

Differential Scanning Calorimetry of Single Acid Triglycerides: Effect of Chain Length and Unsaturation¹

J.W. HAGEMANN² and W.H. TALLENT,
Northern Regional Research Laboratory,³ Peoria, Illinois 61604
and K.E. KOLB, Department of Chemistry,
Bradley University, Peoria, Illinois 61604

ABSTRACT

The polymorphism of 13 single acid triglycerides with acyl group chain lengths ranging from 16-22 was studied by differential scanning calorimetry. In contrast to the single β' -form generally attributed to such triglycerides, at least two intermediate endotherms were found for most samples between the least stable (α) and most stable (β) polymorphs. For saturated triglycerides, two versions of the familiar "tuning fork" model meet the β' -form requirement of alternate fatty acid chains in planes perpendicular to each other. The detection of three intermediate endotherms for triolein, tri-*cis*-11-octadecenoin and trierucin (and possibly also trilinolein) may be rationalized by assuming that the segments of polymethylene chains on either side of double bonds may zigzag in different planes. Four exceptions for which no evidence was found for β' -forms are tri-*cis*-6-octadecenoin, tri-*cis*-6-hexadecenoin, tri-*trans*-6-octadecenoin and trielaidin. Three of these exceptions contain $\Delta 6$ -acyl groups and have in common segments with even numbers of methylene groups on either side of the double bonds. These same three triglycerides also have a shorter than usual polymethylene segment between the ester linkages and the double bonds and a longer than usual distance from the double bonds to the terminal methyl groups. Tri-*trans*-6-octadecenoin and trielaidin are exceptional in still another way. Only they and are exceptional in still another way. Only they and trierucin exhibited significant nonconformity with an empirical relationship between melting points and heats of fusion of β -forms. Otherwise, all points in a plot of the former physical constants vs. the latter closely fit a smooth curve, the positive slope of which gets larger as the X-axis values, i.e., melting points, increase.

INTRODUCTION

Differential scanning calorimetry (DSC) is a relatively new technique (1) similar to differential thermal analysis (DTA) but having the advantage of providing a more direct measurement of the ΔH accompanying the physical and chemical changes studied. Both techniques reveal the temperature at which these transitions occur. In the field of fats and oils, DSC has been used to measure fat solids (2,3), crystallinity of edible fats (4,5), the keeping time of commercial fats (6) and heats of fusion of pure triglycerides (7). Palmitic-stearic (8) and palmitic-stearic-oleic triglycerides (9), natural fats and oils (10-12) and thermal properties of edible fats (13-15) have been examined by DTA. Recently DTA was used in conjunction with X-ray diffraction to study the polymorphism of single-saturated fatty-acid odd-and-even triglycerides, C₈ through C₂₂ (16).

Triglyceride polymorphism has been reviewed well by

Chapman (17), Larsson (18) and Hoerr and Paulicka (19). Briefly, it is now generally agreed that the α -form is the lowest sharp-melting polymorphic form and has a hexagonal crystal subcell. The highest melting polymorph is the β -form, which has a triclinic subcell, and the intermediate melting β' -forms are orthorhombic. The planes in which polymethylene chains zigzag are all parallel in the β -form, while in the β' -form the plane of every second chain is perpendicular to the planes of the others. Some degree of twisting or torsional oscillation in polymethylene chains is believed to take place in α -forms. The pure β -form can be crystallized from solvent.

In the present study, DSC was used to study the effect of chain length and unsaturation on the polymorphism of monoacid triglycerides.

MATERIALS AND METHODS

Tripalmitin, tristearin, trielaidin, triolein, trilinolein, tripetroselinin (tri-*cis*-6-octadecenoin), triecosanoin and tridocosanoin, all 99% pure by thin layer chromatography (TLC), were supplied by The Hormel Institute, Austin, Minnesota. Trierucin, 99% pure by TLC (20) and gas liquid chromatography (GLC) (21), was provided by H. Grynberg of the Institute of General Chemistry, Warsaw, Poland. Tripetroselaidin (tri-*trans*-6-octadecenoin), tri-*cis*-11-octadecenoin, tri-*cis*-6-hexadecenoin and tri-*trans*-13-docosenoin were prepared by conventional esterification of the appropriate fatty acid with glycerol (Fisher Certified Reagent) in the presence of *p*-toluenesulfonic acid as catalyst. The *cis*-11-octadecenoic acid also came from The Hormel Institute. Petroselaidic (*trans*-6-octadecenoic) and *trans*-13-docosenoic acids were made by elaidinization (22) of petroselinic (*cis*-6-octadecenoic) and erucic (*cis*-13-docosenoic) acids, respectively. *Cis*-6-Hexadecenoic acid was isolated from the oil of *Thunbergia alata* Boj. ex Sims (23). After purification by preparative TLC (24), the four triglycerides were estimated to be more than 95% pure by GLC (21) and TLC of the triglycerides and methyl esters prepared from them. Methyl esters were analyzed by GLC in a Packard Model 7401 equipped with a flame ionization detector and a 12 ft x 1/4 in. glass column packed with 5% LAC-2-R 446 on Chromosorb W AW-DMCS. The injection port was held at 220 C and the column at 200 C.

The differential and average temperature controls of the Perkin-Elmer DSC-1B were calibrated using benzene (Baker Analyzed Reagent). Melting point calibration curves were prepared by melting standard materials at scan speeds of 10, 2.5 and 1.25 C/min, and plotting the difference between the literature and instrument temperatures at each scan speed. Standard materials for the calibration curves included methyl esters of octanoic, decanoic, hexanoic, lauric, myristic, stearic and docosanoic acids (The Hormel Institute), CHC₁₃ and CC₁₄ (Matheson Coleman & Bell Spectroquality), and vanillin (a melting point standard, Arthur H. Thomas Co.).

In the DSC of triglycerides, each sample was weighed into an aluminum pan to the nearest 0.01 mg with a Cahn RG Electrobalance Model 2000. A similar empty pan served as a reference. Sample size varied from 2-8 mg for the

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²Submitted as partial MS requirement, Bradley University.

³N. Market. Nutr. Res. Div., ARS, USDA.

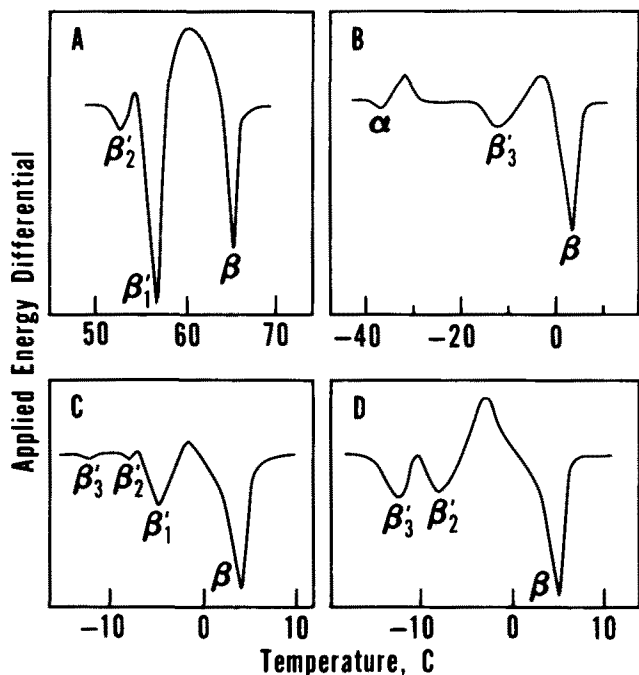


FIG. 1. Typical differential scanning calorimetry curves with endotherms shown as negative peaks. (A) Tripalmitin, heating rate 10 C/min after holding 15 min at 46 C. (An α -form not shown was observed after rapid cooling.) (B) Triolein, heating rate 10 C/min after rapid cooling. (C) Triolein, heating rate 2.5 C/min after holding 1 hr at -14 C. (D) Triolein, heating rate 2.5 C/min after holding 2 hr at -26 C.

saturated and *trans* triglycerides, and from 10-20 mg for the unsaturated triglycerides. Sample pans were surrounded by nitrogen at a flow rate of 30 ml/min as measured at the bypass outlet. Heating scans were run on each sample at 10, 2.5 and 1.25 C/min. Liquid nitrogen was used as coolant. Before each heating scan, the temperature was lowered at 20 C/min to 20 C below an exotherm corresponding to solidification of the sample. To find α -forms, this cooling was preceded by holding the sample at 20-25 C above the melting point of the β -form for 10 min. Samples were conditioned, usually for 15-60 min, at the lowest melting form or slightly below to prepare β' -forms. Melting points were obtained by correcting the peak temperature for thermal lag. As recommended (25), this lag was determined from the slope of the leading edge of an endotherm for 99.999% pure indium (Perkin-Elmer Co.) recorded at the same scan speed and sensitivity as the triglyceride DSC curve.

In the determination of ΔH_f some samples were used as received in the pure β -form and others were converted to this form by crystallization from solvent (18). For triglycerides easily and completely converted to the β -form by thermal conditioning, a single peak for the highest melting polymorphic form was obtained by heating the triglyceride for at least 1 hr at a temperature slightly above the lowest melting form. The values of ΔH_f were found by comparing the area of the endotherm of the pure β -form (also α -form for tridocosanoin and a β' -form for tri-*cis*-11-octadecenoin) with the area of the pure indium ($\Delta H_f = 6.79$ cal/g) (26) endotherm recorded under identical conditions. Peak areas were measured with a No. 2107 Bowen and Company planimeter. The scan speed for ΔH_f determinations was 2.5 C/min.

For slow-cooling scans the temperature was programmed downward at 0.625 C/min from 20 C above the highest melting point.

IR spectra were determined at 22 C with a Perkin-Elmer Model 337 spectrophotometer. Samples were allowed to crystallize from solvent to produce β -forms (18) on an

TABLE I

Melting Points and Heats of Fusion of Triglycerides

Triglyceride	NRRL-Bradley University Study										ΔH_f , cal/g (β -form)		
	Previous reports					Form and mp, C							
	α	β'	β	Reference	α	β_3	β_2	β_1	β	β			
Trilaurin	15.2	34	46.5	(16)								66	49.0
Trimyristin	32.8	45.0	58.5	(16)								73	51.4
Tripalmitin	44.7	56.6	66.4	(17)	46		53					78	54.6
Tristearin	54.7	63.2	73.5	(16)	55		61					83	59.1
Triicosanoin	61.8	69	78.1	(16)	64		69					15	27.7
Tridocosanoin	68.2	74	82.5	(16)	70 ^a		74					41	39.5
Tri- <i>cis</i> -6-hexadecenoin					-15							5	25.8
Trielaidin	15.5	37(?)	42	(28) ^b	15		-8					10	27.1
Triolein	-32	-12	4.9	(28)	-37		-27					28	30.7
Trilinolein ^c	-49-44	-29-27	-10.5	(30)	-84		0					52	43.0
Tri- <i>cis</i> -11-octadecenoin					(-11) ^e							32	33.0
Tripetroselinin					(-2) ^e							58	34.4
Tripetroselaidin					(32) ^e								
Trierucin	6	17,25	30	(28) ^b	(12) ^e								
Tri- <i>trans</i> -13-docosenoin	43	50	59	(28)	40								

^a $\Delta H_f = 32.3$ cal/g.
^bSee also Reference 17.
^cForm I: -12.9; Form II: -45.6 (29).
^dSee text.
^eEstimated from slow-scan cooling curve.
^f $\Delta H_f = 21.5$ cal/g.

TABLE II

Production of β' - and Pure β -Forms by Thermal Conditioning		
Triglyceride	Conditioning time, min ^a	
	β' -forms	Pure β -forms
Tripalmitin	15	30
Tristearin	30	60
Triecosanoin	45	120
Tridocosanoin	60	150
Tri- <i>cis</i> -6-hexadecenoin		30
Trielaidin		60
Triolein	0-120	60
Trilinolein	0-60	60
Tri- <i>cis</i> -11-octadecenoin	0-60	...b
Tripetroselinin		60
Tripetroselaidin		30
Trierucin	0	b
Tri- <i>trans</i> -13-docosenoin	0-30	60

^aSee Materials and Methods section for conditioning temperatures.

^bPure β -form could not be produced by thermal conditioning.

attenuated total reflectance (ATR) prism. Chloroform was the solvent employed for saturated triglycerides, tri-*trans*-13-docosenoin and trielaidin. Acetone was used for trierucin. Each time after the spectrum of the β -form was obtained, the sample on the prism was melted, held above the β -form melting point for at least 10 min and allowed to cool spontaneously. Another spectrum was then recorded.

RESULTS

Our DSC data (NRRL-Bradley University Study) and that of previous workers are summarized in Table I. A few representative DSC curves appear in Figure 1. The lowest melting point found for each triglyceride is ascribed to the α -form and the highest to the β -form. Intermediate endotherms are attributed to β' -forms, and where more than one of these was detected, β'_1 , β'_2 , etc., designations are used following Larsson's recommendation (31) of using subscripts to name similar crystal types in order of decreasing melting points. A generalization apparent from Table I is that these intermediate forms of a given triglyceride differ little in melting point. The only exception is trilinolein, which is also the only one of its kind structurally, i.e., the only triglyceride from a diunsaturated acid, in the table. Whether or not the -47 C form of trilinolein is really a β' -form may be open to question, but multiple β' -forms were clearly observed for many of the triglycerides. The proportions of these β' -forms varied with conditioning time and scan rate as illustrated in Figure 1B, C and D, for triolein. Additional data concerning production of both β' - and pure β -forms by thermal conditioning are given in Table II.

Cooling triolein to -97 C and reheating at 10 C/min did not produce additional forms lower than -37 C. The α -form of trielaidin gradually disappeared as the scan speed was reduced, and the α -form of tri-*cis*-6-hexadecenoin was observed only at a higher than usual instrument sensitivity at 10 C/min. For four of the unsaturated triglycerides in Table I, we were unable to detect α -forms by heating curves regardless of scan speeds used. In these instances we took advantage of the fact that for the other triglycerides slow-scan cooling curves generally showed an exotherm at approximately the melting point of the α -form. These exotherms were taken as an estimate of the α -form melting point in the absence of more accurate values from heating curves. The estimate was in fair agreement with the reported α -form for trierucin (17,28). Lutton and Fehl (16) reported that α -form melting points from cooling curves are in approximate agreement with those from heating curves.

The sharpness and symmetry of endotherms obtained in this study for pure β -forms confirmed the purity of the

samples employed. For ΔH_f determinations DSC curves were recorded for two or three samples, and in most instances duplicate tracings were made for each sample. Results calculated from all curves for a given triglyceride were averaged to provide the data in the last column of Table I. The standard deviation for these data is 0.85 with 32 degrees of freedom. As an indication of accuracy, benzoic acid (NBS microanalytical standard) gave a value of 34.9 cal/g, which compares favorably with the recorded ΔH_f of 35.2 cal/g (27). The value found for tristearin, 51.4 cal/g, was also in good agreement with the value for Hormel tristearin, 50 cal/g, reported by Hampson and Rothbart (7).

IR spectra of β -forms of the four saturated triglycerides, tri-*trans*-13-docosenoin, trielaidin and trierucin showed the characteristic single band near 717 cm^{-1} for the CH_2 rocking vibration (32,33). After the samples were treated on the ATR prism in a manner approximating the procedure used to produce α -forms in the DSC instrument, all but two of them gave spectra showing a single band at 720 cm^{-1} as expected for α -forms (32,33). Trielaidin and trierucin were the exceptions because their α -forms melt below room temperature.

DISCUSSION

The correctness of polymorphic form assignments for most of the melting points listed in the α and β columns under NRRL-Bradley University Study in Table I is supported by one or more of the following: agreement with previous reports, the IR results and (for the β -forms) the same melting point after appropriate thermal conditioning and after crystallization from solvent. Of greater interest are our results regarding β' -forms. So far as we are aware, reproducible endotherms indicating multiple β' -forms on curves of single monoacid triglyceride samples have not been previously reported. Larsson's recommendation concerning subscripts, e.g., β'_1 , β'_2 , etc., had reference to multiple melting points of the same crystal type in triglyceride mixtures (31).

Figures 2 and 3 illustrate speculative proposals we offer to rationalize the multiple β' -forms observed for some triglycerides and the absence of β' -forms for others. Polymethylene chains in the plane of the paper are drawn in the normal zigzag manner and chains in planes perpendicular to the paper are shown as straight lines, with dots representing individual carbon atoms for both. On the basis of these conventions, there are two and only two forms of the saturated triglycerides which can be drawn to satisfy the requirement that every second chain plane of a β' -form must be perpendicular to the others. These are shown in Figure 2A and correspond to the two forms found by DSC. One form shows all polymethylene chains in any one line from the upper terminal methyl end to the lower end to be in the same plane, while the other form shows the zigzag planes to alternate on each side of the glycerol moiety in the middle of the molecules.

IR spectra (34) and X-ray short spacings (35) of unsaturated triglycerides suggest that their crystal forms are analogous to those of saturated triglycerides. Assuming the approximately 130° bend around the *cis* double bond found for oleic (36) and erucic (37) acids also exists in the unsaturated triglycerides, a projection of the β -form would be as pictured for triolein in Figure 2B. Perhaps the two *cis* bonds and intervening methylene group in the acyl chains of trilinolein can be considered as a single group with hydrocarbon sections on either side similar to the other unsaturated triglycerides.

The IR spectrum of the β' -form of triolein shows bands at 729 and 722 cm^{-1} suggesting an orthorhombic structure similar to that of β' -forms of saturated triglycerides (34). If each polymethylene segment is treated independently and if the zigzag planes are arranged perpendicular to each

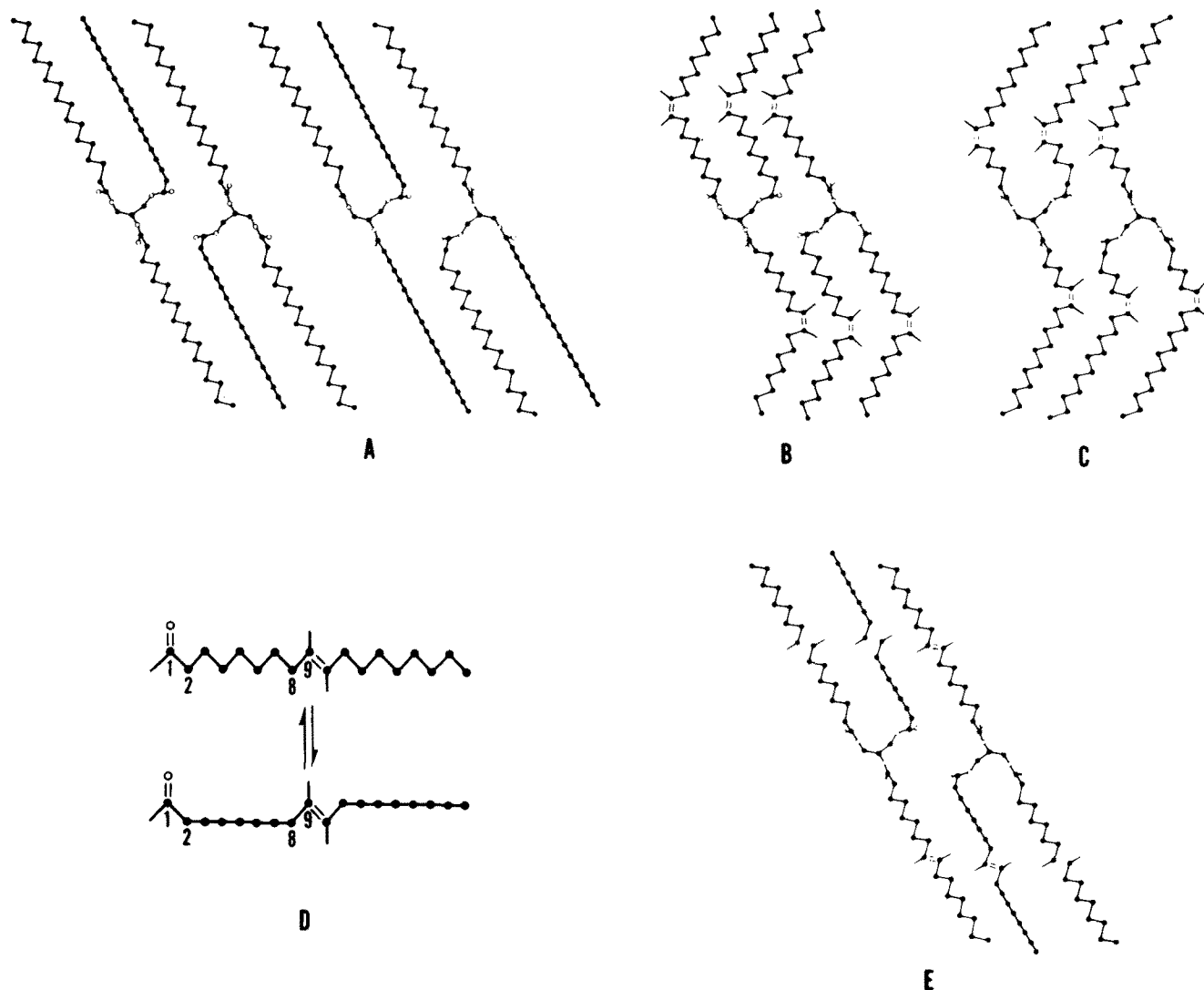


FIG. 2. (A) Proposed b-axis projection of β' -forms of tristearin. (B) β' -form of triolein. (C) β' -form of tripetroselinin. (D) Rotation of elaidic acid. (E) Hypothetical β' -form of trielaidin. (See text for conventions employed in the representations.)

other, it is possible to draw six different forms for a β' crystal of triolein as shown in Figure 3. However a closer examination of these six forms reveals that they can be grouped into three types to agree with the three β' -forms observed by DSC. In form A each of the three parallel "reversed Z" shaped strings of polymethylene segments has its segments either all zigzagging in the plane of the paper or all in planes perpendicular to the paper. Three of the four segments in each string of forms B and C are in the plane of the paper or alternatively in planes perpendicular to it. Each string in forms D, E and F contains two segments in the plane of the paper and two in perpendicular planes. The DSC peaks corresponding to "energy types" B-C and D-E-F may represent mixtures of the two or three component forms, respectively, with melting points of the component forms within each type being too close to be distinguished.

Two of the four monoacid triglycerides showing no β' -forms were tripetroselinin and tri-*cis*-6-hexadecenoin. Observation of β' -forms for triglycerides that have *cis* double bonds in the 9-, 11- and 13-positions but not when the unsaturation is in the 6-position suggests that double bond position affects polymorphism. Two structural features imparted by the Δ^6 unsaturation may be related to the absence of the β' -forms. One is that the Δ^6 double bond divides the chain into two segments containing even numbers of methylene groups. The observation of Lutton

and Fehl (16) that β' -forms of saturated monoacid triglycerides with even-numbered acyl chain lengths are substantially less stable than their odd-numbered counterparts may be pertinent. The second feature common to both triglycerides with Δ^6 unsaturation is the proximity of the 130° bends resulting from the double bonds to the glyceryl moiety in the center of the molecules. As a consequence there are two short and two long polymethylene segments in each "Z-shaped" string in Figure 2C, rather than four segments of the same length as in Figure 2B.

The hydrocarbon chains of trielaidin can take on the form of a saturated hydrocarbon. Carter and Malkin (28) report that the X-ray side spacings of the β' -form of trielaidin are identical with those of saturated triglycerides. Contrary to the saturated triglycerides however, a β' -form was not found in our NRRL-Bradley University Study or by Chapman (34) who used IR to characterize triglycerides. This lack can be rationalized by assuming that the plane of the *trans* double bonds is fixed, e.g., to permit π -electron interactions with double bonds in chains above and below. For trielaidin to form the orthorhombic crystal, with the double bond held rigid, the carbon chain must rotate on both sides of the double bond, as illustrated in Figure 2D, so that every second chain plane can be perpendicular to the others. The rotation of the chain must take place about bonds C_1-C_2 and C_8-C_9 between the carboxyl and double bond, and about the $C_{10}-C_{11}$ bond. This rotation places

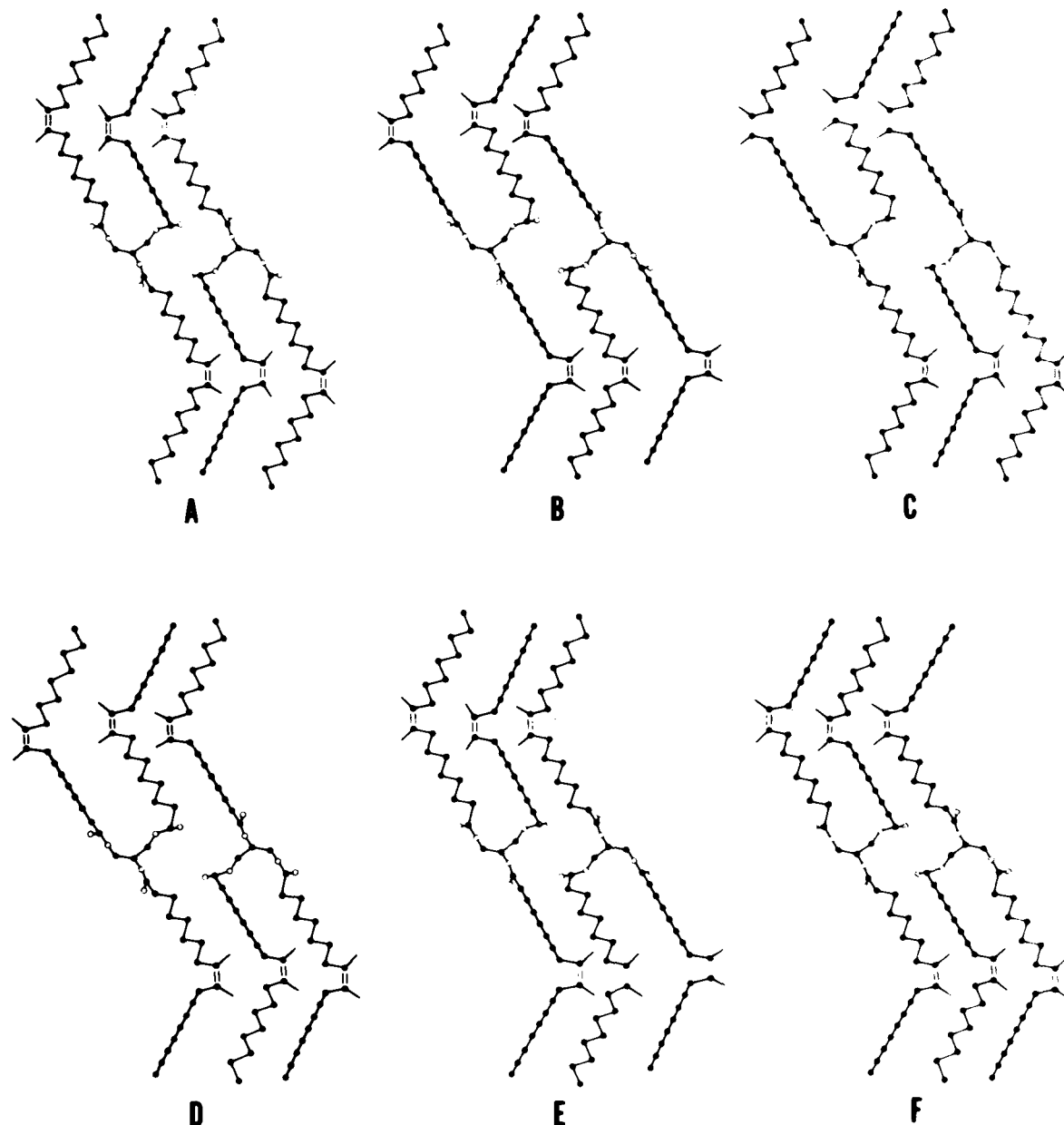


FIG. 3. Proposed b-axis projections of β' -forms of triolein. (See text for conventions employed in the representations.)

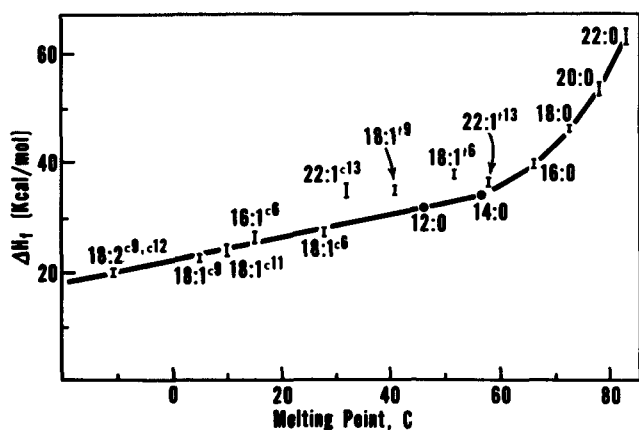


FIG. 4. Triglyceride β melting point vs. ΔH_f . The heights of the vertical bars indicate the 95% confidence intervals for the values of ΔH_f . Data represented by solid circles are from References 7 and 16.

the C_2 to C_8 carbons in a plane different from the C_{11} to C_{18} carbon atoms. The effect on the whole triglyceride structure is a variability in the distance between adjacent chains as pictured in Figure 2E. The distance between the carbon plane C_2 to C_8 and its adjacent chains is not the same as the distance between carbon plane C_{11} to C_{18} and its adjacent chains. The β' structures of tristearin in Figure 2A show adjacent chains to be equidistant apart. It is speculated that this nonuniformity in the distance between chains after chain rotation does not allow β' formation of triolein.

To rationalize the absence of triolein β' -forms, the same arguments can be used as for Δ^6 unsaturated triglycerides or for *trans* unsaturated ones, or both.

Tri-*trans*-13-docosenoin differed from the other two *trans* unsaturated triglycerides studied by showing β' -forms. Rotation of the entire carbon chain including the double bond may be possible because the double bond in tri-*trans*-13-docosenoin is a smaller part of the total molecule than in the *trans* unsaturated C_{18} fatty acid triglycerides and

perhaps has less effect on chain packing. If the entire chain is rotating, then the two β' -forms observed agree with the number that should have been found, the same as for saturated triglycerides. Rotation of the zigzag planes with the double bond rigid, if tolerated in spite of the resulting uneven chain spacing, would lead to a possibility of three β' -forms as found for trierucin.

A plot of the molar heats of fusion of β -forms vs. their melting points is given in Figure 4. Included in the plot are the previously reported ΔH_f values (7) and melting points (16) of trilaurin and trimyristin. Most of the unsaturated triglycerides fall close to a line extended to lower temperatures than the trilaurin melting point. Exceptions are two of the *trans* triglycerides—trielaidin and tripetroselaidin—and trierucin. The points for trielaidin and tripetroselaidin suggest a second line for *trans* triglycerides, whereas more data are required to explain the position of trierucin. The sharp upward trend in ΔH_f values represented in Figure 4 indicates growing stability of the β -forms as the acyl chains lengthened from 16 to 22 carbons. This trend parallels the increase in time required to prepare β' and pure β -forms of the saturated triglycerides as the chain length increased (see Table II). Jackson and Lutton (38) have reported that docosanoyl mixed triglycerides all showed a high β' stability.

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