Beta Prime of 2-Palmitoyldistearin

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A β′ form of 2-palmitoyldistearin (SPS), hitherto unreported for the pure compound is obtained by slow nucleation and crystallization of a slurry of β crystals in hexane. The nucleation process is accelerated by the presence of solid succinic acid. The new β′ form (Long spacing–44.3A.) melts at 69.0° C., 0.5° C. above the β form, and is apparently stable at all temperatures below its melting point.

A β′ FORM, long unobtained for pure 2-palmitoyldistearin (SPS), has now been observed and shown to be a higher melting polymorph than either α or β. The form nucleates and slowly develops in a slurry of β crystals of SPS in hexane. The appearance of β′ is accelerated by presence of finely divided solid succinic acid. The recently reported new metastable β form of 2-stearoyldipalmitin (PSP) (*8*) may be obtained by crystallizing a 2% solution in hexane at 21° C. or lower. While the procedures for obtaining these new forms are significantly different, solvent appears to be necessary for obtaining both β′ SPS and β PSP. Now all six triglycerides obtainable from palmitic and stearic acids have been prepared in authentic α, β′, and β forms.

The monotropic polymorphism of tristearin (SSS), for some time a matter of controversy, is now rather generally agreed to involve α (hexagonal), β′ (monoclinic), and β (triclinic) phases, melting, respectively, at about 55°, 64°, and 73° C. (*7*). Tripalmitin (PPP) behaves similarly. A recent review discusses the situation in detail (*3*). The symbols in parentheses are intended to suggest that there is a correlation, and probably a close one, with the H, M and T phases found in paraffins (*2*).

Over a period of many years the two symmetrical diacid triglycerides PSP and SPS exhibited, respectively, only α and β′ forms (PSP) and only α and β forms (SPS) (*9*). Then it was discovered that a β form of PSP was crystallized from vegetable oil in the presence of finely divided succinic acid. (Subsequently it was found that common solvents were satisfactory and succinic acid, while accelerating, was not essential.) On the basis of the experience with PSP the effects of solvent and succinic acid on SPS crystallization were explored.

The record in the literature on β′ SPS is cloudy. Chapman similarly to this laboratory had not reported β′ for SPS (*4*). It is true that Malkin (*10*) had reported β′ from melt for SPS, but Malkin's procedure does not give β′ for pure SPS in this laboratory. Moreover his proposed β′ melting level, 64° C., is 5° C. below that of the β′ value here reported. That Malkin actually did obtain β′ for his SPS is supported by his x-ray data; but it is believed by the present authors, that β′ SPS is obtainable under Malkin's conditions only in case of substantial proportions of impurity. Strong suggestion of significant impurity lies in the short spacings reported by Malkin for SPS in the β form—3.68A., 3.86A., etc. The degree of separation for his two values here mentioned is typical of other C_{16}–C_{18} triglycerides, while SPS in this laboratory has shown the values—3.72 and 3.81A., with only half the separation reported by Malkin. Malkin's single fatty acid triglycerides and unsymmetrical mixed diacid triglycerides seem unimpeachable, but his symmetrical mixed diacid triglycerides were made via 1,3-diglycerides for which isomerism is a pitfall not properly estimated at the time of Malkin's synthesis of SPS. It is believed that the directed interesterification procedure used for diglyceride intermediates in this laboratory (*1, 5*), but not by Malkin, leads to substantially pure 1,3-isomers, hence to pure symmetrical mixed triglycerides. Two samples of SPS were used in the present work, Sample A via chemical synthesis (*9*) and Sample B, a fractionally crystallized hydrogenated product from the 2-palmitoyl portion of a natural lard (*11*). Sample A was probably slightly purer than Sample B, but they showed little difference in behavior.

EXPERIMENTAL

Solutions of SPS in hexane (approximately 1 to 10) were prepared. To certain of these solutions 1 to 2% (on the SPS basis) of finely divided succinic acid was added which was never completely dissolved. The solutions containing dissolved SPS (and with or without added succinic crystals) were placed at temperatures from 27° to 38° C. Typically the samples were observed approximately daily. Precipitation normally occurred in a day, but took longer at 38° C. The first rapidly grown crystals were β (as established by x-ray in several instances) and showed little or no spherulitic growth. Spherulites developed later, sometimes very large ones. Normally the whole sample was filtered at the end of the storage period and subjected to x-ray diffraction. With the appearance of spherulites, β′ phase was observed. Flat-film patterns of rod pellets were obtained with GE XRD-1 unit employing CuKα nickel-filtered radiation and a 0.025 inch pinhole system.

Melting points on selected samples were obtained in small capillaries (< 1.0 mm. diameter) at a heating rate of 0.5° C. per minute.

In Table I are presented the conditions and phase results of specific experiments. The following data were obtained for the new β′ form: Melting point 69.0° C. (β 68.5° C., α 51.8) (*3*). Short spacings, 4.37 (very weak), 4.23 (medium), 4.10 (very strong), 3.95 (weak), 3.75 (strong). For long spacing see Table II where d/n is measured spacing, I is intensity, n is the order of spacing, and d is the calculated spacing (d/n × n).

Table I. Experiments Defining Conditions for Obtaining β' SPS

Sample dissolved in 20ml. of hexane

Sample	SPS, Grams	Storage Days	Storage Temp., ° C.	Succinic Acid Added, Gram	Remarks on Crystals Obtained	Phase
A	2	14	27	0.04	Spherulites[a]	β'
A	2	14	27	None	Matted needles	β
B	0.5[b]	21	27	0.01	No spherulites	β
B	0.5	49	27	0.01	Spherulites	β'
B	1.5	1	32	0.02	Small crystals	β[c]
B	1.5	8	32	0.02	Spherulites begin	mostly β[c]
B	1.5	19	32	0.02	All spherulites	β'
B	1.5	1	32	None	Small crystals	β[c]
B	1.5	12	32	None	Spherulites begin	mostly β[c]
B	1.5	19	32	None	All spherulites	β'
B	2.0	12	38	0.02	Slow growth	β'
B	2.0	12	38	None	Slow growth	β'

[a] SPS spherulites as large as 2 cm. diam. observed. [b] Sample dissolved in 10ml. of hexane. [c] As judged by appearance of crystals.

Table II. Long Spacing for β' form of SPS

d/n A.	I	n	d A.
43.3	VS	1	(43.3)
22.4	VW	2	44.9
14.7	M	3	44.0
8.88	W–	5	44.4
7.38	VW	6	44.3
6.29	VW	7	44.0
5.52	VW	8	44.1
		Average	44.3[a]

[a] (β 43.1, α 49.2) (*3*).

Table III. Melting Point Data for PMP

Sample	Rapid Complete M.P., ° C. (α) (*3*)	Regular Complete M.P., ° C. (β) (*3*)
I	40.3	59.3
II	40.4	58.4

Table IV. Attempt to Characterize P—S Triglyceride Crystallization

Triglyceride Group	Polymorphic Forms β	β'	α	Relative Estimated Nucleation Rate: High temp. (> 50° C.) (from melt or solvent)	Low temp. (< 40° C.) (from solvent)
Single Acid					
SSS	S	F	F	$\beta' > \beta$[a]	$\beta > \beta'$
PPP	S	F	F	$\beta' > \beta$[a]	$\beta > \beta'$
Unsymmetrical					
SSP (PSS)	S	S	F	$\beta' > \beta$	$\beta > \beta'$
PPS (SPP)	S	U	F	$\beta' > \beta$[a]	$\beta > \beta'$
Symmetrical					
SPS	M	S	U	$\beta > \beta'$	$\beta >> \beta'$
PSP	M	S	very F	$\beta' >> \beta$	$\beta > \beta'$

S = stable
M = metastable
U = unstable
F = fletting

[a] Below β' m.p.

Table I indicates β' stability at lower temperatures. To explore the possibility that β' transforms to β at higher temperatures, β' samples were stored (without solvent) 34 days at 60°, 2 hours at 65° and 2 hours at 67.5° C. All samples remained β'.

In view of Chapman's application (*4*) of infrared examination to fat crystals, spectra were obtained for SPS in β and β' states and similarly for PSP and SSS. It was possible to examine coconut fatty acid nitrile mulls in all cases but that of SSS β' whose instability required elimination of the nitrile. It proved possible to prepare a SSS β' sample, satisfactory for observation, by slicing on a rotary microtome. It was uniformly observed that there was a doubling of the peak in the 13.7 micron wavelength region for all β' samples including SPS β', while all β spectra showed single peaks in that region.

Comparison of closely related homologs can be of much help in polymorphic study. Since two preparations of 2-myristoyldipalmitin (PMP) were available, one from previous study (*6*) and one recently prepared, they were studied for evidence of any behavior analogous to that of SPS.

Melting points of PMP appear in Table III.

Effort was made to prepare β' by holding a precipitate from 1.5 grams in 10ml. of hexane with and without 0.01 gram of succinic acid at 27° C. for 6 months. Only β crystals were observed.

A fleeting β' form of PMP via melt had been reported earlier (*6*). Its melting point was stated to be 47° C., intermediate between α and β melting levels. In the light of the new finding of a high melting β' form for SPS from solvent and negative results from solvent for PMP it was deemed advisable to reexamine the question of β' PMP via melt. Although the best known method of preparation of such a form was used (holding the melt just above the α melting point at a temperature where clouding occurs in 5 minutes but not in 1 minute) only mixtures of α and β phases were obtained. It now appears necessary to conclude that β' PMP is not actually obtainable by any known procedure and hence no form of 47° C. melting level is acceptable.

DISCUSSION

At temperatures below 40° C., SPS typically crystallizes from hexane in fine-grained β crystals. On standing in solvent these β crystals (accelerated by the presence of finely divided succinic acid) slowly transform to spherulitic β' crystals. This β' form, slowly obtained from solvent, is the highest melting and apparently only stable crystalline form of SPS.

It is now clear that the six triglycerides (optical isomerism disregarded) obtainable from palmitic and stearic acids all show α, β', and β forms and apparently no other in the range 0° C. to the completely melting point. In Table IV an effort is made to codify the crystallization behavior of the six different triglycerides in their different forms. Considerable individuality is evident despite the inevitable great similarity. One feature brought out in the table is the high nucleation tendency of β at low temperatures ($<$ 40° C.). This correlates with the observation that nonpolar solvents (the more powerful solvents for triglycerides) favor β crystallization because crystallization from more powerful solvents tends to occur at lower temperatures.

It is tempting to try to account for the highly individual features of polymorphism exhibited by the C_{16}–C_{18} triglycerides, but there is no reasonable hope of doing so before there is a detailed knowledge of crystal structure for at least one β and one β' form.

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Phenol Esters of 3,4,5-Triiodobenzoic Acid

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The 3,4,5-triiodobenzoic esters of fifty phenols have been prepared by reacting the various phenols with 3,4,5-triiodobenzoyl chloride.

WE HAVE PREVIOUSLY reported the use of 3,4,5-triiodobenzoyl chloride as a reagent for the preparation of derivatives of cellosolves (*2*), carbitols (*2*), alcohols (*3*) and mercaptans (*4*). This simple method has now been extended to the preparation of derivatives of a number of phenols. These compounds have proven useful for the characterization of this class of compounds.

EXPERIMENTAL

The phenols were used as obtained from Eastman Kodak with the exception of *p*-chlorophenol which was purified by distillation. The acid chloride was prepared by the method of Klemme and Hunter (*1*) except that cyclohexane was used for crystallization.