Polymorphism of Mixed Triglycerides Containing Odd Fatty Acids

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ABSTRACT

Pairs of $C_nC_{(n+1)}C_n$ (i.e., $C_{16}C_{17}C_{16}$ and $C_{18}C_{19}C_{18}$) and $C_nC_{(n-1)}C_n$ triglycerides ($C_{16}C_{15}C_{16}$ and $C_{18}C_{17}C_{18}$) triglycerides, n even, were prepared to compare with $C_nC_{(n+2)}C_n$ and $C_nC_{(n-2)}C_n$ glycerides, respectively, in polymorphic behavior. It was found that $C_nC_{(n+1)}C_n$ compounds were β' tending and $C_nC_{(n-1)}C_n$ compounds β tending in line with their all-even counterparts. The glyceride $C_{11}C_{13}C_{11}$ is β' stable, like $C_{10}C_{12}C_{10}$ and $C_{16}C_{18}C_{16}$, and seems closely related to them in physical behavior and diffraction characteristics.

INTRODUCTION

The polymorphism of odd single acid triglycerides has recently been reviewed (1) and compared with that of even triglycerides. Odd and even behavior is similar, but β' forms are relatively more stable for odd triglycerides. No mixed odd-even triglycerides had been explored and a natural curiosity existed as to whether such compounds have unique features or represent a blending of odd and even behavior, especially since some mixed C_{16} and C_{18} triglycerides show striking differences from each other in polymorphic behavior.

EXPERIMENTAL PROCEDURES

Four odd-even triglycerides were made: 2-pentadecanoyl-1,3-dihexadecanoin ($C_{16}C_{15}C_{16}$), 2-heptadecanoyl-1,3-dihexadecanoin ($C_{16}C_{17}C_{16}$), 2-heptadecanoyl-1,3-dioctadecanoin ($C_{18}C_{17}C_{18}$), and 2-nonadecanoyl-1,3-dioctadecanoin ($C_{18}C_{19}C_{18}$). In addition one mixed odd triglyceride was made: 2-tridecanoyl-1,3-diundecanoin ($C_{11}C_{13}C_{11}$).

Synthesis of Odd-Even Triglycerides

The 1,3 diglycerides were prepared by directed inter-

TABLE I

Analyses

Triglyceride[a]	Saponification value		Total fatty acids	
	Experiment	Theory	Experiment	Theory
$C_{16}C_{15}C_{16}$	211	212.2	95.1	95.2
$C_{16}C_{17}C_{16}$	205	204.9	93.5	95.4
$C_{18}C_{17}C_{18}$	189	191.8	93.8	95.7
$C_{18}C_{19}C_{18}$	182	185.8	92.8	95.8
$C_{11}C_{13}C_{11}$	267	269.7	94.8	93.9

[a]All show one spot by thin layer chromatography (hexane-ethyl ether-acetic acid 80:20:1 on Silica Gel G).

TABLE II

Polymorphism of Mixed Odd Glycerides

Glyceride	α	β'	β
Thermal behavior, mp, °C			
$C_{18}C_{19}C_{18}$	55.5	69.8	
$C_{16}C_{17}C_{16}$	48.2 (fleeting)	62.8	
$C_{18}C_{17}C_{18}$	53.1		65.0
$C_{16}C_{15}C_{16}$	43.4		56.5
$C_{11}C_{13}C_{11}$	—[a]	42.6	
Diffraction behavior, Å			
Long spacings			
$C_{18}C_{19}C_{18}$	51.5	46.6	
$C_{16}C_{17}C_{16}$	46.5	41.5	
$C_{18}C_{17}C_{18}$	49.7		44.2
$C_{16}C_{15}C_{16}$	43.8		39.5
$C_{11}C_{13}C_{11}$	32.5 (sub α^b)	30.9	
Short spacings			
$C_{18}C_{19}C_{18}$	4.12S	4.22S, 4.08M, 3.80M	In mixed phases from hexane
$C_{16}C_{17}C_{16}$		4.31W+, 4.15S, 3.98W, 3.80S-	In mixed phases from hexane
$C_{18}C_{17}C_{18}$		Traces from acetone	5.30W, 4.54S, 3.83M 3.68W, 3.57W-
$C_{16}C_{15}C_{16}$		Traces from acetone	5.27W, 4.54S, 3.84S 3.71M, 3.58W
$C_{11}C_{13}C_{11}$	4.14S, 3.81 W+ (sub α^b)	4.37S-, 4.17VS, 3.95W 3.80S	

[a]Too fleeting.
[b]At -20 C.

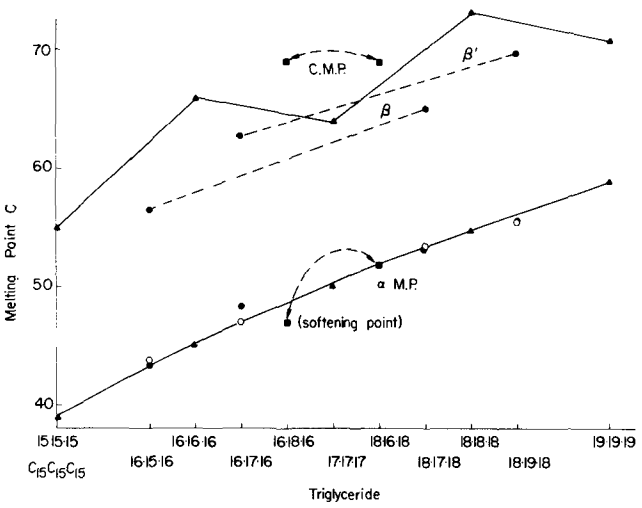

FIG. 1. Melting points. ▲ Single acid triglycerides; ■ mixed even triglycerides; ● mixed odd-even triglycerides; ◇ differential thermal analysis point, mixed odd-even triglycerides. (The curved dashed lines ending in arrows suggest only tenuous relationship between the two mixed even acid triglycerides.)

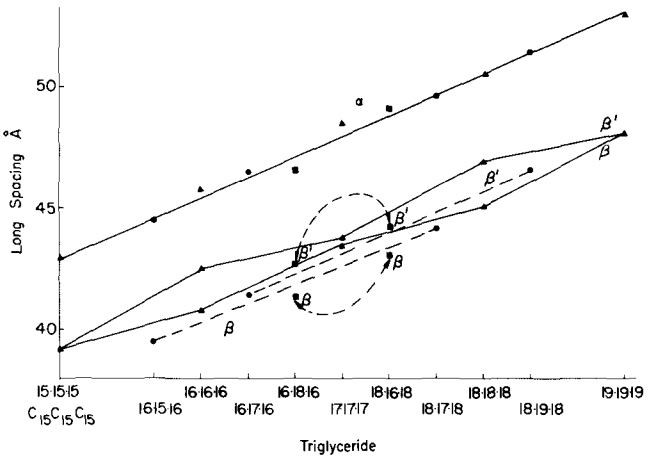

FIG. 2. Long spacings. ▲ Single acid triglycerides; ■ mixed even triglycerides; ● mixed odd-even triglycerides. (The curved dashed lines ending in arrows suggest only tenuous relationship between the two mixed even acid triglycerides.)

esterification (2,3) and purified by crystallization to 97% purity, according to thin layer chromatography (TLC) (benzene-tetrahydrofuran-acetic acid 95:4.5:0.5 on Silica Gel G), about as high purity as is obtainable by crystallization. The fatty acid purity was 97.2%, C_{16} for 1,3-dihexadecanoin and 99.2% C_{18} for 1,3-dioctadecanoin.

The C_{15}, C_{17} and C_{19} acid chlorides were made from the corresponding acids (>99% purity by gas liquid chromatography) used in a previous study (1). Reaction of acid chlorides with appropriate diglycerides in the presence of pyridine (3) yielded the desired triglycerides. These were adsorbed from hexane on a silica gel column (containing 5% H_2O) and eluted with benzene. Final purification was by crystallization from acetone 1:30 at 1 C, 1 C, 10 C and 10 C for $C_{16}C_{15}C_{16}$, $C_{16}C_{17}C_{16}$, $C_{18}C_{17}C_{18}$ and $C_{18}C_{19}C_{18}$, respectively. Final purity as triglycerides was 98, 99, 99 and 99%, respectively, by TLC.

Synthesis of $C_{11}C_{13}C_{11}$

The 1,3-diundecanoin was prepared by reacting 0.11 moles of acid (99% pure [1]) with 0.060 moles dry glycerol in the presence of 0.25 g *p*-toluene sulfonic acid with mechanical agitation under N_2 flow for 4 hr at 140 C. The reaction mix in hexane, washed four times with distilled H_2O, was chromatographed on silica gel (5% H_2O) to recover diglyceride free of mono- or tri-. Two recrystallizations from 10 volumes of acetone at 1 C gave a product of 97% 1,3-diundecanoin as indicated by TLC.

The diundecanoin (0.01 mole) was reacted with 0.0145 moles tridecanoyl chloride (from 99% tridecanoic acid, 99% purity, and thionyl chloride) in the presence of pyridine by familiar procedure (3). The water-washed reaction mix in hexane was dried and chromatographed on anhydrous alumina to remove mono- and diglycerides. Crystallization from petroleum ether at -20 C gave a sample producing a single triglyceride spot by TLC.

Analyses of triglycerides appear in Table I. A combination of saponification value, total fatty acid and TLC is judged superior to elemental analysis for glyceride characterization. Enzymatic analyses were not employed since there is little evidence of acyl wandering under the conditions of synthesis.

Polymorphism was studied by familiar methods employing melting point, differential thermal analysis (DTA) and X-ray diffraction techniques (1,4,5). Briefly α melting points were obtained by "rapid complete mp" on capillary samples melted and chilled in the capillary. Other melting points were obtained by "complete mp" technique on samples treated in the capillary or on stuffed capillaries; X-ray diffraction by film technique was carried out on samples in pyrex glass capillaries, melted and chilled in the capillary in the case of α or other phase prepared via melt, but stuffed into the capillary in case of solvent crystallized phases. DTA generally involved three treatments with small 10 mg samples: (a) heating of solvent-crystallized samples to follow melting of stable forms, (b) cooling of melt to observe crystallization of α, and (c) heating of cooled melt to observe melting of α. Special procedure was necessary for $C_{11}C_{13}C_{11}$, namely the use of liquid nitrogen to cool the sample far enough below zero in order to explore low temperature transformation upon reheating.

The experimental data appear in Table II and Figures 1 and 2.

RESULTS AND DISCUSSION

The behavior of the mixed odd-even triglycerides was very much in keeping with that of similar all-even triglycerides. Thus $C_nC_{(n+1)}C_n$ resemble $C_nC_{(n+2)}C_n$ glycerides, and $C_nC_{(n-1)}C_n$ resemble $C_nC_{(n-2)}C_n$ glycerides.

All four of the odd-even compounds show the expected α. It is a rather fleeting phase for $C_{16}C_{17}C_{16}$, but not so fleeting as that of $C_{16}C_{18}C_{16}$ for which a softening point must be obtained, a complete α melting point not being observable. The α form of $C_{18}C_{19}C_{18}$ is less fleeting.

The $C_nC_{(n+1)}C_n$ glycerides readily show β' from solvent or transformed α; traces of β appeared in some crystallizations from hexane, but pure β was not obtained after varied efforts. Conversely $C_nC_{(n-1)}C_n$ glycerides readily show β from solvent or transformed α; β', in small proportion, was obtainable from acetone, but never approaching purity. Such behavior is in keeping with the normal appearance via melt of β' for $C_{16}C_{18}C_{16}$ and β for $C_{18}C_{16}C_{18}$.

As seen in Figure 1, α melting points fall rather well on a curve (essentially) according to molecular weight. The complete melting points of $C_nC_{(n+1)}C_n$ compounds fall relatively below $C_nC_{(n+2)}C_n$ as $C_nC_{(n-1)}C_n$ values fall below those for $C_nC_{(n-2)}C_n$, in line with typical odd vs. even behavior. The β-tending $C_nC_{(n-1)}C_n$ values fall relatively below β'-tending $C_nC_{(n+1)}C_n$ values in keeping with $C_{18}C_{16}C_{18}$ behavior, with respect to that of $C_{16}C_{18}C_{16}$.

Long spacing values of the present glycerides fall into a rational pattern according to phase and molecular weight. The α values fall reasonably near a single line including values of odd and even neighbors. The values of β-forming compounds lie relatively below, although only a little

TABLE III

β' Diffraction Comparison: Odd vs. Even[a] Mixed Glycerides

Glyceride	Short spacings, Å	Long spacings, Å
$C_{10}C_{12}C_{10}$	4.33S+, 4.11S+, 3.80S	28.9
$C_{11}C_{13}C_{11}$	4.37S-, 4.17VS, 3.95W, 3.80S	30.9
$C_{12}C_{14}C_{12}$	4.43W, 4.23VS, 4.01M, 3.80S	33.8
$C_{14}C_{16}C_{14}$	4.31S, 4.13S-, 3.81S	38.1
$C_{16}C_{18}C_{16}$	4.30M, 4.15VS, 3.98M, 3.79S	42.75

[a]Diffraction pattern re-examined for present study in case of $C_{14}C_{16}C_{14}$ and $C_{16}C_{18}C_{16}$ (6). $C_{10}C_{12}C_{10}$ and $C_{12}C_{14}C_{12}$ prepared and examined. Diffraction data in qualitative agreement with those of Malkin and Meara (7).

below, the values for β'-tending compounds, just as the β values lie below β' values for even (single acid) glycerides and for $C_nC_{(n+2)}C_n$ and $C_nC_{(n-2)}C_n$ glycerides. However it has been observed (1) for odd single acid triglycerides that β long spacings are greater than β' long spacings. (A look at di-odd mono-even glycerides would be interesting.)

In the study of β' forms of odd triglycerides (1) there appeared a variation of diffraction pattern with chain length which was paralleled by the variation in β' forms of even $C_nC_{(n+2)}C_n$ triglycerides. Such a behavior is not so clearly seen with even single acid triglycerides, it is believed, because the low stability and generally very small particle size of β' crystallites of these glycerides results in more diffuse diffraction patterns. It was at first thought that β' of odd $C_nC_{(n+2)}C_n$ glycerides might resemble β' of even $C_nC_nC_n$ as β' of even $C_nC_{(n+2)}$ resemble β' of odd $C_nC_nC_n$, whence part of the interest in $C_{11}C_{13}C_{11}$. While observations on a single member of a series permit only limited conclusions, the short spacings of β' $C_{11}C_{13}C_{11}$ seem to correspond rather well to the even $C_nC_{(n+2)}C_n$ series as seen in Table III rather than to fit specifically the even $C_nC_nC_n$ series.

A second form, here called Subα, was observed for $C_{11}C_{13}C_{11}$ at -20 C. It was too fleeting (as was α if it exists) to permit thermal point determination. This behavior is in line with the notably fleeting character of the α form of $C_{16}C_{18}C_{16}$.

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