Postulated Scheme for β Crystal Structures of Mixed Palmitic-Stearic Triglycerides

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ABSTRACT

A structural scheme is proposed for β phases of the six palmitic-stearic triglycerides, based on known configurations of tricaprin and 2-11-bromoundecanoyl-1,1'-dicaprin. The scheme receives some support from short spacing and binary system data.

INTRODUCTION

Doyne and Gordon (1), in a partial crystal structure determination of the β-form of 2-11-bromoundecanoyl-1,1'-dicaprin, found a molecular packing different from that of tricaprin (2) and trilaurin (3). The difference, arising from the difference in chain length relationships within a molecule, was particularly manifest by the arrangement of the methyl groups at the chain ends. With the help of several simple assumptions it is possible to proceed from the observations of Doyne and Gordon to a postulated classification of β-form structures for the mixed palmitic-stearic triglycerides.

POSTULATED β-FORM STRUCTURES

The following assumptions are made:

1. The bromine atom in 2-(11-bromoundecanoyl)-1,3-

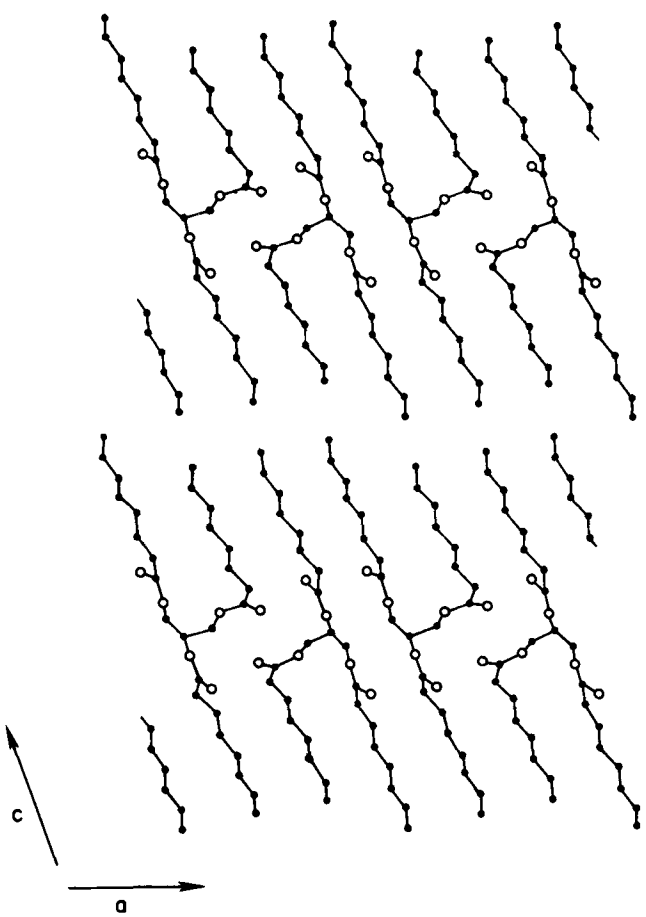

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FIG. 1. Postulated structure scheme for β-form of $C_{18}C_{18}C_{18}$. •, carbon; ○, oxygen.

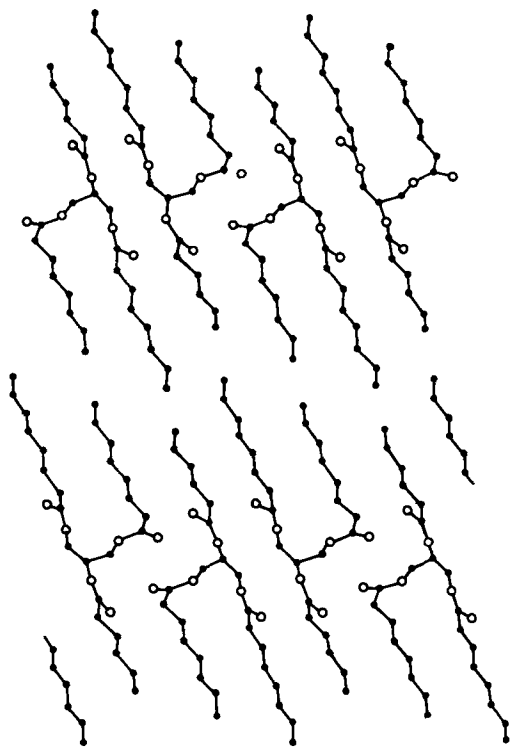

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FIG. 2. Postulated structure scheme for β-form of $C_{18}C_{16}C_{18}$.

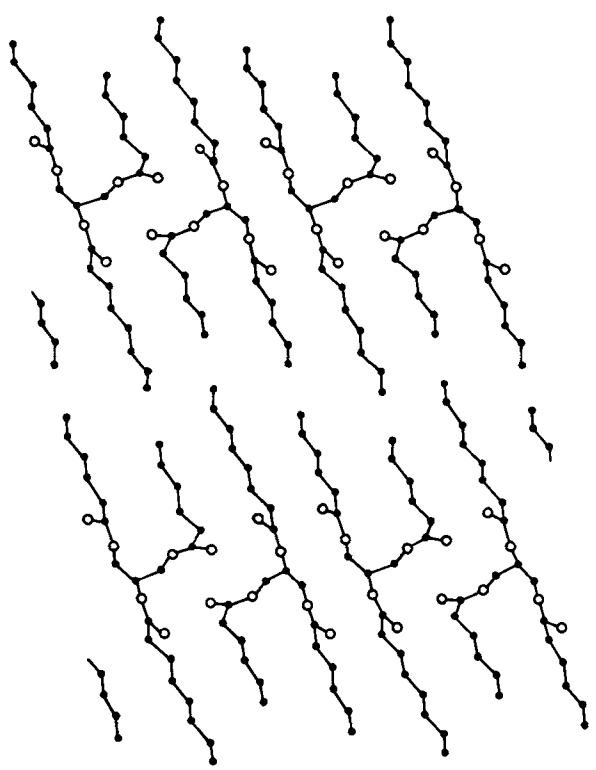

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FIG. 3. Postulated structure scheme for β-form of $C_{16}C_{18}C_{16}$.

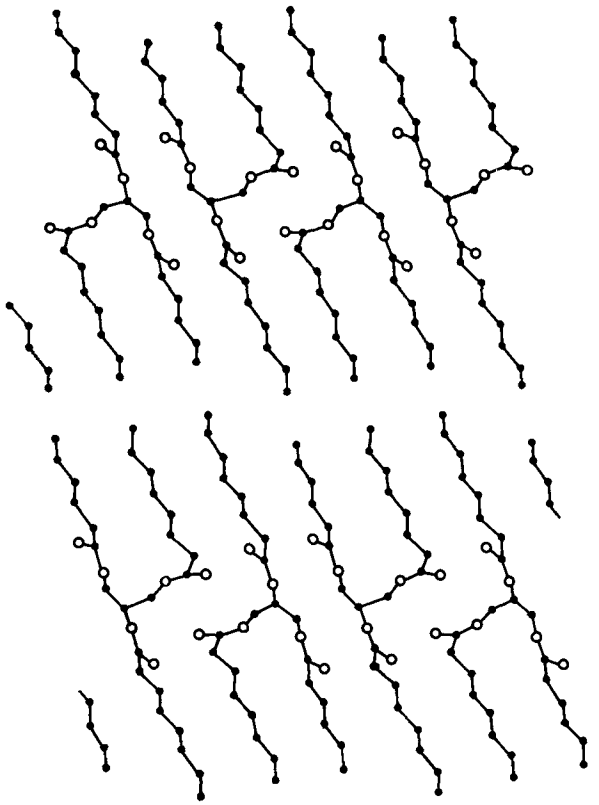


FIG. 4. Postulated structure scheme for β-form of $C_{16}C_{18}C_{18}$.

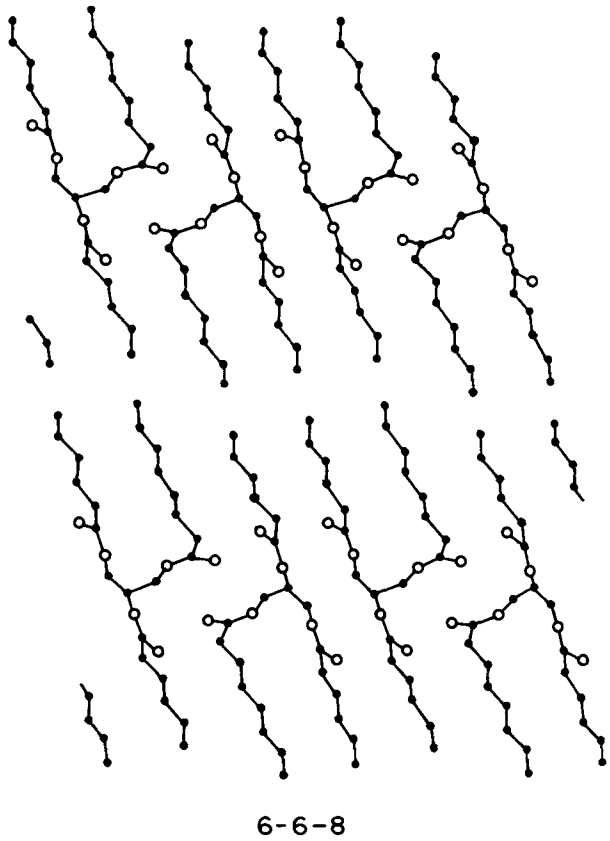


FIG. 5. Postulated structure scheme for β-form of $C_{16}C_{16}C_{18}$.

dicaprin plays the structural role of a methyl group, hence the glyceride crystal structure corresponds to that of 2-lauroyl dicaprin ($C_{10}C_{12}C_{10}$), in a (hypothetical)β-form. While the β-form of $C_{10}C_{12}C_{10}$ has not been reported, that of its homolog, $C_{16}C_{18}C_{16}$, has been (4).

2. The whole family of β-2(double chain length) forming saturated triglycerides comprised of several homologous groups, crystallizes in similar structures, quite similar in cross-sectional arrangement as attested by similar short spacings. (Examples of homologous groups are the $C_nC_nC_n$ and the $C_{n-2}C_nC_n$ types, where, of course, n is the number of carbons in the acyl chain.)

3. Projections of molecular skeletons on the ac plane of the unit cell or hypothetical unit cell are quite similar in all β-2 structures; glyceryl configurations and chain tilts remain identical. A corollary is that the 'tuning-fork' arrangement is maintained, i.e., with 1- and 3-chains in one direction and the 2-chain in the opposite direction.

4. Configurations at the methyl planes may be different, but in such a way as to maintain the most nearly comparable methyl group packing under the restrictions already laid down.

On the basis of the four assumptions, configurations for five types of β structure can be postulated for the palmitic-stearic triglycerides: $C_{18}C_{18}C_{18}$($C_{16}C_{16}C_{16}$), $C_{18}C_{16}C_{16}$, $C_{16}C_{18}C_{16}$, $C_{16}C_{18}C_{18}$, $C_{16}C_{16}C_{18}$. These are represented in Figures 1-5, prepared according to the following procedure: (a) Each molecule, to the extent possible, was traced from Figure 4 of the tricaprin study (2). (b) To reduce the labor of drawing while still keeping the molecules long enough to retain the general aspect of a triglyceride, chain length, n, was reduced by 10 so that, for example, $C_{18}C_{16}C_{18}$ appears as $C_8C_6C_8$. (c) As indicated in assumption 4, methyl relationships are maintained as near as possible to the arrangement in tricaprin, but according to the indication of Doyne and Gordon, the second tier of molecules is shifted by the width of a chain or two to maintain close packing in the methyl region.

DISCUSSION

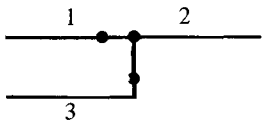
The postulated structures in Figures 1-5 can be systematized according to the following features: (a) A convention for chain numbering as follows:

TABLE I

Characterization of β-Forms of 16-18 Triglycerides

Glyceride	Unchanging Chain No.[a]	Slope (up) of triads of methyl groups	Strong short spacings of corresponding 16-18 triglycerides (4,5)		
$C_{18}C_{18}C_{18}$	2-2	Right	4.61 VS	3.84 S	3.68 S
$C_{18}C_{16}C_{18}$	3-3	Left	4.57 VS	3.81 S	3.72 +
$C_{16}C_{18}C_{16}$	1-1	Left	4.59 S	(3.82 W)	3.73 S
$C_{16}C_{18}C_{18}$	3-3	Right	4.61 S	3.87 S	3.67 S
$C_{16}C_{16}C_{18}$	1-1	Right	4.61 VS	3.85 S	3.67 S

[a]In straight line from tier to tier.



(b) A specification of the chain number which does not change in passing, in an approximately straight line, from a lower to an upper tier of molecules. (c) An indication of whether the zig-zag of methyl groups (which are in sequences of three at the chain ends) slopes upwards to the left or right. These observations are summarized in Table I.

From the short spacings in Table I it seems clear that the cross-sectional structures, while similar, are not identical, a situation which would not be surprising with significantly different packing necessary at the chain ends. It is gratifying that the cross-sectional, i.e., short spacing, variations fall into two groups, $C_{18}C_{18}C_{18}$, $C_{16}C_{18}C_{18}$, $C_{16}C_{16}C_{18}$ and $C_{18}C_{16}C_{18}$, $C_{16}C_{18}C_{16}$ according to whether the methyl groups slope to the right or left, respectively.

It is further gratifying that in binary systems (6), $C_{18}C_{18}C_{18}$ has been seen to better accommodate $C_{16}C_{18}C_{18}$ and $C_{16}C_{16}C_{18}$, of similar methyl slope, than $C_{18}C_{16}C_{18}$ and $C_{16}C_{18}C_{16}$ of different postulated slope. This agreement still leaves much question as to how glycerides would pack in binary systems.

The feature of optical isomerism, as to be reckoned with in $C_{16}C_{18}C_{18}$ and $C_{16}C_{16}C_{18}$ raises some problem as to the validity of present postulations, not answerable by the present two-dimensional analysis. It seems likely, however, from the negligible contribution of optical isomerism to measurable optical activity and its small influence on thermal behavior for saturated long chain triglycerides, that this feature would not be a significant factor in the considerations here advanced.

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