Crystal Packing of Odd-Chain Saturated Triglycerides

Douglas L. Dorset

Electron Diffraction Department, Medical Foundation of Buffalo, Inc. 73 High Street, Buffalo, NY 14203, USA

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Single crystal electron diffraction data from an odd-chain triglyceride, glycerol triheptadecanoate, are compared with the known structure of the even-chain homo-acid triglycerides. Both classes of triglycerides are found to resemble one another in chain packing: they both have the same chain tilt (61 °) for the β-polymorph and, further, the orientation of the $T_{\parallel}$ subcell in the crystal structure is identical. The existence of the $T_{\parallel}$ subcell is quantitatively verified for the first time with the diffraction intensities from suitably tilted crystals. Given these similarities in β-polymorph structure, the major difference between triglycerides with even or odd chains (indicated by published long spacing and melting point alternation) must be due to the methyl end group packing – *i.e.*, the end group packing volume for the odd-chain glycerides must be larger than found for the even-chain materials.

Introduction

Because of the influence of polymorphic crystalline behavior on the properties of products made from edible fats, the crystal structures of triglycerides have been studied. Recently, three-dimensional X-ray determinations [1–4], along with powder X-ray data from a variety of even-chain triglycerides, have been combined to derive a comprehensive description of their polymorphic crystal forms [5–7]. Considering such parameters as chain length(s) and positions of acyl groups on the glyceride backbone it is possible to predict most probable crystal structures, including the identity of the methylene subcell, the acyl chain tilt, and the nature of the terminal methyl packing [6, 7].

The crystal packing of odd-chain triglycerides are less well understood. Powder X-ray data [8–10] suggest the existence of the three polymorphic forms found for the even-chain compounds. A further similiarity is that a β-form packing with $T_{\parallel}$ subcell may also be most stable for the single acid compounds.

Since several types of β-packing have been described [7, 11], dependent upon chain tilt, it is important to establish whether or not the forms preferred by even- and odd-acid glycerides are similar. This is most easily approached with the use of electron diffraction techniques [11–13] whereby single microcrystals can be oriented to derive methylene subcell and chain tilt data [14].

Reprint requests to Dr. D. L. Dorset.

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Experimental

Sample preparation

Samples of glycerol triheptadecanoate for transmission diffraction experiments (Sigma Chemical Co., St. Louis, MO), were dissolved in $CHCl_3$ and reprecipitated by addition of absolute ethanol. After sonication, microcrystals in the cloudy suspension were allowed to settle onto carbon-covered 400 mesh copper electron microscope grids.

Electron diffraction

All electron diffraction and microscopy experiments were carried out 100 kV with a JEOL JEM-100B electron microscope equipped with a side-entry ±60 ° tilt eucentric goniometer stage for transmission studies (selected area diffraction and diffraction contrast imaging). Diffraction camera length was calibrated with a gold powder diffraction standard. To minimize radiation damage to the specimens, a low incident beam current and very fast photographic film (Kodak NS-5T No Screen X-ray) were employed.

The protocols for quantitative use of electron diffraction intensity data from lipids are described elsewhere [14, 15]. For structure factor calculations, Doyle-Turner [16] electron scattering factors were employed. Diffraction intensities were obtained from films by integration of peaks after scanning with a Joyce Loebl MkIIIC flat bed microdensitometer.

Results

The resemblence of diffraction and image data from glycerol triheptadecanoate with those from the

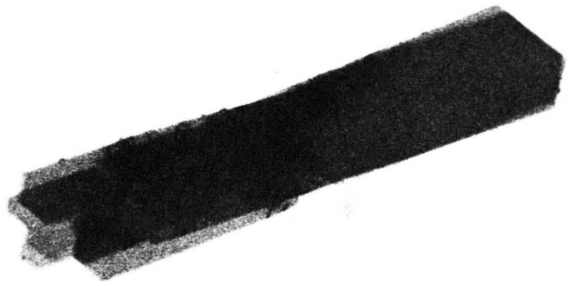

Fig. 1. Lath microcrystal of glycerol triheptadecanoate as grown from chloroform/ethanol.

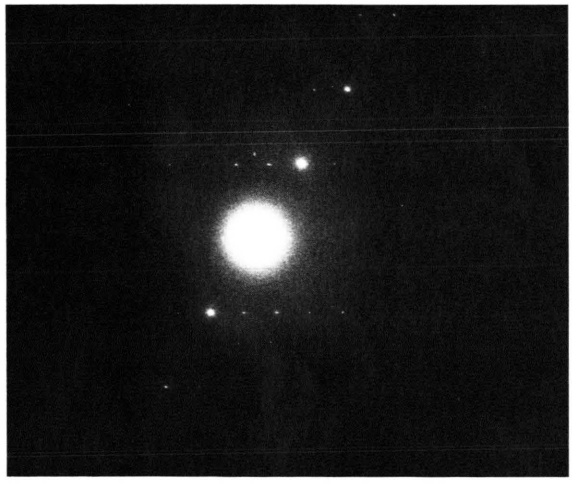

Fig. 2. Electron diffraction pattern from untilted crystal of glycerol triheptadecanoate. Compare to Fig. 3 in ref. 12 to verify similarity with the diffraction from glycerol tripalmitate.

tripalmitate is striking. The lath crystal habit (Fig. 1) is the same found for the crystal growth of simple, even, *homo*-acid, saturated triglycerides [12, 17]. These crystals give an electron diffraction pattern (Fig. 2) with similar unit cell constants (see Table I for comparison to tripalmitin) and expression of the molecular transform in the intensity distribution of the diffraction pattern.

The acyl chain tilt to the crystal face is found to be the same for both compound classes. When the above crystals are tilted by 29 ° (complement of 61 ° chain tilt found for even chain compounds [12]) about the b^*-axis, a transmission electron diffraction pattern is obtained (Fig. 3) which is characteristic of

Table I. Comparison of measured unit cell constants of untilted odd and even chain *homo*-acid triglyceride crystals.

Parameter	Triheptadecanoate	Tripalmitate
d_{100}	$d_{100}=11.95\pm0.15$Å	11.75 ± 0.14Å
d_{010}	$d_{010}=5.32\pm0.03$Å	5.36 ± 0.07Å
γ^*	80 °	80.8 ±0.8 °

Table II. Electron diffraction data from (001) projection of $T_{\|}$ methylene subcell.

	$\|F_{obs}\|$		
(hk0)s	Tripalmitin	Triheptadecanoin	F_{calc}
100	3.97	3.93	3.68
200	0.89	1.89	1.88
010	3.45	3.31	−3.38
$1\underline{1}0$	1.40	1.41	−1.81
$\underline{1}10$	3.70	3.48	−3.55
210	2.13	1.76	−2.36
$0\underline{2}0$	1.28	1.55	0.79
$\underline{1}20$	2.13	1.93	1.50
220	1.53	1.24	1.54
	$R=0.16$	$R=0.14$	

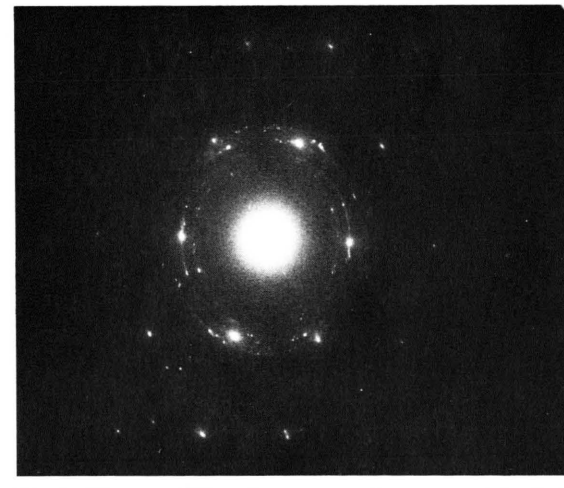

Fig. 3. Electron diffraction pattern from a crystal of glycerol triheptadecanoate tilted 29 ° about the b_5^*-axis to give a view down the chains in the $T_{\|}$ subcell. This may be compared to Fig. 3 of ref. 13 for a similar view down the chain axes for a different tripalmitin polymorph.

a projection down the chains for the $T_{\|}$ methylene subcell [13]. This is verified quantitatively by a comparison (Table II) to measured electron diffraction structure factors from tripalmitin single crystals tilted under the same conditions and to structure factors calculated from the known methylene carbon atomic positions in the subcell [2].

Discussion

The single crystal data presented here verify that the stable β crystal polymorph of even and odd chain *homo*-acid triglycerides are quite similar. Although earlier powder X-ray data [8–10] indicated the long chains in the odd-chain compounds to pack in the $T_{\|}$ methylene subcell, this is quantitatively verified for the first time here. Moreover it is seen that, within the uncertainty of a few degrees imposed by elastic crystal bending [14], the chain tilts for even and odd compounds are identical and that the methylene subcell packing is oriented with respect to the tilted chain axes in the same way.

Some differences in the respective crystal packings must occur, however. The alternation in X-ray long spacings for even and odd compounds found by Lutton and Fehl [9] indicates that much of the difference is due to an alternate methyl end group packing for the odd chain compounds. This difference is also suggested by a more evident melting point alternation [9]. Using an expression for the long spacing L derived by de Jong and van Soest [6],

$$L = (n+n_0)\,\frac{c_s}{3}\,\sin\tau$$

where τ is the molecular tilt, n is the number of chain carbons in the molecule and $c_s = 2.545$Å is the zig-zag chain repeat, it is found that a value $n_0 = 7.25$ gives a good fit to experimental even chain triglyceride long spacings reviewed by Lutton and Fehl [9] whereas $n_0 = 8.25$ gives the corresponding good fit to odd-chain compounds (Fig. 4). The quantity n_0, accounts for the end plane packing component to the long spacing. If the subcell axes and chain tilt do not change, as indicated by our data, then the end plane packing must have a different "terrace" arrangement than found for the β-2A crystal structure [6], which describes the *homo*-acid even chain triglycerides. Just how this is formed is not evident at this stage, but it is apparent that the volume of this region must be larger for odd chain materials, as is consistent with the lower melting points found.

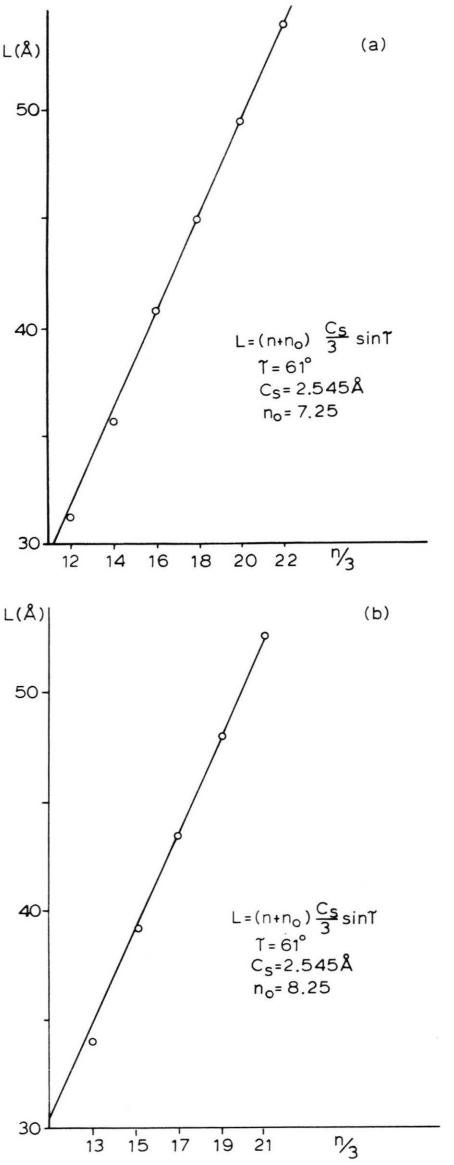

Fig. 4. Comparison of computed long spacings for (a) even-chain and (b) odd-chain *homo*-acid triglycerides using an expression derived by de Jong and van Soest [6, 7]. Note the larger n_0 required for the odd-chain compounds, denoting a larger methyl end group packing volume in the crystal.

Acknowledgements

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