Technical

Polymorphism of Saturated Triglycerides: II.
1,3-Dipalmito Triglycerides

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ABSTRACT

Differential scanning calorimetry was used to examine triglycerides of the 16-N-16 series, where N is an even-carbon, saturated fatty acid of 2 to 18 carbons in length. The procedures used to obtain heats of fusion and crystallization of the various triglycerides and their polymorphs are described. Small samples (ca. 1-2 mg) were used to investigate polymorphs with relatively rapid rats 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 are given.

INTRODUCTION

The polymorphism of individual triglycerides of the 16-N-16 series, where N is an even-carbon, saturated fatty acid of 2 to 18 carbons in length, has been studied and reviewed by a number of investigators (1-5). 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 observe the changes that take place. These procedures permit the study of those polymorphs that are encountered in the normal melting and solidification procedures used in commercial operations with fats.

MATERIALS AND METHODS

The triglycerides of the 16-N-16 series were synthesized and supplied to us by D. Rebello, University of Bombay, India, through a PL-480 cooperative project sponsored by the U.S. Department of Agriculture (6). The triglycerides were prepared using the acylation procedure of Jackson et al. (7) as modified by Craig et al. (8) and were 99.8% pure when checked by thin layer chromatography for absence of partial glycerides and free fatty acids. The structural purity was greater than 99.5% by lipase hydrolysis.

We used a Perkin-Elmer DSC-1 differential scanning calorimeter (DSC) calibrated with indium, tin, and naphthalene to ensure the accuracy of caloric data at different range settings. Calibration of the temperature scale at the scanning rates used and the techniques employed to obtain consistent results have been described previously (9). A sample of 2.0 mg or less was used to study polymorphism to minimize heat transfer problems, and a sample of ca. 12 mg to obtain more accurate caloric values. Routinely, samples were scanned at 5 and 10 C/min. At heating rates below 5 C/min, the temperature lag is negligible, but the baseline is difficult to determine in some instances. The slower heating rates are useful for determining the melting temperature; the temperature lag in heating rates higher than 2.5 C/min is measurable and reproducible.

The highest melting polymorph (form 1, or β) was obtained on solvent-crystallized samples in most cases. Intermediate polymorphs were obtained after a slow, stepwise tempering of the sample in the calorimeter following its crystallization from the melt (9). Certain samples with unstable, lower melting polymorphs were quickly chilled from the melt to ca. -10 C and then heated at higher scanning rates.

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, whereas those melting between, when found, are referred to as intermediate, to facilitate comparison to the polymorphs reported in the literature. The 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. We derived caloric data for the heat of crystallization (ΔH_c) for the α-form from the cooling scans. In some instances, there was little or no melting of the α-form 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.

Capillary melting points were determined in a Thomas-Hoover Uni-Melt capillary apparatus. A heating rate of 0.5 C/min was used for the high melting, stable polymorph. With the more unstable polymorphs a "thrust in" technique was used. The sample was melted, solidified rapidly, thermally treated as desired, then thrust in at the testing temperature to see if it melted. This procedure was repeated at 0.1 C intervals 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 higher melting polymorph. Theoretical melting point data were derived from melting vs. total chain length curves of saturated triglycerides (3).

RESULTS

Initial melting of the 16-N-16 series of saturated triglycerides was on solvent-crystallized samples. Caloric data for
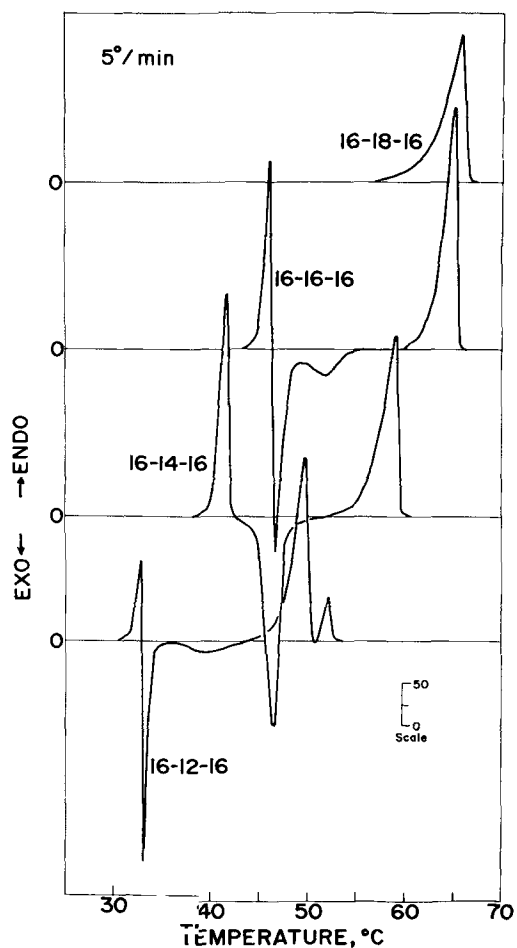
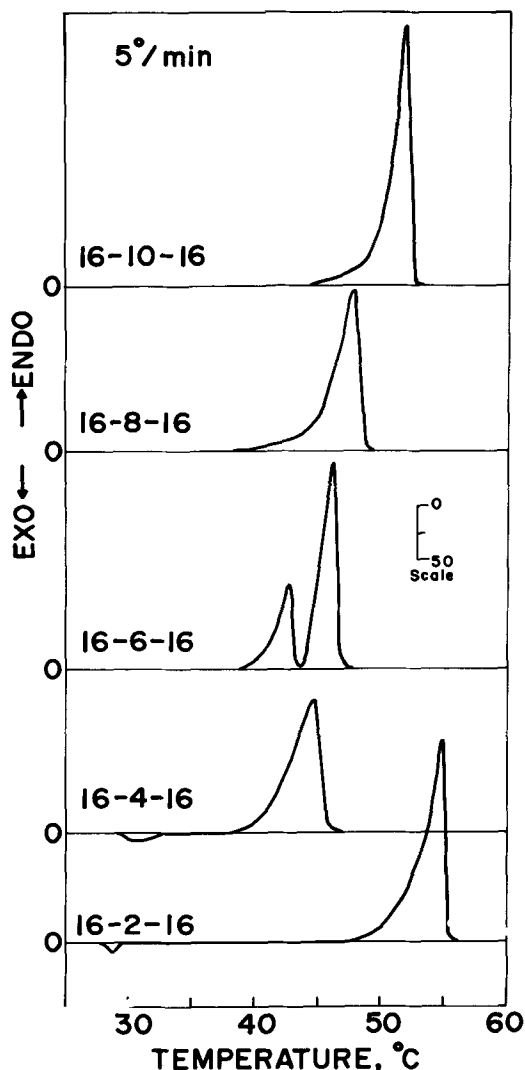FIG. 1. DSC heating curves, cooled from melt and heated at 5 C/min.

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

form 1 (β) were derived from the initial melt of the larger samples that had been heated rapidly to just below the melting temperature of form 1 and held there to permit tempering of any intermediate polymorph present. Three triglycerides, 16-12-16, 16-10-16, 1-8-16, and possibly 16-14-16, contained small amounts of form 2 (β') when the small samples were initially melted. A small amount of a higher melting polymorph was found in 16-4-16. After initial melting, the samples were cooled at either 5 or 10 C/min, then reheated at the same rate. Thermal changes that occur at a heating rate of 5 C/min are shown in Figures 1 and 2; those at 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 when a particular polymorph melts. Some of the lower melting polymorphs are not stable enough to completely melt before being converted 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 the higher polymorph. When a polymorph completely melts and then crystallizes to a higher 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 a measure of ΔH_t.

Calorimetric data for ΔH_f of form 1 (β) and ΔH_c for the 16-N-16 series of saturated triglycerides are given in Table I, and the 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 16-N-16 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.

16-18-16

Two polymorphs at 67 and 47 C were found by both DSC and capillary melting techniques. These melting points correlate well with the 68.6 and 46.5 C reported in the literature (10). Lutton and Hugenberg (11) reported a metastable β-form that melted at 65.5 C, obtained with difficulty and identified with X-ray diffraction, in addition to α, mp 47 C, and β', mp 69 C. Initial melting of our solvent-crystallized sample occurred at ca. 61.5-67 C, and over an even broader range of 58-66.5 C after solidification and remelting at 5 C/min (Fig. 1). Form 4 (α) is very un-

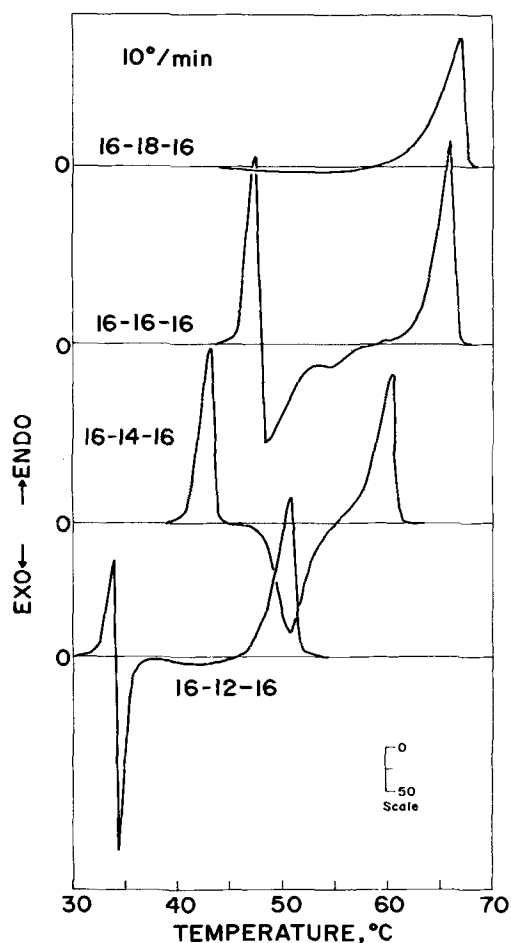FIG. 3. DSC heating curves, cooled from melt and heated at 10 C/min.

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

stable, and partial melting did not occur at a heating rate below 40 C/min, although conversion from form 4 (α) occurred to some extent without melting at 10 C/min (Fig. 3). There is a slight displacement of the peaks from the 5 C/min to 10 C/min DSC scans, caused by temperature lag.

16-16-16

Two polymorphs at 67 and 45 C were found by both DSC and capillary melting and an intermediate polymorph at 56 C by capillary melting. These melting points correlate well with the 66.4, 56.6, and 44.7 C cited in the literature (10). However, a recent DSC study (12) lists four polymorphs for tripalmitin that melt at 66, 57, 53, and 46 C, but we found no DSC evidence for one at 53 C. Initial melting of the solvent-crystallized sample occurred at ca. 63-67 C with a minimum of tailing. At a heating rate of 5 C/min, form 4 (α) melted, converted to the intermediate polymorph and then, without melting, converted to form 1 (β), which melted at 61.5-65.5 C (Fig. 1). A heating rate of 10 C/min gave similar results (Fig. 3).

16-14-16

Two polymorphs at 59.8 and 40 C were found by both DSC and capillary melting. These melting points correlate well with 60.3, 47.0, and 40.1 C but not so well with 60, 55, 46, and 37 C melting points cited in the literature (10). Initial melting of the solvent-crystallized sample occurred at ca. 53-60 C, with the major melting occurring at 56-60 C. When the sample was tempered for 1.5 hr near 55 C, form 1 (β) melted primarily at 57-60 C and a trace melted at 52-57 C. The melting range is broad for a pure
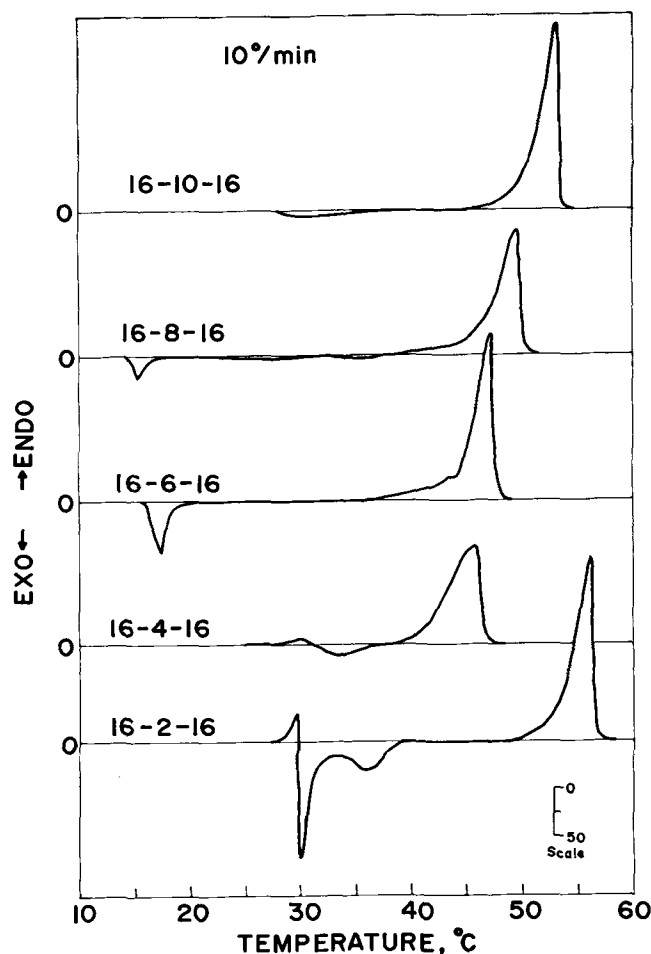
triglyceride, and 16-14-16 either encounters difficulties in forming an ordered crystal structure during crystallization, or an intermediate polymorph is present. At a heating rate of 5 C/min, form 4 (α) melted and converted to form 1 (β), which melted at 55-59.5 C (Fig. 1). A heating rate of 10 C/min gave similar results (Fig. 3). At a heating rate of 20 C/min, however, 16-14-16 melted almost entirely in form 4 (α), although there is a small amount of conversion at 53-58 C and form 1 (β) melted at 58-61 C.

16-12-16

Three polymorphs at 55, 49.1, and 31.2 C were found by both DSC and capillary melting. The correlation with the 53.5, 50, 47, and 34 C melting points cited in the literature (10) is only fair. Initial melting of the solvent-crystallized sample occurred at ca. 49.5-56 C and consisted primarily of form 1 (β), with a small amount of form 2 (β'). On tempering for 25 min at 51 C, all of the sample converted to form 1 (β) and melted at ca. 52-56 C. At a heating rate of 5 C/min, form 4 (α) melted, rapidly crystallized, and converted at 33-34 C. A slow conversion from 37-44 C followed, then an intermediate polymorph melted at ca. 44-50, and a small amount of form 1 (β) melted at 50.5-53 C (Fig. 1). At a heating rate of 10 C/min, the results were similar except that less conversion to form 1 (β) took place. The intermediate polymorph melted at 46-52.5 C; the small amount of form 1 (β) appeared as a tailing at 52.5-54 C (Fig. 3).

16-10-16

Three polymorphs at 52, 41, and 20 C were found

TABLE I

Calorimetric Data for 16-N-16 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	42.2	53.3	32.2	37.8
16	49.5	52.6	31.4	37.1
14	44.7	51.7	29.7	36.4
12	43.4	50.8	27.1	35.6
10	40.2	49.9	36.0[b]	34.8
8	39.2	48.8	16.3	33.9
6	41.4	47.7	26.4	32.9
4	44.7	46.5	25.3	31.8
2	42.1	45.1	28.1	30.6

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

[b]Crystallized in mixture of α- and β'-forms.

by both DSC and capillary melting. There is good correlation with three of the four melting points (51.5, 48, 42, and 20 C) reported in the literature (10). The lower melting polymorphs of 16-10-16 are very unstable, and their melting points cannot be determined by DSC. At heating rates of 20 and 40 C/min, the DSC scans show evidence of conversion of form 4 (α) to an intermediate polymorph, followed by a slow conversion to a higher polymorph. The intermediate polymorph (mp 41 C) melted, was followed by conversion, and form 1 (β) melted. There is evidence for a second intermediate polymorph because three conversions take place, two before the melting of the intermediate polymorph, and a third sharp conversion between the melting of the intermediate polymorph and form 1 (β). However, we were unable to determine the melting point of this unstable polymorph by either DSC or capillary melting. Initial melting of the solvent-crystallized sample occurred at ca. 45-53.5 C, and the major melting of form 1 (β) at 51-53.5 C. At a heating rate of 5 C/min, the sample melted as form 1 (β) at ca. 44-53 C, and the major melting took place at 48.5-53 C (Fig. 2). It is possible, in both the initial melt and the 5 C/min melt, that 16-10-16 is a mixture of form 1 (β) and an intermediate melting polymorph that melted and converted to form 1 (β) during heating. At a heating rate of 10 C/min, a slow conversion took place at 28-36 C, and the sample melted as form 1 (β) at ca. 44-54.5 C, and major melting was at 48-53.5 C (Fig. 4).

16-8-16

Two polymorphs at 48.5 and 13.2 C were found by both DSC and capillary melting. No melting point data are reported in the literature for this triglyceride. Initial melting of the solvent-crystallized sample was at ca. 40-51 C. An intermediate polymorph melted at ca. 40-45 C, and form 1 (β) melted at ca. 45-51 C. At a heating rate of 5

C/min, the sample melted at ca. 38-49.5 C; the major melting was at 44-48.5 C (Fig. 2). When the sample was tempered at 46 C for 33 min, chilled, then heated at 5 C/min, melting was over a norrower range of 45-49 C. This melt may be a mixture of form 1 (β) and an intermediate polymorph that melted and converted to form 1 (β) during heating. At a heating rate of 10 C/min, there is conversion of form 4 (α) without melting at 14-17 C, two slow conversions at 23-30 C and 32-37 C, and melting form 1 (β), along with probable melting and conversion of some form 2, at 38-51 C (Fig. 4). At heating rates of 20, 40, and 80 C/min, form 4 (α) melted at 14 C in successively larger amounts then rapidly converted to a mixture of form 1 (β) and an intermediate polymorph. There is evidence in the DSC heating scans for four polymorphs for 16-8-16 in that three conversions took place after form 4 (α) partially melted. The two intermediate polymorphs were very unstable. At a heating rate of 80 C/min, a small amount of form 3 melted before conversion, but none of form 2. At all heating rates, it appears that the small amount of form 2 present melted in the lower temperature range of the melting curve for form 1 (β).

16-6-16

Three polymorphs at 45.8, 44.1, and 15.7 C were found by both DSC and capillary melting. These are somewhat higher than the 44.5, 40.5, 40.5, and 13.4 C reported in the literature (13). Neither DSC nor capillary melting lends itself to the differentiation of the two intermediate polymorphs that melt at 40.5 C, which were based on microscopic examination and X-ray diffraction. Initial melting of the solvent-crystallized sample took place at 43-48.6 C with a minimum of tailing and no evidence of an intermediate polymorph. When the sample was tempered at ca. 43 C for 75 min, chilled, then heated at 5 C/min, melting was almost entirely over a narrower range of 45-49 C. At a heating rate of 5 C/min, form 2 melted at ca. 38.5-43.5 C and was followed immediately by the melting of form 1 (β) at ca. 43.5-47.5 C (Fig. 2). At a heating rate of 10 C/min, form 4 (α) converted without melting at 15.5-20.5 C, polymorph 2 partially melted and converted at ca. 36-43.5 C, and polymorph 1 (β) melted at ca. 43.5-48.5 C. At a heating rate of 20 C/min, a small amount of form 4 (α) melted at ca. 15 C then rapidly converted at 16-17.5 C, form 2 melted at 38.44 C, and form 1 (β) at 44-48 C.

16-4-16

Four polymorphs at 56, 46, 27.2, and 20.6 C were found by both DSC and capillary melting. Three polymorphs, based on microscopic examination and X-ray diffraction, have been reported in the literature at 46.5, 32.6, and 20.6 C (13). The polymorphs we found that melt

TABLE II

Capillary Melting Point Data for 16-N-16 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	67.0	67.8			47.0	48.6
16	67.0	65.4	56.0		45.0	45.0
14	59.8	62.8			40.0	41.3
12	55.0	59.9	49.1		31.2	37.2
10	52.0	57.0	41.0		20.0	33.0
8	48.5	53.9			13.2	28.7
6	45.8	50.4	44.1		15.7	23.6
4	56.0	46.8	46.0	27.2	20.6	18.5
2	54.8	42.8	33.6		28.1	12.8

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

at 46 and 20.6 agree closely with those reported. The intermediate polymorph, mp 27.2 C, melted considerably lower than that reported at 32.6 C. The higher melting polymorph, mp 56 C, has not been reported previously. It was obtained on the initial melt of two capillary tubes and on the initial DSC scan of 16-4-16 at 5 C/min, where it was ca. 10% of the observed melt. In the initial melting of the larger (13.7 mg) solvent-crystallized sample, form 2 melted at ca. 41-50.5 C and form 1 at ca. 50.5-55.8 C. This polymorph (mp 56 C) was not obtained by tempering after the initial melt. Apparently 16-4-16 converts to this higher polymorph with difficulty and only a limited amount formed during solvent crystallization. The fact that evidence for this polymorph is found only on initial melting and is not in later melts, even after tempering in the calorimeter, essentially rules out the possibility that the sample contains an impurity. At a heating rate of 5 C/min, conversion to form 2 took place without melting, and melted at ca. 38-47 C. (Fig. 2). Form 2 corresponds to the β-form reported in the literature (13). At a heating rate of 10 C/min, a small amount of form 3 melted at ca. 27.5-31.5 C; converted to form 2 at ca. 31.5-36.5 C; and melted at ca. 38.5-48 C (Fig. 4). At a heating rate of 80 C/min, a small amount of form 4 (α) melted before being converted to form 3, a small amount of which melted, converted to form 2, and then melted.

16-2-16

Three polymorphs at 54.8, 33.6, and 28.1 C were found by both DSC and capillary melting. There is close correlation with the two polymorphs, 54.8 and 28.4 C, reported in the literature for the β- and α-forms (13). The intermediate polymorph was not reported previously. The solvent-crystallized sample initially melted at 49.3-56.6 with a moderate amount of tailing. At a heating rate of 5 C/min, form 4 (α) converted without melting at ca. 27.5-29 C, and form 1 (β) melted at ca. 47.5-56 C (Fig. 2). At a heating rate of 10 C/min, form 4 (α) started to melt at ca. 27-30 C, rapidly converted to form 2 at ca. 30-33 C, converted without melting to form 1 (β) at ca. 33-39 C, and form 1 melted at ca. 49-58 C. Similar results were obtained at 20 and 40 C/min heating rates except that increasingly larger amounts of form 4 (α) melted before conversion to the higher forms took place.

Crystallization

The 1,3-dipalmito triglycerides crystallized from the melt at a cooling rate of 5 C/min in one of two forms, or a mixture of these forms in varying proportions depending on the stability of form 4 (α). Three triglycerides, 16-16-16, 16-14-16, and 16-12-16, crystallized in form 4 (α). The next two triglycerides of the series, 16-10-16 and 16-8-16, crystallized in an intermediate form. A cooling rate of 20 C/min was necessary before 16-10-16 crystallized partially in form 4 (α), but 16-8-16 crystallized partially in form 4 (α) at 10 C/min. Four triglycerides, 16-18-16, 16-6-16, 16-4-16, and 16-2-16, crystallized in a mixture of form 4 (α) and a higher melting form when cooled at 5 C/min, and 16-18-16 crystallized primarily in form 1 (β) with a small amount in form 4 (α). A cooling rate of 20 C/min was required before the major portion of 16-18-16 crystallized in form 4 (α). At a cooling rate of 10 C/min, 16-6-16 crystallized about equally in two forms, α and intermediate. At more rapid cooling rates, the proportion of crystallization in form 4 (α) increased. At a cooling rate of 5 C/min, 16-4-16 crystallized, with ca. 80% in form 3 and 20% in form 4 (α). At a 20 C/min cooling rate, about half crystallized in form 4 (α). At a cooling rate of 5 C/min, 16-2-16 crystallized, with ca. 33% in an intermediate form and 67% in form 4 (α). At 10 C/min, all of 16-2-16 crystal-
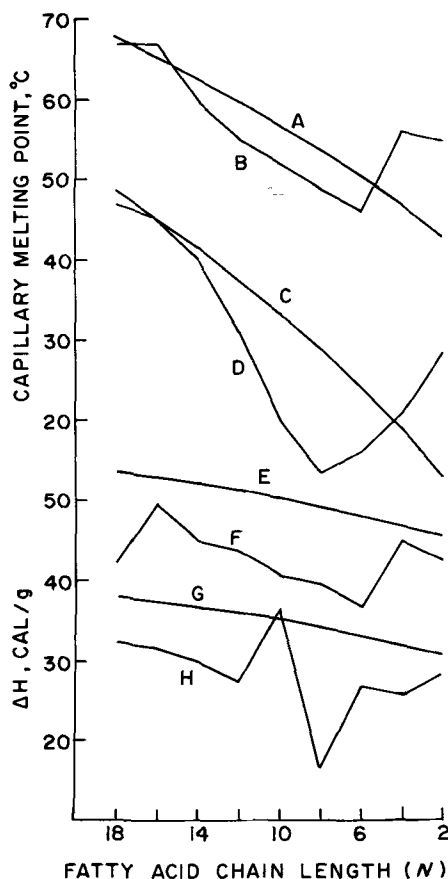

FIG. 5. Capillary melting points and calorimetric data for 16-N-16 series of saturated triglycerides. *Capillary melting points:* A, theoretical, β; B, form 1 (β); C, theoretical, α; and D, form 4, (α). *Calorimetric data:* E, theoretical ΔH_f, β; F, ΔH_f, form 1, (β); G, theoretical ΔH_f, α; and H, ΔH_c.

lized in form 4 (α).

Calorimetry

The calorimetric data for the 16-N-16 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 the 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 most cases. The exception was 16-16-16, which crystallized partially in a higher polymorph at all cooling rates. 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, 49.5 cal/g for form 1 (β) of tripalmitin is lower than the 53 and 53.2 cal/g previously obtained by calorimetry (14) or the 52.8 and 53.4 cal/g obtained by differential thermal analysis (15), but is slightly higher than the 49.2 cal/g obtained by DSC (16). The ΔH_c, 31.4 cal/g, is considerably lower than the ΔH_f of 37.4 cal/g for form 4 (α) obtained by calorimetry (14). Calorimetric data for other triglycerides of the 16-N-16 series have not been reported previously. Calorimetric data are not given for intermediate polymorphs, when present, because conversion to a particular intermediate polymorph is either incomplete or conversion to a higher polymorph occurs during melting.

In the lower part of Figure 5 the calorimetric data for ΔH_f, form 1 (β), and ΔH_c for the 16-N-16 series have been plotted. The calculated ΔH_f's of form 1 (β) and form 4 (α)

are included for comparison. The unusually high value for the ΔH_c of 16-10-16 includes calories from the higher polymorph. The instability of form 4 (α), precluded measurement of calories for the pure form 4 (α).

Capillary Melting Points

The capillary melting point data for the 16-N-16 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 all triglycerides in the series except for 16-18-16, 16-14-16, and 16-8-16. Form 3 was obtained only for 16-4-16.

The capillary melting point technique provides an accurate method for the determination of the form 1 (β) melting point of triglycerides. The "thrust in" technique, previously described, is useful for the determination of form 4 (α) and the intermediate melting points. In some instances, the melting point of form 4 (α) and certain intermediate melting points could be determined only by this technique. DSC was unsuitable where the polymorphs were unstable and where melting and transition to a higher form took place rapidly.

DISCUSSION

There is poor correlation between the caloric data obtained experimentally for the 16-N-16 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, and 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 melting polymorphs and the ease with which conversion to higher polymorphs takes place. The variation in configuration in the polymorphs and consequent differences in chain packing account for the lack of correlation between the experimental and theoretical calorie values.

The melting point data for the 16-N-16 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) have been plotted. The calculated melting points of the two polymorphs are included for comparison. The correlation between the melting point data obtained experimentally for the 16-N-16 series and the theoretical values is poor, but is somewhat better for form 1 (β) than for form 4 (α). This would be expected when the fatty acid in the 2-position varies in length.

In the 18-N-18 and 16-N-16 series of triglycerides, the lowest form 4 (α) melting and the lowest ΔH_c occurred where N was the 8-carbon fatty acid. There is similarity in

polymorphic behavior in 18-18-18 and 16-16-16, 18-16-18 and 16-14-16, and 18-14-18 and 16-12-16. The various triglycerides in the 16-N-16 series convert more rapidly to higher polymorphs than do the corresponding triglycerides in the 18-N-18 series. No data have been reported previously on 16-8-16, for which there is DSC evidence for three polymorphs. Two polymorphs, form 1 (β) (mp 48.5 C) and form 4 (α) (mp 13.2 C), were found by capillary melting. A polymorph of 16-4-16, mp 56.0 C, not previously reported, was found by capillary melting and DSC in the initial melting of the solvent-crystallized sample. Form 2 (mp 46.0 C) corresponded to the β-form reported in the literature (13). The 56.0 C polymorph may be comparable to the metastable β'-form reported by Lutton and Hugenberg for 16-18-16 and 18-16-18 (11). An intermediate polymorph of 16-2-16 (mp 33.6 C), not previously reported, was found by capillary melting and DSC. We have designated this polymorph form 2 (β'), but have not confirmed the polymorphism by X-ray diffraction.

DSC heating scans of the 16-N-16 series of saturated triglycerides are useful in determining the polymorphs and the rate of conversion to higher polymorphs that would be encountered under normal working 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 for a better understanding of the stability, rate of polymorphic change, and the energy requirements of natural and modified fats and oils.

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