Polymorphism of 1-Behenoyldistearin and 2-Stearoyldibehenin

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ABSTRACT

The triglyceride 1-behenoyldistearin shows α-2, β-2, β′-2 and β-3 forms in order of increasing stability. The previously unobserved β-2 form of the closely related homolog 1-stearoyldimyristin has now been observed on crystallization from hexane. The triglyceride 2-stearoyldibehenin shows an α-2 form and two modifications of β′-2 type. No β-3 form was observed such as has been previously observed for the related homolog 2-myristoyldistearin.

INTRODUCTION

The glycerides 1-behenoyldistearin $C_{22}C_{18}C_{18}$ and 2-stearoyldibehenin $C_{22}C_{18}C_{22}$ are important components of highly hydrogenated rape and crambe oils. Their crystallization behavior is therefore of interest.

It is also of interest to compare their behavior with that of closely related lower homologs and with previously studied 2-behenoyldistearin $C_{18}C_{22}C_{18}$ and 1-stearoyldibehenin $C_{22}C_{22}C_{18}$ (1).

EXPERIMENTAL PROCEDURES

As previously described (2) isomerically pure 1-monobehenin was prepared and found to be 99% 1-monoglyceride, which was 99% 1-isomer, by thin layer chromatography (TLC). The C_{22} percentage was 97.5 by gas liquid chromatography.

The triglyceride 1-monobehenoyldistearin ($C_{22}C_{18}C_{18}$) was prepared from 1-monobehenin by reaction with stearoyl chloride, 99.5% C_{18}, in the presence of pyridine (3).

The crude product was purified by chromatography on silica gel, then crystallized successively from hexane and acetone to yield a pure triglyceride by TLC and by analyses given in Table I.

By directed interesterification (3,4) 1,3-dibehenin of 98% isomeric purity and 99.8% C_{22} was prepared.

The triglyceride 2-stearoyldibehenin ($C_{22}C_{18}C_{22}$) was prepared from 1,3-dibehenin (of 98% C_{22}) and stearoyl chloride of 99.7% C_{18} in the presence of pyridine (3). The reaction product was chromatographed on silica gel and crystallized from heptane. Analyses appear in Table I. (A preparation via 2-monostearin and behenoyl chloride gave substantially identical results.)

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

Phase behavior was explored by familiar melting point, differential thermal analysis (DTA) and X-ray diffraction techniques. The procedures are indicated in a companion paper on mixed glycerides containing odd acids (5).

Because of a lack of correspondence in phase behavior between $C_{22}C_{18}C_{18}$ and previously explored 1-stearoyldimyristin, $C_{18}C_{14}C_{14}$ (6), the latter glyceride was further examined, specifically after crystallization from hexane.

Results of phase study of the three glycerides are reported in Table II.

DISCUSSION

There are four polymorphs of $C_{22}C_{18}C_{18}$—α-2, β-2, β′-2 and β-3, in order of increasing melting point. There is nothing unusual about α, obtained by chilling the melt, except perhaps its considerable stability. However the present β-2 from hexane is less familiar in behavior. Unlike the stable β-2 of tripalmitin ($C_{16}C_{16}C_{16}$) or tristearin ($C_{18}C_{18}C_{18}$), the present β-2 transforms to either β′-2 or β-3 depending on conditions. This metastability of β-2 is not unprecedented, for it has been observed in $C_{16}C_{18}C_{16}$ and, indeed, in $C_{18}C_{16}C_{18}$. So far it has not been possible to get β-2 via melt for $C_{22}C_{18}C_{18}$ (nor for $C_{16}C_{18}C_{16}$, but β-2 is easily obtained from melt for $C_{18}C_{16}C_{18}$).

There seems little doubt that β-3, while not readily accessible, is the stable form, at high temperatures at least; although β′-2 is quite stable and, when well formed, resists conversion to β-3. While results are somewhat erratic, it appears that at 60 C β-2 transforms in 1 week to β′-2 and in 2 weeks to mainly β-3, but after standing 4 weeks at room temperature will not transform in 2 weeks at 60 C nor in 1 hr at 68 C.

Because of the β-2 phase from hexane observed for $C_{22}C_{18}C_{18}$ and since β-2 had not been found for $C_{18}C_{14}C_{14}$, it was decided to explore hexane crystallization for the latter glyceride; β-2 phase was indeed found. It was confirmed that β′-2 phase is obtainable for $C_{18}C_{14}C_{14}$ by crystallization from melt just above the α melting point. Thus $C_{22}C_{18}C_{18}$ and $C_{18}C_{14}C_{14}$ each show four distinct and comparable phases, with these differences (a) β′-2 and β-2 are close in melting point in the case of $C_{18}C_{14}C_{14}$, but β′-2 is much higher than β-2 in the case of $C_{22}C_{18}C_{18}$, (b) β-3 and β′-2 are close in melting point in the case of $C_{22}C_{18}C_{18}$, but β-3 is much higher than β′-2 in the case of $C_{18}C_{14}C_{14}$.

Because of the considerable interest in the uncommon β-2 to β′-2 transformation, the possibility of actual β-2 stability at low temperatures was explored for both

TABLE I

Analysis of Triglycerides

Triglyceride	*SV*[a]	*TFA*[b]	*TLC*[c]
$C_{22}C_{18}C_{18}$	173(177.6[d])	95.4(96.0)	100% Triglyceride
$C_{22}C_{18}C_{22}$	170(170)	94.9(97.8)	99% Triglyceride

[a]Saponification value.

[b]Total fatty acid.

[c]Thin layer chromatography with solvent system:—Hexane-ethyl ether-acetic acid 80:21:1 on Silica Gel G.

[d]Theory in parentheses.

TABLE II

Phase Behavior

$C_{22}C_{18}C_{18}$				$C_{18}C_{14}C_{14}$				$C_{22}C_{18}C_{22}$		
α-2[a]	β-2[b]	β'-2[c]	β-3[f]	α-2[a]	β-2[b]	β'-2[d]	β-3[e]	α-2[a]	β'_{II}[b]	β'_{I}[f]
Melting points, C										
56.3	65	69.7	70.7	35.9	46	46.5	56.4	61.1	71.0	72.5
Diffraction data, Å										
Long spacings										
55.0	48.1	49.0	75.5	44.5	39.5	41.3	61.7	58.0	53.0	51.5
Short spacings[g]										
4.11S	5.30W+	4.26W	5.16W	4.14VS	5.32W	4.33S	5.27W	4.11S	4.42W	4.45W
	4.58S	4.13S	4.52S		4.57VS	4.19S	4.58S		4.17S	4.18S
	3.86M+	3.95W	3.78VS		3.87S		4.24W+		3.95VW+	3.98M
	3.72M-	3.76M+			3.74M-	3.81S	3.78VS		3.76S	3.82M
	3.58W+				3.62M					

[a]From chilled melt.
[b]From hydrocarbon solvent.
[c]From acetone.
[d]From melt, held near α mp.
[e]From polar solvent.
[f]By transformation.
[g]VW, very weak; W, weak; M, medium; S, strong; VS, very strong.

$C_{22}C_{18}C_{18}$ and $C_{16}C_{18}C_{16}$. Mixtures of 1:1 β-2: β'-2 were prepared and digested in 1:10 hexane at various temperatures. Even at 10 C, the lowest temperature of test, 100% β'-2 is always more stable than β'2 for both $C_{22}C_{18}C_{18}$ and $C_{16}C_{18}C_{16}$.

$C_{22}C_{18}C_{22}$ showed α and β' forms. It appeared from minor changes in both long and short spacings that two β'-type forms must be distinguished, β'-2_{II} when freshly prepared and β'-2_{I} when stored. Preparations by both synthetic routes each showed the two structure types. No evidence of β-2 or β-3 forms was obtained, although β-3 was previously observed for the related homolog 2-myristoyl distearin (6).

The $C_{22}C_{18}C_{18}$ and $C_{22}C_{18}C_{22}$ forms compare with the earlier observed α-2, β'-2 and β-3 for $C_{22}C_{18}C_{22}$ and α-2, β'-2 and β-2 for $C_{18}C_{22}C_{22}$ (1).

GENERAL COMMENT ON TRIGLYCERIDE POLYMORPHISM

Problems persist in triglyceride polymorphism (7); some of these are unavoidable, some quite unnecessary. Discovery of new forms is always possible; the total field is complex, and the complete crystal structure is known in only two cases, namely the β forms of tricaprin and trilaurin. Any departure from tristearin, the behavior of which seems well established, must be considered with caution. But on the side of simplicity let it be said that very many fats and glycerides, indeed most of practical significance, behave like tristearin, with its three polymorphs, or vary only slightly from tristearin, e.g., by lacking a polymorph or by having relative stabilities of two polymorphs reversed.

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[Received October 15, 1971]