p functions; (6) is retarded to an increasing extent by *ortho* substituents with increasing steric requirements.

Evidence that basic ester interchange and basic ester hydrolysis are similar is provided.

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[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE COMPANY]

The Polymorphism of Certain Behenyl Mixed Triglycerides. A New Metastable Crystalline Form of Triglycerides

BY F. L. JACKSON AND E. S. LUTTON

Previous communications have discussed the X-ray diffraction and thermal behavior of mixed saturated diacid triglycerides.[1,2,3] These compounds, like the single fatty acid triglycerides,[4] *e. g.*, tristearin, in most cases exhibit three polymorphic forms (alpha, beta prime and beta) each with a characteristic melting point. Some differ in having only two such forms, *e. g.*, 2-stearyldipalmitin with no beta form,[2] while others have four forms each with characteristic melting level, *e. g.*, 2-myristyldistearin with alpha-2, beta prime-2, beta prime-4, and beta-3 forms.[1] Glycerides have been found to show a notable individuality in degree of stability of metastable forms. In no case has the vitreous-type form of Clarkson and Malkin[5,6] been observed.

In the present paper there are discussed the X-ray diffraction and thermal characteristics of the new diacid triglycerides, 2-behenyldipalmitin ($PC_{22}P$), 2-behenyldistearin ($SC_{22}S$), 1-palmityldibehenin ($PC_{22}C_{22}$), and 1-stearyldibehenin ($SC_{22}C_{22}$). These glycerides are of practical interest in that some probably occur in hydrogenated rapeseed and mustard seed oils.

The polymorphism of these behenyl-containing glycerides is similar in type to that reported for shorter chain compounds. However, the behenyl compounds all show rather high beta prime stability, $PC_{22}C_{22}$ exhibiting no beta form at all. The beta forms of the symmetrical compounds are beta-3, that of $SC_{22}C_{22}$ is beta-2.

A feature of considerable interest is the new sub-alpha form clearly manifested by the unsymmetrical behenyl glycerides at low temperatures (−50°). At higher temperatures, it transforms reversibly to alpha; it appears to be analogous to the sub-alpha form of monoglycerides.[7]

Experimental

The four mixed triglycerides were made by treating the corresponding mono- and diglycerides with an excess of behenyl chloride in the presence of pyridine according to established methods. The mono- and diglycerides were prepared by directed rearrangement according to the method of Eckey.[8] The behenyl chloride was prepared by treating an excess of oxalyl chloride with behenic acid, which had been obtained by complete hydrogenation of carefully purified erucic acid ($\Delta^{18:14}$-docosenoic acid).[9] Constants for the starting materials and the final products are given in Table I.

TABLE I

ANALYTICAL CONSTANTS OF STARTING MATERIALS AND PRODUCTS

	I. V.		Saponification value		Hydroxyl value		% Monoglyceride[10]	M. p., °C.		
	Calcd.	Found	Calcd.	Found	Calcd.	Found		Found	Lit.	Ref.
Erucic acid	74.5	74.5						33.4	33.5	10
Behenic acid	0	0.2						80.2	80.0	10
1-Monopalmitin	0	0	169.6	169			98.4	76.5	77.0	7
1-Monostearin	0	0.1	156.4	156.3			101.9	81.5	81.5	7
1,3-Dipalmitin	0	0	197.3	197.4	98	99	0.5	72.4	72.9	11
1,3-Distearin	0	0.1	179.7	179.4	90	92	0.4	78.2	78.2	11
$PC_{22}P$			188.8	190.6				66.6		
$SC_{22}S$			177.7	177.3				70.6		
$PC_{22}C_{22}$			172.5	172.3				66.1		
$SC_{22}C_{22}$			167.7	167.8				73.5		

Final purification of the glycerides was accomplished by four to six crystallizations from Skellysolve B or Skellysolve B–ethyl ether mixtures.

The polymorphism of the glycerides was studied by X-ray and melting point techniques described previously.[4] A General Electric XRD unit was used to obtain flat film patterns using a 0.025" pinhole. The film distances were 5.0 cm. for most short spacing determinations, and 10.0 cm. for detailed short spacing and for long spacing patterns. Detailed X-ray data are reported in Table II. For identification purposes and quick reference, the characteristic thermal and X-ray data for the various poly-

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[1] Jackson and Lutton, THIS JOURNAL, **71**, 1976 (1949).

[2] Lutton, Jackson and Quimby, *ibid.*, **70**, 2441 (1948).

[3] Lutton, *ibid.*, **70**, 248 (1948).

[4] Lutton, *ibid.*, **67**, 524 (1945).

[5] Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934).

[6] Clarkson and Malkin, *ibid.*, 985 (1948).

[7] Lutton and Jackson, THIS JOURNAL, **70**, 2445 (1948).

[8] Eckey and Formo, *J. Am. Oil Chem. Soc.*, **26**, 207 (1949).

[9] Handschumacher and Linteris, *ibid.*, **24**, 143 (1947).

[10] Ralston, "Fatty Acids and Their Derivatives," John Wiley & Sons, Inc., New York, N. Y., 1948.

[11] Baur, *et al.*, THIS JOURNAL, **71**, 3363 (1949).

TABLE II

DETAILED d/n VALUES FOR BEHENYL MIXED TRIGLYCERIDES

	$PC_{22}P$			$SC_{22}S$			$PC_{22}C_{22}$			$SC_{22}C_{22}$			
(hkl)	Alpha-2	Beta Prime-2	Beta-3	Alpha-2	Beta Prime-2	Beta-3	Sub-alpha-2	Alpha-2	Beta Prime-2	Sub-alpha-2	Alpha-2	Beta Prime-2	Beta-2
						Long Spacings Å.							
001	50.15VS	45.8VS	70.00VS	53.00VS	50.00VS	74.00VS	59.00VS	56.8VS	52.7VS	62.5S	59.20VS	52.30VS	55.6VS
002		22.8W	35.30S	26.50VW	24.80VW	37.20S		29.0VW	26.2VW		29.70VW	27.00W	27.0W+
003	16.60S	15.45S	23.60VW−	17.78S	16.35S	25.5W	19.55W	19.18S	17.28S	20.1W+	19.70S	17.78S	18.35S
004			17.57VW−	13.40VW				14.20W	13.47VW				
005		9.40W	14.18M	10.63W	9.80M	15.00S		11.55W	10.52W		11.70W	10.65W	10.90W
006		7.65W+	11.81W−		8.15VW	12.50VW−					9.88VW−		
007		6.15VW	10.00VW−	7.82W	7.14VW−				7.50VW−			7.65VW−	
008		5.69W−	8.80VW−		6.24W	9.40W						6.32VW−	6.85VW−
009			7.72VW		5.62VW−	8.35VW−						5.72VW−	
0010						7.57W							
0011						6.73VW−							
Av. d	50.0	46.0	70.4	53.2	49.4	75.1	58.9	57.4	52.4	61.4	59.1	53.3	54.6
						Short Spacings Å.							
	4.14VS	4.19VS	5.80W	4.14VS	4.94VW	5.78VW−	4.20S	4.15VS	4.20VS	4.20S	4.15VS	4.78VW−	5.42M
	2.39W	3.97W−	5.21VW	2.40VW	4.18VS	5.16W	3.72M	2.39VW	3.78S	3.77W+	2.43VW−	4.20VS	5.06VW−
		3.76S+	4.58S		3.78S	4.58S	2.52VW		3.45W	2.52VW		3.78S	4.72W
		3.45VW	4.27W		3.45VW−	4.28W			3.06W	2.24VW		3.50W	4.59S
		3.08W	3.79VS		3.07W	3.78VS			2.79VW			3.15VW	3.87S
		2.80VW	3.62W		2.77W	3.62VW			2.54W+			3.03VW−	3.70S
		2.54W	3.47VW		2.55W	3.46VW−			2.26W+			2.83VW−	3.42VW
		2.29W+	3.32VW		2.36VW−	3.26VW			2.07VW−			2.53W	3.26VW
		2.12VW−	2.73VW		2.26W+	2.72VW−			1.98VW−			2.28W+	3.12W
			2.48M+		2.07VW−	2.48M			1.88VW			2.08VW−	2.81W+
			2.24VW		1.88VW−	2.27W			1.75VW			1.97VW−	2.77VW−
			2.10W+		1.76VW−	2.11W						1.87VW−	2.65VW−
			1.90VW			1.90VW−							2.55M
													2.41W
													2.34W−
													2.28VW
													2.15W+
													2.07W+
													1.94VW
													1.86VW−

morphic forms of the behenyl mixed glycerides are given in Table III in comparison with data for the related 2-stearyldipalmitin (PSP) and 1-palmityldistearin (PSS).

Discussion

The behenyl triglycerides resemble their corresponding shorter chain homologs in many features of their polymorphism. Alpha and beta prime forms are apparently typical double-chain-length structures. The symmetrical $SC_{22}S$ and $PC_{22}P$ compounds crystallize from solvent as beta-3 structures, in keeping with shorter chain symmetrical compounds which show triple-chain-length structures for 4 and 6 carbon difference in the fatty acid chains. Moreover, $SC_{22}C_{22}$ gives a beta-2 structure like 1-myristyldistearin and $PC_{22}C_{22}$ gives a stable beta prime-2 form, like 1-lauryldistearin.[3]

The beta prime stabilities of $SC_{22}S$ and $SC_{22}C_{22}$ were so great that beta forms were not obtainable from the melt.

The very interesting new sub-alpha form ($SC_{22}S$ and $PC_{22}P$) somewhat resembles beta prime in short spacings but is nearer alpha in long spacings. The "perpendicular" long spacing is actually longer by 1-2 Å. than "perpendicular" alpha, presumably as a result of a denser more highly ordered structure. Sub-alpha has no melting point, for it transforms reversibly to the higher temperature alpha form near −20°. Subsequent studies at temperatures of −5 to −50° indicate that sub-alpha is not uncommon among other triglycerides and may indeed be quite general although apparently much

TABLE III

CHARACTERISTIC THERMAL AND X-RAY DATA FOR BEHENYL MIXED TRIGLYCERIDES

	PSP[a,3]	$PC_{22}P$	$SC_{22}S$	PSS[a,3]	$PC_{22}C_{22}$	$SC_{22}C_{22}$
			Melting points, °C.			
Sub-alpha	..	..	..	..	*b*	*b*
Alpha	46.5	47.4	56.0	50.6	55.9	61.3
Beta Prime	68.6	61.5	64.0	61.1–65.0	66.1	71.5
Beta	..	66.6	70.6	65.2	..	73.5
			X-Ray data: long spacings, Å.			
Sub-alpha	..	..	..	..	58.9	61.4
Alpha	46.65	50.0	53.2	48.5	57.4	59.1
Beta Prime	42.75	46.0	49.4	45.1	52.4	53.3
Beta	..	70.4	75.1	44.7	..	54.6
			Short spacings, Å.			
Sub-alpha					4.20S 3.72M	4.20S 3.77M
Alpha	4.13VS	4.14VS	4.14VS	4.14VS	4.15VS	4.15VS
Beta Prime	4.34M 4.18VS 3.99M 3.75S	4.19VS 3.76S+ 2.29W+	4.18VS 3.78S 2.26W+	4.37VS 4.23VS 4.07M 3.81S	4.20VS 3.78S 2.54W+	4.20VS 3.78S 2.53W
Beta	..	4.58S 3.79VS 2.48M+	4.58S 3.78VS 2.48M	5.34M 4.61VS 3.87S 3.67S	..	5.42M 4.59S+ 3.87S 3.70S
			Polymorphic stability			
Sub-alpha	..	..	..	..	*c*	*c*
Alpha	v. unstable	unstable	m. unstable	unstable	m. unstable	m. stable
Beta Prime	t. stable	m. stable	v. stable	v. or t. stable	t. stable	v. stable
Beta	..	t. stable	t. stable	t. stable	..	t. stable

m, moderately, v, very, t, thermodynamically. [a] PSP and PSS data included for comparison. [b] Transforms at −20 to −15°. [c] Transforms reversibly to alpha.

more readily obtained with unsymmetrical compounds. Tristearin as well as the symmetrical glycerides of this report do show a diffuse darkening of patterns in the 3.8 Å. region at −50°. This strongly suggests incipient sub-alpha formation. These reversible alpha to sub-alpha transformations appear to be analogous to similar reversible transformations in other long chain compounds, notably hydrocarbons.[12]

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Summary

The thermal and X-ray diffraction characteristics of four behenyl diacid triglycerides have been described and compared with those of shorter chain triglycerides. The forms observed are indicated in the following tabulation.

$PC_{22}P$	$SC_{22}S$	$PC_{22}C_{22}$	$SC_{22}C_{22}$
		Sub-alpha-2	Sub-alpha-2
Alpha-2	Alpha-2	Alpha-2	Alpha-2
Beta prime-2	Beta prime-2	Beta prime-2	Beta prime-2
Beta-3	Beta-3		Beta-2

In most respects the phase behavior of these glycerides closely resembles that of corresponding shorter chain homologs. The beta prime stabilities of $SC_{22}S$ and $SC_{22}C_{22}$ are so great that beta forms were obtainable only from solvent.

Sub-alpha-2 is a new form for triglycerides. It is a low temperature "perpendicular" form, transforming reversibly to "perpendicular" alpha. It appears to be analogous to monoglyceride sub-alpha and certain forms of other long chain compounds, *e. g.*, hydrocarbons. It is suspected that sub-alpha may be formed by most if not all triglycerides, but it is more readily obtained with unsymmetrical compounds.

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[12] Muller, *Proc. Roy. Soc. (London)*, **138**, 514 (1932).