

form for each of these 1,3-unsaturated diglycerides. X-Ray diffraction data for the three compounds are highly distinctive as indicated by long spacings—diolein, 39.3; dilinolein, 45.2; dilinolenin, 40.3 (1,3-distearin in the  $\beta$ -form,

49.5). The forms are therefore not so closely comparable as are the stable (and unstable) forms of many groups of glycerides.

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## X-Ray Investigation of Glycerides. VI. Diffraction Analyses of Synthetic Triacid Triglycerides<sup>1</sup>

BY S. S. SIDHU AND B. F. DAUBERT

Ferguson and Lutton<sup>2</sup> in their review on the polymorphic phases of fats excellently discussed and summarized the significance of the X-ray diffraction work on glycerides of Malkin and his co-workers.<sup>3</sup> Although it is not our intention to review again previous X-ray investigations, it is perhaps desirable to present briefly some of the background of the X-ray diffraction of glycerides in order to provide an explanation of the basis for the present research.

From X-ray diffraction studies of the different polymorphic forms of the simple triglycerides, Malkin proved by the magnitude of the long spacings of the different polymorphic forms the structural units of the crystalline simple triglycerides to be of a double chain length. In later work on symmetrical mixed diacid triglycerides where the chain length of the two fatty acids differed by two carbon atoms, the long spacings corresponded to two chain lengths in line with the structure for the simple triglycerides. However, when the fatty acids in the molecule differed by more than two carbon atoms, the long spacings, with few exceptions, corresponded to a structural unit of four chain lengths according to Malkin. The same relationships appeared to be true in the case of the unsymmetrical mixed diacid triglycerides. As pointed out by Ferguson and Lutton,<sup>2</sup> "The significance of this behavior is obviously related in some manner to the disparity in length between fatty acid chains."

Filer, *et al.*,<sup>4</sup> were not able to postulate a molecular arrangement in the crystalline state of a series of triacid triglycerides based upon X-ray diffraction, because it was not known whether they represented a series of compounds whose long spacings could be related to some theoretical concept of molecular structure; neither was it possible to fit them into the schematic arrangement of Malkin for diacid triglycerides. As a matter of fact, it was found by Filer, *et al.*, that the triacid triglycerides fell into four distinct groups on the

bases of their molecular weight, melting point and long-spacing relationships. Recently Lutton,<sup>5</sup> on a re-examination of the abnormally large long-spacing values reported by Malkin for some of the symmetrical and unsymmetrical saturated diacid triglycerides and by Filer, *et al.*,<sup>4</sup> for some of the saturated triacid triglycerides, found that these abnormal values could be interpreted as due to triple chain structures.

In the present investigation, in order to determine whether a molecular configuration in the crystalline state could be postulated for a homologous series of triacid triglycerides, three glycerides were synthesized in which the fatty acids in the 1-position of the glycerol molecule were of a chain length two and four carbon atoms greater, respectively, than the fatty acids in the 2- and 3-positions, the difference in corresponding chains between homologs being two carbon atoms. X-Ray diffraction patterns were then made of the solvent-crystallized forms.

### Experimental

**Preparation of Intermediates.**—The fatty acids and fatty acid chlorides were prepared by previously described methods.<sup>6</sup>

The diacid diglycerides, 1-myristyl-3-caprin, m. p. 48.0°, 1-palmityl-3-laurin, m. p. 59.5°, and 1-stearyl-3-myristin, m. p. 67.0°, were prepared after the method of Verkade, *et al.*,<sup>7</sup> as described by Sidhu and Daubert.<sup>8</sup>

**Preparation of Triacid Triglycerides.**—All three of the triacid triglycerides reported in this communication were prepared essentially by the same procedure. The method is given in detail for 1-palmityl-2-myristyl-3-laurin: 1-palmityl-3-laurin (5 g.) was dissolved in a mixture of quinoline (7 ml.) and chloroform (20 ml.). To this mixture there was added slowly myristyl chloride (2.8 g., 1 mole = 2.4 g.). The mixture after refluxing on a steam-bath for four hours, was cooled, and taken up in ethyl ether (300 ml.). The solution was washed successively with water, cold 0.5 N sulfuric acid, 5% potassium carbonate solution, water, and then dried over anhydrous sodium sulfate. The ethyl ether was removed *in vacuo* from the filtered liquid, and the solid residue remaining was dissolved in warm 95% ethanol. After cooling to 5° for several hours the crystal mass was suction-filtered and recrystallized several times

(1) The generous financial assistance of the Buhl Foundation in support of this investigation is gratefully acknowledged.

(2) Ferguson and Lutton, *Chem. Rev.*, **28**, 355 (1941).

(3) Malkin, *et al.*, *J. Chem. Soc.*, 666 (1934); 1628 (1936); 1409 (1937); 103, 577, 1141 (1939).

(4) Filer, Sidhu, Chen and Daubert, *THIS JOURNAL*, **67**, 2085 (1945).

(5) E. S. Lutton, paper presented at a meeting of the American Society for X-Ray and Electron Diffraction, Mellon Institute, Pittsburgh, Pa., December 5-7, 1946.

(6) Daubert, Fricke and Longenecker, *THIS JOURNAL*, **65**, 1718 (1943).

(7) Verkade and van der Lee, *Rec. trav. chim.*, **55**, 267 (1936).

(8) Sidhu and Daubert, *THIS JOURNAL*, **68**, 2603 (1946).

from a 1:1 mixture of ethyl ether and alcohol, and finally once from acetone. After drying *in vacuo* for several hours, the triglyceride melted at 49.0°; molecular weight,<sup>9</sup> 726 (calculated 723).

Anal.<sup>10</sup> Calcd. for C<sub>45</sub>H<sub>86</sub>O<sub>6</sub>: C, 74.73; H, 11.98. Found: C, 74.57, 74.65; H, 11.86, 11.91.

1-Stearyl-2-palmityl-3-myristyl glycerol, m. p. 59.0° (Verkade, *et al.*,<sup>7</sup> 58.5–59.0°), mol. wt. 803 (calcd. 807), and 1-myristyl-2-lauryl-3-capryl glycerol, m. p. 37.0°, mol. wt. 639 (calcd. 641), were prepared as indicated by essentially the same procedure. As in previous publications from this Laboratory on glyceride synthesis, carbon and hydrogen values were determined for one compound only as proof against errors of synthesis.

Each of the triglycerides was found to be chromatographically homogeneous as determined by the procedure described for symmetrical diacid diglycerides.<sup>8</sup>

Transition temperatures of the different polymorphic forms of the triglycerides were determined by the methods of Daubert and Clarke,<sup>11</sup> and are listed in Table I.

TABLE I  
LONG SPACINGS AND TRANSITION TEMPERATURES OF THE  
TRIACID TRIGLYCERIDES

	Long spacing $d \times 10^{-8}$ cm.	Transition temperature, °C.		
		Form I	Form II	Form III
1-Stearyl-2-palmityl-3-myristin ( $\beta$ )	40.7	59.0	54.0	43.5–44
1-Palmityl-2-myristyl-3-laurin ( $\beta$ )	35.7	48.5–49	44.0	36–37
1-Myristyl-2-lauryl-3-caprin ( $\beta'$ )	33.4	36.5–37	33–34	22

**X-Ray Diffraction Analyses.**—The X-ray diffraction patterns were obtained by the same procedure as described by Sidhu and Daubert<sup>8</sup> for symmetrical diacid diglycerides.

### Discussion

It may be noted from the data in Table II that the strong side-spacing lines for 1-stearyl-2-palmityl-3-myristin and 1-palmityl-2-myristyl-3-laurin are typical and characteristic of the *beta* form of triglycerides. The side-spacing lines for 1-myristyl-2-lauryl-3-caprin, however, are similar to those reported previously for the *beta-prime* form of the same type of triacid triglycerides,<sup>4</sup> *i. e.*, those containing a capryl group in the 3-position of the glycerol molecule. It appears that here again, even though these data differ somewhat from side spacings characteristic of the *beta-prime* form of the simple triglycerides and mixed diacid triglycerides, they are sufficiently different from those of the *beta* form to indicate a degree of uncertainty in the naming of the form. Although it has been observed in this Laboratory that rapid crystal growth of triacid triglycerides from solvent gave rise to the *beta-prime* form, repeated slow and rapid crystallization of 1-myristyl-2-lauryl-3-caprin always resulted in a form having similar side-spacing data. The magnitude of the long-spacing data for this compound, since they are out of line with the long-spacing data for the other two ho-

(9) Hanson and Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939).

(10) The microanalysis was performed by Mr. George Stragand.

(11) Daubert and Clarke, *THIS JOURNAL*, **66**, 690 (1944); *Oil & Soap*, **32**, 113 (1945).

TABLE II  
INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF  
TRIACID TRIGLYCERIDES<sup>a</sup>

$\beta$ Phase		$\beta$ Phase		$\beta'$ Phase	
$d \times 10^{-8}$	$I/I_0^b$	$d \times 10^{-8}$	$I/I_0^b$	$d \times 10^{-8}$	$I/I_0^b$
1-Stearyl-2-palmityl-3-myristin		1-Palmityl-2-myristyl-3-laurin		1-Myristyl-2-lauryl-3-caprin	
20.1	W	17.4	W <sup>+</sup>	16.7	W <sup>+</sup>
15.9	VW	12.0	S	11.2	S
13.5	S	9.36	W	6.60	W
9.84	VW	7.91	W	5.76	VW
8.20	VW	5.69	VW	5.35	W <sup>+</sup>
6.66	VW	5.33	M	4.98	W <sup>+</sup>
5.34	M	5.08	M	4.78	W
5.21	W <sup>+</sup>	4.79	W	4.60	M
4.98	W	4.57	VS	4.33	VS
4.80	VW	4.42	W	4.13	VS
4.57	VS	4.22	W	3.82	VS
4.28	VW	4.05	W	3.62	W
4.16	VW	3.83	S	3.44	W
4.05	W	3.74	S	3.28	W
3.82	VS	3.60	W	3.17	W <sup>+</sup>
3.72	VS	3.43	W	3.01	W
3.59	W	3.30	W	2.85	W <sup>+</sup>
3.47	W	3.21	VW	2.64	VW
3.35	W	3.05	W <sup>+</sup>	2.55	W <sup>+</sup>
3.11	W	2.71	VW	2.40	W
3.00	VW	2.57	M	2.28	M
2.71	W	2.49	VW	2.10	W <sup>+</sup>
2.56	M	2.42	M	2.00	VW
2.40	M	2.31	W	1.91	W
2.28	M	2.22	W	1.81	W
2.22	W <sup>+</sup>	2.14	VW		
2.14	W <sup>+</sup>	2.10	M		
2.09	W <sup>+</sup>	1.93	W <sup>+</sup>		
2.02	VW				
1.96	W				
1.93	W				
1.87	W				
1.80	VW				

<sup>a</sup> The interplanar spacings listed are those below 22 Å.  
<sup>b</sup> V = very, S = strong, M = medium, W = weak.

mologous compounds (Table I), serves also as added proof that the form obtained by rapid and slow crystallization of the 1-myristyl-2-lauryl-3-caprin from solvent conforms to a *beta-prime* type pattern. *Beta-prime* type pattern is used here as a means of distinguishing it from a typical *beta-prime* pattern. There are not yet sufficient X-ray diffraction data available on all crystalline forms of triacid triglycerides to enable one to draw specific conclusions to explain away the anomalies in side-spacing data.

Although the original goal of establishing a degree of similarity in the structure of the triacid triglyceride was not completely attained, the fact that a *beta-prime* type form of 1-myristyl-2-lauryl-3-caprin crystallized from solvent in apparently its most stable form is highly significant. The magnitude of the long-spacing data, however, does indicate that the three triacid triglycerides con-

sist of molecules of double chain length in the crystalline state, at least in the form obtained by solvent crystallization.

Although evidence for three melting phases was determined from warming and cooling curves and from capillary tube data, difficulty was experienced in obtaining X-ray diffraction patterns on the different forms because of relatively rapid phase transition. The transition temperatures of the different polymorphic forms are listed in Table I together with the long-spacing values of the solvent-crystallized form.

### Summary

Long and short spacing X-ray data are reported for three homologous triacid triglycerides, two of which are new compounds, namely, 1-palmityl-2-myristyl-3-laurin and 1-myristyl-2-lauryl-3-caprin.

It appears from the X-ray evidence presented that the homologous triacid glycerides in the crystalline state are of a double chain length, and that the solvent-crystallized form (*beta-prime type*) for 1-myristyl-2-lauryl-3-caprin is its most stable form.

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## The Effect of Molecular Weight Distribution on the Reduced Viscosity-Concentration Coefficient

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### Introduction

During the past ten years, the determination of the solution viscosity of high polymers has assumed increasing importance as a means of estimating their molecular weights. The generally accepted procedure now is to relate molecular weight to intrinsic viscosity (limiting value of specific viscosity/concentration at infinite dilution), as suggested by Kraemer,<sup>1</sup> rather than to specific viscosity/concentration at a "sufficiently low" concentration, as originally proposed by Staudinger.<sup>2</sup> The determination of this quantity, intrinsic viscosity, therefore requires an extrapolation of viscosity data to infinite dilution. Such a procedure attains its maximum accuracy when the extrapolation is linear, and a number of equations expressing specific viscosity/concentration or some related quantity as a linear function of concentration have been proposed and used. Among the most frequently used of these equations are the following

$$\eta_{sp}/c = [\eta](1 + k'[\eta]c) \quad (1)$$

$$\log \eta_{sp}/c = \log [\eta] + ac \quad (2)$$

where

$\eta_{sp}$  = specific viscosity  
 $c$  = concentration  
 $[\eta]$  = intrinsic viscosity  
 $k'$  and  $a$  = constants

Equation (1) has been used by Guth<sup>3</sup> and others, and is directly related to another equation (making the substitution  $[\eta]c \rightsquigarrow \eta_{sp}$ )

$$\eta_{sp}/c = [\eta](1 + k'\eta_{sp}) \quad (3)$$

derived on a hydrodynamical basis by Huggins<sup>4</sup> and used empirically by Schulz and Blaschke.<sup>5</sup>

(1) E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

(2) H. Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

(3) E. Guth, *Kolloid-Z.*, **74**, 147 (1936); **75**, 15 (1936).

(4) M. L. Huggins, *THIS JOURNAL*, **64**, 2716 (1942).

(5) G. V. Schulz and F. Blaschke, *J. prakt. Chem.*, **158**, 130 (1941).

Equation (2) has been used by Staudinger<sup>6</sup> and others, and is particularly useful because it appears to be valid over a rather wide range of concentration. This equation has been modified by Martin,<sup>7</sup> who presented data indicating that the constant,  $a$ , is a linear function of intrinsic viscosity for a given solute-solvent system, *i. e.*, that

$$a = k[\eta] \quad (4)$$

so that equation (2) should be written

$$\log \eta_{sp}/c = \log [\eta] + k[\eta]c \quad (5)$$

where  $k$  is a constant independent of all factors except the chemical nature of solute and solvent. It is readily shown, by writing equation (5) in exponential form

$$\eta_{sp} = [\eta]c \cdot 10^{k[\eta]c}$$

expanding in powers of  $[\eta]c$  and dropping the higher terms that equations (1) and (3) are approximations to equation (5), valid at low concentration, and that the following relation holds between the constants:

$$k' = 2.303k \quad (6)$$

In determining intrinsic viscosity, the usual procedure is to plot the viscosity data according to equation (5) (or, at sufficiently low concentration, according to equation (1) or (3)) and extend the straight line obtained to zero concentration (or to zero  $\eta_{sp}$  in equation (3)). It is obvious that this procedure could be greatly shortened if the contention of Martin,<sup>7</sup> that the constant  $k$  (and therefore also  $k'$ ) has a single characteristic value for a given solute-solvent system, were true. In that case it would not be necessary to make viscosity determinations at several concentrations in order to establish a good straight line; once the correct value of  $k$  or  $k'$  was known, one viscosity

(6) H. Staudinger and W. Heuer, *Z. physik. Chem.*, **A171**, 129 (1934).

(7) A. F. Martin, Am. Chem. Soc. Meeting, Memphis, April 23, 1942.