The Crystal Structure of a Diacid Triglyceride

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Abstract

The x-ray structure analysis of a single crystal of the β-form of 2-11-bromoundecanoyl-1, 1′-dicaprin has revealed an arrangement of carbon atom chains within a molecular layer that is identical to that found in the β-form monoacid triglycerides. However the packing of the molecular layers within the crystal lattice is substantially different because of the unequal fatty acid chain-lengths in the symmetrical diacid triglyceride of this investigation.

Insufficient diffraction data owing to difficulty in preparing crystals of adequate size prohibits computation of precise interatomic distances and angles for this triglyceride.

Introduction

THE SINGLE CRYSTAL STRUCTURE analysis of the β-form of 2-11-bromoundecanoyl-1, 1′-dicaprin has been completed. The purpose in undertaking the investigation was to determine the change in triglyceride crystal structure as the result of replacing one of the fatty acids of a simple β-form monoacid triglyceride with an acid of differing chain-length. The compound chosen for the study was a heavy atom analogue of, and thus a crystallographic substitute for, the β-form of 2-lauryl-1, 1′-dicaprin in which the fatty acid chain attached to the 2-glyceryl oxygen was two carbon atoms greater in length than the chains in the 1-positions. Comparison of the structure, which was determined, with those of the β-forms of the monoacid triglycerides tricaprin (3,4) and trilaurin (6,7) and the isomorphous heavy atom analogue of trilaurin, tri-11-bromoundecanoin (6,7), is made below.

Experimental Procedure and Data

The compound for study, 2-11-bromoundecanoyl-1, 1′-dicaprin, was synthesized by the method of Hartman (2) and crystallized from petroleum ether (39.4–53.2C) in moderately thick plates, mp 35.5–36.5C. The crystal is triclinic and was assigned to space group $P\bar{1}$ on the basis of intensity distribution. The unit cell dimensions are: $a = 12.35 \pm 0.10$ Å, $b = 5.51 \pm 0.05$ Å, and $c = 29.3 \pm 0.4$ Å; $\alpha = 96 \pm 1°$, $\beta = 102 \pm 1°$, and $\gamma = 96 \pm 1°$. There are two molecules of structural formula $[CH_3(CH_2)_8CO_2CH_2]_2CHCO_2(CH_2)_{10}Br$ in the unit cell. A pronounced tendency toward twinning necessitated the selection of a very small crystal for study. The crystal was mounted on its b-axis, and three layers of intensity data were collected on film at room temperature by using an equi-inclination Weissenberg camera and an average initial exposure time of 91 hr. A total of 857 reflections were evaluated, including those accidentally absent and those too weak or too intense for accurate visual measurement by means of a calibrated film strip.

The bromine atom positions were located by means of a three-dimensional Patterson function, and the structure was solved by means of a bromine-phased, three-dimensional Fourier synthesis. Atomic coordinates and isotropic temperature factors for carbon, oxygen, and bromine atoms were refined by block-diagonal least squares to an R factor of 0.15 for the 365 observed reflections. However this represents an over-refined state leading to unnatural bond lengths and angles, particularly for carbonyl and glyceryl atoms, a not unexpected finding in view of the low reflection to parameter ratio which resulted from small crystal size and the consequent paucity of intensity data. Results were essentially the same when calculated hydrogen atom positions were included in the structure factor computations during the refinement process. The carbonyl and glyceryl atoms can be adjusted to positions which give acceptable interatomic distances and angles for the molecule as a whole. The resultant R factor, or reliability index, is 0.19, based on the coordinates listed in Table I and an isotropic temperature factor of 2.0 $Å^{-2}$ for all atoms. The increase in R factor can be minimized by retaining refined temperature factors, but there appears to be little other justification for doing so.

Discussion

Although precise interatomic distances and angles cannot be obtained from the data collected in this study, essential features of the structure and its chain-packing scheme are revealed. In the final structure the bromoundecanoyl chain and one capryl chain, together with their respective glyceryl atoms, form a continuous zigzag chain. The other capryl chain, together with its glyceryl atoms, branches at the 2-glyceryl carbon atoms and folds back parallel to and alongside the first capryl chain so that all chain

TABLE I

Atomic Coordinates of One Molecule in the β-Form of 2-11-Bromoundecanoyl-1, 1′-dicaprin

Fatty Acid Chain Carbon Atoms		
0.143	0.723	0.100
0.168	0.920	0.140
0.116	0.847	0.182
0.125	1.055	0.217
0.079	0.986	0.261
0.091	1.222	0.295
0.039	1.143	0.336
0.056	1.362	0.373
0.005	1.290	0.418
0.045	1.075	0.445
0.499	0.250	0.051
0.520	0.488	0.085
0.471	0.386	0.129
0.476	0.613	0.160
0.432	0.549	0.201
0.455	0.762	0.239
0.402	0.699	0.284
0.421	0.922	0.317
0.373	0.853	0.363
0.374	1.076	0.395
0.126	1.988	0.960
0.197	2.040	0.926
0.151	1.815	0.889
0.211	1.877	0.852
0.189	1.660	0.808
0.245	1.744	0.768
0.229	1.514	0.734
0.282	1.599	0.690
0.265	1.363	0.660
0.309	1.411	0.617
0.327	1.185	0.588
Glyceryl Carbon Atoms		
0.200	0.980	0.486
0.397	1.200	0.475
0.326	1.090	0.505
Oxygen Atoms		
−0.020	0.900	0.445
0.160	1.100	0.445
0.429	1.265	0.390
0.384	0.980	0.438
0.303	0.999	0.596
0.329	1.280	0.541
Bromine Atom		
0.163	2.288	1.008

axes in a molecular layer lie in one plane. Although there is parallel orientation of most of the bonds of the two capryl chains, their carbonyl groups are on opposite sides of the molecular-layer plane because of the rotation of the β-carbon to γ-carbon bond of the folded capryl chain, facilitating close packing of the structure. Both of these structural features are found in the published structures of β-tricaprin (4) and β-trilaurin (7).

However the projection down the b-axis (Fig. 1) reveals that the packing of the layers differs from that of the β-form monoacid triglycerides. In order to accommodate the longer chain in the 2-glyceryl position, the angle of tilt of the chain axes with respect to the normal to the end plane is less so that the 2-glyceryl chains (bromoundecanoyl chains) are oriented end-to-end with the folded and therefore shortened

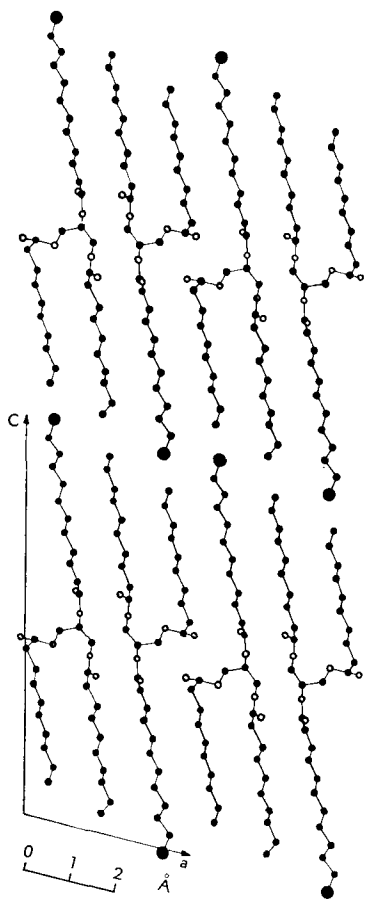

FIG. 1. The crystal structure of the β-form of 2-11-bromoundecanoyl-1, 1'-dicaprin as projected along the b-axis.

1-glyceryl chains (capryl chains) instead of with other 2-glyceryl chains in the adjacent layers as in β-trilaurin and β-tricaprin. Thus a greater degree of interlocking of molecular layers is achieved than with those structures, but the view of Kitaigorodskii that the principles of closest packing severely limit the variations in crystal structure to be found in long-chain organic compounds (5) is nevertheless corroborated. The observation that the crystals are thickened plates is in agreement with Larsson's finding that the terracing of the end methyl groups in β-trilaurin prevents the mechanical slipping of layers past each other along the axis (7).

Programs to compute distances between planes and distances of all atoms in a structure from any plane and from their least squares plane were written in SPS for the IBM 1620 computer. The short spacings indicated by the most intense reflections: 3.82 Å, (301) planes; 3.77 Å, $(2\bar{1}3)$ planes and 4.70 Å, $(11\bar{2})$ planes, as well as the repeat distance on the b-axis, 5.51 Å, are in good agreement with the short spacings listed for all β-form monoacid triglycerides for which there are x-ray powder data by Chapman in his review of glyceride polymorphism (1). The average distance of all carbon, oxygen, and bromine atoms in one molecule from their least squares plane is 0.57 Å and demonstrates the flatness of the molecular arrangement. The chain or zigzag planes are found to be parallel, and the crystal is confirmed as a β-form. Although the zigzag planes are not quite coincident with the $(2\bar{1}3)$ planes, the average distance of all atoms in the zigzag chains from their respective $(2\bar{1}3)$ planes is only 0.39 Å. The distance of all chain atoms in one molecular layer from their least squares plane was computed for two and for four adjacent molecules and is 0.44 Å. The molecular-layer planes lie between the $(11\bar{2})$ planes, symmetrically oriented with respect to the $(22\bar{4})$ planes but not parallel to those planes. The result is that, when the structure is viewed in a-axis projection, the chain axes are discontinuous at the b-axis in contrast to the structure of β-trilaurin (7).

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REFERENCES

1. Chapman, D., Chem. Revs. *62*, 444 (1962).
2. Hartman, L., J. Chem. Soc. 3572–3575 (1957).
3. Jensen, L. G., and A. J. Mabis, Nature *197*, 681–682 (1963).
4. Jensen, L. G., and A. J. Mabis, Acta Cryst. *21*, 770–781 (1966).
5. Kitaigorodskii, A. I., "Organic Chemical Crystallography," Consultants Bureau Enterprises Inc., New York, N. Y., c. 1961, pp. 177–208.
6. Larsson, K., Proc. Chem. Soc. 87–88 (1963).
7. Larsson, K., Arkiv Kemi *23*, 1–22 and 41 (1964).