Beta Phase of 2-Stearoyldipalmitin

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FOR SOME TIME controversy had existed in the field of triglyceride polymorphism, disagreement arising from a different association of x-ray pattern with melting point. The main points at issue seem finally to have been settled by the independent work of Chapman (*1*, *2*) using infrared as a principal tool. With neither solvent nor additives of any kind in the picture, it is generally clear that pure tristearin and pure tripalmitin will develop α, β' and β forms and only these, while pure 2-palmitoyldistearin (SPS) develops α and β, and pure 2-stearoyldipalmitin (PSP) develops only α and β' (α being characterized by a single strong short spacing near 4.2A., β' by having multiple short spacings with one, usually the strongest, near 4.2A., and β by having multiple strong short spacings with one, usually the strongest, near 4.6A.). Possible sub-α forms, sometimes obtainable by chilling α to low temperatures (*3*), are not considered here.

Now it has been observed that a metastable β form of PSP can be obtained from solvent. Without additive, the conditions must be controlled with unusual care. But the presence of solid dicarboxylic acid,—e.g. succinic, facilitates obtaining the form from oil or solvent. Indeed discovery of β PSP resulted from the observation of a fine-grained β precipitate obtained from oil in the presence of succinic and contrasting with the normal spherulitic β' growth.

EXPERIMENTAL

PSP was prepared by recrystallization of a completely hydrogenated disaturated fraction of cottonseed oil. It is believed that PSP is more easily prepared in high purity by this procedure than by synthesis. Typical polymorphic behavior and sharp dilatometric melting point characterize such preparations. The present PSP preparation had normal β' diffraction pattern and melted at 69° C.; a fleeting α form typically prevented determination of a minimum melting point (*4*), but a normal softening point of 47° C. was obtained.

The unexpected β phase can be grown from hexane by rapidly cooling a 5% PSP solution to 33° C., then setting it at 21° C. (not 27° or 10° C.). Similar cooling and seeding at 27° C. with β PSP also yields β. Growth from a 1% solution in xylene at 0° C. gave 25% β. A 0.25% solution in xylene evaporated on a microscope slide at 10° C. to give beautiful β rhomboids.

The easiest way to obtain β is through the agency of succinic acid. If a 5% mixture of PSP in oil or hexane with 0.1% powdered succinic acid is heated to 50° C., the PSP dissolves but not the succinic acid; crystallization of the PSP at 27° C. gives β phase. Crystallization temperature was varied from 0° to 32° C. Benzene and isopropyl alcohol were tried as solvents. Several dicarboxylic acids and other additives were tested. See Table I for a summary of data on conditions for growth of β PSP with a variety of solvents, temperatures, and additives.

Table I. Inducing β 2-Stearoyldipalmitin

% PSP	Solvent	Additive, % Succinic	Crystallization Conditions, ° C.	Phase
5	Vegetable Oil	0.1[a]	32	β
5	Hexane	0.1[b]	27[b] (also 21, 10, 0)	β
5	Hexane	. . .	27	β'
5	Hexane	0.1	32 (no crystals), 27	β'
5	Hexane	. . .	32 (no crystals), seed 0.5 g. PSP, 27	β
7.5	Hexane	0.1	32	β
2	Hexane	. . .	27–32 (no crystals), 21	β
5	Benzene	0.1	10	β
5	Isopropyl alcohol	1, 5, 10	32	β'
1	Xylene	. . .	0	25% β

[a] Under these same conditions, the following additives were ineffective-inositol hexapalmitate, sucrose octapalmitate, distearin carbonate.

[b] Under these same conditions, the following additives gave β-oxalic series through suberic, fumaric, maleic, citraconic, mesaconic, malic, diglycolic, tartaric acid, succinic anhydride; partially β-glycolic acid; β'-citric and salicylic acid, glycine, β-alanine.

Diffraction data for the new β phase appear in Table II. Flat film patterns of rod pellets were obtained with a G.E.

Table II. Diffraction and Thermal Data

	PSP			MPM		
	α (*4*)	α (*4*)	β	α	β'	β
LS (A.)	46.6	42.75	41.4	41.5	38.3	37.6
SS (A.)	4.14 vs	4.57 m	5.33 w	4.11 s	4.79 vw	5.18 vw
		4.23 vs	4.59 s		4.32 s	4.59 s
		4.07 m	3.96 w		4.11 s	
		3.81 s	3.82 w		3.80 m+	3.79 m
			3.73 s			
MP (Exptl)	47°[a]	69°		34.5°[a]	60.8°	
(Lit.)	46.5° (*4*)	68.6° (*5*)		37° (*5*)	58.5° (*5*)	

s = small, vs = very small, m = medium, w = weak, vw = very weak, LS = long spacing, SS = short spacing, MP = melting point

[a] Softening point

XRD-1 unit employing $CuK\alpha$ nickel-filtered radiation and a 0.025-inch pinhole system.

A close comparison of melting behavior of the three PSP phases is given in Table III.

The closely related lower homolog of PSP, 2-palmitoyldimyristin (MPM), was prepared from 1,3-dimyristin with palmitoyl chloride in pyridine. It was subjected to typical polymorphic examination with results shown in Table II and then treated, in a manner identical to PSP, with succinic acid in hexane and crystallized at 10° C. to test for appearance of β phase.

DISCUSSION

The entirely unexpected and accidental discovery of the β form of PSP can be seen in proper perspective if the phase sequence α, β, β' for PSP is considered in relation to the sequence α, β', β for tristearin (SSS). In the more familiar SSS case, supercooling of the melt occurs well below the highest β melting point and considerably below the intermediate β' melting point, but very little below the α melting point. Accordingly, sufficiently rapid cooling results in α crystallization; intermediate cooling permits β'; very slow cooling gives β which also arises by transformation of α and β'. The conditions for β' must be nicely established to avoid α on the one hand and β on the other. In fact, the intermediate phase disappeared for a time from the literature. Purer (and faster transforming) SSS demanded improved techniques of observation before revealing its intermediate polymorphic form.

The situation appears to be analogous for PSP, but here β is the intermediate form. It is so elusive that it has not yet been obtainable from melt. Obtaining it from solvent, without other additive, was a late observation.

Once β PSP is obtained, it can serve as seed for further β crystallization (Table I); likewise β tripalmitin (PPP), SSS, and tribehenin seed β PSP, but not without a considerable proportion of β'. However, β SPS has no seeding action for β PSP.

The first and simplest way of obtaining β PSP was through the action of succinic acid, 0.1% in a 5% solution of PSP in vegetable oil or mineral oil at 32° C. or lower, or hexane at 27° C. or lower. So insoluble is the succinic acid (<0.001% at 27° C. in hexane) that crystals exist at any significant concentration. The function of the solid additive is promotion of β crystallization rather than suppression of beta prime. This is evident visually and was shown by comparative cooling curves of 75 gram samples of 5% PSP in cottonseed oil with and without succinic acid. An earlier and faster crystallization was observed in the presence of the β-promoting succinic.

Attempts to grow β on large crystals of succinic were either unsuccessful or involved secondary small crystals of succinic deposited from heated systems. Consequently no preferred orientation has been observed. Nevertheless it appears quite possible that epitaxy,—i.e. oriented overgrowth, is involved.

The phenomenon of epitaxy has been discussed critically by Pashley (*6*). For epitactic growth a correspondence is required (but not a close one) between the arrangement of structural elements (atoms) in the contacting faces of substrate and overgrowth. Epitaxy normally involves the growth of a familiar structure type on the substrate; it is rare that an abnormal structure such as β PSP is produced. However, RbBr crystallizes in a "CsCl structure" (*6*) on Ag although it normally crystallizes in a NaCl structure. Evidence of epitaxy with organic structures is uncommon, but overgrowth of polyethylene on NaCl has been reported (*7*).

Effects of Storage. The relative stability of β PSP is a question of major interest. With due allowance for the complexities of melting point observation, indicated in Table III, it seems proper to regard the β melting point as 2–3° C. below the β' melting point. β is the stable for at least 1 month at 38° C. At 44° C. it is stable for 1 week (but not 1 month), for less than 1 week at 49° C., for less than 1 day at 60° C., and at 65° C. transforms (via melt) to β' in less than 1 hour. In solvent or in oil at 25° C., β is converted to β' in less than 6 months.

Table III. Thermal Data for 2-Stearoyldipalmitin

Phase	Preparation	Softening Point (*5*)	Complete Melting Point
α	Chilled melt	47.0 ± 0.5	(68.0)[a]
β'	Transformation of α 15 min. 47° C.	64.6 ± 0.5[b]	67.9
β'	Solvent crystallization	68.0 ± 0.5	68.7
β	Solvent crystallization	65.5 ± 0.5	(68.2)[a]

[a] Probably transformed to β'.

[b] Probably microcrystalline and poorly organized.

It is possible that β PSP is thermodynamically stable at low temperatures. Such a situation is known for triclinic hydrocarbon and fatty acid phases (of similar short spacings), but stability of both β' and β is so great at 0° to −20° C. that a 50 to 50 β' to β slurry in hexane is changed little or none in 1 month.

A considerable range of additives was tested. All dibasic acids of the series oxalic through sebacic are effective in β promotion as well as a number of other dibasic acids. Tartaric acid and succinic anhydride are effective, glycolic acid partially so. The variety of effective additives is large, with no clear-cut indication of common character except the necessity of existing in the solid state.

The importance of solvent seems to lie mainly in whether or not it dissolves the additive.

Predictable departures from Malkin's evidence (*5*) were observed for the polymorphism of MPM. It shows, like PSP, stable β' and fleeting α. Like PSP it is induced into the β phase by 0.1% succinic in hexane at 10° C. This β was converted about 50% to β' in one month at 27° C. β was not obtained from melt or solvent without succinic added.

It is not to be assumed that the β crystalline states here reported for PSP and MPM can be equated with those reported by Malkin. Under his conditions, PSP and MPM are believed to be dimorphic (α and β'), not tetramorphic as he suggested.

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LITERATURE CITED

(1) Chapman, D., *J. Chem. Soc.* **1956**, p. 2522.
(2) Chapman, D., *Ibid.*, **1957**, 2715.
(3) Jackson, F.L., Lutton, E.S., *J. Am. Chem. Soc.* **72**, 4519 (1950).
(4) Lutton, E.S., Jackson, F.L., Quimby, O.T., *J. Am. Chem. Soc.* **70**, 2441 (1948).
(5) Malkin, T., Meara, M.L., *J. Chem. Soc.* **1939**, p. 103.
(6) Pashley, D.W., Advances in Physics, Vol. **5**, 173 (1956).
(7) Willems, J., *Discussions Faraday Soc.*, No. **25**, 111–113, 204–207 (1958).

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