

or weakly covalent sp^3 bonds in each compound measured seems, therefore, justified, with the possible exception of the cupric complexes, for which there is no magnetic criterion of bond type. However, the formation of essentially ionic complexes throughout the rest of this series makes such a structure for copper at least probable. The large orbital contribution to total moment, which was encountered in all compounds except (XII), is also an indication of the largely ionic character of the bonds.⁵

It is also found that the color change of cobaltous salts from red to blue cannot be explained on the basis of a change in complex structure,

(5) Russell, Cooper and Vosburgh, *THIS JOURNAL*, **65**, 1301-1306 (1943).

since both the red (VII) and the blue (VIII), cobaltous complexes measured are found to be essentially ionic.

Summary

It has been possible to synthesize several glycol complexes of some of the light transition metals and of cupric ion. As far as can be determined from magnetic data all the complexes measured magnetically are essentially ionic. The probability of ionic cupric complexes in the series is increased by the fact that related metal complexes are ionic in form. It has been found that the color change of the cobaltous complexes investigated is independent of geometrical form.

CLAREMONT, CALIF.

RECEIVED APRIL 10, 1944

[CONTRIBUTION NO. 523 FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, UNIVERSITY OF PITTSBURGH]

X-Ray Investigation of Glycerides. I. Diffraction Analyses of Isomeric Monoglycerides¹

BY L. J. FILER, JR., S. S. SIDHU, B. F. DAUBERT AND H. E. LONGENECKER

The presence of a large number of isomeric glycerides of closely related physical properties complicates the study of the glyceride composition of natural fats. Since the complexity of these glyceride mixtures has militated against the effective separation of individual glyceride components, an alternative and necessary approach to the study of natural fats has been through the synthesis of glycerides of known configuration and their subsequent characterization.

The glycerides which have thus far been obtained by synthesis usually have been characterized by measurements of their refractive indices, determination of solubility data, melting points of their polymorphic forms, and, in a few instances, heats of combustion. For the purpose of providing more complete identification, X-ray diffraction data for pure synthetic glycerides should be made available. The value of the diffraction diagram for further characterization of synthetic compounds has been fully appreciated only recently in the study of natural fats. When complete long and short spacing data, characteristic for each synthetic glyceride, can be obtained from diffraction diagrams, a supplementary means will have been provided for the positive identification of those glycerides isolated from natural sources. From these accumulative data it is entirely probable that single components in simple glyceride mixtures may be correctly identified as to structure and configuration. Furthermore, it is quite possible that the correlation of all data from thermal curves, X-ray diffraction diagrams, measurements and observations of other physical

properties will help in the fundamental interpretation of the relationships of these properties and also provide the necessary data for the identification of naturally occurring glycerides. In a recent review, Ferguson and Lutton² have already indicated the desirability of such information. "To identify a single glyceride by X-ray alone without known materials for comparison would be difficult even if the number of possible glycerides could be limited to a few. However, the first steps have been taken to make such identification a real possibility, and, combined with multiple melting points, the X-ray method should serve in many instances to give far more certain results than have hitherto been possible."

In 1934 it was recognized clearly by McElroy and King³ that powder diffraction diagrams could provide independent evidence of the difference in structure between synthetic isomeric mixed triglycerides. Their data⁴ clearly indicated that a specific diffraction pattern was associated with a given triglyceride and that isomeric triglycerides were distinguished on the basis of individual patterns. These investigators, however, reported only limited short spacing data on the solvent crystallized (stable form) compounds.

In a study of the thermal and X-ray properties of many glyceride types, Malkin and associates⁵ showed the tremendous supplementary importance of diffraction data for characterization of the different polymorphic forms of synthetic glycerides. Unfortunately, their data are insuffi-

(2) Ferguson and Lutton, *Chem. Rev.*, **26**, 379 (1941).

(3) McElroy and King, *THIS JOURNAL*, **56**, 1191 (1934).

(4) McElroy, Ph.D. Thesis, University of Pittsburgh, 1934, *University of Pittsburgh Bulletin*, **31**, 263 (1934).

(5) Malkin and Meara, *J. Chem. Soc.*, 1141 (1939); see other papers of the series.

(1) A grant by the Buhl Foundation in support of this investigation is gratefully acknowledged. Presented at the 107th meeting of the American Chemical Society, Cleveland, Ohio, April 2-6, 1944.

TABLE I
 INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF 1-MONOGLYCERIDES

Capryl		Lauryl		Acyl radical in monoglycerides				Stearyl		Elaidyl	
<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>	Myristyl	Palmityl	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>
16.3	S	14.2	VW	15.4	VW	22.4	S	25.5	S	25.5	S
13.2	VW	11.4	VW	13.7	S	15.2	VS	19.9	W	21.1	W
10.8	VW	10.3	VW	11.3	W	11.4	VS	17.5	W	19.1	W
9.12	VW	9.24	M	10.3	VS	11.0	W	16.6	VS	17.6	VW
8.19	S	8.15	W	8.46	VW	9.05	W	14.3	W	17.1	S
7.12	VW	6.44	W	8.27	M	8.52	W	12.5	S	13.4	VW
6.59	M	6.27	W	7.13	W	7.62	M	11.1	VS	12.6	S
5.46	M	5.91	W	6.25	W	7.48	W	10.7	VW	11.3	VW
5.03	W	5.45	W	5.97	M	6.47	W	9.93	M	10.4	VW
4.70	VS	5.02	W	5.24	W	5.72	W	9.01	W+	9.19	VW
4.49	W	4.85	W	5.00	W	5.30	W+	8.33	S	8.95	W
4.36	S	4.56	VS	4.58	S	5.04	M	7.55	W	8.36	M
4.13	M	4.41	S	4.36	M+	4.88	W	6.90	VW	6.88	VW
3.96	S	4.32	S	4.30	M	4.73	VS	6.64	W	6.79	M
3.88	M	4.27	M	4.19	M	4.55	VS	6.17	W	6.19	M
3.81	S	4.05	M	4.09	W	4.37	S	5.96	VW	5.64	W+
3.76	W	3.91	S	3.89	S	4.27	VS	5.60	W	5.24	W
3.64	M	3.81	M	3.80	S	4.12	M	4.98	W	4.94	W+
3.40	W	3.71	M	3.71	M	3.94	VS	4.89	W	4.77	W+
3.17	M	3.62	W+	3.51	W	3.84	VS	4.74	W	4.57	VS
2.98	W	3.45	M	3.34	W	3.74	S	4.55	VS	4.37	S
2.80	W	3.33	M	3.13	M	3.63	W	4.37	S	4.18	W+
2.67	VW	3.26	M	2.95	W	3.47	M	4.13	M	4.08	W
2.57	W	3.13	M	2.75	W	3.29	M	3.84	VS	3.96	S
2.47	S	2.98	VW	2.59	W	3.11	M	3.74	W	3.86	W+
2.40	VVW	2.78	W	2.45	W	2.99	W	3.64	W	3.76	W+
2.31	M	2.62	W	2.30	W	2.78	W	3.59	W	3.56	W
2.24	VVW	2.46	S	2.17	W	2.53	W	3.52	S	3.35	W
2.17	W	2.31	M			2.48	W	3.44	W	3.16	M
		2.21	VW			2.39	W	3.30	W	2.93	W
		2.16	VW			2.29	W	3.14	M	2.78	W+
		2.09	W			2.25	W	2.97	W	2.62	W
						2.19	W	2.65	VW	2.46	S
						2.15	W	2.62	VW	2.38	VW
						2.07	W	2.54	W	2.25	W
								2.45	M	2.13	W
										2.04	W
										1.96	W

ciently complete for positive identification purposes.

Inasmuch as powder diffraction data suitable for the identification of synthetic glycerides are not available in the literature, part of this Laboratory's program on the study of fats is concerned with the collection of such data on all glyceride types. We believe that a systematic study must of necessity begin with the isomeric monoglycerides, although we are fully aware that monoglycerides do not normally occur in appreciable amounts as components of natural fats. Certain fundamental relationships have been established in the present investigations which may be of considerable value in later interpretations on other glyceride types. While Malkin and Shurbagy⁶ have previously reported some long and short spacing data for the polymorphic forms

of 1-monoglycerides, their short spacing data consisted only of the interplanar spacing of the most intense lines (3.94 and 4.65 Å.). Since these data are of limited value as a means of identification, the purpose of this communication is to report more complete diffraction data not only for the 1-monoglycerides, but also for the stable form of the isomeric 2-monoglycerides which have not previously been investigated by X-ray methods.

Experimental Procedures

Preparation of Monoglycerides.—The 1-monoglycerides were prepared by the esterification, in quinoline-chloroform solution, of acetone-glycrol with the appropriate acyl chloride, prepared from highly purified acids, and the subsequent cold hydrolysis of the intermediate with concentrated hydrochloric acid.⁷ The monoglycerides, in all instances, were crystallized repeatedly from ethyl ether, and finally from a 1:1 mixture of ethyl ether and petro-

(6) Malkin and Shurbagy, *J. Chem. Soc.*, 1628 (1936).

(7) Fischer, *Ber.*, 53, 1621 (1920).

TABLE II
INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF 2-MONOGLYCERIDES

Capryl		Lauryl		Myristyl		Palmityl		Stearyl	
<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>
29.9	VS	10.8	M	18.0	M+	20.4	W	17.0	S
14.9	W+	8.38	M	12.5	W	19.8	S	14.6	VS
9.85	S	7.22	VVW	12.0	S	13.9	W	13.9	M
8.05	VW	5.66	VW	10.0	VW	13.3	VS	10.8	W
7.35	S	5.13	S	9.32	W	11.1	VW	8.67	W
5.89	VW	5.06	W	9.00	M	9.97	W	7.34	W
5.39	VW	4.70	W	6.12	W+	6.73	M	6.20	VW
5.18	M	4.64	S	5.59	VW	5.72	VW	5.68	W
4.90	S	4.57	W	5.27	W	5.12	W	5.43	M
4.86	W	4.38	VS	5.17	VW	5.03	M	5.10	M
4.56	S	4.26	W	4.92	M	4.91	VW	4.99	W
4.32	VS	4.18	W	4.84	M	4.75	VW	4.89	M
4.13	VS	4.00	S	4.65	S	4.66	M	4.69	S
4.04	VS	3.94	VS	4.56	M	4.46	S	4.44	VS
3.93	S	3.89	M	4.42	VS	4.38	M	4.26	M
3.88	VS	3.77	VW	4.36	VS	4.27	W	4.15	W+
3.69	S	3.59	W+	4.20	M	4.16	W	4.01	W
3.57	W	3.34	M	4.07	M	4.09	M	3.88	VS
3.48	W	3.17	W	3.93	VS	4.00	S	3.77	VS
3.23	W	3.09	W	3.82	S	3.90	S	3.58	M
3.05	VW	2.97	W	3.56	W	3.84	VS	3.42	W
2.90	W+	2.76	M	3.34	W	3.77	S	3.30	W
2.78	M	2.61	S	3.15	W	3.65	W	3.09	M
2.69	M	2.49	M	2.93	W	3.58	W	2.93	W
2.61	S	2.40	W+	2.85	W	3.43	VW	2.84	VW
2.47	M	2.33	W	2.77	M	3.15	VW	2.71	M
2.37	VW	2.27	W	2.68	M	2.94	W	2.58	S
2.29	VW	2.18	W+	2.60	S	2.72	M	2.48	M
2.25	VW	2.09	W	2.48	M	2.59	M+	2.34	W
2.20	W+	2.01	W+	2.41	W	2.48	W+	2.31	W
2.16	W			2.31	W	2.40	VW	2.26	W
2.11	VW					2.30	W	2.17	M
2.04	VW					2.18	W		
1.96	VW								
1.89	W								

TABLE III
LONG SPACING VALUES AND MELTING POINTS OF
MONOGLYCERIDES

Number of carbons in fatty acid chain	1-Monoglycerides			2-Monoglycerides		
	Long spacing (Å.)	Melting point ^a		Long spacing (Å.)	Melting point ^a	
10	32.6	32.7	53.0	29.4	29.3	40.4
12	36.9	37.0	63.0	32.8	32.9	51.0
14	41.6	41.4	70.5	36.2	36.5	61.2
16	45.7	45.7	77.0	40.1	40.1	68.5
18	49.9	50.1	81.5	43.8	43.7	74.5
(Elaidin)	50.5		58.5			

^a Determined by capillary tube method using a calibrated Anschütz thermometer.

leum ether, and then dried in a vacuum desiccator. Melting points for the compounds are listed in Table III.

The method of Bergmann and Carter,⁸ as modified by Stimmel and King,⁹ was used to prepare the isomeric 2-monoglycerides. Esterification of 1,3-benzylidene glycerol and hydrogenolysis of the resulting acetal, in alcohol solution, with hydrogen under pressure (35 lb.) and palladium black as a catalyst, yielded 2-monoglycerides of a high

degree of purity. Each monoglyceride was crystallized repeatedly from absolute alcohol and finally from petroleum ether and dried in a vacuum desiccator. Melting points for the compounds are listed in Table III.

X-Ray Diffraction Analyses.—The X-ray diffraction patterns of the monoglycerides were made by the usual powder method. A small portion of the solvent crystallized material, ground to a fine powder, was packed into a nylon tube of internal diameter of 0.8 mm. The tube was then mounted in a cylindrical camera of 17.19 cm. effective diameter and rotated during the exposure. The patterns were repeated with a pin-hole type of camera using specimen-to-film distances of both 8 and 24 cm.

The radiation employed was filtered $\text{CuK}\alpha$ of effective wave length of 1.5386 Å. and was supplied by a diffraction tube with beryllium windows.

The typical photographs of the diffraction patterns made with the cylindrical and the pin-hole camera are shown in Figs. 1 to 3. The photograph in Fig. 2 was made with specimen-to-film distance of 8 cm. and that in Fig. 3 was made with a specimen-to-film distance of 24 cm. and is typical of the type of photographs made to measure the first order reflection of the long spacing. The observed interplanar spacings and visually estimated relative intensities of diffraction lines obtained from photographs similar to those given in Figs. 1 and 2, are given in Tables I and II. The observed long spacing dif-

(8) Bergmann and Carter, *Z. physiol. Chem.*, **191**, 211 (1930).

(9) Stimmel and King, *THIS JOURNAL*, **56**, 1724 (1934).

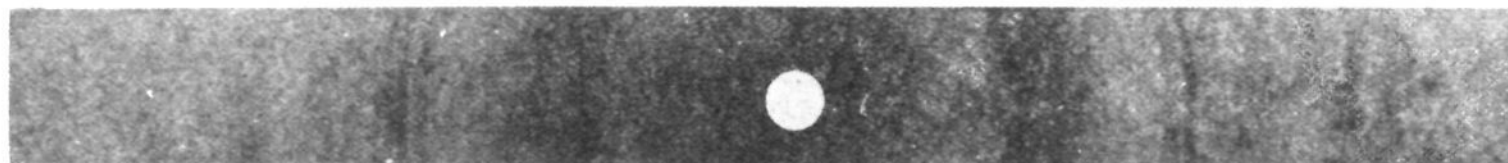


Fig. 1.—Diffraction pattern for 2-monostearin; cylindrical camera, $\text{CuK}\alpha$.

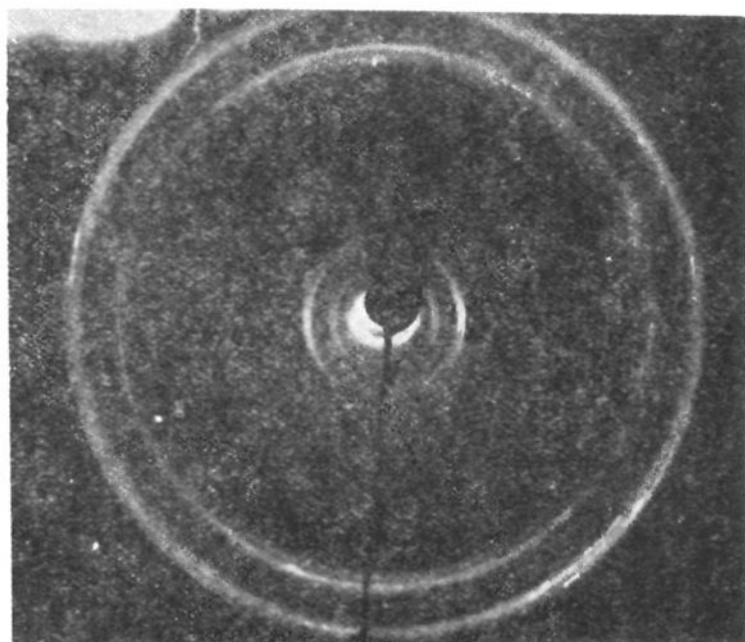


Fig. 2.—Diffraction pattern for 2-monostearin; pinhole camera, $\text{CuK}\alpha$.

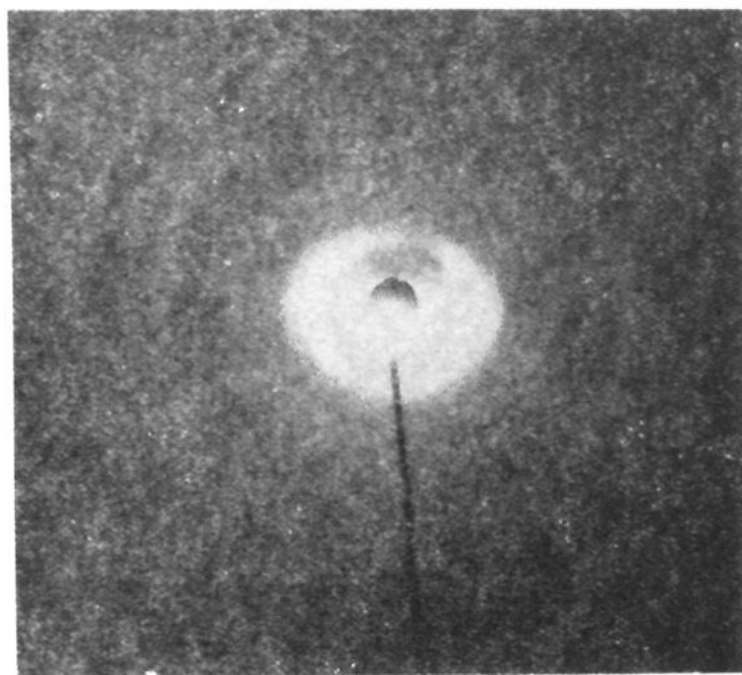


Fig. 3.—Diffraction pattern for 1-monostearin; pinhole camera, $\text{CuK}\alpha$.

fraction data, together with the calculated long spacing values are listed in Table III. The observed values presented here are the composite of data obtained with both the 8-cm. and 24-cm. cameras. They were weighted according to the accuracy with which they could be measured.

The spacings measured on the diffraction pattern of a typical physical mixture of 1-monolaurin (90%) and 1-monostearin (10%) have been plotted on semilogarithmic coordinate paper. Identification of the components can be made readily by viewing the chart of the data obtained

from the mixtures and superimposing it on reference charts for each component (Fig. 4).

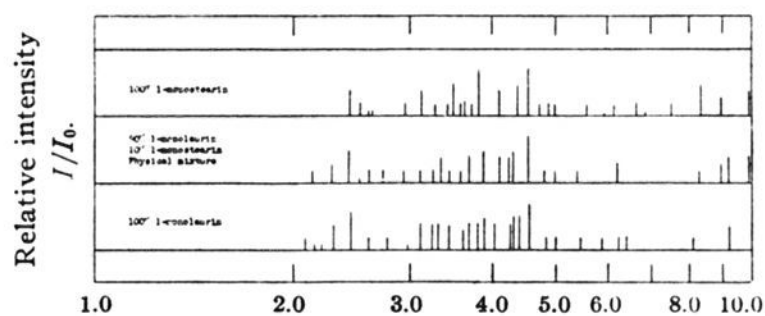


Fig. 4.—Interplanar spacing (d) in Å.

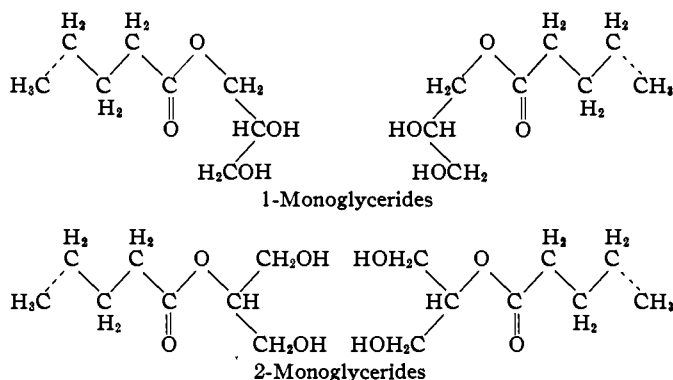
Discussion

Both short and long spacing X-ray diffraction data have been obtained for the isomeric 1- and 2-monoglycerides. Each set of data characterized a compound. The short spacing data have been employed to identify a compound in its pure state or in a physical mixture of two compounds. It is possible to identify a compound present in the amount of 10% in a simple admixture of two adjacent homologs or isomeric pairs. Such identification is not so positive when less complete long or short spacing data are employed.

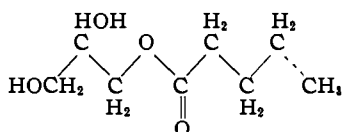
When long spacings of monoglycerides are plotted against the number of effective carbon atoms, straight lines are obtained. An empirical relation between the long spacings and the effective number of carbon atoms was calculated for each line by the method of least squares. It is of the form of $y = ax + b$ where x equals two times the number of carbon atoms in the hydrocarbon chain.^{9a} For 1-monoglycerides the values of a and b are 1.085 and 11.0 Å., respectively, and for 2-monoglycerides, 0.903 and 11.2 Å. This relationship was used to obtain the calculated values of the long spacings given in Table III. The slope of the line, a , represents the increment in long spacing per one CH_2 group. The intercept, b , represents that distance contributed to the total long spacing by the two glyceryl residues and their nearest distance of approach in a double molecule.

The fact that the intercept, b , is approximately the same for the isomeric monoglycerides leads to the suggestion that the glycerol residues in the double molecule of the monoglycerides in the solid state are similarly oriented. One reasonable interpretation for the orientation of a 2-monoglyceride is in terms of the skeleton structure

(9a) This value of x was chosen because the long spacing data best fit the conception of a double molecule.



Although the data reported here best fit the above conception, our interpretation for the isomeric monoglycerides is not in harmony with the considerations of Malkin and associates who visualized the structure of 1-monoglycerides as



Our data are equally capable of this interpretation in the case of the 1-monoglycerides. However, the same model does not fit the data for the 2-monoglycerides. If Malkin's model for 1-monoglycerides could be applied equally to the 2-monoglycerides, then a constant difference in the long spacing between the isomeric pairs should have been observed. The measured differences (*cf.* Table III) increased as the carbon chain length of the acyl radical was increased. Thus, the difference for the isomeric pair of mono-laurins was 4.1 Å., whereas for the monostearins, it was 6.1 Å.

The measured difference in long spacing for any single pair of isomeric monoglycerides is interpreted to be due to a difference in the angle of tilt of the hydrocarbon chain. When the hydrocarbon chain is perpendicular to the diffracting planes giving long spacings, the increment per one CH₂ group is calculated to be 1.27 Å., based on an angle of 111° between carbon atoms.¹⁰ For monoglycerides in the stable phase investigated the chains are tilted. The angle of tilt (ϕ), as shown in Fig. 5 for 1-monoglycerides is 58°41' and for 2-monoglycerides it is 45°19'. These values were calculated as follows

$$\begin{aligned} \cos \theta &= \frac{d_1}{OA} = \frac{\text{long spacing at tilted angle, } \phi}{\text{long spacing when perpendicular}} \\ &= \frac{\text{increment per CH}_2 \text{ when chain is tilted}}{\text{increment per CH}_2 \text{ when chain is perpendicular}} \end{aligned}$$

For 1-monoglycerides

$$\begin{aligned} \cos \theta &= 1.085/1.270 = 0.8543 \\ \theta &= 31^\circ 19' \\ \phi &= 90^\circ - \theta = 58^\circ 41' \end{aligned}$$

(10) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1942, p. 84.

For 2-monoglycerides

$$\begin{aligned} \cos \theta &= 0.903/1.270 = 0.7110 \\ \theta &= 44^\circ 41' \\ \phi &= 90^\circ - \theta = 45^\circ 19' \end{aligned}$$

The observed difference in angle of tilt between 1- and 2-monoglycerides is such that a 1-monoglyceride has approximately the same long spacing as a 2-monoglyceride of a chain length of two carbons greater. For example, 1-monolaurin and 2-monomyristin have long spacings of 36.9 and 36.2 Å., respectively. It should be further observed that these monoglycerides have approximately the same melting points; 1-monolaurin, 63°, and 2-monomyristin, 61.5°. Thus, when the long spacings of the isomeric monoglycerides are plotted as a function of their melting points a smooth curve results for the range of monoglycerides investigated.

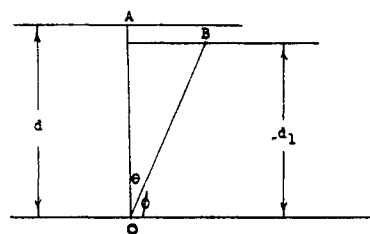


Fig. 5.—OA = OB = d = increment per CH₂ when hydrocarbon chains are perpendicular to the end methyl groups. d_1 = increment per CH₂ when hydrocarbon chains are tilted to the planes produced by the end methyl groups. $\phi = 90^\circ - \theta$ = angle of tilt of hydrocarbon chain.

For comparison with the saturated 1-monoglycerides, short spacings and long spacings for the unsaturated monoglyceride, 1-monoelaidin, are given in Tables I and III. It is to be noted that the long spacing value for 1-monoelaidin is of slightly greater magnitude than for 1-monostearin which contains the same number of carbon atoms. Although several possible theories have been considered to account for the difference in long spacing values, we feel that additional experimental data are necessary before any conclusive explanation is advanced.

Summary

Both short spacing and long spacing diffraction data are reported for isomeric pairs of monoglycerides. These data are characteristic for each compound. Application of the data for identification of simple admixtures is indicated.

An empirical equation was derived to express the long spacing values in terms of the number of effective carbon atoms. The 1-monoglycerides were observed to have a larger angle of tilt than 2-monoglycerides. A direct relationship between the long spacings and the melting points of the monoglycerides is indicated.