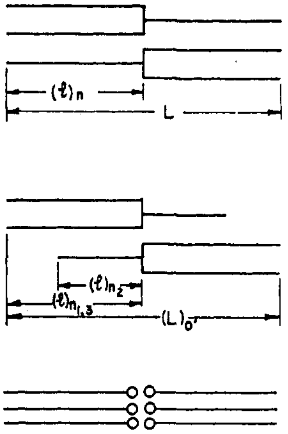
[CONTRIBUTION FROM THE PROCTER AND GAMBLE CO.]

Triple Chain-Length Structures of Saturated Triglycerides[1]

BY E. S. LUTTON

The nature of the polymorphism of the glyceride series, tristearin, tripalmitin, etc., has been made clear by the work of Clarkson and Malkin[2] and others.[3,4,5] The "triple-melting" phenomena of these glycerides are due to three crystalline forms—α, β' and β. These forms are of double-chain-length (DCL) structure, with their molecules presumably in Malkin's "tuning fork" type of configuration. The arrangement is indicated schematically in Fig. 1 along with other DCL structures, one for a fatty acid and another for a mixed triglyceride.



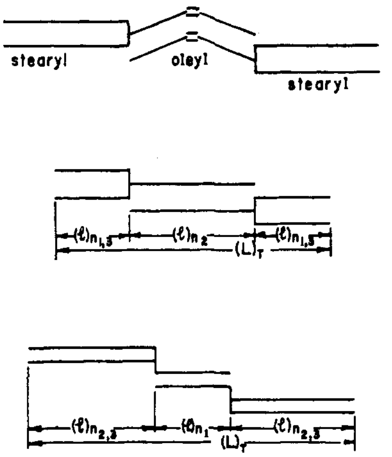
(a) Simple triglyceride

(b) Mixed triglyceride

(c) Fatty acid

Fig. 1.—Double-chain-length structures.

According to Malkin, *et al.*,[6] and others[7,8] many mixed saturated triglycerides are analogous to tristearin in their polymorphic forms. But these authors have shown that there may be serious departures from the tristearin plan, notably with regard to long spacings and DCL structure. No comprehensive scheme has been advanced which treats in any clear-cut way these departures from DCL structure. The presentation of such a scheme is attempted in this paper. It is shown that most, but not all, departures from normal long spacing values can be explained by crystallization of the mixed glycerides in triple-chain-length (TCL) structures similar to those proposed for the mixed saturated-unsaturated triglyceride 2-oleyl distearin.[5,9] In the saturated case, as in the unsaturated case, the TCL structures are presumed to arise from the sorting of chains, short chains from long chains instead of unsaturated from saturated chains. This process of sorting apparently gives rise to both tuning fork structures and a newly proposed "chair" type of molecular arrangement (see Fig. 2).



(a) 2-Oleyldistearin

(b) Symmetrical or "tuning fork" arrangement

(c) Unsymmetrical or "chair" arrangement

Fig. 2.—Triple-chain-length structures.

The quadruple-chain-length (QCL) structures which are discussed later are regarded as doubled DCL structures.

A simple geometric basis is proposed for classifying the various reported triglyceride forms as DCL, TCL or QCL structures. In developing this basis the following assumptions are made:

1. With regard to cross-sectional structures, as characterized by short spacings, there are three structure types which may be identified according to Table I.

TABLE I

CROSS-SECTIONAL STRUCTURE TYPES

Type	Identification
α	A single strong line corresponding to approx. 4.15 Å.
β'	Usually two (but occasionally more) strong lines corresponding to approx. 4.2 and 3.8 Å.
β	A strong (usually strongest) line corresponding to approx. 4.6 Å.

2. With regard to longitudinal structure, as revealed by long spacings, there are three structure types which are distinguished as indicated in Table II. Each of these conceivably may be, and one of them actually is, associated with all three cross-sectional types.

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[1] Presented in part to the American Society for X-Ray and Electron Diffraction, December 5, 1946.

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

[3] Bailey, *et al.*, *Oil & Soap*, **22**, 10 (1945).

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

[5] Filer, *et al.*, *ibid.*, **68**, 168 (1946).

[6] (a) Malkin and Meara, *J. Chem. Soc.*, 103 (1939); (b) Carter and Malkin, *ibid.*, 577 (1939); (c) Malkin and Meara, *ibid.*, 1141 (1939); (d) Carter and Malkin, *ibid.*, 1518 (1939).

[7] Filer, *et al.*, THIS JOURNAL, **67**, 2085 (1945).

[8] Sidhu and Daubert, *ibid.*, **69**, 1451 (1947).

[9] Lutton, *ibid.*, **68**, 676 (1946).

TABLE II

LONGITUDINAL STRUCTURE TYPES

Type	Identification
DCL	Long spacings of approx. normal length
TCL	Long spacings approx. 50% longer than normal
QCL	Long spacings approx. twice normal

There is, in theory, no exclusion of the possibility of other cross-sectional and longitudinal structure types.

Calculation of Long Spacings

If it be assumed that for any specified cross-sectional type the angle of tilt and consequently the contribution to long spacing per chain is approximately the same as in single fatty acid triglycerides, a simple calculation for long spacings can be postulated. Contributions per chain are indicated by (l) values shown in Table III.

TABLE III

CONTRIBUTIONS OF SINGLE CHAINS

Triglyceride	n	Long spacings of simple triglycerides $L\alpha$[b]	 $L\beta'$[c]	 $L\beta$[b]	Long spacing per chain $(l\alpha)_n$	 $(l\beta')_n$	 $(l\beta)_n$
Tricaprin	10	(30.6)[a]	(28.2)[a]	26.8	15.3	14.1	13.4
Trilaurin	12	35.6	32.85	31.2	17.8	16.4	15.6
Trimyristin	14	41.2	37.65	35.8	20.6	18.8	17.9
Tripalmitin	16	45.6	42.3	40.6	22.8	21.15	20.3
Tristearin	18	50.6	46.8	45	25.3	23.4	22.5

[a] Extrapolated. [b] Malkin, *et al.*, ref. 2. [c] Lutton, ref. 4.

Obviously $(l_\alpha) = {}^1/_2 L_\alpha$, etc.

Now it follows from the linear variation of (l) values with number of carbons that the following simple expressions can be given

$$(l_\beta)_n = 2.0 + 1.138\,n \qquad (1)$$
$$(l_{\beta'})_n = 2.5 + 1.163\,n \qquad (2)$$
$$(l_\alpha)_n = 2.8 + 1.250\,n \qquad (3)$$

Arithmetically the long spacing calculation for mixed glycerides is simply a matter of obtaining the average chain length contribution, C, and multiplying by the right "multiplicity factor," *i. e.*, 2 for DCL, as indicated in Table IV.

TABLE IV

CALCULATED LONG SPACING VALUES IN TERMS OF (l) VALUES

β Cross-sectional type

Long spacing type	Calculated value	
DCL	$(L\beta)_D = 2 \times \frac{(l\beta)_{n_1} + (l\beta)_{n_2} + l\beta)_{n_3}}{3} = 2\,C\beta$	(4)
TCL	$(L\beta)_T = 3 \times \frac{(l\beta)_{n_1} + (l\beta)_{n_2} + (l\beta)_{n_3}}{3} =$ $(l\beta)_{n_1} + (l\beta)_{n_2} + (l\beta)_{n_3} = 3\,C\beta$	(5)
QCL	$(L\beta)_Q = 4 \times \frac{(l\beta)_{n_1} + (l\beta)_{n_2} + (l\beta)_{n_3}}{3} = 4C\beta$	(6)

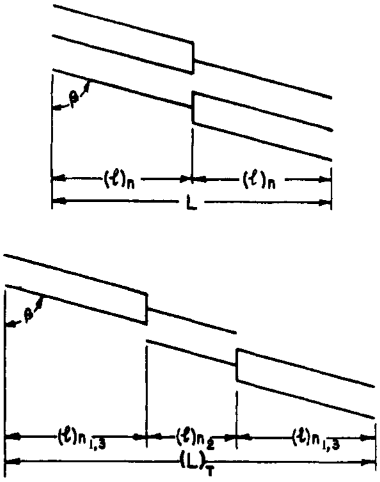
Similar values are postulated for beta prime and alpha cross-sectional types.

Now, from relations (1), (2) and (3), (L) values may be simply derived from the total number of acyl carbons, *e.g.*: letting $(n_1 + n_2 + n_3) = N$

$$(L_\beta)_T = 3\,C_\beta = 6.0 + 1.138\,N \qquad (7)$$
$$(L_{\beta'})_T = 3\,C_{\beta'} = 7.5 + 1.163\,N \qquad (8)$$
$$(L_\alpha)_T = 3\,C_\alpha = 8.4 + 1.250\,N \qquad (9)$$

with corresponding relations for DCL and QCL structures. By these equations, all calculated long spacing values were derived.

Geometrically, TCL structures may be represented as in Fig. 2 (in projection) or Fig. 3 (with the tilt indicated). It is not possible to represent DCL structures neatly for mixed glycerides. In Fig. 1 such a structure is represented with long spacing value designated as $(L)_{D'}$ to distinguish it from the shorter $(L)_D$ value defined as in equation (4). QCL structures are regarded as essentially doubled DCL structures, the manner and basis for doubling not being understood except that they are in some way associated with chain length difference in the glycerides.



(a) Double

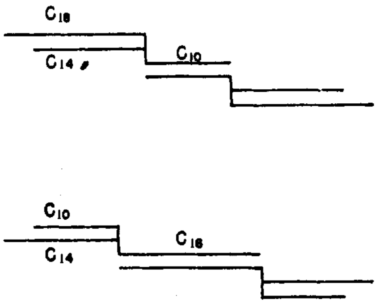
(b) Triple

Fig. 3.—Assumed constancy of tilt angle for given "form."

Additional quantities are defined to express the departure of experimental from calculated values

$$(\Delta_\beta)_D = L_\beta - (L_\beta)_D \qquad (10)$$
$$(\Delta_\beta)_T = L_\beta - (L_\beta)_T \qquad (11)$$
$$(\Delta_\beta)_Q = L_\beta - (L_\beta)_Q \qquad (12)$$

where L_β is the experimental value, (L_β) values are calculated as previously described and (Δ_β) values represent the differences.



(a) β'-3,C_{10}

(b) β'-3,C_{18}

Fig. 4.—Alternative triple structures for C_{18}, C_{14}, C_{10}.

Similar (Δ) values are defined for alpha and beta prime forms.

In Tables V and VI, the experimental L and derived (Δ) values are recorded for all mixed saturated glycerides for which data have been published.

Fortunately only one (Δ) value needs to be calculated for a given form. It is generally evident by inspection if, for instance, $(\Delta)_T$ is preferable to $(\Delta)_D$ or $(\Delta)_Q$.

The L values of Tables V and VI are plotted in Figs. 5 and 6 along with lines which express the calculated (L) values. It is these plots which most strikingly reveal that all the available long spacing data with one exception correspond with the concept of either DCL, TCL or QCL structure.

TABLE V

DIFFERENCES BETWEEN EXPERIMENTAL[60,b,c,d,e] AND CALCULATED LONG SPACINGS

Recording of $(\Delta)_D$, $(\Delta)_T$ or $(\Delta)_Q$ value signifies, respectively, double, triple, or quadruple (doubled double) chain length structure.

Diacid triglycerides

		Alpha		Beta prime				Beta		
Triglyceride	N	$L\alpha$	$(\Delta)_D$	$L\beta'$	$(\Delta)_D$	$(\Delta)_T$	$(\Delta)_Q$	$L\beta$	$(\Delta)_D$	$(\Delta)_T$
$C_{10}C_{12}C_{12}$	34	[c]		30.4	−1.0			31.8	+1.9	
$C_{12}C_{14}C_{14}$	40			35.3	−0.8			36.5	+2.1	
$C_{14}C_{16}C_{16}$	46	43.9	−0.2	40.3	− .4			41.5	+2.6	
$C_{16}H_{18}C_{18}$	52	48.8	− .1	44.7	+ .7			46.5	+3.0	
$C_{12}C_{10}C_{12}$	34							30.0	+0.1	
$C_{14}C_{12}C_{14}$	40	39.6	+ .7	36.7	+ .6			34.7	+0.3	
$C_{16}C_{14}C_{16}$	46	44.4	+ .3	42.4	+1.7			39.0	+0.1	
$C_{18}C_{16}C_{18}$	52	50.5	+1.6	47.5	+2.1			44.2	+0.7	
$C_{12}C_{10}C_{10}$	32							28.4	+0.1	
$C_{14}C_{12}C_{12}$	38			34.5	−0.1			33.0	+0.1	
$C_{16}C_{14}C_{14}$	44	42.8	+0.5	39.5	+ .3			37.7	+0.2	
$C_{18}C_{16}C_{16}$	50	47.8	+ .5	43.9	+ .1			42.5	+0.5	
$C_{10}C_{12}C_{10}$	32			29[a]	− .9			[d]		
$C_{12}C_{14}C_{12}$	38			33.6[a]	−1.0			[d]		
$C_{14}C_{16}C_{14}$	44	45.0	+2.7	38.1[a]	−1.1			[d]		
$C_{16}C_{18}C_{16}$	50	50.2	+2.9	43.2[a]	−0.6			[d]		
$C_{10}C_{14}C_{14}$	38			33.8	− .8			35.2	+2.3	
$C_{14}C_{16}C_{16}$	44	43.4	+1.1	38.5	− .7			39.8	+2.5	
$C_{14}C_{18}C_{18}$	50	48.5	+1.2	43.4	− .4			45.0	+3.1	
$C_{14}C_{10}C_{14}$	38			33.7	− .9			52.5		3.2
$C_{16}C_{12}C_{16}$	44	44.6	+2.3	77.0			−0.7 × 2	59.0		2.9
$C_{18}C_{14}C_{18}$	50	49.5	+2.2	44.7	− .9			65.8		2.9
$C_{14}C_{10}C_{10}$	34			31.3	− .1			47.5		2.8
$C_{16}C_{12}C_{12}$	40			36.2	+ .1			54.6		3.0
$C_{18}C_{14}C_{14}$	46	46.4	+2.3	41.7	+1.0			61.4		3.1
$C_{10}C_{14}C_{10}$	34			30.3	−1.1			46.5		1.8
$C_{12}C_{16}C_{12}$	40			35.5[a]	−0.6			[d]		
$C_{14}C_{18}C_{14}$	46	44.0	−0.1	40.0[a]	− .7			[d]		
$C_{10}C_{16}C_{16}$	42			74.1			− .55 × 2			
$C_{12}C_{18}C_{18}$	48	47.4	+1.8[e]	42.8	+ .5					
$C_{16}C_{10}C_{16}$	42	39.0	−1.6	74.0			− .6 × 2	56.5		2.7
$C_{18}C_{12}C_{18}$	48	47.1	+1.5	42.4	+ .1			63.7		3.7
$C_{16}C_{10}C_{10}$	36							49.7		2.7
$C_{18}C_{12}C_{12}$	42	(41.7)[e]	(+1.1)[e]	38.7, (38.0, 55.0)[e]	+1.1 (0.4)[e],	 (−1.4)[e]		57.0 (57.2)[e]		3.2 (3.4)[e]
$C_{10}C_{16}C_{10}$	36							49.5		2.5
$C_{12}C_{18}C_{12}$	42	40.8	+0.2	37.5	− .1			56.8		3.0
$C_{10}C_{18}C_{18}$	46	73.7[b]		60.0[e]		−1.1				
$C_{18}C_{10}C_{18}$	46			76.3			−2.55 × 2	61.2		2.9
$C_{18}C_{10}C_{10}$	38			51.0		−0.8		52.6		3.3
$C_{10}C_{18}C_{10}$	38							51.6		2.3

[a] Malkin's listing changed from beta to beta prime on the basis of short spacing data. [b] $(\Delta\alpha)_T = 7.8$, $(\Delta\alpha)_Q = -7.3 \times 2$. [c] Blank, no data. [d] Probably no form exists. [e] Data of E. S. L.

TABLE VI

DIFFERENCES BETWEEN EXPERIMENTAL[7,8] AND CALCULATED LONG SPACINGS TRIACID TRIGLYCERIDES

		Beta prime				Beta		
Triglyceride	N	$L\beta'$	$(\Delta)_D$	$(\Delta)_T$		$L\beta$	$(\Delta)_D$	$(\Delta)_T$
				I	II			
$C_{18}C_{10}C_{16}$	44					60.0		3.9
$C_{18}C_{12}C_{16}$	46					61.2		2.9
$C_{18}C_{14}C_{16}$	48	41.5	−0.8			63.4		2.7
$C_{18}C_{10}C_{14}$	42					57.3		3.5
$C_{18}C_{12}C_{14}$	44					59.8		3.7
$C_{18}C_{16}C_{14}$	48					40.5	0.0	
$C_{18}C_{10}C_{12}$	40					54.9		3.3
$C_{18}C_{14}C_{12}$	44	40.1	−2.2			59.6		3.5
$C_{18}C_{16}C_{12}$	46	43.3	−0.8			62.4		4.0
$C_{18}C_{12}C_{10}$	40	35.6[a,b]	− .5					
		53.0		−1.1 (β'-3, C_{18})				
$C_{18}C_{14}C_{10}$	42	54.3,		−2.1 (β'-3, C_{18})				
		56.1[a,b]			−0.3 (β'-3, C_{10})			
$C_{18}C_{16}C_{10}$	44	38.5[a,b]	− .7					
		59.0			−0.3 (β'-3, C_{10})			
$C_{16}C_{14}C_{12}$	42					35.7	− .2	
$C_{14}C_{12}C_{10}$	36	33.4	.4					

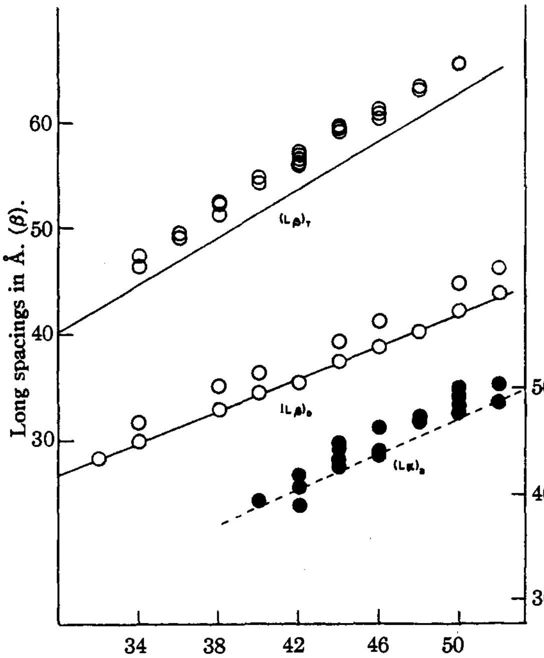
[a] Higher melting form. [b] Filer's listing changed from β to β' on the basis of short spacing data.

Agreement of Calculation and Experiment

Alpha Form (None reported for triacid triglycerides)

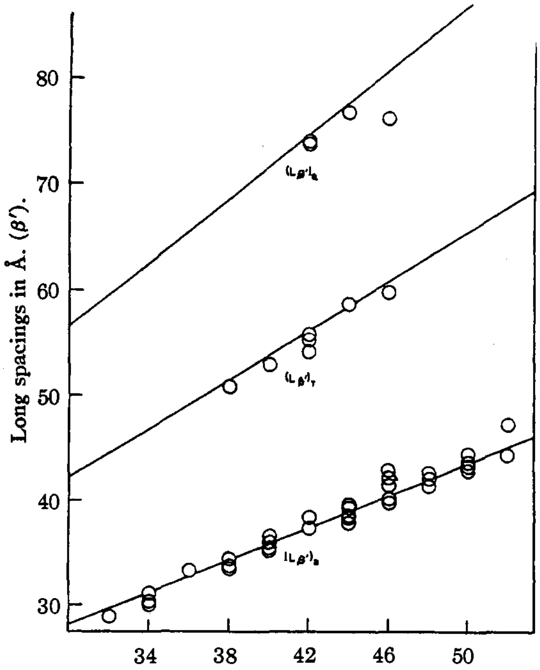
Among the cases for which data are reported for alpha forms, there are fourteen examples of agreement within 1.6 Å. between experiment and calculated DCL structure. Experimental error is usually of the order 0.5 Å. (but in individual cases it may be greater). In the untilted hydrocarbon chain each carbon corresponds to 1.27 Å. of length, wherefore it might be said that the correspondence between calculation and experiment is, in these cases, within about 1 carbon atom.

The six cases of rather poor agreement (1.6 < (Δ), absolute value <2.9) involve glycerides having a large difference (4, 6 or 8 carbons) between



N = total no. acyl carbons per triglyceride.

Fig. 5.—O—experimental long spacings (β), ●—experimental long spacings (α); solid lines—calculated long spacings for β-2 and β-3, dashed line—calculated long spacings for α-2.



N = total no. acyl carbons per triglyceride.

Fig. 6.—Circles, experimental long spacings (β'); solid lines, calculated long spacings for β'-2, -3, and -4.

longer and shorter chains. It might be expected that the fit in these cases would be irregular at the chain ends. In the case of $C_{10}C_{18}C_{18}$ agreement is so poor for any basis of calculation that (Δ) values are given only in a footnote.

Beta Prime Form

Diacid Triglycerides.—Agreement between experiment and calculation is better for the beta prime form. There are twenty-seven examples of DCL structure showing agreement within 1.1 Å. and two with (Δ) values of 1.7 and 2.1 Å. For three glycerides, the evidence points to TCL structure with agreement within 1.4 Å. (For $C_{18}C_{12}C_{12}$, the author's data indicate both double and triple structures, of which Malkin reported only the double structure.) Only for the beta prime form are QCL (or doubled DCL) structures obtained. There are three cases whose agreement is within 2 × 0.7 Å. and a single case of poor agreement, 2 × 2.5 Å.

It should be pointed out that the stable forms of the $C_{n-2}C_nC_{n-2}$ glycerides are tabulated as beta prime. Both the data of Malkin[5a] and data of this Laboratory[10] are best interpreted as indicating that these compounds are dimorphous exhibiting alpha and beta prime forms but not beta. Likewise Malkin's so-called beta forms of $C_{12}C_{16}C_{12}$, $C_{14}C_{18}C_{14}$, and $C_{10}C_{18}C_{18}$ seem to be best classified as beta prime.

Triacid Triglycerides.—The designation of forms for the $C_{18}C_{n2}C_{n3}$ glycerides by Filer, *et al.*,[7] was stated by them to be tentative. They simply labelled the lower melting of two forms beta prime and the higher melting beta. Several changes are here made to bring the designations more nearly in line with the recognized short spacing basis for labelling glyceride forms. These designations should perhaps be as tentative as those of Filer, *et al.*,[7] and they lead into as yet untested speculations.

There are five forms recorded as DCL beta prime. Experiment and calculation agree within 0.8 Å. except in the case of $C_{18}C_{16}C_{12}$ which shows a (Δ) value of −2.2 Å.

There are four forms designated as TCL beta prime, two for one compound, $C_{18}C_{14}C_{10}$. Agreement with experiment is within 1.1 Å. except in one case where (Δ) = 2.1 Å. The form of $C_{18}C_{12}C_{10}$ is interpreted to be analogous with the beta prime form of $C_{18}C_{10}C_{10}$. That of $C_{18}C_{16}C_{10}$ is probably analogous with the beta prime form of $C_{10}C_{18}C_{18}$ (listed by Malkin as beta, but here as beta prime). All four of these structures are presumably of the chair type as opposed to the tuning fork type of structure.

The forms of $C_{18}C_{14}C_{10}$, because of alternative possibilities are of special if somewhat speculative interest. They can be interpreted to be of the chair type, but as differing according to whether C_{14} goes with C_{10} or C_{18}, *i.e.*, whether C_{10} or C_{18} is the lone chain (see Fig. 4). An alternative "tuning fork" type structure seems to be ruled out because it is unlikely that C_{10} and C_{18} would line up side by side.

It is assumed simply on the basis of $(\Delta)_T$ values that the lower melting form of $C_{18}C_{14}C_{10}$ is more nearly analogous to the TCL beta prime form of $C_{18}C_{12}C_{10}$, and is therefore β'-3,C_{18} (C_{18} being the lone chain) and the higher melting form corresponds to that of $C_{18}C_{16}C_{10}$, and is therefore β'-3,-C_{16}. Examination of the detailed short spacing data of Filer, *et al.*,[7] gives little support to this association of forms, but does not preclude it in any way.

Beta Form

Diacid Triglycerides.—There are 15 DCL beta structures indicated. Of these eight show (Δ) values of 0.7 or smaller. Seven show values near 2.5 Å. It will be noted that where (Δ) values are large, the glycerides are of the general types $C_{n-2}C_nC_n$ and $C_{n-4}C_nC_n$.

It is of special interest that more than half of the reported beta forms or 18 out of 33 correspond to TCL structure. In these cases $(\Delta_\beta)_T$ has an average value of +2.9 Å. Deviations from this value in no case exceed 1.1 Å. It might be that the greater number of glyceryl groups per chain (2 for 3 instead of 1 for 2) accounts for the increased length, or, of course, a real difference in angle of tilt between DCL and TCL structures may be involved.

TCL structures do not appear for beta forms of these diacid glycerides unless one chain is 4 carbons longer than the other and not then for $C_{n-4}C_nC_n$ glycerides.

Of further interest is the absence of any beta form for $C_{12}C_{16}C_{12}$ and $C_{14}C_{18}C_{14}$ which are near relatives of $C_{n-2}C_nC_{n-2}$ glycerides whose stable forms appear to be beta prime. The glyceride $C_{10}C_{14}C_{10}$ does show a beta form but of TCL structure.

Triacid Triglycerides.—Of the forms that are unequivocally beta, all are of TCl structure except those of $C_{18}C_{16}C_{14}$ and $C_{16}C_{14}C_{12}$ which are DCL in analogy to the beta forms of $C_{18}C_{16}C_{16}$ and $C_{16}C_{14}C_{14}$ or $C_{16}C_{16}C_{14}$ and $C_{14}C_{14}C_{12}$ but unlike those of $C_{18}C_{14}C_{14}$ and $C_{18}C_{12}C_{12}$. The glycerides $C_{18}C_{14}C_{16}$ and $C_{16}C_{12}C_{14}$ which are more nearly symmetrical show TCL structure.

The $(\Delta)_T$ values for the TCL structures show an average of +3.4 in good agreement with the +2.9 value for diacid triglycerides. Perhaps a better relation than (7) for calculating TCL values for beta forms would be

$$(L_\beta)_{T'} = 3C_\beta + 3.0 = 9.0 + 1.138\,N \quad (13)$$

Evidence from Intensities.—The postulated triple (or sextuple) structure for 2-oleyldistearin was supported by approximate agreement of observed relative intensities with those calculated from a very simple model.[9] No adequate intensity data on long spacings for the saturated

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[10] Quimby and Lutton, unpublished.

glycerides here considered have been reported. To observe such intensities the compound 1-stearyldilaurin was prepared after the manner of Malkin, *et al.*[6d] It was obtained in four polymorphic forms characterized in Table VII.

TABLE VII

FORMS OF 1-STEARYLDILAURIN

	Preparation	Main short spacings	M. p., °C.[a]
α	Melted, chilled 0°	4.13 VS	21.0
β'-2	Melted, crystallized 30 min. 22.0°	4.23 VS, 4.06 S−, 3.77 S+	31.0
β'-3	β'-2, held 10 min. 32°	4.30 M, 4.17 M, 3.94 S	38.0
β	Solvent crystallized 16°, or β'-3 held 1 day 38°	4.60 VS, 3.84 S	44.6

[a] Malkin, ref. 6d, gave m. p's. as 20, 31, 41.5 and 45°.

Two of the 1-stearyldilaurin forms are called "beta prime" in an effort to follow as closely as possible the basis for nomenclature outlined at the beginning of this paper. Long spacing observations distinguish sharply between the so-called "beta prime" forms. A partial record appears in Table VIII.

TABLE VIII

LONG SPACING DATA FOR 1-STEARYLDILAURIN

Form	Magnitude of L. S.	Relative intensity 2nd and 3rd orders	Probable structure type	(Δ) Å.
α	41.7	3 >> 2	Double	$(\Delta\alpha)_D = 1.1$
β'-2	38.0 (38.7[a])	3 ≧ 2 (2 << 1)	Double	$(\Delta\beta')_D = 0.5$
β'-3	55.0	2 >> 3	Triple	$(\Delta\beta')_T = -1.25$
β	57.2 (57.0[a])	2 > 3	Triple	$(\Delta\beta)_T = 3.8$

[a] Malkin, ref. 6d.

Support for the TCL concept is given in Table VIII. The intensity results, so far as shown, correlate with postulated structure type. It is according to expectations that *a double structure for 1-stearyldilaurin should have a weak second order* and that *a triple structure should have a weak third order*. Attempts to find a more detailed agreement between observed and calculated intensities, according to previous procedure,[9] were unsuccessful. Failure was due, it is thought, to the degree of imperfection of the highly simplified model that was employed.

It is presumed that QCL structure would show intensity distributions similar to those of DCL structures, *i. e.*, weak fourth (instead of second as for DCL) and probably strong sixth (instead of third) order.

Conclusions

The following generalizations apply to the data now available. These can be best understood by reference to Tables VI, for triacid glycerides, and IX, a summary table for diacid triglycerides.

Alpha Forms.—DCL structures prevail among alpha forms. Long spacing values, all indicating DCL, have been reported for compounds having a difference of as much as 6 carbons in chain length, but no values have been reported for a difference of 8 carbons. It is possible that triple structures might occur for the larger difference.

TABLE IX

DESIGNATION OF STRUCTURE LENGTH FOR DIACID TRIGLYCERIDES. A SUMMARY FOR C_{10} TO C_{18}

Triglyceride type	No. compds.	α	β'	β
$C_{n-2}C_nC_n$	4	D[a]	D	D
$C_nC_{n-2}C_n$	4	D	D	D
$C_nC_{n-2}C_{n-2}$	4	D	D	D
$C_{n-2}C_nC_{n-2}$	4	D	D	[d]
$C_{n-4}C_nC_n$	3	D	D	D
$C_nC_{n-4}C_n$	3	D	D, (Q)[c]	T
$C_nC_{n-4}C_{n-4}$	3	(D)[c]	D	T
$C_{n-4}C_nC_{n-4}$	3	(D)[c]	D	[d] (T)[c]
$C_{n-6}C_nC_n$	2	(D)[c]	D), (Q)[c]	(T)[c]
$C_nC_{n-6}C_n$	2	D	(D), (Q)[c]	T
$C_nC_{n-6}C_{n-6}$	2	[D][c]	(D), [T][c]	T
$C_{n-6}C_nC_{n-6}$	2	[b]	(D)[c]	T
Mixed C_{10}-C_{18}	4	(?)[c,e]	T, (Q)[c]	T

[a] D = DCL; Q = QCL; T = TCL. [b] No data. [c] ( ) = one example; [ ] = one example, data of ESL. [d] Probably no form exists. [e] Uncertain from data, (Δ) > 7 Å.

Beta Prime Forms.—DCL structure is the usual one for beta prime forms. However, according to the data of Malkin, *et al.*, and Filer, *et al.*, if there is a chain length difference of as much as eight carbons, TCL structures predominate among beta prime forms of unsymmetrical triglycerides. (The author has found TCL structure with the six carbon difference in 1-stearyldilaurin.) In the case of beta prime only, QCL structures appear to be possible for chain length differences of four or more carbons.

Beta Forms.—Triple structure is much more likely for beta forms but seems not to occur unless there is a chain difference of at least four carbons. For difference of six carbons or greater there are no reported cases of other than TCL beta. The reported behavior of samples of *four carbon difference* can be described by the following four statements:

1. $C_{n_1}C_{n_2}C_{n_3}$, $n_1 > n_3 < n_2$ (or $n_3 > n_1 < n_2$)—Structures are double.
2. $C_{n_1}C_{n_2}C_{n_3}$, $n_1 > n_2 < n_3$—Structures are triple.
3. $C_nC_{n-4}C_{n-4}$—Structures are triple.
4. $C_{n-4}C_nC_{n-4}$—No beta form (beta prime may be stable as for $C_{n-2}C_nC_{n-2}$) except for $C_{10}C_{14}C_{10}$ which shows beta of triple structure.

It is a reasonable hope that, as further experimental evidence rounds out the record on triglyceride polymorphism, an increasing degree of order will become apparent.

Acknowledgment.—The author is indebted to Dr. R. H. Ferguson and others of this laboratory for many helpful discussions of this subject.

Summary

Polymorphic forms of many mixed saturated triglycerides show long spacing values which are abnormally large, that is, they are too large to per-

mit their associated crystal structures to be classified as typical double-chain-length structures. It is shown in this paper that most of these abnormal values can be interpreted as due to triple-chain-length structures analogous to that of the mixed unsaturated C_{18} triglyceride, 2-oleyldistearin. This triple structure presumably arises from a sorting of chains—sorting of short from long chains in the case of mixed saturated triglycerides, in manner similar to the sorting of unsaturated from saturated chains for 2-oleyldistearin.

These considerations lead to the proposal of a new type of molecular configuration in triglyceride crystals, a "chair" type of arrangement for certain unsymmetrical compounds in contrast to the generally accepted "tuning fork" arrangement.

Long spacings corresponding to quadruple-chain length structure have also been noted.

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[CONTRIBUTION FROM THE DIVISION OF MEDICINAL CHEMISTRY, THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH]

The Skraup Reaction with Acrolein and its Derivatives[1]

BY HARRY L. YALE AND JACK BERNSTEIN

A recent report[2] from these laboratories has described the synthesis of 6-methoxy-8-nitroquinoline in 42.3% yield, by a modified Skraup reaction. Some additional studies on the utilization of this reaction in the preparation of quinoline derivatives have now been completed. The results are summarized in Table I. Method A refers to the reaction conditions previously reported[2] while Method B is a new modification of the Skraup reaction employing acrolein and 85% phosphoric acid with arsenic acid as the oxidizing agent at 100°.

TABLE I

SKRAUP REACTION WITH ACROLEIN AND ITS DERIVATIVES

Amine	Quinoline derivative Yield, % Method A	Method B	M. p., °C. Found
Aniline[a]	Trace	3[b]	199–200
o-Nitroaniline	32	26	87–88
p-Nitroaniline	28	32	147–148
p-Anisidine	13	...	27
p-Bromoaniline	5[b]	5[b]	209
2-Amino-4-nitroanisole	5	59	148–149
2-Amino-5-nitroanisole[c]	30	67	147–148[g]
4-Amino-5-nitroveratrole	36	51	125–126
3-Nitro-4-aminoanisole[d,e,f]	42	60	157–158

[a] Ardashev, *J. Gen. Chem.* (*U. S. S. R.*), 16, 47 (1946), recently has reported the synthesis of quinoline in poor yield from aniline and acrolein in the presence of sulfuric and hydrochloric acids. [b] Isolated as the picrate. [c] β-Ethoxypropionaldehyde by Method B gave 60% yield. [d] The acetylated amine with acrolein by Method A gave 43% yield. [e] The amine with various acrolein derivatives by Method A gave: with β-ethoxypropionaldehyde, 39%; with β-ethoxypropionaldehyde diethyl acetal, 34%; with acrolein diethyl acetal, 21%. [f] The amine with α-methylacrolein gave the corresponding methyl quinoline in 19% yield by Method A; in 59% yield by Method B, m. p. 173–174°. *Anal.* Calcd. for $C_{11}H_{10}O_3N_2$: C, 60.55; H, 4.59; N, 12.84. Found: C, 60.87; H, 4.64; N, 12.96, 12.76. [g] *Anal.* Calcd. for $C_{10}H_8O_3N_2$: N, 13.72. Found: N, 13.52.

In the preparation of 6-methoxy-8-nitroquinoline by Method B a 60% yield is obtained at 100°, however, at 25°, the yield is 25% and at 65°, 54%; The use of 100% phosphoric acid has only a very slight advantage over 85% acid (65% yield as compared to 60%) but a marked decrease in yields occur with 75% acid (35%) and 50% acid (24%).

Acrolein diethyl acetal, β-ethoxypropionaldehyde and β-ethoxypropionaldehyde diethyl acetal, each of which is capable of yielding acrolein under the modified Skraup conditions, were substituted for acrolein in the reaction with 3-nitro-4-aminoanisole and 2-amino-5-nitroanisole; each gave slightly lower yields of the substituted quinoline.

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Experimental

All temperatures are uncorrected.

Method B.—Skraup Reactions with Phosphoric Acid.—A mixture of 33.6 g. (0.2 mole) of 3-nitro-4-aminoanisole and 56.8 g. (0.4 mole) of arsenic acid in 200 ml. of 85% phosphoric acid was placed in a 1-liter, 3-necked flask fitted with a thermometer, dropping funnel, reflux condenser and mercury-sealed stirrer. The reaction mixture was warmed to 100° and 19 ml. (0.3 mole) of acrolein added dropwise with vigorous stirring. The rate of addition was regulated so as to maintain the temperature at 100 ± 2°. After all the acrolein had been added (twenty-five minutes), the reaction mixture was stirred for an additional thirty minutes during which time the temperature was maintained at 100° by warming with an oil-bath. The solution was poured into 800 ml. of water, treated with Hyflo and decolorizing carbon and filtered. The filtrate was made alkaline with aqueous ammonia and the precipitated product filtered. The dried solid was refluxed with 600 ml. of ethyl acetate and decolorizing carbon, filtered, and concentrated until crystallization started. The product weighed 25 g. (60% yield), m. p. 157–158°.

Summary

A modified Skraup reaction with acrolein and α-methylacrolein has been carried out with substituted anilines. The reaction has been extended to include compounds capable of yielding acrolein, *in situ*.

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[2] Yale, THIS JOURNAL, 69, 1230 (1947).