Polymorphism of Saturated Triglycerides: I. 1,3-Distearo Triglycerides

N.V. LOVEGREN and **M.S. GRAY**, Southern Regional Research Center,
Agricultural Research Service, U.S. Department of Agriculture,
New Orleans, Louisiana 70179

ABSTRACT

Triglycerides of the 18-*N*-18 series, where *N* is an even-carbon saturated fatty acid of 2 to 18 carbons in length, were examined by differential scanning calorimetry. The procedures used to obtain heats of fusion and crystallization of the various triglycerides and their polymorphs are described. When small samples (ca. 1-2 mg) were used, the temperature lag was minor at rapid scanning rates thus permitting investigation of polymorphs with relatively rapid rates of conversion, but more accurate calorimetric data were obtained with larger samples. Capillary melting points were also obtained for the various triglycerides and their polymorphs. Calorimetric and melting point data were given.

INTRODUCTION

The polymorphism of individual triglycerides of the 18-*N*-18 series, where *N* is an even-carbon, saturated fatty acid of 2 to 18 carbons in length, has been studied by a number of investigators. Divergent viewpoints are illustrated in reviews by Lutton (1) in 1950 and Malkin (2) in 1954. Bailey (3) was the first to compile comprehensive polymorphic data on fats. Chapman (4,5) has critically reviewed the various experimental methods and the state of knowledge of the polymorphism of glycerides. However, no systematic study of the entire series has been made to determine the changes in polymorphic properties in relation to changes in the chain length of the fatty acids in the 2-position.

We restricted this study to the use of capillary melting points and differential scanning calorimetry to determine the changes that take place. These procedures permit the study of those polymorphs that are encountered in the normal melting and solidification procedures that might be used in commercial operations with fats.

MATERIALS AND METHODS

The triglycerides of the 18-*N*-18 series were synthesized and supplied to us by Prof. D. Rebello of the University of Bombay, India, through a PL-480 cooperative project sponsored by the U.S. Department of Agriculture (6). The synthesized triglycerides were 99.8% pure when checked by thin layer chromatography for absence of partial glycerides and fatty acids. The structural purity was greater than 99.5% by lipase hydrolysis.

The differential scanning calorimeter (DSC) employed was a Perkin-Elmer Model DSC-1 calibrated with indium, tin, and naphthalene to ensure the accuracy of the caloric data at different range settings. The instrument was calibrated by melting samples of palmitic acid, lauric acid, methyl palmitate, and ice, whose equilibrium melting-solidification temperatures had been previously determined with a calibrated thermometer to ensure accuracy of the temperature readings. Two sample sizes were used. Polymorphism was studied with samples of 2.0 mg or less to minimize heat transfer problems. Caloric values were measured on samples of ca. 12 mg to obtain more accurate results. The crystallized samples were weighed into DSC pans to the nearest 0.1 mg, and the covers were crimped into place. An empty, covered sample pan was used as a reference. After the sample and reference pans were placed in the calorimeter at room temperature, the low temperature Dewat flask sample cover was put in place and the sample area was flushed with nitrogen. The nitrogen flow rate was then adjusted to a slower rate, sufficient to maintain a dry, inert atmosphere within the sample area without changing the temperature, and the sample cover was filled with dry ice. To obtain consistent results, all samples were stabilized for 30 min or longer with dry ice cooling before the scans were started.

In the case of the small samples, which were used to study polymorphism, all samples were run in the following sequence: (a) crystalline samples heated at 5 C/min for initial melt; (b) cooled at 5 C/min; (c) heated at 5 C/min; (d) cooled at 10 C/min; and (e) heated at 10 C/min. Stepwise tempering, described below, was used to obtain and to verify form 1 (β) and to determine the ease of conversion to higher polymorphs.

When certain triglycerides had unstable lower melting polymorphs, the sample was quickly chilled from the melt to ca. -10 C, then immediately heated at scanning rates of 20-80 C/min depending on the degree of instability of the polymorph.

All large samples, which were used for caloric data, were heated to just below melting and held there to ensure as near complete conversion to form 1 (β) as was possible (based on information obtained from the initial melt of the small sample). The samples were then cooled to 15-20 C below the holding temperature, then heated at 5 C/min for the initial melt. After stepwise tempering, the sample was melted to verify caloric data. Crystalization to form 4 (α) was obtained by cooling the completely melted sample at an appropriate rate determined by cooling data from the small samples. Two criteria are used to determine whether the sample has crystallized entirely in form 4 (α): (a) crystallization starts below the temperature at which form 4 (α) starts to melt, and (b) ca. 2 C below this temperature crystallization takes place rapidly. To obtain accurate caloric data, the sample must be entirely in the state to be measured. Another limiting factor of the accuracy of caloric data is the accuracy with which the peak area of the DSC scan can be measured with the planimeter rather than the performance of the calorimeter.

Numeous heating and cooling cycles were made on both the large and small samples for each triglyceride. When exact conditions for sample treatment were reproduced, the DSC scans were identical.

Stepwise tempering consists of (a) heating the sample until melting just starts, (b) holding the sample at this temperature to allow time for conversion to a higher polymorph, and (c) cooling the sample 4 to 10 C below the holding temperature. This cycle was repeated, the temperature at which the sample started to melt being somewhat higher each time, until the sample had converted to a particular polymorph. The number of times the cycle had to be repeated depended on the degree of stability of the lower polymorphs and the ease with which conversion took place. Samples that converted slowly were held at the incipient melting temperature for 2 hr or more, thus reducing the

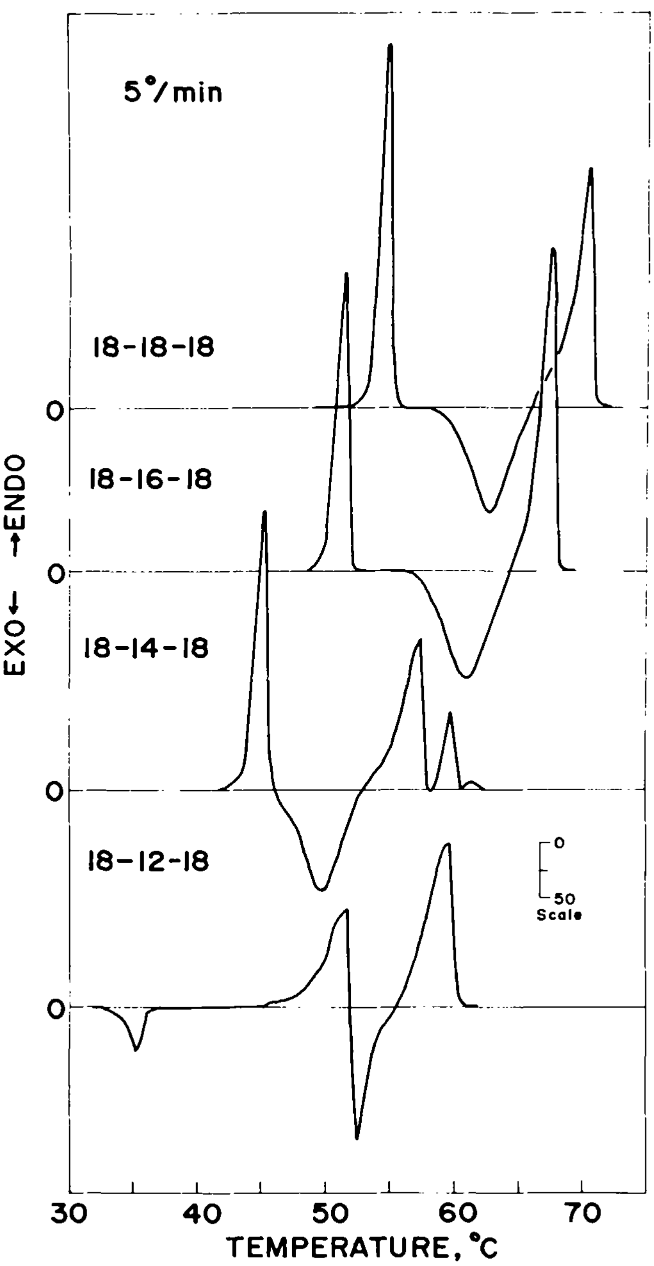

FIG. 1. DSC heating curves, samples cooled from melt and heated at 5 C/min.

number of repeat cycles required to attain a polymorphic conversion.

The melting point for the various triglycerides is that temperature at which the highest polymorph melts completely. The polymorphs referred to in the heating curves and tables are designated as 1, 2, 3, and 4, in order of their decreasing melting points. In addition, β is used for the highest melting polymorph and α for the lowest melting, while those melting between, when found, are referred to as intermediate to facilitate comparison to the polymorphs reported in the literature. These designations, β and α correspond to the polymorphs found by others with X-ray diffraction.

Crystallization studies were made by solidifying samples at various cooling rates after thermal history had been erased by melting. Caloric data for the heat of crystallization (ΔH_c) for the α-form were derived from the cooling scans. In some instances, little or no melting of the α-form occurred during the heating scans, precluding determination of its heat of fusion (ΔH_f). For the α-form, ΔH_c is equivalent to the ΔH_f. Caloric data obtained from the DSC scans were calculated to a unit weight basis to facilitate comparison. Theoretical caloric data were calculated according to the equations for simple triglycerides (3). Equations for the β-form were based on the members trilaurin (12-12-12) to tristearin (18-18-18) and on only three members for the α-form.

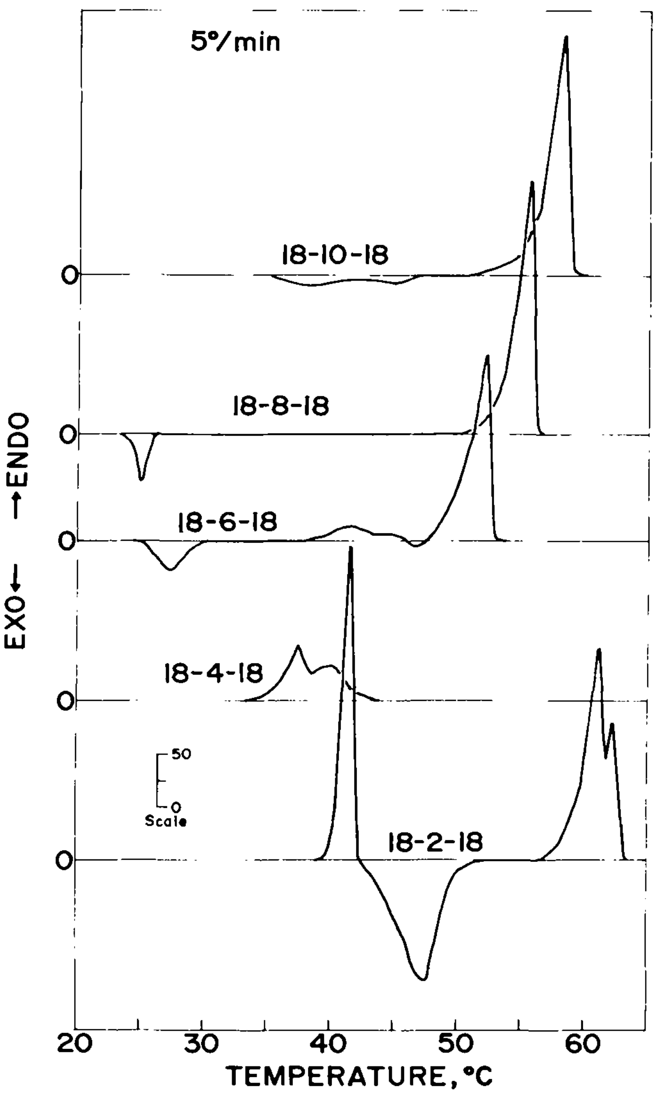

FIG. 2. DSC heating curves, samples cooled from melt and heated at 5 C/min.

Capillary melting points were determined in a Thomas-Hoover Uni-Melt capillary melting apparatus. Normal procedure were used for the high melting, stable polymorph. The more unstable polymorphs were determined by the "thrust in" technique, in which the sample is melted, solidified rapidly, thermally treated as desired, then thrust in at the testing temperature to see if it melts. This procedure was repeated at various bath temperatures until the melting point was determined. For some of the more elusive polymorphs, melting could be observed only in the small droplets on the capillary tube wall. Between tests, samples were held in an ice water bath to prevent transformation to a high melting polymorph. Theoretical melting point data were derived from melting vs. total chain length curves of saturated triglycerides (3).

RESULTS AND DISCUSSION

Initial melting of the 18-*N*-18 series of saturated tryglycerides was determined on solvent-crystallized

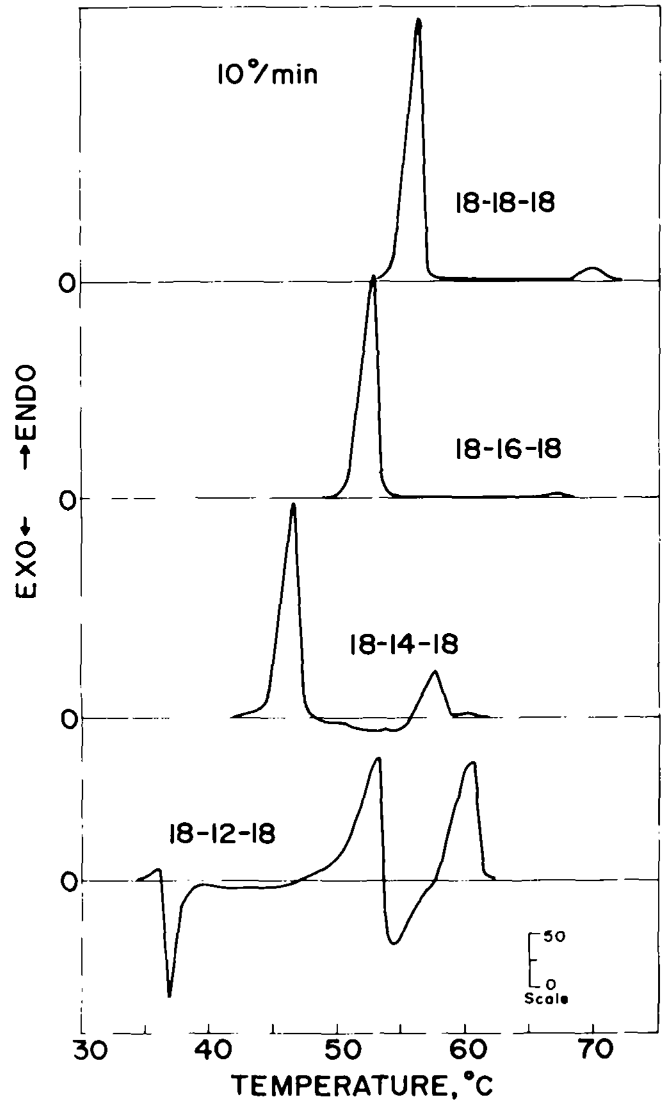

FIG. 3. DSC heating curves, samples cooled from melt and heated at 10 C/min.

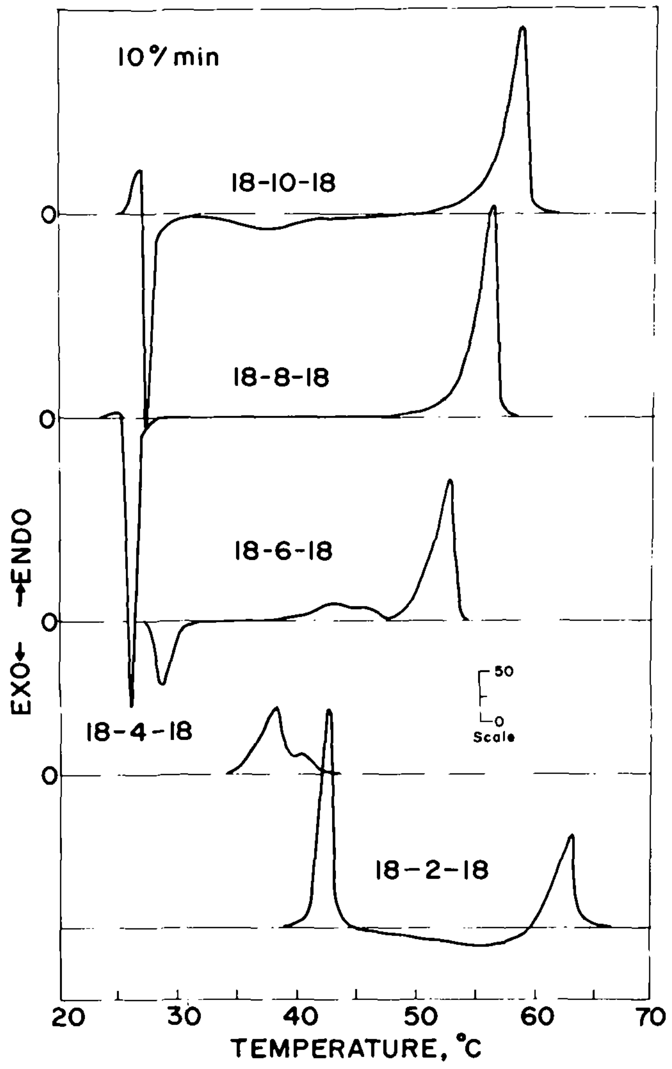

FIG. 4. DSC heating curves, samples cooled from melt and heated at 10 C/min.

samples. DSC heating scans gave a sharp melting peak for form 1 (β), from which the caloric data for this polymorph were derived. After initial melting, thermal changes that take place after cooling and heating of the samples at a rate of 5 C/min are shown in Figures 1 and 2, and after cooling and heating at a rate of 10 C/min are shown in Figures 3 and 4. The samples were not tempered between cooling and heating cycles, and any polymorphic changes that occurred were due to the instability of the low melting polymorphs.

The endothermic changes appear above the baseline, and the peak area is a direct caloric measure of the heat absorbed during melting of a particular polymorph. Some of the lower melting polymorphs are not stable enough to completely melt before conversion to a higher polymorph. When a partial melting of a polymorph accompanied by a conversion or transition to a higher polymorph takes place, both endothermic and exothermic changes are represented in the endothermic peak. The peak area in such a case is a measure of the heat absorbed during melting less the heat given off during the transition and crystallization to a higher polymorph. When a polymorph completely melts and then crystallizes to a higher polymorphic form, the endothermic peak area is a measure of the ΔH_f for that particular polymorph. The exothermic changes appear below the baseline, and the area of the exothermic peak that follows the melting of the polymorph is a measure of the ΔH_t for the transition and crystallization to a higher melting polymorph. The transition to a higher melting polymorph sometimes takes place without melting. In this case, only an exothermic change takes place, and the exothermic peak area below the baseline is the measure of ΔH_t.

Calorimetric data for ΔH_f of form 1 (β) and ΔH_c for the 18-*N*-18 series of saturated triglycerides are given in Table I, and capillary melting point data appear in Table II. In Figure 5, the melting points and the calorimetric data for the β and α polymorphs of the 18-*N*-18 series are compared with their theoretical values. The melting points and calorimetric data for the β and α polymorphs are given in the same figure to facilitate comparison with each other.

18-18-18

Two polymorphs melting at 73 and 55.3 C were found by both DSC and capillary melting techniques, and there was good correlation of the melting temperatures. An intermediate polymorph, cited in the literature (3) as occurring at ca. 64-65 C during rapid scanning by infrared, was not detected. Also reported (7) are polymorphs found by DSC that melt at 73, 64, 61, and 54 C. The one melting at 61 C had not been reported previously. There is possible DSC evidence for an intermediate form in the broad melting range of form 1 (β), which melts from 66 to 71.5 C when heated at 5 C/min (Fig. 1). After tempering for 2 hr at 67

C, the melting range became 68-72 C. The high purity of the tristearin may be responsible for our inability to find this intermediate polymorph. In a less pure sample of tristearin, the intermediate form was readily found by both DSC and capillary melting. The apparent stabilization of a lower melting transient polymorph by an impurity is similar to that previously noted (8) where cocoa butter, in 2-oleodipalmitin-cocoa butter mixtures, appeared to stabilize the low-melting polymorph of 2-oleodipalmitin (POP), whose melting is indicated only at a scanning rate of 10 C/min for POP alone. At a scanning rate of 10 C/min (Fig. 3), 18-18-18 melts as form 4 (α), with a small amount converting form 1 (β). There is a slight displacement of the peaks in the DSC scans caused by temperature lag.

18-16-18

Two polymorphs at 68 and 52 C were found by both DSC and capillary melting, and there was excellent correlation of the melting temperatures. Two intermediate polymorphs, cited in the literature as occurring at 64 and 56 C (3), were not detected by capillary melting. Hugenberg and Lutton (9) reported a higher melting β′ form, mp 69 C, which is obtained under special crystallizing conditions and is apparently stable at all temperatures below its melting point. There is DSC evidence for the polymorph that melts at 64 C, a small amount of which melts at the beginning of the peak for form 1 (β) when heated at 5 C/min (Fig. 1). There is no DSC evidence for a polymorph melting at 56 C. At a heating rate of 10 C/min (Fig. 3) 18-16-18 melts as form 4 (α) with a negligible amount converting to form 1 (β). Tempering at 49 C for 5 min is sufficient to permit extensive conversion to form 1 (β) when scanned at 10 C/min.

18-14-18

Four polymorphs at 63, 61, 53, and 48 C were found by DSC and two (1 and 4) at 63 and 44 C by capillary melting. There was good correlation of the melting temperatures. The two intermediate polymorphs cited in the literature as occurring at 59 and 56 C (3) were present when the sample was heated at 5 C/min (Fig. 1), although these forms were not obtained by capillary melting. At a heating rate of 10 C/min (Fig. 3), 18-14-18 melts as form 4 (α), with a moderate amount converting to forms 3 and 2, which appear in a broad peak melting at 56-59 C, and a negligible amount converting to form 1 (β). Rapid solidification followed by tempering at 45 C for 2 min, then heating at 5 C/min, gave nearly complete conversion to form 2 with only a trace of form 1 (β). Tempering to 57 C and holding there for ca. 40 min, then heating at 5 C/min, gave almost complete conversion to form 1 (β).

TABLE I

Calorimetric Data for 18-*N*-18 Series of Triglycerides (cal/g)

Carbons in fatty acid chain	ΔH_f Form 1 (β)	ΔH_f β theoretical[a]	ΔH_c	ΔH_f α theoretical[a]
18	51.1	54.5	32.9	39.0
16	46.7	54.0	41.4	38.4
14	41.5	53.3	30,2	37.8
12	39.5	52.6	31.2	37.1
10	43.3	51.7	22.5	36.4
8	45.0	50.8	17.0	35.6
6	41.2	49.9	26.1	34.8
4	37.0	48.8	24.2	33.9
2	48.8	47.7	27.8	32.9

[a] Bailey (Ref. 3, p. 154).

18-12-18

Four polymorphs at 60.5, 58, 52, and 36 C were found by both DSC and capillary melting, and there was good correlation of the melting temperatures. The capillary melting points were identical to those reported in the literature (3). Form 1 (β) was obtained in the pure form only from the solvent-crystallized sample. After the initial DSC melting, conversion progressed to the state wherein the sample melted as a mixture of forms 1 (β) and 2. At a heating rate of 5 C/min (Fig. 1), the only evidence of form 4 (α) is the crystallization and conversion to form 3, which, in turn, converts to a mixture of forms 1 (β) and 2. At a heating rate of 10 C/min (Fig. 3), form 4 (α) melts slightly, rapidly converts to form 3, and then converts to a mixture of forms 2 and 1 (β). At a heating rate of 20 C/min, somewhat more of form 4 (α) melted before conversion to higher melting polymorphs, indicating that this polymorph is quite unstable and rapidly converts to higher melting polymorphs.

18-10-18

Two polymorphs at 58.2 and 30 C were found by both DSC and capillary melting, and the correlation of the melting temperature for form 1 (β) was good. However, at a heating rate of 10 C/min (Fig. 4), form 4 (α) started to melt at ca. 25 C and rapidly converted at ca. 27 C, well below the capillary melting pont. Two intermediate polymorphs cited in the literature (3) as occurring at 53 and 47 C were not detected by capillary melting. The DSC evidence for these two intermediate polymorphs is primarily the two conversions that take place during heating. Form 1 (β) was obtained in the pure form from the solvent-crystallized sample and melted over a range of 57-59 C. There is evidence for form 2, which melts at 53 C, in the broad melting range of form 1 (β), which melts from ca. 50-60 C when heated at 5 C/min (Fig. 2). At a heating rate of 10 C/min, form 4 (α) begins to melt at 25 C and rapidly crystallizes at 27 C, with two corversions taking place before melting over a range of ca. 51-52 C as a mixture of form 1 (β) with some form 2.

TABLE II

Capillary Melting Point Data for 18-*N*-18 Series of Triglycerides (°C)

Carbons in fatty acid chain	Form 1 (β)	β theoretical[a]	Form 2 (β′)	Form 3	Form 4 (α)	α theoretical[a]
18	73.0	72.0			55.3	54.6
16	68.0	70.0			52.0	51.7
14	63.0	67.8			44.0	48.6
12	60.5	65.4	58.0	52.0	36.0	45.0
10	58.2	62.8			30.0	41.3
8	55.8	59.9			27.2	37.2
6	53.0	57.0	46.0		27.8	33.0
4	58.0	53.9	53.0	38.0	33.4	28.7
2	62.8	50.4			40.4	23.6

[a] Bailey (Ref. 3, p. 158).

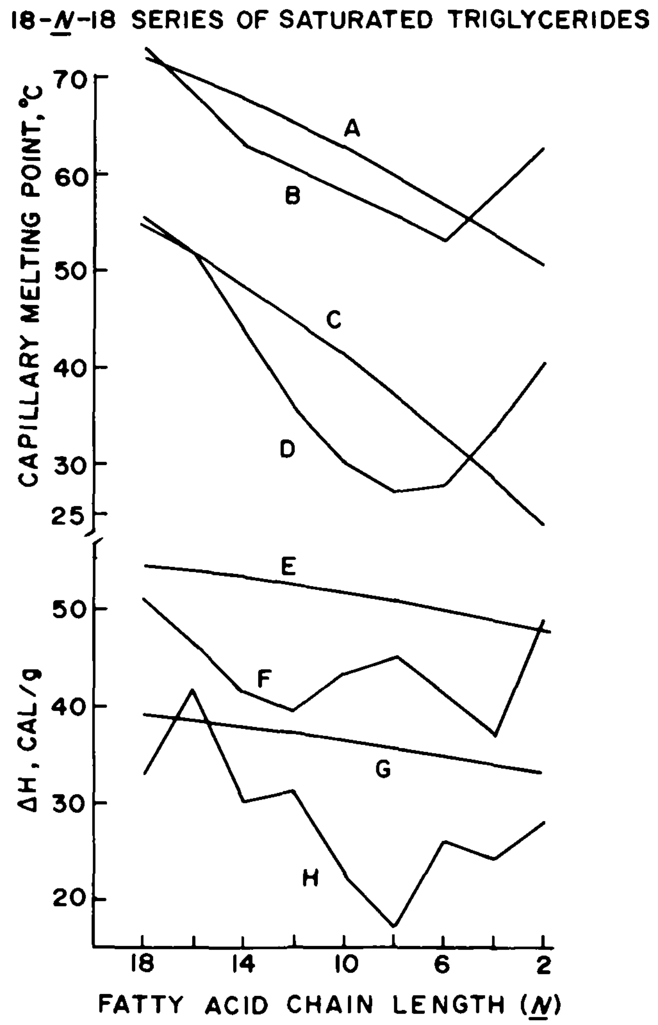

FIG. 5. Capillary melting points and calorimetric data for 18-*N*-18 series of saturated triglycerides. *Capillary melting points:* A, theoretical, β; B, form 1, (β); C, theoretical, α; and D, form 4, (α). *Calorimetric data:* E, theoretical ΔH_f, β; F, ΔH, form 1, (β); G, theoretical ΔH_f, α; and H, ΔH_c.

18-8-18

Two polymorphs at 55.8 and 27.2 C were found by both DSC and capillary melting, and there was good correlation of the melting temperatures. Only one polymorph was cited in the literature that melted at 51.8 C (3). This lower melting point is probably due to the presence of impurities since the work cited was reported in 1932. In the initial DSC heating at 5 C/min, 18-8-18 melted over a range of 54-57 C. After solidification and reheating at 5 C/min (Fig. 2), there was conversion without melting at 24-25.5 C, followed by melting of form 1 (β) at 50-56 C. At a heating rate of 10 C/min (Fig. 4), there was a small amount of melting at 23.5-25.5 C of form 4 (α), which almost immediately converted to form 1 (β) and melted over a range of ca. 48-58 C. At a heating rate of 80 C/min, the sample partially melted at ca. 25 C, then crystallized and converted to form 1 (β).

18-6-18

Three polymorphs at 53, 46, and 27.8 C were found by both DSC and capillary melting. Correlation of the melting temperatures was excellent. Two intermediate polymorphs melting at 46 C, based on microscopic examination and X-ray diffraction, are cited in the literature (9). Neither DSC nor capillary melting point determination lends itself to the differentiation of polymorphs having identical melting points. At a heating rate of 5 C/min (Fig. 2), form 4 (α) of 18-6-18 converted without melting at 25-30 C, then form 2 melted at 46 C and form 1 (β) at 53 C. A heating rate of 10 C/min (Fig. 4) gave similar results except for peak displacement due to temperature lag. A heating rate of 20 C/min was necessary before partial melting of form 4 (α) could be observed before it converted to form 2. The intermediate polymorph, at heating rates of 5 and 10 C/min, melted ober a wide range as a double peak. At higher heating rates, the intermediate polymorph melted essentially as a single form, the amount increasing as the heating rate increased. There was also an increase in the amount of form 4 (α) that melted before crystallization and conversion to form 2. The amount of form 1 (β) decreased as the heating rate increased, becoming negligible at 80 C/min. The double intermediate peak found at heating rates of 5 and 10 C/min probably is the result of the melting of form 2 and the simultaneous conversion, with accompanying exothermic change, to form 1 (β). At a heating rate of 5 C/min, a small amount of crystallization and conversion continues to take place at 46-47 C after form 2 completes melting at 46 C and before melting of form 1 (β) at 47-53 C.

18-4-18

Three polymorphs at 53, 38, and 33.4 C were found by both DSC and capillar melting. There was good correlation of the melting temperatures. Three polymorphs melting at 54.8, 42.7, and 33.4 C, based on X-ray diffraction, are cited in the literature (10), but only form 4 (α), melting at 33.4 C, correlated with our findings. A form melting at 58 C was observed in the initial capillary melting of two separate samples of 18-4-18. The major melting took place at a lower temperature, but a persistent cloudiness continued until complete melting took place at 58 C. It is possible that 18-4-18 converts very slowly and with difficulty to a higher melting polymorph. After initial melting, carefull tempering did not produce a polymorph melting at higher than 53 C. Apparently, the polymorph that melts at 58 C in so small an amount that it cannot be detected by DSC.

Initial DSC melting of 18-4-18 at 5 C/min was over a 45-53 C range. When the sample was reheated at 5 C/min (Fig. 2), melting occurred as a double peak at 33.5-38-43 C. Approximately the same melting behavior occurred when the sample was heated at 10 C/min (Fig. 4), except that more melting occurred in the lower range since there was less time for conversion to the higher melting form. These appear to be the two low melting polymorphs, although the melting of each begins at the temperature at which capillary melting occurs. When the sample is cooled and immediately reheated, its crystal structure may be such that heat transfer within the sample is slower than is usual for the other similarly treated triglycerides in the series. The temperature lag is ca. 1 min at the 5 C/min heating rate. With slow and tedious tempering, the sample can be converted to the high melting polymorph, which melted over a 51-53 C range. This melting range is considerably sharper than that found during initial melting (45-53 C). 18-4-18 appears to encounter difficulties in forming an ordered crystal structure during crystallization and tempering. The original sample, which was crystallized from solvent, had a broad melting range on initial DSC melting and also gave evidence during initial capillary melting of a higher melting polymorph heretofore unreported.

18-2-18

Three polymorphs at 62.8, 60.8, and 40.4 C were found by both DSC and capillary melting, and there was very good correlation of the melting temperatures. Two polymorphs melting at 62.8 and 40.4 C, based on X-ray diffraction, are cited in the literature (10). In the initial heating at 5 C/min, 18-2-18 melted over a range of 59-63 C, primarily in form 1 (β) with ca. 10% form 2. After solidification and remelting at 5 C/min (Fig. 2), form 4 (α) melted sharply at 40-42 C, then crystallized and converted at 42-51 C. At ca. 57 C, form 2 starts to melt and at ca. 62-63.5 C, form 1 (β) melts. At a 5 C/min heating rate, conversion is primarily to form 2, with 15-20% to form 1 (β). At a heating rate of 10 C/min (Fig. 4), form 4 (α) melted at ca. 40-44 C, slowly crystallized and converted from 44-60 C, then form 2 melted at 60-65 C. Apparently, there was insufficient time for complete conversion to form 2 to take place, and there is no evidence of the presence of form 1 (β). At a heating rate of 20 C/min, very little of the sample converted to form 2. Stepwise tempering from 58 C up to 61 C for ca. 50-60 min converted all of the sample to form 1 (β), which melted at 61-63 C.

Crystallization

Crystallization of the 1,3-distearo triglycerides from the melt at a cooling rate of 5 C/min gave form 4 (α) except in the case of 18-10-18 and 18-8-18. 18-10-18 crystallized in an intermediate form but, at a cooling rate of 10 C/min, began crystallizing in an intermediate form and completed crystallization in form 4 (α). 18-8-18 began crystallizing in an intermediate form but completed crystallization in form 4 (α). At a cooling rate of 10 C/min, a small amount of 18-8-18 crystallized in the intermediate form followed by rapid crystallization in form 4 (α). At a cooling rate of 20 C/min, 18-8-18 crystallized in the intermediate form followed by rapid crystallization in form 4 (α). The two 1,3-distearo triglycerides, 18-10-18 and 18-8-18, with fatty acids ca. half the length of the stearic acid have the least stable low melting polymorphs and rapidly convert to form 1 (β).

Calorimetry

The calorimetric data for the 18-*N*-18 series of triglycerides (Table I) include the heat of fusion (ΔH_f) for form 1 (β) and the heat of crystallization (ΔH_c). The ΔH_c values were reported rather than ΔH_f because melting of form 4 (α) was obtained by DSC for less than half of the series, although crystallization for form 4 (α) could be obtained in all instances. The theoretical values for ΔH_f of form 1 (β) and form 4 (α) of the series of triglycerides were calculated according to the equations given in Bailey (3).

The ΔH_f, 51.1 cal/g, for form 1 (β) of 18-18-18 is lower than the 54.6 and 54.5 cal/g previously obtained by calorimetry (11) or the 54.5, 54.9, and 55.0 cal/g obtained by differential thermal analysis (DTA) (12, 13), but is higher than the 50.0 and 50.7 cal/g previously obtained by DSC (14). The ΔH_c, 32.9 cal/g, is considerably lower than the ΔH_f of 38.9 cal/g for form 4 (α) previously obtained by calorimetry (10). Calorimetric data for other triglycerides of the 18-*N*-18 series have not been reported previously. Calorimetric data for intermediate polymorphs, when present, are not given because conversion to a particular intermediate polymorph is either incomplete or conversion to a higher polymorph occurs during the melting.

In the lower part of Figure 5 the calorimetric data for ΔH_f, form 1 (β) and ΔH_c for the 18-*N*-18 series have been plotted along with the calculated ΔH_f's form 1 (β) and form 4 (α), for comparison. The three triglycerides of the series, 18-10-18, 18-8-18, and 18-6-18, which have low ΔH_c values have the least stable lower melting polymorphs and rapidly convert to form 1 (β). There is poor correlation between the calorimetric data obtained experimentally for the 18-*N*-18 series of triglycerides and the theoretical values.

The theoretical values are derived from single saturated acid triglycerides. Chain packing in this series would be similar for the various members. The experimental values are derived from diacid saturated triglycerides in which the fatty acid in the 2-position varies in length. The variation in the configuration of the triglycerides in this series affects the chain packing of the individual members, thus their polymorphic behavior. There is considerable variation in the stability of the lower polymorphs and the ease with which conversion to higher polymorphs takes place. The variation in configuration in the triglycerides and the consequent differences in chain packing account for the lack of correlation between the experimental and theoretical caloric values.

Capillary Melting Points

The capillary melting point data for the 18-*N*-18 series of triglycerides (Table II) include the melting points for four polymorphic forms. Form 1 (β) and form 4 (α) were obtained for all samples. Form 2 (β') was obtained for 18-12-18, 18-6-18, and 18-4-18. Form 3 was obtained for 18-12-18 and 18-4-18. The theoretical melting points for form 1 (β) and form 4 (α) of the series of triglycerides were derived from melting vs. total chain length curves of saturated triglycerides (3).

The capillary melting point, 73.0 C, for form 1 (β) of 18-18-18 is slightly higher than the 72.5 C previously obtained by calorimetry (10) and slightly lower than the 73.5 C obtained by DTA (14). The capillary melting point, 55.3 C, of form 4 (α) is higher than the 54.0 C obtained by calorimetry or the 54.7 C obtained by DTA (15). Two intermediate polymorphs, one melting at 63.2 C (DTA) (15), and two at 61 and 64 C (infrared) (7) were not obtained except for one at ca. 63 C in a sample of tristearin that was determined to be slightly impure by gas liquid chromatography.

The melting point data for the 18-*N*-18 series have been covered extensively, along with the DSC data, during the discussion of the polymorphism of the individual triglycerides.

In the upper part of Figure 5, the melting point data for form 1 (β) and form 4 (α) for the 18-*N*-18 series have been plotted along with the calculated melting points of the two polymorphs, for comparison. The three triglycerides of the series, 18-10-18, 18-8-18, and 18-6-18, which have low melting points for form 4 (α), correspond to the three low ΔH_c values determined by DSC. The correlation between the melting point data obtained experimentally for the 18-*N*-18 series and the theoretical values is poor, but is somewhat better for form 1 (β) than for form 4 (α).

DSC heating scans of the 18-*N*-18 series of saturated triglycerides are useful in determining the polymorphs that would be encountered under normal melting and solidification conditions. Cooling scans, in some instances, are useful in indicating triglycerides that convert very rapidly to higher polymorphs. A knowledge of the polymorphic behavior and caloric requirements of pure triglycerides can be applied to an understanding of the stability, rate of polymorphic change, and the energy requirements of natural and modified fats and oils.

REFERENCES

1. Lutton, E.S., JAOCS 27:276 (1950).
2. Malkin, T., "Progress in the Chemistry of Fats and Other Lipids," Vol. 2, Academic Press, Inc., New York, 1954.
3. Bailey, A.E., "Melting and Solidificaiton of Fats," Interscience Publishers, Inc., New York, 1950.
4. Chapman, D., Chem. Rev. 62:433 (1962).
5. Chapman, D., "The Structure of Lipids," John Wiley and Sons, New York, 1965.
6. Rebello, D., "Technical Report of Grant Number FG-In-118, Project Number UR-A7-(40)-3," Bombay University Press, 1967.

7. Hagemann, J.W., and W.H. Tallent, JAOCS 49:118 (1972).
8. Gray, M.S., N.V. Lovegren, and R.O. Feuge, Ibid. 53:727 (1976).
9. Hugenberg, F.R., and E.S. Lutton, J. Chem. Eng. Data 8:606 (1963).
10. Jackson, F.L., R.L. Wille, and E.S. Lutton, J. Am. Chem. Soc. 73:4280 (1951).
11. Charbonnet, G.H., and W.S. Singleton, JAOCS 24:140 (1947).
12. Moran, D.P.J., J. Appl. Chem. 13:91 (1963).
13. Yoncoskie, R.A., JAOCS 44:446 (1967).
14. Hampson, J.W., and H.L. Rothbart, Ibid. 46:143 (1969).
15. Lutton, E.S., and A.J. Fehl, Lipids 5:90 (1970).

[Received April 4, 1977]