21.23	–8.386	–	–	–

Table 5 Transition temperature and enthalpy during melting of untreated commercial fish oils: No. 1 processed from sardine, herring, anchovies, mackerel; Nos 2, 3 and 4 of unknown origin each and No. 6 processed from cod liver, Nos 7, 8 and 9 of unknown origin each

Fish oil	T_{ons}/°C	T_{max}/°C	ΔH/J g^{-1}	Fish oil	T_{max}/°C			ΔH/J g^{-1}		
					Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
1	–22.60	–7.47	15.347	6	–33.90	–16.53	–7.90	8.909	1.434	9.342
2	–20.82	–5.40	14.739	7	–	–	–6.30	–	–	14.477
3	–21.61	–6.83	16.747	8	–35.07	–	–6.77	4.505	–	20.771
4	–23.78	–7.60	7.510	9	–17.17	2.33	14.87	2.211	0.244	9.007

Its content of ω-3 fatty acids was comparable low. As indicated in Table 4, T_{max} of the other samples 7 and 8 laid in between. Of the vegetable oils rape oils had lowest T_{max} with almost no difference between the oils from organic and conventional cultivation, but both were less intense. On the other hand, sesame oil had the highest temperature of transition. In general, DSC traces of the crystallisation curves of both fish oils and vegetable oils were almost comparable and displayed one exothermic peak.

The T_{ons} reported for extra virgin olive oils [15] were lower than those found in this study (not shown). A possible explanation is the different scanning rate used (2 *vs.* 10°C min^{-1}). DSC cooling curves are affected by chemical composition of extra virgin olive oil [15]. Some thermal properties (crystallisation peak onset and temperature range) were influenced not only by major but, probably, also by minor components. When hazelnut oil was added to olive oil the transition shifted to lower temperature and the ΔH enhanced possibly due to the lower content of saturated fatty acids in hazelnut oil [17]. When correlating DSC pattern of vegetable oils with their chemical composition it was found that oil samples with a high degree of saturation showed DSC melting and crystallisation profiles at higher temperature regions than the oil samples with high degree of unsaturation [11]. Triacylglyceride fractions rich in either PUFA or MUFA from menhaden oil and partially hydrogenated menhaden oil were crystallised by DSC and it was found that DSC pattern for the fractions in conjunction with their fatty acid

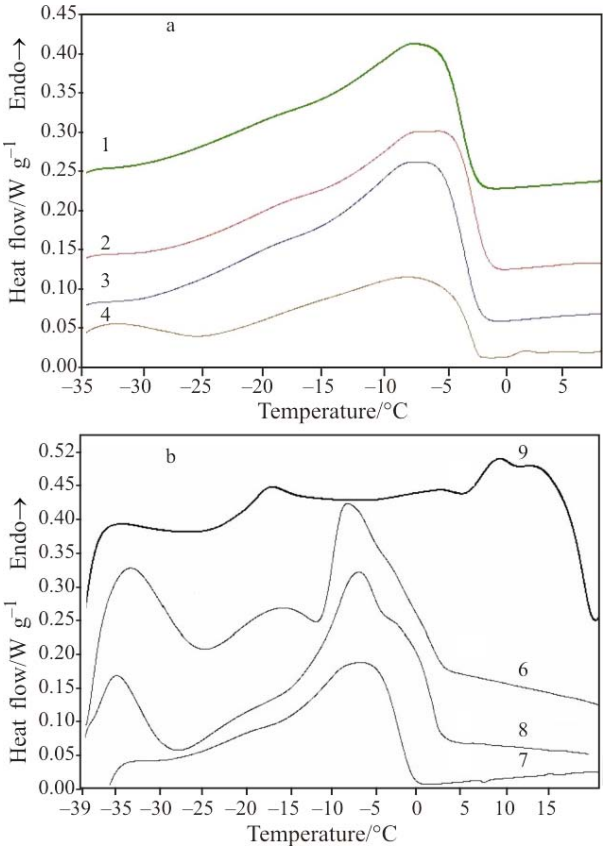

Fig. 4 DSC melting curves taken on a – untreated commercial fish oils: a – 1 – processed from sardine, herring, anchovies, mackerel; 2, 3 and 4 – of unknown origin each, b – 6 – processed from cod liver, 7, 8 and 9 – of unknown origin each

Table 6 Transition temperature and enthalpy during crystallisation and melting of fish oil capsules: No. 10 from marine fish oil, Nos 11, 12, 13 and 15 from salmon oil, No. 14 from salmon and other fish oil, and No. 17 from krill oil (Table 1)

Sample	Crystallization				Melting			
	T_{max}/°C		ΔH/J g^{-1}		T_{max}/°C		ΔH/J g^{-1}	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
10	–15.53	–	–11.24	–	–7.73	–	12.46	–
11	–12.77	–	–13.44	–	–7.50	–	15.22	–
12	–11.40	–	–13.47	–	–7.43	–	15.94	–
13	–14.57	–	–12.14	–	–7.43	–	14.70	–
14	–13.70	–	–10.28	–	–7.83	–	11.76	–
15	–11.70	–	–12.09	–	–6.80	–	14.64	–
17	–8.67	–13.97	–2.33	–9.05	–14.90	2.37	21.67	22.73

compositional data allow for the optimisation of the fractionation schemes developed [19].

Melting

When fish oil after cooling down was heated from –40 to 25°C the melting curve was obtained by DSC. Those taken on the different fish oils are displayed in Fig. 4 and their respective T_{max} and ΔH in Table 5. It becomes obvious that curves are partly of different shape. While DSC curves taken on samples 1–4 exhibit only one major peak that deviated marginally in both T_{ons} and T_{max} from the curves taken on samples 6–9, only fish oil 7 exhibits one major peak. Compared with T_{max} of the crystallisation curve its transition temperature when melting is more than 10°C higher. The number of peaks of the oils 6, 8 and 9 varies between two and three. The lowest melting points were found for samples 8 and 7 with about –35°C. Taking into account that melting points occur at higher temperature than the respective crystallisation transitions possible due to the phenomenon of undercooling, it can be assumed that the cooling curve shows probably more than one transition, which however, occurs at lower temperature (<–40°C) as detectable with the method applied in this study.

Two distinct endothermic peaks for oils from red and pink salmon heads ranging from –69.0 to –0.36°C and from –64.7 to 20.8°C, respectively, were observed in DSC investigation of these fish oils. The peaks at –13.4°C for red salmon oil and at –8.8°C for pink salmon oil were not sharp. The ΔH was 40 and 39 J g^{-1} for red and pink salmon oil, respectively [20]. DSC investigations on catfish visceral oil during the purification process revealed that there were changes in melting points during purification. Because impurities were gradually removed, melting point peaks of catfish oil became sharper after each purification step [21]. The melting points of the fatty acids may define the properties of the triglycerides, of which they are a part. The melting points of saturated fatty acids increased with increasing chain lengths, possibly due to the intermolecular dispersion force which increases with the increased number of carbons in chains [24]. In the case of unsaturated fatty acids, the increased number of double bonds decreased the melting point. The lowest melting point (T_{ons}= –47.4°C) was observed for DHA [21].

Fish oil capsules

Figure 5 depicts the different fish oil capsules, which were included in the investigation. Figure 6 displays the crystallisation and melting curves obtained when their oily content was subjected to DSC and Table 6 shows their respective transition temperatures and enthalpies.

It becomes obvious that the DSC curves are relatively comparable in shape and size as well as in their T_{max} and ΔH. The reason for the uniformity can

Fig. 5 Collection of fish oil capsules included in the investigation: 10 – from marine fish oil, 11, 12, 13, 15 and 18 – from salmon oil, 14 – from salmon and other fish oil, 16 – from fish oil of unknown origin and 17 – from krill oil (Table 1)

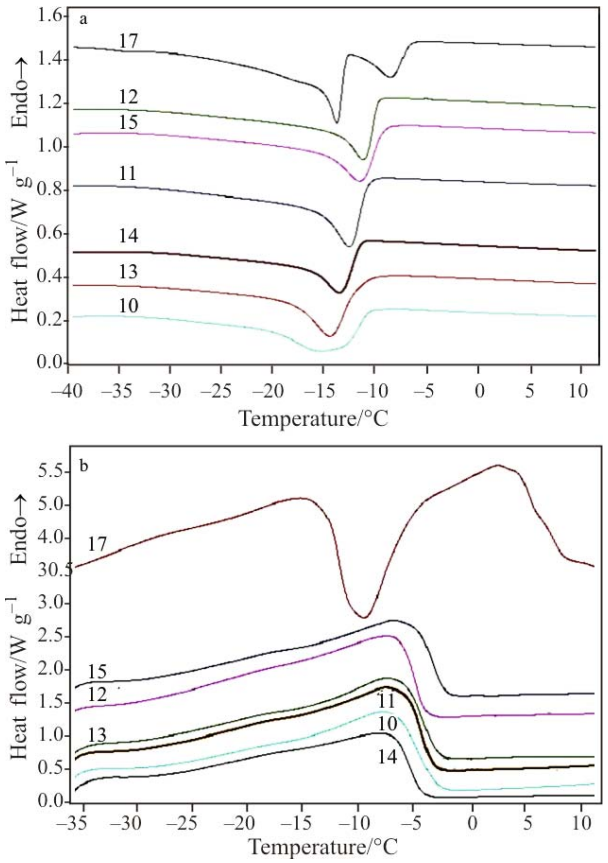

Fig. 6 DSC a – crystallisation and b – melting curves taken on different fish oil capsules: 10 – from marine fish oil, 11, 12, 13 and 15 – from salmon oil, 14 – from salmon and other fish oil, 17 – from krill oil (Table 1)

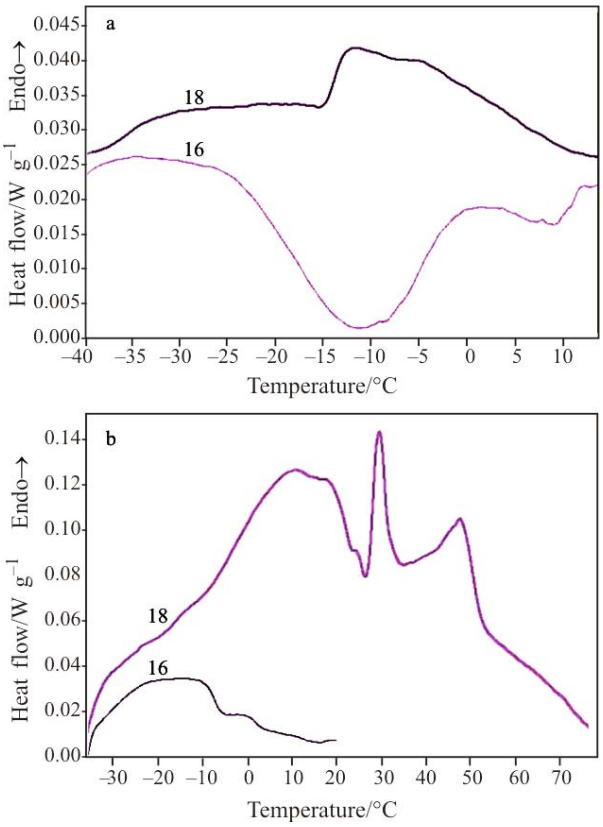

Fig. 7 DSC a – crystallisation and b – melting curves taken on the fish oil capsules 16 – from fish oil of unknown origin and 18 – from salmon oil

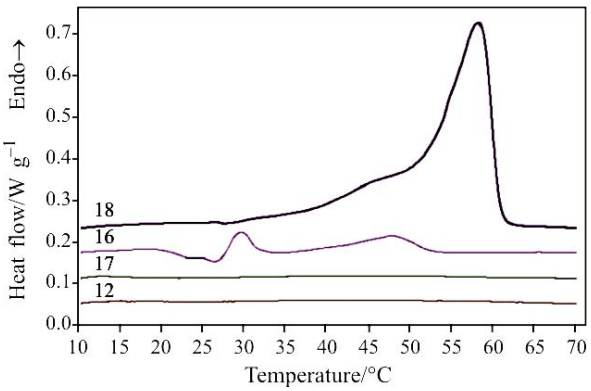

Fig. 8 DSC curves taken on different fish oil capsules in the temperature range 10–70°C, 12 – from salmon oil, 16 – from fish oil of unknown origin, 17 – from krill oil and 18 – from salmon oil

be seen in that most of fish oil capsules on the market today are blends of natural fish oil and their derivates [4]. Processors have the aim to assure a consistent quality and therefore, they possibly use the same blends, which should be available for moderate prices. DSC pattern are also comparable with those of the fish oils shown above (Figs 1–3). The exception from the homogeneity is sample 17, a capsule that contains krill oil. This oil exhibits two distinct peaks in both the crystallisation and melting curves. Furthermore, two abnormalities were found too (Fig. 7). The DSC crystallisation and melting pattern deviate from the normal behaviour of a fish oil and are difficult to explain. These were capsules that were labelled as product rich in EPA and containing green shell mussel powder (sample 16) and as product containing a special fish oil with 65% ω-3 fatty acid, especially developed for elderly people over fifty. However, the DSC patterns obtained differ markedly from those, which are characteristic for fish oil. Therefore, these products were also subjected to DSC measurement in the temperature range 10–70°C (Fig. 8). Both samples exhibit one (sample 18) or two (sample 16) peaks in that range, which are in general not found with fish oil or krill oil (samples 12 and 17, respectively). Therefore, it can be considered that these both products do not contain fish oil in the amount labelled.

From the results obtained it can be concluded that thermal treatment of fish oil at 50°C before crystallisation or melting did not change significantly the DSC pattern. However, the DSC curves appear to

be markedly influenced by the degree of saturation or unsaturation of fatty acids of the fish oils investigated. The lowest crystallisation temperature was found for cod liver oil with –26.5°C. The comparable melting and crystallisation behaviour found for fish oil capsules point to the use of similar fish oils or blends of oils and concentrates, particularly salmon oil. A different melting and crystallisation behaviour was observed when investigating capsules containing krill oil. Their DSC curves showed two distinct melting and crystallisation peaks. Two of the fish oil capsules labelled as dietary supplement did not show the typical melting and crystallisation behaviour of fish oil although a content of ω-3 fatty acid was labelled at packaging.

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