Computer Modeling of Packing Arrangements and Transitions in Saturated-cis-unsaturated Mixed Triglycerides

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Conformational analysis of modeled cis-unsaturated chains in triunsaturated and symmetrical monounsaturated triglycerides has identified pseudo-linear chain orientations that allow lower molecular mechanical energies than are possible with conventional cis-chains. Energy plots recorded during bond rotations near the double bond show that energy barriers between linear and normal cis-configurations are often less than 5 Kcal/mol. Pseudo-linear orientations, which allow compatible side-by-side packing of saturated and unsaturated chains in double-chainlength mixed triglycerides, also provide a route for efficient transformation between double-chainlength and triple-chainlength configurations in solid polymorphic triglycerides.

KEY WORDS: Computer modeling, double-chainlength, molecular mechanics energy, phase transitions, polymorphism, tri-cis-11-eicosenoic triglycerides, triple-chainlength.

One of many unanswered questions regarding triglyceride polymorphism concerns the phase transitions of saturated-unsaturated mixed triglycerides (e.g., oleoyl distearin, SOS, and oleoyl dipalmitin, POP). Recent studies by Gibon, Durant and DeRoanne (3) and Sato et al (4) on the thermal transitions of mixed triglycerides reveal dramatic reversible changes in X-ray long spacings that would be consistent with a substantial increase in the distance between molecular end group planes and a shift in molecular arrangement from double- to triple-chainlength configurations of the type illustrated in Figure 1(b). Such molecular transformation allows unsaturated chains to pack with other unsaturated chains in the triple-chainlength configuration, but in double-chainlength arrangements saturated and unsaturated chains must pack side-by-side, presumably in chain orientations quite different from that normally associated with cis-unsaturated structure. Insight into how such molecular arrangements might arise and contribute to unusual dimensional shifts of crystalline lipids is allowed by computer-aided analysis of cis-chain orientations in unsaturated triglycerides.

EXPERIMENTAL PROCEDURES

Chain and atom labeling. A schematic of the triglyceride structure used in these modeling studies is shown in Figure 1(a). Chains are numbered according to Lutton (5). Individual atoms in each chain are numbered from the terminal methyl carbon (i.e., chain 1 equals 1 through 20; chain 2, 21 through 40; and chain 3, 41 through 60). Double bond locations are identified according to standard convention for fatty acids, in which the carbonyl carbon is number one. Thus, for example, Δ11 unsaturation in chain 3 of Figure 1(a) occurs between carbons 49 and 50 of the triglyceride model.

Unsaturated bond orientations. Tri-cis-11-eicosenoic was modeled in a symmetrical tuning fork arrangement, Figure 1(a), from triarachidin (6) by removing hydrogen atoms to create cis-Δ11 unsaturation. The unsaturated carbon-carbon bond distance was adjusted to 1.34 Å. Initially, each unsaturated chain was oriented with an average 137° bend at the cis bond. To search for low-energy conformational forms, portions of the triglyceride were treated as separate entities. Chain 2 [Fig. 1(a)] was altered independently, but changes made in chain 1 were made simultaneously in chain 3 to achieve synchronous movement and to avoid chain contact and overlap.

Carbon-carbon bonds were rotated in 5- or 10-degree increments except near energy minima, where rotations were reduced to 1 or 2 degrees. Bond rotations were confined to the adjacent single bonds on either side of the double bond to keep the bulk of each chain segment in an all-trans configuration. This constraint, which essentially expresses any scattered gauche orientation effects as four equivalent single bond rotations, is not inconsistent with predominant trans methylene orientation observed by X-ray. It also was favored due to practical limits on computation times. Bonds nearest the glycerol region were rotated first; e.g., C11-C12 and C51-C52 for chains 1 and 3, and C51-C52 for chain 2. The low-energy form, having a normal cis orientation identified by the first rotations, i.e., C11-C12 and C51-C52 bonds, was used as a starting point for the next set of bond rotations, C30-C31 and C50-C51.

Mixed saturated-unsaturated triglycerides. A 2-oleo-1,3-distearin molecule (SOS) was prepared from a triarachidin model. Two methylene units were removed from each chain, and the double bond was placed in the C9 position of chain #2. For best-fit and transformation studies, the low-energy configuration found for chain #2 in tri-cis-11-eicosenoic was assigned to the SOS molecule.

Arrangements and transitions. Minimum energy positions for two molecules in both the double- and triple-chainlength arrangements were determined by placing the molecules in close proximity in an arbitrary starting position. One molecule remained stationary while the other was allowed movement along the X-, Y- and Z-axes, and rotation about the long verticle Y-axis through the central glycerol carbon until a minimum energy position was found. Between values for initial and final axes positions, whole molecule rotations and bond rotations were divided into 100 steps. At each step, mathematically adjusted parameters were incremented a portion of their total value, and the molecular mechanics energy (MME) was calculated to produce an energy curve for the transition.

Modeling system. The Chem-X molecular modeling system, developed and distributed by Chemical Design Ltd. (Oxford, England), was used for bond rotations, axes shifts, calculation of MME's (7) and display studies of orientations and transitions. A Digital MicroVAX 2000 computer (Digital Equipment Corp., Marlborough, MA) and a Tektronix 4255 high-resolution terminal (Tektronix Inc., Beaverton, OR) were used to run the Chem-X software.

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RESULTS

Crystalline monoacid triglycerides, both saturated and unsaturated, generally occur in double-chainlength (DCL) structures [refs. 8–10; Figure 1(b)], which have long spacings, \( L \), approximately equivalent to the length of two extended fatty acid chains. This methyl-to-methyl distance is reduced when chains are tilted with respect to the methyl group plane. As the name implies, triple-chainlength (TLC) structures have a long spacing that approximates the length of three fatty acid chains minus a reduction for chain tilt. In TLC structures of POP and SOS, the oleic acid moieties (chain #2) pack together, thereby segregating saturated and unsaturated chains in stable, high-melting polymorphs.

If a normal cis orientation were maintained in DCL structures, side-by-side packing of saturated and unsaturated chains should produce many voids in the crystal lattice and result in unstable liquid-like substances. Yet DCL forms of saturated-unsaturated mixed triglycerides are relatively stable and display definite melting points and X-ray spacings (4).

Low-energy forms of chains #1 and #3. A flow chart of transformations employed during the search for optimal energy forms of chains #1 and #3 is shown in Figure 2, which identifies bonds rotated, the extent of rotation at an energy minimum, the observed MME in Kcal and, in schematic, the general shape of the molecule.

Rotating bonds \( C_{11}-C_{12} \) and \( C_{51}-C_{52} \) in chains #1 and #3 at \(-72^\circ\) disclosed a nearly linear configuration that had a MME slightly lower than the MME’s for either of the other forms, normal cis or pseudo-linear. An energy plot for rotation about these bonds is given in Figure 3, which also shows the distance between methyl groups \( C_3 \) and \( C_{41} \) in chains #1 and #3, respectively, during bond rotation. MME’s for the normal cis orientation at \( 19^\circ \) and the pseudo-linear structure at \(-72^\circ\) differ by 3.3 Kcal but, as Figures 2 and 3 reveal, the two forms are separated by an energy barrier of approximately 8 Kcal. A larger 22-Kcal barrier separates the \(-72^\circ\) structure from an unusual, though apparently stable, orientation at \(-222^\circ\). The \( C_1:C_4 \) distance, indicative of chain spacing, shows that the closest approach of end groups on chains #1 and #3 coincides with conformational stability, which occurs at \(-72^\circ\) when the end groups are separated by 4.45 Å. This spacing approximates the 4.15 Å short spacing for \( \alpha \)-forms of saturated monoacid triglycerides (11), the 4.21 Å spacing for \( \alpha \)-forms of SOS and POP (1,4), and the 4.36 Å spacing for \( \alpha \)-forms of triolein (12).

Rotation about the \( C_{10}-C_{11} \) and \( C_{50}-C_{51} \) bonds of chains #1 and #3 (Fig. 4) also proved interesting. It produced two distinctly different orientations, \( 45^\circ \) and \(-18^\circ\), separated by a barrier of less than 1 Kcal and slightly lower in energy than the \( 19^\circ \) starting structure (Fig. 4). Together these interconvertable orientations represent a conformational switch point from which molecules might proceed via different paths to ultimately different configurations. In the present case, additional \( C_7:C_7:C_4 \) rotations led to minimized structures with slightly lower MME’s. A final normal cis structure at \( 21^\circ \) was about 1.5 Kcal lower in energy than an analogous counterpart at \( 9^\circ \). Both were separated from quite different configurations by 5 Kcal barriers.

Low-energy forms of chain #2. The search for low-energy...
normal cis and pseudo-linear forms of chain #2 began with
the same initial structure [Fig. 1(a)] used in the analysis
of chains #1 and #3. Figure 5 details the bond rotations
applied to chain #2. Rotation about the C_{31}-C_{32} bond pro-
duced a normal cis orientation at $-21^\circ$ and a pseudo-
linear form at $80^\circ$ separated by an energy barrier of 8
Kcal, which is identical to the barrier between normal cis
and pseudo-linear forms of chains #1 and #3 (Fig. 2).

C_{10}-C_{11};C_{20}-C_{21} rotations in chains #1 and #3 produced
two normal cis forms. However, rotation of the equivalent
bond, C_{30}-C_{31} in chain #2, formed one normal cis con-
figuration and two orientations with acute bends in the
chain. On the proximal side of the double bond in chain
#2, rotations of the C_{26}-C_{27} bond did not produce a nor-
mal cis orientation, and were a useless source of starting
structures for C_{27}-C_{28} rotations. Forms generated from
the C_{30}-C_{31} $-16^\circ$ configuration by rotation of the C_{27}-C_{28}
bond to $88^\circ$ and $-124^\circ$ also appeared linear. But when
viewed from another angle (Fig. 5), these structures ex-
hibited a more normal cis bend and, therefore, were not
true pseudo-linear forms.

Minimal energy forms. Final low-energy configurations

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FIG. 2. Flow chart of search for low-energy forms of chains #1 and #3 in tri-cis-
d11-eicosenoin in terms of bonds rotated, degree of rotation at energy minimum, molecular
mechanics energy (Kcal) and schematic triglyceride shape. Double arrows indicate energy
barriers between orientations.
for pseudo-linear and normal cis structures were obtained by combining bond rotations identified in the analyses of chain conformations (Figs. 2 and 5). Skeletal drawings of three of these structures are shown in Figures 6–8. The MME, 23.43 Kcal, of the lowest-energy linear form (Fig. 6) is lower than that for any of the other configurations. This minimal structure was derived by a $-72^\circ$ rotation in chains #1 and #3 (Fig. 2) and an $80^\circ$ rotation in chain #2 (Fig. 5). Carbon-carbon zigzag planes on opposite sides of the double bond are approximately perpendicular to each other on opposite sides of the double bond are an interesting feature clearly shown by the two views in Figure 6. A similar (MME, 23.61 Kcal), though less linear, form (not shown) can be made by combining a $-72^\circ$ rotation in chains #1 and #3 (Fig. 2) with rotations of $-21^\circ$, $-16^\circ$, and $-124^\circ$ in chain #2 (Fig. 5).

Figures 7 and 8 each show two views of low-energy forms (MME, 23.55 and 23.62, respectively) that have nearly normal cis bends in the acyl chains. Chain #2 of the structure in Figure 7 contains one unusual bond orientation, $C_{39}C_{29}$, but MME calculations indicate that this is a low-energy conformation. Chains #1 and #3 of both structures were derived by the $19^\circ$, $45^\circ$, $10^\circ$, and $21^\circ$ rotations of Figure 2. Chain #2 of Figure 7 resulted from $-21^\circ$, $-16^\circ$, and $88^\circ$ rotations, whereas the structure in Figure 8 was made by $-21^\circ$, $-16^\circ$, and $-19^\circ$ rotations. The two structures differ most in the chain #2 configuration. Carbon-carbon zigzag planes on opposite sides of the cis bond are approximately perpendicular in Figure 7 but are nearly parallel in Figure 8.

**DCL to TCL conversion.** Conversion of the SOS molecule from DCL to the TCL arrangement required that chain #2 of each molecule start in the pseudo-linear orientation and end in the normal cis configuration. A total of nine parameters, which included bond and whole-molecule rotations and axes shifts, were changed at each step in the conversion. Initial experiments with linear change in each parameter, i.e., with each step equal to $1/100$th of the total change of each parameter, produced unrealistically high MME values due to close approaches and, sometimes, overlap in portions of the molecule.

Comparing initial and final structures in Figure 9, it is evident that one molecule must move upward ($Y = 24.5$ Å) and to the left ($X = -6.4$ Å), while both molecules are rotated on axes (Z-axis) vertical to the plane of the Figure, one molecule clockwise and the other counterclockwise about glycerol centers. Review of conditions at intermediate steps in the initial linear-increment experiments suggested that delays in the X-axis shifts and Z-axis rotations (through an increasing function), combined with relatively large initial Y-axis shifts (a decreasing function), might eliminate atom-atom overlap and reduce total...
COMPUTER MODELING OF MIXED TRIGLYCERIDES

Starting Structure
31.63 Kcal

\[ \begin{align*}
\text{C}_{31-32} & \quad 21^\circ \\
30.94 \text{ Kcal} & \quad 8 \text{ Kcal} \\
\text{C}_{30-31} & \quad 79^\circ \\
30.63 \text{ Kcal} & \quad 2.5 \text{ Kcal} \\
\text{C}_{28-29} & \quad 111^\circ \\
30.31 \text{ Kcal} & \quad 1.5 \text{ Kcal} \\
\text{C}_{27-28} & \quad 88^\circ \\
30.20 \text{ Kcal} & \quad 1.5 \text{ Kcal} \\
& \quad 1.6 \text{ Kcal} \\
30.47 \text{ Kcal} & \quad 2.5 \text{ Kcal} \\
\end{align*} \]

FIG. 5. Flow chart of search for low-energy forms of chain #2 in tri-cis-Δ11-eicosenoin in terms of bonds rotated, degree of rotation at energy minimum, molecular mechanics energy (Kcal), and schematic triglyceride shape. Double arrows indicate energy barriers between orientations.

MME. Parameter values at each of the 100 steps were calculated as follows:

\[
\text{X-shift/Z-rotation} = [(F-S)/(Total steps)]^2 \times (\text{Step No.})^2
\]

\[
\text{Y-shift} = [(F-S)/(Total steps)]^2 \times [(\text{Total steps} + 1) - \text{Step No.}]^2
\]

where F and S are final and starting value.

Effects of these adjustments are reflected in computer-generated images of molecular positions at every 20th step of the transition (Fig. 9), and in the energy curve for the DCL to TCL conversion (Fig. 10). Contact between oleic acid and the adjacent molecule is eliminated and, at the same time, the overall spacing between molecules remains relatively constant. The energy profile for the first half of the conversion (Fig. 10) shows a series of high-energy transitions, which may or may not arise from interactions representative of activation processes. Overall, the energy barrier (approximately 34 Kcal) presented by these high-energy intermediate steps is not inconsistent with apparent phase excitation energies for monoacid triglycerides (13).

DISCUSSION

Previous modeling studies (6) have shown that several tuning-fork arrangements meet a requirement for α-forms of saturated triglycerides; namely, symmetry in the glycerol region (14). Little else, however, is known in detail of α-form structure, even though many studies have focused on the polymorphism of saturated mono-acid triglycerides (15). Even less is known about mixed saturated-unsaturated triglycerides. Thus, any of the proposed theoretical α-forms (6) is suitable for examining the feasibility of chain packing alternatives and possible conversion pathways for saturated-unsaturated triglycerides. Our findings affirm the conviction that subtle molecular differ-
ences regulate lipid behavior. Logically, knowledge of how minute kinetic and energetic differences segregate lipid populations is the key to selective exploitation of lipid properties.

Most of the minimal configurations identified for chains #1 and #3 (Fig. 2) and chain #2 (Fig. 5) differed little from each other in terms of calculated mechanical energy. MME’s for configurations in Figure 2 (chains #1 and #3) averaged 4.9 Kcal less than that for the starting configuration; extremes were separated by 3.5 Kcal. Similarly, MME’s for chain #2 were reduced from the starting value by only 1.2 Kcal, on average, and were spread over a range of 0.8 Kcal. MME’s calculated for minimized whole-molecule configurations (Fig. 6-8) were consistent with the energy reductions achieved by selected bond rotations in the separate chains. It is possible that several of these minimal molecular forms, though somewhat unusual in shape, may coexist in lipid populations during polymorphic transitions. It remains to be seen how many will be observed by improved detection methods.

The minimal structures identified in this study present evidence for two especially interesting features: i) Pseudo-linear alkene chains with trans bond orientation adjacent to the double bond; and ii) nonparallel zigzag planes on opposite sides of cis bonds. Pseudo-linear alkene chains, as illustrated in Figure 6, are not theoretical curiosities. A similar conformation was reported by Sawzik and Craven after X-ray analysis of cholesteryl nervonate (16) and cholesteryl palmitoleate (17). de Jong (18) also recognized the feasibility of overall straight configurations for unsaturated triglycerides with a trans-skew-cis-skew-gauche torsion angle sequence through the double bond (gauche = ± 60°; skew = ± 120°; trans = 180°; cis = 0°). De Jong pointed out that single bonds adjacent to a cis double bond cannot be cis. His analysis of available X-ray data on cis unsaturated compounds further suggested that the skew conformation would be favored for such single bonds.

Bond torsion angle data in Table 1 are consistent with such observations, but they suggest that angles adjacent to the double bond will be nearer trans and skew, which would affect the ability of the molecule to pack orderly among neighboring molecules. Significantly, one of two independent molecules in the unit cell of cholesteryl palmitoleate (17) exhibits a single bond torsion angle of −165° adjacent to the double bond, which is essentially identical to the preferred conformation (± 167° ave.) at double bonds in the pseudo-linear form identified by this study. In the identified favored configurations (Table 1), chains #1 and #3 are nearly identical to each other, which emphasizes the advantage of similar structure in adjacent chains. Chain #2 is approximately the same except for the direction of rotation and the C26-C27-C28-C29 angle of Form I.
Elements of structure in Figures 6–8 are similar to those found in single crystal studies of oleic (19) and erucic (20) acids, which show parallel zigzag planes on opposite sides of the cis double bond. Chains #1 and #3 in Figure 7 exhibit this structure, as do the three chains of the second low-energy normal cis structure in Figure 8. In Figures 7 and 8, however, portions of the chains between the double bonds and methyl groups at opposite ends of the molecule point in directions approximately 180° from each other. This is similar to the pattern found for double chain layers of oleic and erucic acids hydrogen bonded through their carboxyl groups.

Nonparallel zigzag planes on opposite sides of cis bonds are prominent in the pseudo-linear structure (Fig. 6) and chain #2 of Form I (Fig. 7). This segmented chain configuration was proposed originally to rationalize the observation of multiple β'-forms for some triglycerides and the absence of β'-forms for others during differential scanning calorimetry of monoacid cis triglycerides (21). It is comforting to find, two decades later, that such unusual structure is indeed preferred in low-energy forms. X-ray data indicate that zigzag planes alternate in β'-forms (9). Perhaps chain configurations of the type shown in Figure 7 do contribute to the polymorphic behavior displayed by all-cis and mixed triglycerides.

Unfortunately, little information is available by which to evaluate models composed of 20-carbon cis-unsaturated chains (Figs. 6–8). A shorter molecule, triolein, can be made by removing two methylene units, approximately 2.5 Å per repeating unit (22), from the vertical zigzag portion between glycerol and the double bond of each chain. A shortened molecule’s vertical axis length should approximate known X-ray long spacing dimensions for C18 triglycerides. Long spacing values reported for triolein α-forms vary from 44.8 to 47 Å, β-forms, 44.8 to 45.8 Å and β’-forms, 43 to 45 Å (12,23,24). While there is no evidence that α-triolein has pseudo-linear chains like those in Figure 6, the length of the triolein model, 44.2 Å, approximates the lowest reported long spacing value. Models with nearly normal cis bends, Figures 7 and 8, have lengths (approximately 40.2 Å) 3–5 Å shorter than those reported for β-forms, but this small difference can easily be corrected by a slight change in the angle of chain bend at the cis bond. Increasing the angle adjacent to each double bond by 2° will increase the long spacing by nearly 0.7 Å and the chain bend approximately 2.7°.

Better agreement with known dimensions was found by comparing published X-ray long spacings (4) to lengths for modeled DCL and TCL structures of SOS. In Figure 9, the starting (α-2) structures assigned pseudo-linear configurations (Fig. 6) have an overall length of 48.1 Å which compares well with a recently reported X-ray value of 48.3 Å. The observed length is slightly longer than the single molecule length because one molecule is shifted slightly with respect to the other in the long axis direction to improve interaction energetics. The final TCL structures in Figure 9 have an observed overall length of 67.6 Å as compared with X-ray values of 65.0 Å for β and 70.0 Å for β’ (4). The model essentially represents an average of β and β’ dimensions. Again, the precise molecular length depends on the cis-bend angle. This close correlation between modeled and observed long spacings lends credence overall to the schematic mechanism in Figure 9, but much remains to be learned about how intermolecular forces focus and redistribute to compel the drastic DCL to TCL change in configuration. Processes leading to α-form activation likely determine when and at what rate the transition occurs. Accordingly, further modeling will consider interactions that might promote or inhibit the bond rotations summarized in Figure 9. Final structural proof will most likely depend on single crystal X-ray, but 13C-nuclear magnetic resonance, which is sensitive to gauche configurations, also could prove beneficial.

Obviously, polymorphic transitions occur in temporal environments composed of different rate processes. Therefore, algorithms that incorporate kinetic parameters are appropriate. Adjusting molecular shifts and rotations relative to one another maintained molecular proximity and reduced the transition energy barrier substantially to about 34 Kcal (Fig. 10). In unadjusted transitions, individual steps produced six-digit energy values due to atom-atom contact. Throughout the first half of the parameter-adjusted transition (Fig. 10), energy peaks occurred at steps 13, 19, 25, 32 and 39 when protons near the end of cis-chain #2 passed close to protons on the adjacent saturated chain (Fig. 10, steps 20 and 40). By Step 60, cis-chain methyl protons on the upper SOS molecule clear the saturated chain of the lower molecule and little remains to interfere with concerted collapse into a more stable configuration. From the general shape of the curve...
in Figure 10, it appears that added experimentation with kinetic adjustments might further reduce the energy spikes, and that the activation energy for a DCL to TCL conversion of SOS might be near 15 Kcal.

These computational experiments intentionally explored options available to unsaturated chains in triglyceride configurations that represent but a few of many that might be consistent with accepted knowledge of crystalline lipids. Systematic extensions of such analyses that identify local features of defined molecular contexts will, in turn, provide larger contexts in which to conduct the more difficult search for conditions that regulate transformations into and out of global minima in lipid populations. The current experiments, for example, do not consider changes in the glycerol region, which might also contribute to DCL to TCL conversions. Some such additions may be necessary to account for X-ray data that evidence a rather more complex DCL to TCL to DCL conversion in the SOS homologue POP (4). Within the defined context, however, the work identifies low-energy configurations in which unsaturated chains pack efficiently with saturated chains, and it provides an appealing mechanism by which such triglyceride populations could undergo polymorphic transitions in unison through relatively simple bond rotations with a minimum of molecular separation.
TABLE 1
Torsion Angles Around cis-Bonds of Theoretical Unsaturated Triglycerides

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<th>Torsion angle</th>
<th>Pseudo-linear&lt;sup&gt;a&lt;/sup&gt;</th>
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<th>Form II&lt;sup&gt;c&lt;/sup&gt;</th>
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<sup>a</sup>Fig. 6.
<sup>b</sup>Figure 7.
<sup>c</sup>Figure 8.

FIG 10. Molecular mechanics energy vs. step number for DCL to TCL conversion of SOS.

REFERENCES

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