

The Phases of Saturated 1-Monoglycerides C₁₄-C₂₂

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ABSTRACT

Phase behavior of a homologous series of saturated even 1-monoglycerides, starting with monomyristin, has been reviewed and their study extended to monoarachidin and monobehenin. The occurrence of sub α , α' , β' and β polymorphs was confirmed for all compounds, except in the case of β' for monomyristin. It has been firmly established that there is a reversible sub $\alpha_2 \rightleftharpoons$ sub α_1 transition, (indicated by Malkin for monostearin) below the reversible sub α (sub α_1) \rightleftharpoons α transition, for C₁₈ through C₂₂ compounds; it occurs at about 50 C and is apparently almost independent of chain length. The sub α_2 to sub α_1 transformation is particularly sensitive to impurity and disappears for 1-monobehenin at about 10% 2-monobehenin as produced by heating at 96 C. Heats of transformation are, for β' and β crystal melting, about 50 cal/g; for α melting, about 35; for sub $\alpha \rightarrow \alpha$ transition, about 15 and for sub α_2 to sub α_1 transition about 3, which is several times as large as typical heats of melting of mesomorphic states. Diffraction data confirm the essential identity of all long spacing values and the occurrence of tilted chains for all polymorphs of a given compound. Much similarity is encountered between sub α and β' patterns. Sub α_2 and sub α_1 are difficult to distinguish by diffraction pattern.

INTRODUCTION

The crystallization of monoglycerides is complex, probably more complex than that of triglycerides.

It was shown earlier (1) that 1-monostearin, for example, has a stable β form normally obtained from solvent or transformation of metastable forms, a metastable β' form from solvent and 2 metastable forms from chilled melt, these forms transforming reversibly one to another. Malkin and el Shurbagy (2) had previously indicated some but not all of these points and had reported an extra solid transformation between metastable states of 1-monostearin. Larsson (3) has indicated further complexity by report of another crystalline form of racemic 1-monoglycerides

TABLE I
Analysis of Monoglycerides

1-Monoglyceride	Chain length purity, GC ^a	% 1-Mono, TLC ^b
Behenin	I	>99.9
	II	100.0
	III	88
Arachidin	99.9	ca. 100
Stearin	I	100.0
	II	99.6
	III	98.3
	IV	97.9
Palmitin	I	99.6
	II	>99
	III	96.2
Myristin	99.5	ca. 99

^aGas chromatography.

^bThin layer chromatography.

^cPeriodic acid anal.

which resembles the familiar stable β form but which has alternating chain directions. (The present study deals only in a very limited way with the possibility of two β forms.)

It is remarkable that all well-established long spacing values for the solid states of 1-monostearin are equal within experimental error. The same situation holds for homologs.

EXPERIMENTAL PROCEDURES

Two pure samples each of 1-monobehenin, 1-monostearin and 1-monopalmitin and one each of 1-monoarachidin and 1-monomyristin were prepared by interesterification of methyl or other ester, of high chain length purity, i.e., low percentage of homologs, with an excess of glycerol in the presence of alkaline catalyst such as sodium glyceroxide. The monoglyceride was concentrated and purified by recrystallization or by a combination of column chromatography on silica gel and crystallization. Favorable solvent composition for chromatography is 4:1 hexane-chloroform.

In addition less pure samples of some of the aforementioned saturated monoglycerides were explored. No systematic addition of impurities was involved, but analyses help to explain interesting deviations from the behavior of pure samples. Analyses appear in Table I.

Samples were studied by familiar techniques involving capillary melting points, differential thermal analyses and X-ray diffraction.

Complete melting points on solvent crystallized samples were obtained at a heating rate of 0.5 C/min. Rapid complete melting points were obtained for α forms by thrust-in technique.

A standard procedure was adopted for differential thermal analysis (DTA) with a DuPont 900 unit. Solvent crystallized sample was ground with mortar and pestle and packed into standard DTA capillary (2 mm OD) to a height

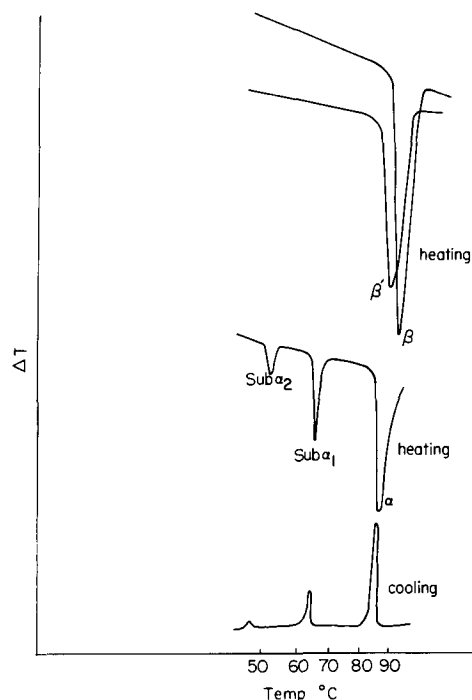


FIG. 1. Differential thermal analysis curves for 1-monobehenin (I) in different polymorphic states.

of 3-4 mm (ca. 3 mg). With chromel-alumel thermocouples inserted in the sample and into glass bead samples for reference and for temperature programming, the sample was heated in a silver block at 10 C per min just to melting (with avoidance of overheating and consequent partial isomerization to 2-monoglyceride). The curve thus obtained normally registered melting of the most stable form and was confirmatory of capillary melting point level. A cooling curve immediately following the heating curve explored supercooling to α melting level, α solidification and solid-solid transformations. Cooling was accelerated by flow of N_2 through the channel provided. Alpha melting and the solid-solid transformations were then explored by heating curve. DTA curves for monobehenin, as representative, are shown in Figure 1, and for sub α and α states of the various homologs in Figure 2. Calorimetric studies were carried out on the phases identified by DTA in the DuPont 900350 cell. (None were performed with the later prepared monomyristin.) Calibration was based on tin, indium, palmitic and stearic acids. In the calorimetric cells there are matching silver cups for sample and reference. Aluminum (or platinum) liners for the sample make good thermal contact with the silver cup. Chromel-alumel thermocouples make contact with the underside of the cups. Into the liners was weighed approximately 6 mg of sample. In the assembled apparatus, heating rate was 10 C/min. From areas under the thermal curves enthalpy changes were calculated. Resolution of peaks is not quite so good as with the DTA cell. In the case of monostearin for which the peaks for solid-solid transformations were unresolved with the calorimetric cell, DTA curves showing definite resolution were compared with DTA curves for monoarachidin.

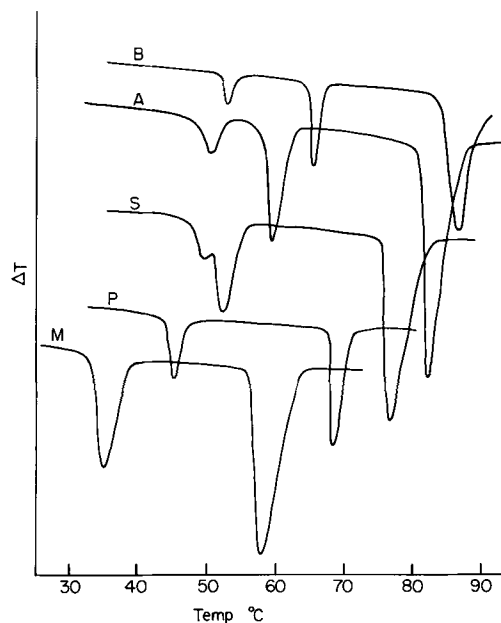


FIG. 2. Differential thermal analysis curves for sub α and α states of 1-monoglycerides.

Because of the same ratio for areas of transformation peaks by DTA for the two compounds, it was assumed for monostearin a ratio of heats of transformation identical to that for monoarachidin.

Melting and transformation points appear in Table II and Figure 3, calorimetric data in Table III.

TABLE II

Melting and Transformation Points of 1-Monoglycerides

Monoglyceride		Transformation point, C		Melting point, C		
		Sub $\alpha_2 \rightarrow$ Sub α_1	Sub $\alpha_1 \rightarrow \alpha$	α mp ± 0.2	β' mp	β mp
Behenin	I	53	64	85.1	86.0 \pm 0.6	88.5 \pm 0.5
	II	49	63	85.0		89.0 \pm 0.5
	III	— ^b	61	82 ^a		
Arachidin		50	58	80.1	82.2	85.2
Stearin	I	50	52.5	74.2	78 ^c	81.6 \pm 0.5
	II	50	52.5	74.2		81.0 \pm 0.5
	III	42	47	73 ^a		80.0
	IV	44	47	73.9		80.7
Palmitin	I	— ^b	45 ^d	66.8	74.6 ^c	76.5
	II	— ^b	46 ^d	67.0		76.5
	III	— ^b	— ^b	66.5		74.8
Myristin		— ^b	35(24 ^e)	57.9(56 ^e)	— ^b (67.5 ^e)	70.3(70.5 ^e)

^aDifferential thermal analyses.

^bNot found.

^cPrevious data (1).

^dHigher than earlier value (1) by cruder methods.

^eMalkin and el Shurbagy (2).

TABLE III

Heats of Transition, cal/g

	C ₁₆	C ₁₈	C ₂₀	C ₂₂	Probable accuracy
Sub α_2 to α	18.2	17.0	(15.1 ^b)	(18.3 ^b)	
Sub α_2 to sub α_1		(2.7 ^a)	2.4	3.6	± 0.5
Sub α_1 to α		(14.3 ^a)	12.7	14.7	± 1
α to melt	34.2	33.7	35.7	34.7	± 1.5
β' to melt			55.8	54.8	± 3
β to melt	50.7	54.4	53.2	51.6	± 3

^aEstimated from differential thermal analyses.

^bBy addition.

TABLE IV

Diffraction Data for 1-Monoarachidin and 1-Monobehenin

Long Spacings		Short Spacings	
1-monoarachidin	1-monobehenin	1-monoarachidin	1-monobehenin
sub α_1 54.3, α 53.8, β' 53.9, β 54.4; all $54.2 \pm 0.3\text{\AA}$	sub α_1 58.1, sub α_2 58, α 58.9, β' 58.2, β 58.7; all $58.5 \pm 0.5\text{\AA}$	sub α_1 (4.26W, 4.12S, 3.87M, 3.72M, 3.58M), α (4.60W, 4.18VS, 3.87W), β' (4.17S, 4.05W+, 3.79M-, 3.64M-, 3.90S, 3.75M, 3.34W)	sub α_1 (4.14VW, 4.09S, 3.84W+, 3.70W, 3.55W+), sub α_2 (4.22VS, 4.00W-, 3.88W, 3.80W, 3.66M), α (4.63W, 4.19VS, 3.88W), β' (4.51VW, 4.14S, 3.86W, 3.73W, 3.59W), β (4.54S, 4.35S, 4.09VW, 3.85S, 3.71W)

Diffraction data on flat films, 5 cm sample-to-film distance for exploratory tests and 10 cm sample-to-film distance for accurate measurement, were obtained for the various polymorphs as suggested by thermal tests. See Table IV for previously unpublished diffraction information on monoarachidin and monobehenin.

A low temperature solid-solid transformation below sub α - α transformation has been a source of uncertainty and mystery for 30 years and proved particularly easy to study with monobehenin. A series of DTA runs on monobehenin was made after increasing periods of time at 96 C. The curves are reproduced in Figure 4; in Figure 5 are shown the results from thin layer chromatography (TLC) on the treated 1-monobehenins, with evidence of increasing degree of isomerism. The TLC adsorbent was Silica Gel G (Brinkmann Instruments, Inc.) on plates of 250 μ thickness; the solvent system was benzene-triethyl borate 85:15, which separates 1- from 2-monoglycerides. Spots were revealed by charring with a spray of 25% H_2SO_4 .

RESULTS AND DISCUSSION

The main investigation was of the C_{20} and C_{22} monoglycerides since monostearin, monopalmitin and monomyristin have been explored earlier (1,2). New data on both monopalmitin and monomyristin show higher sub α and α transformation points than previously reported.

It was found that 1-monobehenin readily crystallizes in the β' form from solvent, e.g., with a 10 g sample dissolved in 300 ml of benzene and set at 25 C. The β form is more difficultly obtained, but 1 g in 10 ml acetone cooled in a

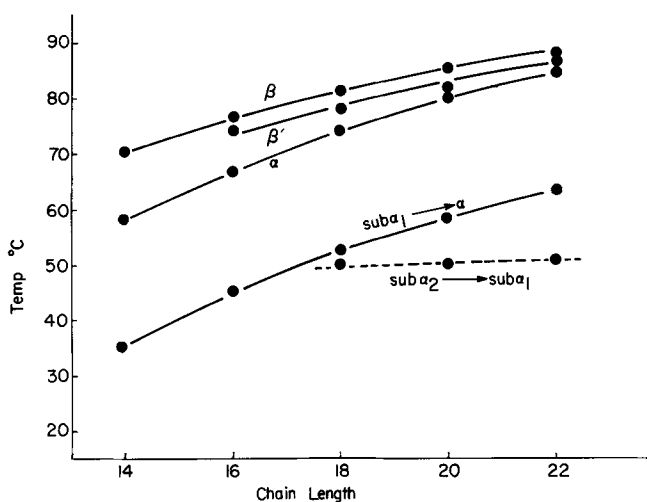


FIG. 3. Melting and transformation points of saturated 1-monoglycerides, C_{14} - C_{22} .

thermos bottle of H_2O from 60 C to 25 C gave 100% β . Three metastable forms, α , sub α_1 and sub α_2 , are observed on chilling the melt and are particularly easy to study because each has a range of existence of more than 10 C.

Monoarachidin is in every important feature, similar to monobehenin and intermediate in behavior between behenin and stearin.

Metastable Forms From Melt

Monomyristin and monopalmitin each show one solid-solid transformation, but monostearin, as reported by Malkin and el Shurbagy (2), shows two. Present values within 2 or 3 deg of each other are closer than Malkin's. For monoarachidin, which also shows two such transformations, the points are farther apart, and for monobehenin the points are separated by more than 10 C. The lower transition point at about 50 C appears to be almost independent of chain length for monostearin through monobehenin.

In most respects monomyristin behaves comparably to monopalmitin. However we were unable to obtain a β' form even by rapid chilling of dilute solutions in hexane.

While the difference in X-ray diffraction pattern be-

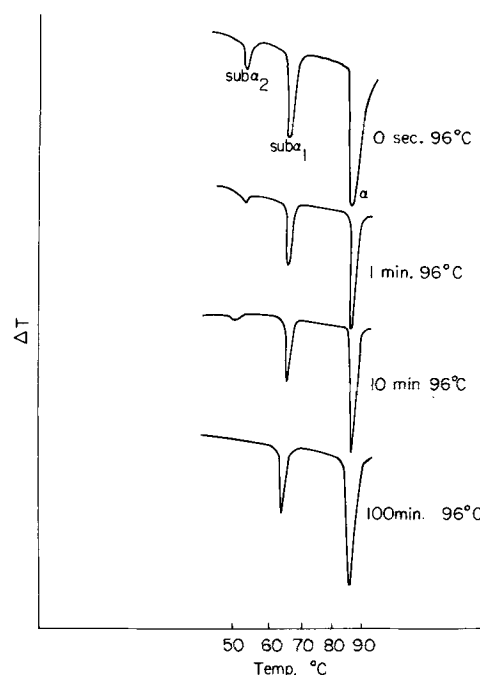


FIG. 4. Differential thermal analysis curves for 1-monobehenin (I) after holding at 96 C; differential thermal analysis samples melted and chilled.

tween sub α and α is major, only minor difference is discernible between sub α_2 and sub α_1 (for 1-monobehenin only, because of too rapid transformation with lower molecular weights).

It was found that the lower solid-solid transformation in particular is extraordinarily sensitive to composition change. A careful exploration was made with monobehenin of the effect of heating, which proved to be essentially the effect of 1- to 2-monobehenin transformation, on the lower transformation point. The results are shown in Figures 4 and 5. Figure 5, being a print from a photograph of the actual TLC plate, leaves something to be desired as far as detail is concerned. It shows some 2-isomer contamination, actually about 1%, in the original sample. Spots at the origin are intensified with any time lapse before separation. They were also intensified relatively by photography. In no case do they indicate more than 0.5% of actual impurity.

As time of sample at 96 C increased, 2-monobehenin increased and the lower DTA transformation peak faded so that with formation of about 10% 2-monobehenin, after 100 min at 96 C (as indicated by near match of 2-isomer spot with the 1-isomer spot at 10% strength, spot No. 3), the lower DTA peak disappeared completely. With the isomerization other thermal phenomena were only slightly affected in level and peak magnitude. Undoubtedly monoglyceride isomerism is the major factor in the erratic behavior of the thermal peaks. In the experiment described TLC indicates little other composition change than isomerization. However diglyceride content and chain length impurity are factors of importance, as indicated by other evidence. Thus in 1-monobehenin III, of low chain length and 1-monoglyceride purity, the sub $\alpha_2 \rightarrow$ sub α_1 transformation is missing. With 1-monopalmitin III, of good monoglyceride purity but only fair chain length purity, the sub $\alpha \rightarrow \alpha$ transformation is missing, suggesting that the sensitivity of transformation point phenomena increases with decreasing chain length.

Heats of Transformation

Over the years from several sources has developed a limited lore on heats of transformation in long chain compounds. Thus highly crystalline forms show heats of melting of 40-50 cal/g, α forms about 30 and mesomorphic states, about 0.5. These values are indicative of the changes in degree of order upon change of state. It seemed desirable to obtain quantitative calorimetric information on the monoglyceride transformations.

From Table III it is seen that the heat of melting of β' or β forms is about 50 cal/g; the values for the two forms are nearly within experimental error, but it may be that the lower melting β' form has actually a higher heat of fusion which would mean that β' is actually more stable than β at low temperatures.

Heats of fusion for α are only about 35 cal/g, in line with the presumed random orientation of the long chain axis.

Heats of transition, sub $\alpha \rightarrow \alpha$ are about 15 cal/g which means that sub α is very nearly as well ordered as β and β' , as it would appear to be from its diffraction pattern.

The sub $\alpha_2 \rightarrow$ sub α_1 heat of transformation is about 3 cal/g, quite small, yet several times the magnitude of heats of melting of mesomorphic forms.

The sub $\alpha \rightarrow \alpha$ change represents largely the passage of the hydrocarbon chains from a well ordered close-packed state to a state of randomly oriented (in axis) but still parallel chains. It is hard to imagine to what the sub $\alpha_2 \rightarrow$ sub α_1 change can be owing. A similar change in acetyl monostearins (Lutton and Martin, in preparation) has been clearly associated with an extra partial chain ordering phenomenon.

It appears probable that, sensitive as the transformation is, an interesting study of molecular influence could be

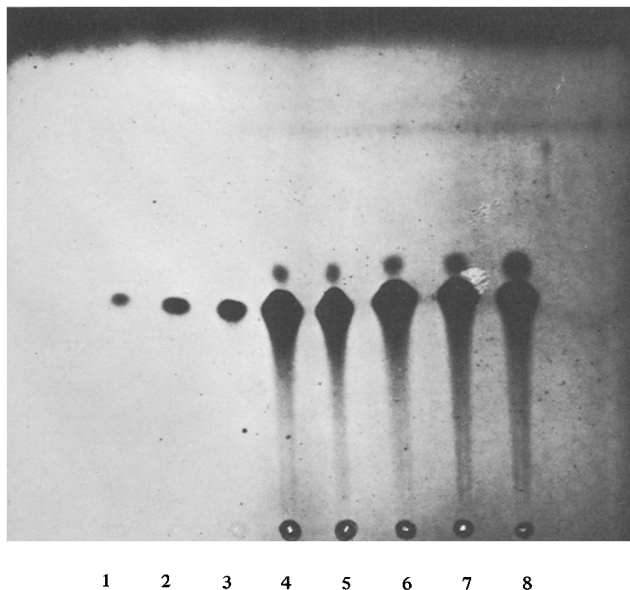


FIG. 5. Thin layer chromatography record of isomerism in 1-monobehenin held at 96 C: spot No. 1, 2.5 μ g, 0 sec 96 C; 2, 5 μ g, 0 sec 96 C; 3, 10 μ g, 0 sec 96 C; 4, 100 μ g, 0 sec 96 C; 5, 100 μ g, 10 sec 96 C; 6, 100 μ g, 1 min 96 C; 7, 100 μ g, 10 min 96 C; 8, 100 μ g, 100 min 96 C.

developed simply by controlled addition of impurities to 1-monobehenin and following the sub $\alpha_2 \rightarrow$ sub α_1 transition. The influences of molecular size, shape and polarity might be quite instructive.

Diffraction Patterns

There is not much to be said about diffraction patterns of 1-monoglycerides that has not been said before. Several interesting puzzles remain: (1) The near identity in long spacings for all polymorphs of a given compound has been mentioned. The bulky polar group requires, for space filling reasons, considerable tilting of the hydrocarbon chain. It is remarkable that the tilting remains so nearly constant from polymorph to polymorph; (2) Sub α and β' are remarkably alike in diffraction pattern and in thermal energy, but are very distinct structure types; (3) It has been difficult to find characterizing differences between sub α_2 and sub α_1 structures, but minor differences have been noted in the case of 1-monobehenin. Chances of understanding the structure differences in any detail in the near future seem remote.

β Diffraction Change with Crystal Variation

A chance variation was noted in " β " crystals of 1-monopalmitin from 20 volumes of hexane. Large shiny crystals had distinctive short spacings of 4.55S, 4.35W, 2.45M, 2.22VW and 2.15W as compared with small powdery crystals of distinctive spacings 4.53W, 4.37S, 2.44M, 2.20M. Both types of crystals were ground prior to obtaining diffraction patterns, but not all orientation effects were eliminated. It is believed that the distinctive features are not artifacts, but whether, for instance, they relate to Larsson's reported β variations (3) is not known.

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