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The Polymorphism of 1-Stearyl- and 1-Palmityldiacetin, -dibutyrin, -dicaproin and 1-Stearyldipropionin

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The polymorphism of seven unsymmetrical diacid triglycerides, whose acyl chains differ by 10 to 16 carbon atoms, is reported. The solid polymorphic forms observed are: sub-alpha, alpha and beta for 1-palmityl- and 1-stearyldiacetin and for 1-stearyldipropionin; sub-alpha and alpha for 1-palmityl- and 1-stearyldibutyrin; sub-alpha and beta prime for 1-palmityldicaproin; and sub-alpha, beta prime and beta for 1-stearyldicaproin. All polymorphic forms are of triple chain length structure. The relationship of the melting points and X-ray long spacings of these glycerides to others of the SC_nC_n and PC_nC_n series has been shown. A new waxy, translucent and relatively stable alpha form was observed for the five lower molecular weight members.

Recent reviews[1,2] have dealt, in part, with the polymorphism of *mixed saturated diacid triglycerides*. Since their publication two other studies in this field have been reported from this Laboratory. The first[3] involved the behenyl radical, with a chain substantially greater than C_{18}; the second[4] involved very short acyl radicals in symmetrical triglycerides. Where chain length difference of 2 or less occurs within triglycerides, it is typical to observe three polymorphic forms—alpha. beta prime and beta—each of double-chain-length structure. With greater chain length difference there are many and varied exceptions to this behavior.

Particularly interesting is the present group of 1-stearyl and 1-palmityl compounds, SC_nC_n and PC_nC_n, where n is a low number and hence C_n represents a very short acyl radical. All forms of all members of this group show triple chain length structure. The triglycerides with $n = 2$ to 4 are chiefly notable for their relatively stable alpha forms. A summary of observed forms for the seven triglycerides of the present study appears in Table I where, for example, SC_4C_4 signifies 1-stearyldibutyrin.

TABLE I

POLYMORPHIC FORMS OF SC_nC_n AND PC_nC_n TRIGLYCERIDES WHERE n IS SMALL

SC_2C_2, PC_2C_2 and SC_3C_3	SC_4C_4 and PC_4C_4	SC_6C_6	PC_6C_6
Sub-alpha-3	Sub-alpha-3	Sub-alpha-3	Sub-alpha-3
Alpha-3	Alpha-3		
		Beta prime-3	Beta prime-3
Beta-3			Beta-3

Experimental

The seven unsymmetrical mixed triglycerides were synthesized by treating 1-monostearin or 1-monopalmitin with an excess of the appropriate acid chloride in the presence of pyridine according to established methods. The 1-monoglycerides were prepared by directed rearrangement according to the method of Eckey and Formo.[5] The acetyl, propionyl and butyryl chlorides were purchased from Eastman Kodak Co. Caproyl chloride was prepared from purified sorbic acid.[4]

The crude triglycerides were purified by 4–6 crystallizations from ethanol, ethanol–ether or ethanol–Skellysolve B mixtures as required by the solubility of the triglyceride being purified. The final product was carefully dried *in vacuo* over phosphorus pentoxide. Acid values were all less than 0.4; saponification values were as follows: SC_2C_2, 380.4 (theory 381.0); PC_2C_2, 406.9 (406.2); SC_3C_3, 353.5 (357.6); SC_4C_4, 336.4 (337.5); PC_4C_4, 355.8 (357.6); SC_6C_6, 301.3 (303.3); PC_6C_6, 317.9 (319.5).

Glyceride polymorphism was studied by the same X-ray and m.p. techniques used in earlier studies. A General Electric XRD unit with 0.025″ pinhole system was used to obtain flat film patterns. Short spacing determinations were made with a sample-to-film distance of 5.0 cm. while 10 cm. distance was used for long spacing and detailed short spacing determinations. Characteristic thermal and X-ray data for the various polymorphic forms of the seven triglycerides are given in Table II.

Discussion

Polymorphic Behavior.—These glycerides show considerable uniformity within pairs, but various pairs differ from each other. SC_3C_3 behaves like the -diacetin pair. The five lower members show no beta prime form; the -dibutyrins show no forms melting higher than alpha. The -dicaproins apparently lack a true alpha form, sub-alpha existing up to the lowest metastable m.p.; both show beta prime, but the stearyl compound lacks beta, shown by the palmityl compound.

The triple-chain-length structure shown by all forms of all seven glycerides is not surprising in view of the fact that triple structures are common for glycerides whose acyl chains differ by four or more carbon atoms. This is the first observation of triple chain length alpha, however.

Fig. 1.—Postulated schematic triple chain length structure.

A likely schematic configuration for the triple chain length structure is the so-called "chair type"[2] (Fig. 1) in which the longer acyl residues are paired.

Waxy Translucent Form of Unsymmetrical Triglycerides.—One of the most interesting features in this work was the observation of a waxy translucent alpha form of matter for five of the seven triglycerides investigated, namely, SC_2C_2, PC_2C_2, SC_3C_3, SC_4C_4 and PC_4C_4. The translucent alpha form of each of these five triglycerides is unusually stable; in fact, the alpha form of each dibutyryl member appears to be indefinitely stable between its melting point and the sub-alpha transformation point, for no higher melting polymorphic forms were observed.

Sub-Alpha to Alpha Reversible Solid Transformation.—Five of the seven unsymmetrical tri-

(1) A. E. Bailey, "Melting and Solidification of Fats," Interscience Publishers, Inc., New York, N. Y., 1950.

(2) E. S. Lutton, *J. Am. Oil Chem. Soc.*, **27**, 276 (1950).

(3) F. L. Jackson and E. S. Lutton, THIS JOURNAL, **72**, 4519 (1950).

(4) F. L. Jackson, R. L. Wille and E. S. Lutton, *ibid.*, **73**, 4280 (1951).

(5) E. W. Eckey and M. W. Formo, *J. Am. Oil Chem. Soc.*, **26**, 207 (1949).

TABLE II

CHARACTERISTIC THERMAL AND X-RAY DATA

r = transforms reversibly to alpha in solid state; m = moderately; t = thermodynamically.

	SC_2C_2	PC_2C_2	SC_3C_3	SC_4C_4	PC_4C_4	SC_6C_6	PC_6C_6
Melting points, °C.							
Sub-alpha-3	..	..	..	..	..	6.0	−7.4
Alpha-3	34.1	22.4	23.5	15.6	2.9	..	..
Beta prime-3	..	..	..	..	..	16.9	12.0
Beta-3	47.8	42.3[a]	31.7	..	..	21.2	..
X-Ray data: long spacings, Å.							
Sub-alpha-3	37.1	34.7	40.5	42.1	39.9	45.5	43.2
Alpha-3	36.5	34.1	39.5	42.3	39.6	..	..
Beta prime-3	..	..	..	..	..	41.2	39.7
Beta-3	34.0	31.5	34.1	..	..	38.3	..
Short spacings, Å.							
Sub-alpha-3	4.13 VS 3.65 M 2.96 W 2.52 W		4.20 VS 3.77 S 2.53 W	4.20 VS 3.71 S 2.55 W		4.18 VS 3.71 S 2.55 W	
Alpha-3	4.13 VS 2.41 VW		4.14 VS 2.41 VW	4.14 VS 2.40 VW		.....	
Beta-prime-3	.....		.....	.....		4.15 S 3.69 M	4.22 S 4.03 S 3.74 M
Beta-3	4.85 M 4.64 S 4.13 M 3.77 VS 2.50 W 2.16 M		5.50 M 4.60 VS 4.35 M 4.11 M 3.94 S 3.60 M 3.50 W+ 2.59 W+	.....		5.28 M 4.68 M 4.54 S 4.38 M 4.11 M 3.93 S	.....
Polymorphic stability							
Sub-alpha-3	r	r	r	r	r	Unstable	Unstable
Alpha-3	m. stable	m. stable	m. stable	Stable	Stable	.....	.....
Beta prime-3	.....	.....	.....	....	....	Unstable	Stable
Beta-3	t. stable	t. stable	t. stable	....	....	t. stable	.....

[a] No literature values found for these triglycerides except for PC_2C_2 (m.p. 42.5–43.5°) prepared as a derivative of 1-monopalmitin in characterizing the monoglyceride obtained from hog pancreas.[6]

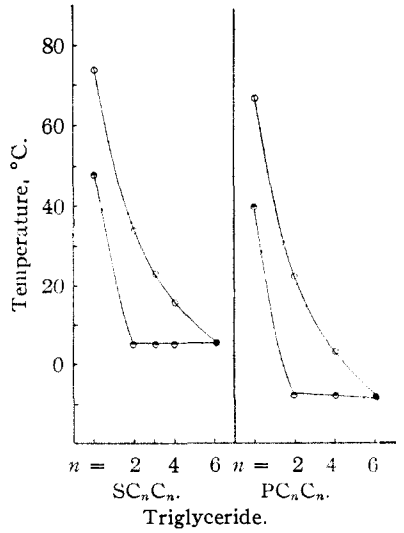

Fig. 2.—Region for existence of alpha: ○, alpha m.p.; ◓, alpha ⇄ sub-alpha transformation point; ●, apparent sub-alpha m.p.

glycerides investigated here show a reversible solid-solid alpha to sub-alpha transformation. The plots of alpha melting points and of reversible transformation temperatures in Fig. 2 are interesting in that the spread between alpha m.p. and alpha to sub-alpha transformation temperature decreases with increasing chain length of the diacyl members. The failure to find an alpha form for the dicaproyl members (SC_6C_6, PC_6C_6) could be due to a very small temperature range of existence for the alpha form. It will be noted (Fig. 2) that the monoglycerides[7] were considered as end members for the series, an assumption which may not be entirely warranted because of dissimilarity of thermal and X-ray behavior to be discussed later.

Melting Point Behavior: Relationship to Homologs.—The melting point behavior of the seven unsymmetrical triglycerides reported here is correlated graphically in Fig. 3 with data[1-3,7,8] for other SC_nC_n and PC_nC_n glycerides in Figs. 3 and 4. The SC_6C_6 and PC_6C_6 triglycerides are the minimum melting members of each of their respective series. The fact that most of the m.p. values fall on

(6) M. E. Jones, F. L. Koch, A. E. Heath and P. L. Munson, *J. Biol. Chem.*, **181**, 755 (1949).

(7) E. S. Lutton and F. L. Jackson, THIS JOURNAL, **70**, 2445 (1948).

(8) F. L. Jackson and E. S. Lutton, unreported data.

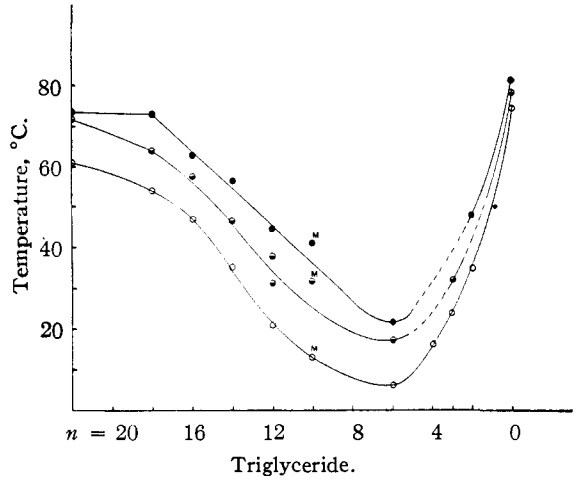

Fig. 3.—M.p. data for SC_nC_n series (data of Jackson, Lutton, *et al.*, except M-data of Malkin, *et al.*): O, alpha (sub-alpha); ◒, beta prime; ●, beta.

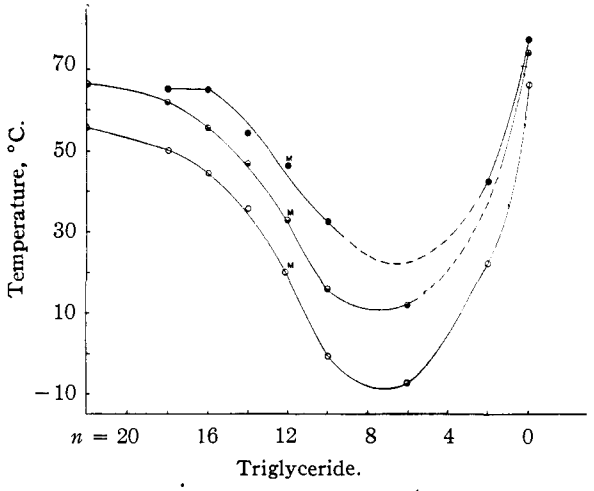

Fig. 4.—M.p. data for PC_nC_n series (data of Jackson, Lutton, *et al.*, except M-data of Malkin, *et al.*): O, alpha (sub-alpha); ◒ beta prime; ●, beta.

smooth curves lends support to the reliability of individual values. The extremely high m.ps. of the monoglycerides do not fit too well as end values of the diacyl series.

The low melting behavior of SC_6C_6 and PC_6C_6 is in agreement with previously reported data[4] in which the SC_6S and PC_6P triglycerides were found to have the minimum melting points of the SC_nS and PC_nP series. The low melting behavior of the caproyl-containing triglycerides is further correlated with the fact that for the normal saturated fatty acids, a m.p. minimum is observed in the region of the four or five carbon acids.[1]

X-Ray Long Spacings: Relationship to Homologs.—X-Ray long spacing data for the unsymmetrical stearyl- and palmityldiacetins, dibutyrins and dicaproins and for stearyldipropionin are shown in relationship to others of the SC_nC_n and PC_nC_n series in Figs. 5 and 6. It will be noted that in general the long spacing values fall on straight lines. There is a sharp break in long spacing values at $PC_{10}C_{10}$ and at SLL[8] for the alpha and

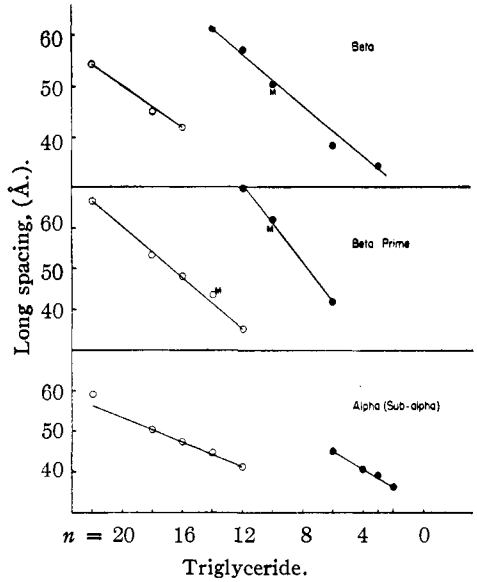

Fig. 5.—Long spacings for SC_nC_n series (data of Jackson, Lutton, *et al.*, except M-data of Malkin *et al.*): O, double chain length structure; ●, triple chain length structure.

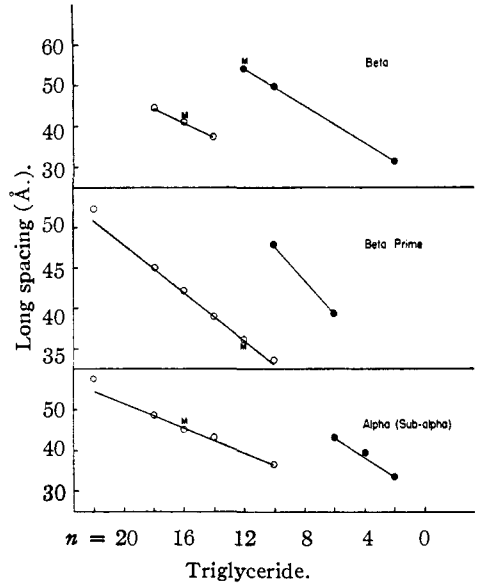

Fig. 6.—Long spacings for PC_nC_n series (data of Jackson, Lutton, *et al.*, except M-data of Malkin, *et al.*): O, double chain length structure; ●, triple chain length structure.

beta prime forms. At this point the higher molecular weight homologs assume double chain length structures. However, beta forms of the SC_nC_n and PC_nC_n series crystallize in triple chain length structures if the acyl chain lengths differ by as much as four carbon atoms.

With respect to long spacing values, the 1-monoglycerides do not fit as end members of the two series.

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