bath was heated to 150° before immersing the reaction flask in it.

The distillates from the two runs were combined, diluted with benzene, most of the water separated, and then the benzene layer was distilled from hydroquinone through a Vigreux column. The product was 69 g. (49% yield) of material boiling at 89–90° (2 mm.), n^{25}_{D} 1.5568 (supercooled liquid), m. p. 33–34°. An analytical sample melted at 35.0–36.5° (35–36°).[1]

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.0; H, 6.18; sapon. equiv., 162. Found: C, 74.1; H, 6.44; sapon. equiv., 162.

Summary

The liquid phase oxidation of methyl *p*-ethylbenzoate to methyl *p*-acetylbenzoate has been achieved in 54% conversion and 66% yield. This reaction, followed by hydrogenation and dehydration, constitutes a convenient synthesis of methyl *p*-vinylbenzoate.

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[CONTRIBUTION FROM THE PROCTER AND GAMBLE CO.]

The Identity and Polymorphism of Oleyldistearin from Kokum Butter

BY E. S. LUTTON

In 1897 Heise[1] isolated an oleyldistearin from kokum butter and from mkányi fat. Hilditch[2] in 1933 by study of the azelayldistearin from the naturally occurring oleyldistearin indicated the latter glyceride was the symmetrical isomer. The synthesis of pure 2-oleyldistearin and its homologs by Jackson, Daubert, King and Longenecker[3] afforded the opportunity to establish the structure of the natural glyceride with finality. Daubert and Clarke[4] investigated thermally the polymorphism of these compounds. Meara[5] had already found thermal points for the natural oleyldistearin very similar to those reported by Daubert and Clarke for 2-oleyldistearin. He later[6] published additional melting point data on the natural glyceride from several sources including kokum butter, all agreeing quite satisfactorily with the data of Daubert and Clarke.[4]

The weight of evidence is rather convincing, but further confirmation is to be found in X-ray diffraction data. Filer, *et al.*,[7] have very recently reported diffraction patterns for two solvent crystallized forms of (1) synthetic 2-oleyldistearin and (2) a natural oleyldistearin prepared from kokum butter in this laboratory. The corresponding patterns for the two glycerides are practically identical.

By X-ray diffraction and thermal methods an extensive investigation of the polymorphism of the oleyldistearin from kokum butter has been carried out in this laboratory. Through the courtesy of Drs. Longenecker and Daubert it has been possible to make a briefer but similar investigation of their synthetic 2-oleyldistearin. Again the results for the two materials are nearly identical. Deviations from the aforementioned data[7] were observed and will be discussed in a later section.

Materials

1. **Naturally Occurring 2-Oleyldistearin.**—A typical sample of kokum butter was received from the British Food Mission. Analyses of a portion which had been melted and filtered were as follows: iodine value = 36.3, thiocyanogen value = 35.2, acid value = 6.0, saponification value = 189.2, unsaponifiable = 1.36. The filtered portion was then subjected to these steps of fractional crystallization: (a) Three hundred grams was once crystallized from four volumes of acetone at 70°F. (b) The precipitate was crystallized four times from four volumes of acetone at 80°F. (c) The final precipitate of step (b) was crystallized from twenty volumes of petroleum ether at 50°F. The precipitate, Fraction I, was rejected. (d) The filtrate from (c) was crystallized at 32°F. (precipitate = Fraction II, evaporated filtrate = Fraction III). The yield of the main sample, Fraction II, corrected for material removed for analysis was 39%. The stage of purification reached is indicated in some measure by the data of Table I.

TABLE I

FINAL CRYSTALLIZATION FRACTIONS

Fraction	Wt., g.	Iodine value
I	12	28.1
II	75.5	28.3
III	1.3	29.0
Calcd. for 2-oleyldistearin		28.6

2. **Synthetic 2-Oleyldistearin.**—Two solvent crystallized samples in 1-mm. Nylon capillaries were received from Drs. Daubert and Longenecker. The triglyceride had been prepared as described in the literature.[3]

Methods Employed

Samples of the natural glyceride were subjected to examination by m. p., thermal curve and X-ray diffraction as previously described in the case of tristearin and homologs.[8]

The synthetic glyceride was exposed for X-ray diffraction in the Nylon capillaries. For temperature treatment and melting point determination the Nylon capillaries were enclosed in slightly larger thin-walled Pyrex capillaries. Thermal data and X-ray diffraction data appear in Table II.

The various forms were prepared in a variety of ways, but the following are typical. The lowest melting form was obtained by melting the sample and chilling in ice water. The intermediate melting form was obtained by

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(1) Heise, *Tropenflanzer*, **1**, 10 (1897).

(2) Hilditch and Saletore, *J. Soc. Chem. Ind.*, **52**, 101T (1933).

(3) Jackson, Daubert, King and Longenecker, THIS JOURNAL, **66**, 289 (1944).

(4) Daubert and Clarke, *ibid.*, **66**, 690 (1944).

(5) Hilditch, *et al.*, *J. Soc. Chem. Ind.*, **60**, 16–18 (1941).

(6) Meara, *J. Chem. Soc.*, 22 (1945).

(7) Filer, Sidhu, Daubert and Longenecker, THIS JOURNAL, **68**, 167 (1946).

(8) Lutton, *ibid.*, **67**, 524 (1945).

TABLE II

THERMAL AND DIFFRACTION DATA FOR 2-OLEYLDISTEARIN

		Sample from Kokum butter			Synthetic sample		
		Alpha-3	X-3	Beta-3	Alpha-3	X-3	Beta-3
M. p., °C.[a]		22.4	36.2	44.3	23	37	42.0[b]
Break in thermal curve, °C.[c]		23.2	37.7	44.0	22.3	37.3	41.6
C Sin β in Å.[d]		80.9	71.8	64.8	80.4	72.9	64.1
	(001)		(69) Present	(*66.3*) *S*			(61.5) Present
	(002)	*40.8 S*	*35.8 V.S.*	*32.6 S*	*41.3 V.S.*	*36.6 V.S.*	*31.9 V.S.*
	(003)		24.0 M.	21.5 W.		24.0 M.+	
	(004)		17.7 V.W.	16.2 W.			
Long spacings	(005)	*16.3 W.+*	*14.4 M.*	*13.0 M.*	*16.15 M.−*	*14.6 M.+*	*12.89 M.*
	(006)			10.9 V.W.			
	(007)			9.15 V.W.			
	(008)	*9.93 W.*	*9.00 W.*	*8.04 M.*	*9.9 V.W.*	*9.15 W.*	*8.13 M.*
	(009)		(*7.75 W.*)	7.16 W.		(7.83 W.−)	7.01 W.
Diffraction data (*d*/*n* in Å.)	(0010)		(7.00 V.V.W.)				
			5.22 W.	5.44 M.		5.22 M.−	5.44 M.
			4.73 S.	*4.62 V.S.*		*4.74 S.*	*4.62 V.S.*
			4.50 W.+			4.55 M.−	4.01 M.
		4.22 V.S.	4.17 W.	4.26 W.	*4.19 V.S.*	4.23 W.	3.86 M.
				4.03 M.		*3.88 V.S.*	3.78 W.
			3.88 V.S.	3.83 M.		3.60 M.+	3.64 M.
				3.65 M.+		3.08 V.W.	3.31 V.W.
Short spacings			3.58 M.	3.30 W.		2.83 V.W.	3.06 V.W.
			3.04 V.W.			2.56 W.+	2.59 W.+
			2.85 V.W.	3.07 V.W.		2.44 V.W.	2.39 V.W.
			2.55 W.+	2.59 M.−		2.23 V.W.	
			2.41 V.W.	2.37 W.		2.05 V.W.	2.05 V.W.−
			2.32 V.W.	2.27 W.		1.94 V.W.−	1.94 V.W.−
			2.25 V.W.	2.20 V.W.			
			2.05 V.W.	2.12 V.W.			
			1.93 V.W.	2.04 W.			
				1.96 V.W.			

[a] Data of E.S.L. [b] Value of 42.5–43.0 reported in ref. (3). [c] Data on natural sample—E.S.L.; data on synthetic sample—ref. (4) where the value, 29.8, is also given. [d] C Sinβ is the average of long spacing values, $d/n \times n$, except those in parentheses which are (1) first orders uncertain in measurement or (2) apparent higher orders in which short spacings are suspected to be involved.

bringing the lowest melting form to 22.5° for fifteen minutes, or by melting the sample for fifteen minutes at 22.5° or, finally, by melting the sample and crystallizing at room temperature (approximately 25°). The highest melting form was obtained either by recrystallizing from a solvent or storing any of the lower melting forms for two days or more at 80–100°F.

Results and Discussion

Thermal Data.—The thermal data recorded in Table II scarcely need discussion except concerning the question of a fourth point near 30°. Early data[5,9] indicated only three points. Meara,[6] however, now agrees with Daubert and Clarke that there are four, one of them near 30°. Although there has been observed in this Laboratory some fleeting evidence of an apparent change near 30°, a detailed thermal curve study revealed no halt near 30° in any way comparable with the halts at 23, 37 and 44°. If a 30° point is a reality, it represents something definitely more transitory than do the other points. Only three distinctive X-ray diffraction patterns were obtained, and each of these could be readily related to one of three thermal points observed at 23, 37 and 44°. A careful search failed to reveal any evidence of a distinctive pattern which could be related to the fleeting thermal effects near 30°.

X-Ray Diffraction Data.—The identity of the corresponding crystal structures of the natural oleyldistearin from kokum butter and synthetic 2-oleyldistearin is indicated by Table II. The evidence from X-ray diffraction adds to the previous and present thermal evidence in establishing that the natural oleyldistearin is the symmetrical isomer.

Such small differences in spacings as appear in Table II between the natural and synthetic samples are mostly attributable to normal errors in measurement and minor differences in technique (*e. g.*, use of glass capillaries or no capillary for the natural sample but Nylon capillaries for the synthetic sample). A minor but real difference between the samples is indicated by the difference in spacings in the neighborhood of 3.8 Å. in the case of the stable form. With a 2° difference in melting point such differences in spacings

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(9) "Lewkowitsch," 5th ed., Macmillan and Co., Ltd., St. Martin's Street, London, 1913, p. 36.

are not surprising. Such real differences in melting point and spacings are probably attributable to presence of minor impurities in one or both samples.

Short Spacings.—The alpha, beta prime and beta forms of tristearin may be characterized by their strong short spacings as indicated in Table III.

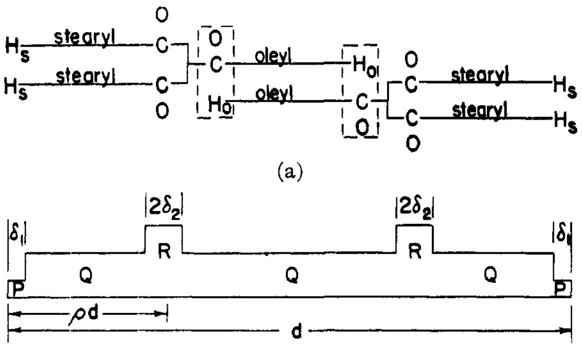
Table III

Characterizing Strong Short Spacing of Tristearin Forms[8]

Alpha	4.15 Å. only
Beta prime	4.2 (strongest) and 3.8 Å.
Beta	4.6 Å. (strongest)

On this basis the lowest and highest melting forms of 2-oleyldistearin are readily classified as alpha and beta, respectively.

The evidence of this Laboratory, however, does not permit regarding the intermediate form as a beta prime form, since at least four short spacing lines are observed to be stronger than any line corresponding to approximately 4.2 Å. For the time being the form is called X. (Other designations such as "beta double prime" or "B" might be preferable.) The form may bear some structural relationship to beta prime, difficult as that is to conceive on the basis of pattern difference. (For solvent crystallized samples Filer, *et al.*,[7] do report a pattern for an intermediate form, which they call beta prime, with strongest spacing near 4.2 Å. but with other features similar to those of the present X-pattern. Perhaps the fact that they crystallized from solvent accounts for the difference in experience with this intermediate form. Several attempts in this Laboratory to obtain an unstable form from solvent, although carried out under a variety of conditions, have all resulted in the stable form.)



(a)

(b)

Fig. 1.—Schematic representation of 2-oleyldistearin crystal structure.

Long Spacings.—The long spacings of the various forms of 2-oleyldistearin show striking differences from those of tristearin. As a group they are roughly 3/2 as long, and the intensities of the various long spacing orders show a different relationship. Both these facts indicate a fundamental structural difference between crystalline 2-oleyldistearin and crystalline tristearin.

A schematic representation of the structure proposed by this laboratory for crystalline 2-oleyldistearin is shown in Fig. 1. It is seen to be a "triple-chain-length structure" and contrasts with the "double-chain-length structure" usually accepted for tristearin. In most essential features it does not differ from that proposed by Filer, *et al.*[7] A somewhat analogous structure for certain phospholipids has been proposed by Bear, *et al.*[10]

The structure of Fig. 1(a) is readily seen to correspond to just half of the sextuple-chain-length structure of Filer, *et al.*[7] Very likely they would have proposed the simpler triple chain length structure had they not observed a weak line corresponding to a fractional order ($1^1/_2$) which, of course, had to be converted to an integral (3) order by doubling the long spacing.

No evidence of such a fractional order has been detected in this Laboratory. It is simpler, therefore, to assume the shorter long spacing value with the consequent triple-chain-length interpretation. It will probably require more powerful X-ray methods to establish finally whether the unit of structure is of triple or of sextuple chain length.

It should be noted that there is a possible pitfall in the conception of sextuple-chain-length structure. In a phase mixture, an actual 40 Å. (double) spacing could not be distinguished from a real or supposed 120 Å. (sextuple) spacing, although it could be distinguished from a real or supposed 60 Å. spacing on the basis of long spacing magnitudes alone.

Particular attention to the relative intensities of the various long spacing orders can be of great aid in distinguishing between double and triple (sextuple) chain length structures. Single-chain-length structures such as are observed for paraffins show a gradual decline in intensity as the long spacing order increases. Double-chain-length structures such as are found for fatty acids and for tristearin, *etc.*, show (in the case of low orders) strong intensity for odd orders and weak intensity for even orders. It is characteristic of the presumed triple-chain-length structure of 2-oleyldistearin, however, that maxima in intensity occur for the 2nd, 5th and 8th (or 4th, 10th and 16th on the sextuple-chain-length basis) orders. This, as clearly as the abnormal long spacing magnitudes, denotes a structure type which is not of double chain length.

Justification of Triple-Chain-Length Structure by Long Spacing Intensities.—That a reasonable triple (or sextuple)-chain-length structure will give a 2, 5, 8 sequence for intensity maxima can be deduced from a simple calculation according to the method of Shearer.[11] The method is not modern, but it has the virtue of simplicity. It

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[10] Bear, Palmer and Schmitt, *J. Cellular Comp. Physiol.*, **17**, 355 (1941).

[11] Shearer, *Proc. Roy. Soc.* (London), **A108**, 655 (1925).

should be very nearly as reliable in dealing with the main structural features in the present case as it was in so many cases successfully treated by Shearer.

A partial conception of the molecular arrangement in crystalline 2-oleyldistearin is represented in Fig. 1(a). The figure may be regarded as a projection on a plane through the long spacing axis. It is analogous to the representation of Filer, *et al.*[7] In Fig. 1(b) is represented "the distribution of scattering power" P, Q, R along the long spacing axis direction after the manner of Shearer.[11] In Fig. 1, H_s = final hydrogen in stearyl chain, H_0 = final hydrogen in oleyl chain, d = the long spacing, δ = the length corresponding to a final hydrogen, $2\delta_2$ = the length corresponding to a carbonyl group, ρd = the distance from the end of the structure to the center of the nearest carbonyl groups. (In the present case ρ should be slightly less than $^1/_3$.) Further assumptions in accordance with Shearer are: $\delta_1 = \delta_2$, in approximate accord with the lengths involved, $Q - P = R - Q$, in approximate accord with the electron densities involved.

The additional simplifying assumptions are made in the present case: (1) that in the oleyl portion of the structure, Fig. 1(a), the sum of the scattering powers of each final hydrogen, H_1, and of the carbonyl nearest to it is equal to Q, which is the scattering power of the main portion of the structure, (2) that the unsaturated in the oleyl chains does not alter the scattering power, Q, in any significant way, (3) that the scattering power for the glyceryl groups is approximately Q.

By still following the lead of Shearer the intensity of X-ray scattering power, I, for such a structure can be shown to follow the relationship

$$I \propto \left[\frac{\sin^2 2\pi n\delta_1/d}{n^2}\right] (1 - 2\cos 2\pi n\rho)^2$$

where n = order of long spacing.

This relationship is analogous to relations derived by Shearer for long chain fatty acids, esters and ketones.

The bracketed term is a factor slowly decreasing with increasing magnitude of n. Maxima for calculated intensities occur for the same values of n as do maxima for the term $(1 - 2\cos 2\,\pi\, n\, \rho)$.^{2} It is sufficient, therefore, to evaluate the latter term for values of n from 1 to 10 and for values of ρ near $^1/_3$ but preferably on the low side, to see if any such value of ρ gives maxima for the sequence of n = 2, 5, 8. In Table IV are shown values of the term for ρ = 0.27, 0.30 and 0.333.

TABLE IV

VALUES OF $(1 - 2\cos 2\,\pi n\rho)^2$

n	$p =$ 0.27	$p =$ 0.30	$p =$ 0.333	n	$p =$ 0.27	$p =$ 0.30	$p =$ 0.333
1	1.6	2.8	$\underline{4}$	6	$\underline{6.0}$	0.1	1
2	$\underline{8.7}$	$\underline{6.9}$	$\underline{4}$	7	0.3	0.1	$\underline{4}$
3	0.1	0.4	1	8	0.0	$\underline{7.0}$	$\underline{4}$
4	0.6	0.1	$\underline{4}$	9	$\underline{7.9}$	2.6	1
5	4.9	$\underline{9.0}$	$\underline{4}$	10	2.7	1.0	$\underline{4}$

The sequence of values of n giving maxima in the term $(1 - 2\cos 2\pi n\rho)^2$ is seen to be quite sensitive to small changes in ρ. At a value of ρ = 0.30, which is very reasonable for the structure type of Fig. 1, the sequence is found to be 2, 5, 8 which is the sequence for intensity maxima experimentally obtained for crystalline 2-oleyldistearin. The proposal of triple (or sextuple)-chain-length structure is therefore supported.

Nomenclature.—A problem in nomenclature arises from the fact that, however similar it may be in short spacings, a triple-chain-length form of 2-oleyldistearin should not be too closely identified with a double-chain-length form of tristearin. It has been thought best to retain the short spacing designation on the basis of Table III but, where any doubt may arise, to specify the structure from the standpoint of chain length also. By this procedure the various forms of tristearin and 2-oleyldistearin would be represented as in Table V.

TABLE V

PROPOSED SYSTEM OF NOMENCLATURE

Order of melting of form	Tristearin	2-Oleyldistearin
Lowest	Alpha-2	Alpha-3
Intermediate	Beta prime-2	X-3
Highest	Beta-2	Beta-3

Whether the 2-oleyldistearin structures are finally established as triple or sextuple in chain length the proposed nomenclature would still indicate the significant distinction between the 2-oleyldistearin and tristearin forms.

Acknowledgment.—The writer expresses his appreciation to Dr. R. H. Ferguson and to others of this Laboratory for many helpful discussions and assistance.

Summary

Thermal and X-ray diffraction data on three crystalline forms of the oleyldistearin from kokum butter agree closely with similar data on the synthetic 2-oleyldistearin of Filer, *et al.*,[7] and lend further confirmation to previous conclusions of others that the naturally occurring glyceride is the symmetrical isomer.

The three forms melting at 22.4, 36.2 and 44.3° are called alpha-3, X-3 and beta-3, respectively. They are called alpha, X and beta on the basis of short spacing data, X giving a pattern not encountered hitherto with other glycerides. The designation "-3" indicates their triple (or possibly sextuple as proposed by Filer, *et al.*)-chain-length structure which contrasts with the double-chain-length structure of tristearin.

The postulated triple structure is supported not only by the magnitudes of the long spacings but also by consideration of the 2, 5, 8 sequence of long spacing orders showing maxima in intensity.

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