Structural Investigations of β' Triacylglycerols: An X-Ray Diffraction and Microscopic Study of Twinned β' Crystals

Paul J.M.W.L. Birker*, Sijmen de Jong, Eli C. Roijers and **Ton C. van Soest**
Unilever Research Laboratorium Vlaardingen, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands

To reveal the structure of β' triacylglycerols in detail, LML ($C_{12}C_{14}C_{12}$) was purified by a zone-melting procedure, and twinned crystals of β' stable LML were obtained from a melt. β' LML crystallizes in the monoclinic space group $C2$, with eight molecules in the unit cell. A powder X-ray diffraction study of solid compounds of 1:1 mixtures of selected triacylglycerols led to the conclusion that the triacylglycerol molecules in the β' modification have a 1,2 chair-conformation (*i.e.*, the fatty acid chains on glycerol positions 1 and 2 are adjacent, with the chain on the 3-position forming the back rest of the chair). Packing studies and the positions of two-fold axes and two-fold screw axes in the unit cell require that the molecules are bent at the glycerol site. The fatty acid chains make an angle of 25° with the long axis of the unit cell. Electron micrographs and precession photographs indicate that the twinning results from the stacking of a large number of thin crystalline platelets in two distinct orientations.

KEY WORDS: **β', crystal structure, electron microscopy, fat, polymorphism, triacylglycerol, twinning, X-ray diffraction.**

Polymorphism is a well-known feature of triacylglycerol crystallization. It is now generally accepted (1,2) that four major types of crystal modification play a role in fat crystallization processes, known as sub-α, α, β' and β. The sub-α and α modifications are always unstable and transform easily to β' or β when heated or during prolonged storage. The β form is the stable modification for most pure triacylglycerols and for some fats of simple composition, like cocoa butter (3). The β' modification is the most stable form for some special types of triacylglycerol (*e.g.*, the saturated $C_nC_{n+2}C_n$ type), and for most complex fat blends. The β' modification is, therefore, of major importance in fat products such as margarines.

Only the structure of the β-2 modification is known in exact detail from several single crystal structure determinations (4–6). The structure of β-2 $C_{10}C_{10}C_{10}$ (5) is shown in Figure 1. It forms a relatively simple crystal structure with a triclinic unit cell containing two triacylglycerol molecules in chair conformations, related by an inversion center. β-2 and β-3 structures which are compatible with X-ray powder diffraction data and melting points have been derived from these structures for a wide range of triacylglycerols (7,8).

Much less is known about the β' structure in spite of considerable efforts to obtain good quality single crystals. β' crystallization often leads to the formation of spherulitic conglomerates of thin needles, which are not suitable for single crystal X-ray structure determination.

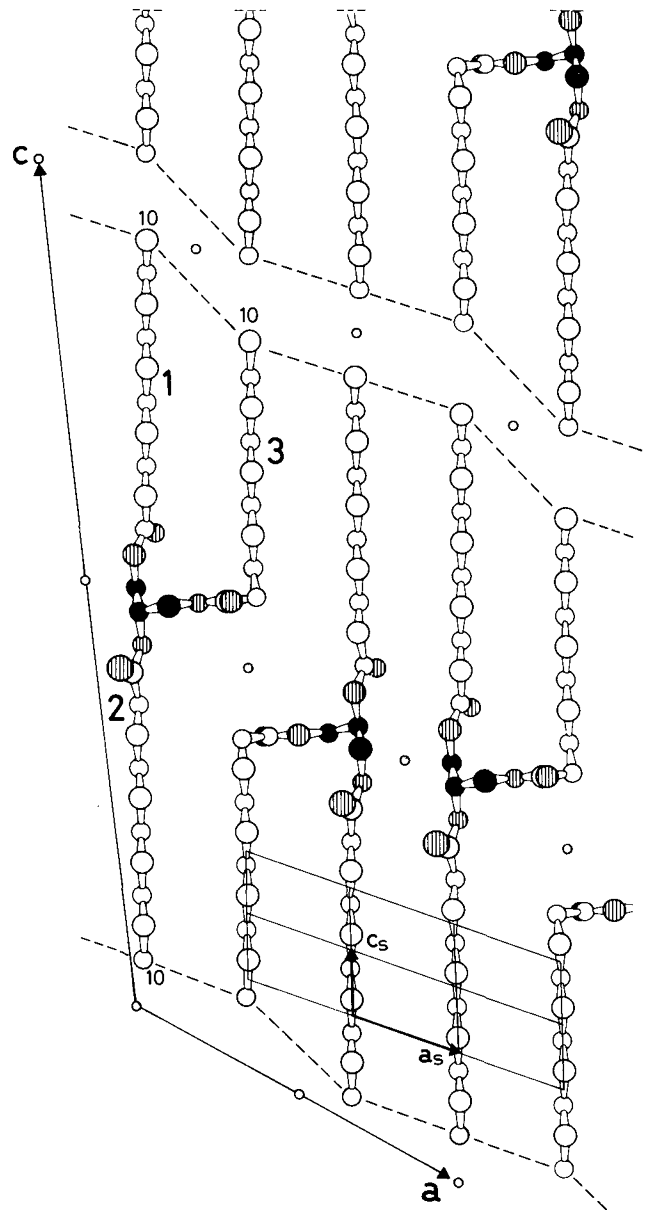

FIG. 1. The β-2 crystal structure of $C_{10}C_{10}C_{10}$ projected on the a_sc_s plane. The methyl terrace and some subcells are indicated (see text). Open circles, chain carbon; closed circles, glycerol carbon; and striped circles, oxygen.

The present paper describes how separate crystals can be obtained after exhaustive sample purification and careful control of experimental conditions during nucleation and growth. Even in this case the resulting crystals are often twinned and have unfavorable dimensions for single crystal X-ray diffraction work—very long thin needles, typically a few centimeters by a few tenths of a millimeter, are often obtained.

Hernqvist and Larsson (9,10) have studied β' triundecanoin ($C_{11}C_{11}C_{11}$), crystallized in space group $P2_1/C$.

---

*To whom all correspondence should be addressed at Unilever Research Laboratorium Vlaardingen, P.O. Box 114, 3130 AC Vlaardingen, The Netherlands.

The complete crystal structure was not solved. The directions of the alkyl chains in the unit cell could be determined, but the chains could not be connected to glycerol groups forming complete molecules. These authors also gave evidence for the existence of two β' modifications supporting earlier observations on SSS ($C_{18}C_{18}C_{18}$) by Simpson and Hagemann (11). A recent detailed study of PPP ($C_{16}C_{16}C_{16}$) by time-resolved X-ray diffraction with a synchrotron radiation source (12) did not demonstrate unambiguously the existence of two distinct and independent β' polymorphs. The two β' phases merely seemed to differ in degree of crystal perfection and crystallinity, but were essentially similar at the molecular level.

Undoubtedly, there is a great deal of structural variation within the β' class, which is simply defined as covering all solid triacylglycerols with two or more short-spacing (d<6 Å) reflections around 3.8 Å and 4.2 Å, but without the strong reflection at 4.6 Å that is typical for the β phase (1). β' crystals of even- *vs.* odd-chain triacylglycerols, of saturated *vs.* unsaturated triacylglycerols or of monoacid *vs.* di- or triacid triacylglycerols necessarily differ in structural detail. As the β' modification is predominant in solidified complex fat blends, it is important to know at least the structure of one type of β' crystal in detail.

The plate-like crystal habit of β triacylglycerol crystals has been explained on the basis of a detailed crystal structure (13). The unusual needle-shaped morphology of β' crystals may also be understood better when the complete crystal structure becomes known.

EXPERIMENTAL PROCEDURES

Materials. Triacylglycerols were synthesized by our Department of Organic Chemistry. Recrystallized LML ($C_{12}C_{14}C_{12}$) was further purified by zone-refinement in an ENRAF-Nonius zone-melting apparatus (ENRAF-Nonius, Delft, The Netherlands). The sample was contained in a vertical glass tube of 30 cm × 0.5 cm, which was heated by 6 ovens (3-cm long) separated by air-cooled regions. The set of ovens travelled along the tube at 0.6 cm/hr. At the end of the purification process, the material had solidified in the form of a thin, hairy mass of crystals oriented in the longitudinal direction of the zone-melting tube. A central section of 15 cm was subsequently cut out of the tube and its contents were remelted in a boiling water bath and then accurately temperature-controlled in a test tube at 51.5°C by means of a Lauda thermostat bath with a Lauda PTR-R52 temperature control unit. Crystallization was induced by a tiny seed crystal from the zone-melting tube mounted on a metal wire. Crystals of 1-cm length can thus be grown in about one day.

Single crystal X-ray diffraction. Measurements were carried out on ENRAF-Nonius Weissenberg and precession X-ray diffraction cameras, and on an ENRAF-Nonius CAD-4 single-crystal X-ray diffractometer with Cu $K\alpha$ radiation (λ = 1.5418 Å).

X-ray powder diffractograms. These were measured with standard ENRAF-Nonius Guinier cameras under Cu $K\alpha$ radiation. Micrographs were made with a Philips 505 SEM (Philips, Eindhoven, The Netherlands), and a Zeiss light microscope. Compounds of two different triacylglycerols were made by evaporation from a 25% w/w chloroform solution of a 1:1 mixture of these triacylglycerols.

RESULTS AND DISCUSSION

Unit cell dimensions and crystal habit. β' LML crystals grown as described in the Experimental section had the appearance of flat, needle-shaped single crystals, but in reality none of them appeared to be truly single. Weissenberg and precession photographs often showed multiple reflections in the X-ray diffraction patterns in places where single crystals should have had single reflections (see Figs. 2 and 3). At best (and, in fact, in most cases), twinned crystals were obtained.

In the twinned β' LML crystals, two different unit cell orientations can be distinguished, but the difference in orientation is small and easily can be overlooked if the quality of the crystals is poorer than in the present study. Figures 2 and 3 show X-ray diffraction patterns of twinned β' LML crystals. The unit cell dimensions calculated from these patterns are:

a = 22.9 Å $\qquad$ α = 90° $\qquad$ V = 8718 Å^3
b = 5.7 Å $\qquad$ β = 91° $\qquad$ Z = 8
c = 66.8 Å $\qquad$ γ = 90°

The calculated density assuming eight molecules of LML ($C_{41}H_{78}O_6$, MW = 667.07) per unit cell is 1.016 g/cm^3, which is in good agreement with the known density of solid triacylglycerols of 1.01–1.06 g/cm^3 (14). Figure 4 shows the orientation of the unit cell in the macroscopic β' LML crystal.

The relative crystal growth rates on the different crystal faces rank as expected, *i.e.*, the crystal grows most rapidly in the direction of the shortest unit cell axis (b = 5.7 Å; the [010] direction), and growth in the direction of the longest unit cell axis (c = 66.8 Å, [001]) is slowest. The

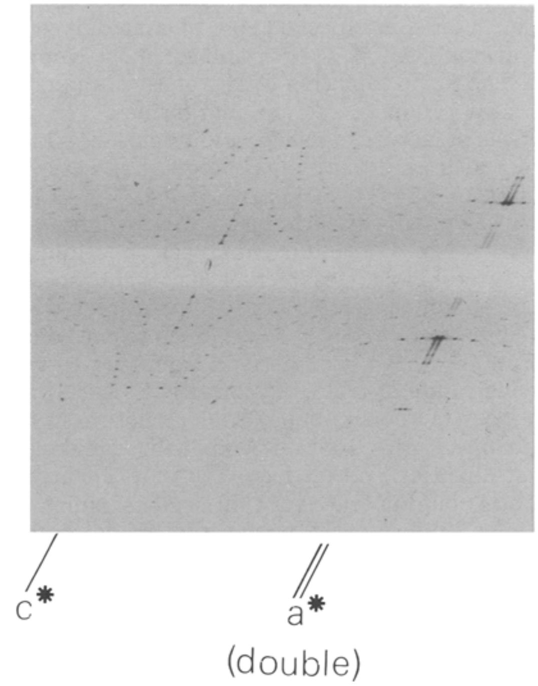

FIG. 2. Weissenberg diffraction pattern of the *h0l* layer in β' LML. The double *a axis is the result of twinning.**

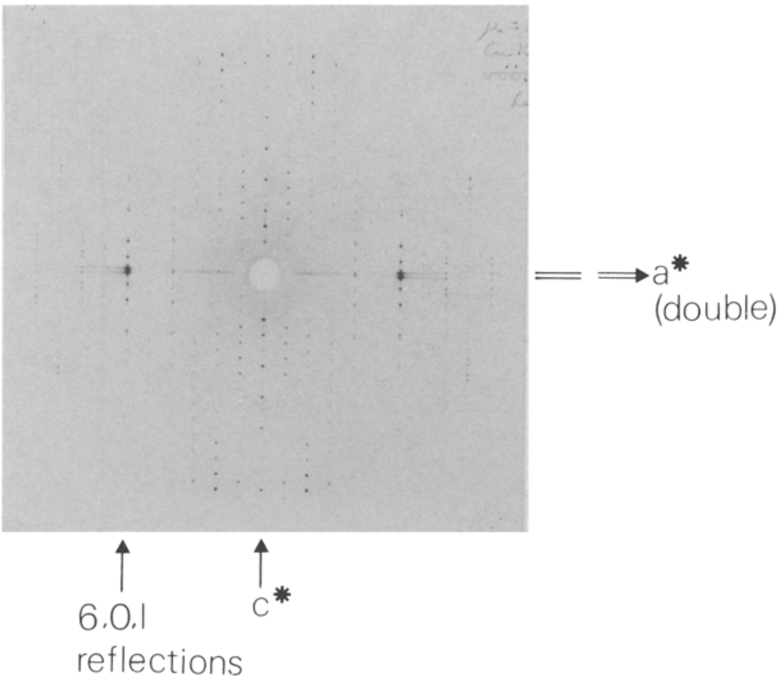

FIG. 3. Precession diffraction photograph of the *h0l* layer of β′ LML (crystal-to-film distance, 60 mm). The two *a directions are caused by twinning. Adjacent *60l* reflections have different intensities.**

size of the LML molecule requires that the long unit cell axis, c, corresponds roughly with the direction of the fatty acid chains. One would indeed expect that crystal growth would be slowest in this direction because the incorporation of molecules in the growing crystal is easier in the other two directions (the *a* and *b* directions in Fig. 4). Growth along a and b involves incorporation of new molecules alongside (and not on top of) molecules in the growing crystal lattice. On the other hand, it is surprising that the growth rates in the *a* and *b* directions still differ considerably, even though both involve lateral incorporation of molecules. One would expect long-chain molecules to form plate-like crystals [as β triacylglycerols often do (15)], instead of long thin needles.

The space group. The crystals are monoclinic (nearly orthorhombic) with an oblique angle of 91°. The preferred setting of axes is dictated by the convention that the unique monoclinic axis (5.7 Å) is called *b*, and that the *c* axis is the long axis in crystals of long-chain molecules.

The deviation from orthorhombicity is also clear from the intensity-weighted reciprocal lattice, which should have *mmm* symmetry in the orthorhombic case. The symmetry of the *h0l* pattern of each individual crystal orientation in the β′ LML twin (Figs. 2 and 3) is, in fact, only a two-fold axis rather than the *mm* symmetry expected for the orthorhombic case. The *60l* reflections (Fig. 3), especially, are split in unequal pairs. It must, however, be stressed that the symmetry of the overall structure can be very close to orthorhombic.

In the present setting (a = 22.9 Å, b = 5.7 Å and c = 66.8 Å) we observe the following systematic absences in Weissenberg and precession photographs: hkl, $h + k + l = 2n + 1$; $hk0$, $h = 2n + 1$ ($k = 2n + 1$); $0kl$, $l = 2n + 1$ ($k = 2n + 1$); $h0l$, ($h + l = 2n + 1$); $00l$, ($l = 2n + 1$); $h00$, ($h = 2n + 1$); and $0k0$, ($k = 2n + 1$). Not all of these reflections are necessarily truly absent. They may be present but unobservably weak due to the pseudoorthorhombic symmetry. The following arguments also show that some of the above conditions for absence cannot be symmetry-imposed.

The set of systematic absences is consistent with a (nonstandard) space group *Ic2a* or *Im2a*, but because the crystals are monoclinic, glide or mirror planes can only be present perpendicular to **b**. The space group then cannot be higher than *I*2 or *Im*. Symmetry operation *m* can also be ruled out, as it is impossible to locate a mirror plane perpendicular to **b** in the unit cell, which is only one molecule thick (b = 5.7 Å), unless all molecules lie in the mirror plane. This can only be so if the molecules themselves have mirror symmetry, but this is highly unlikely for triacylglycerol molecules.

The only remaining possibility then is space group *I*2, which is not a standard space group as listed in the International Tables for Crystallography (16). An appropriate transformation of unit cell axes carries body-centered *I*2 over into face-centered *C*2, listed as space group No. 5 (16):

$$\mathbf{a}(C2) = \mathbf{a}(I2) - \mathbf{c}(I2), \qquad \mathbf{b}(C2) = \mathbf{b}(I2), \qquad \mathbf{c}(C2) = \mathbf{c}(I2)$$

The *I*2 and *C*2 unit cells are shown in Figure 5.

Orientation of the alkyl chains. The long unit cell axis of 66.7 Å corresponds with (twice) the so-called long spacing (*LS*) observed in the X-ray powder diffraction pattern. Figure 6 shows the long spacings (17) and the melting points (18) of four β′ triacylglycerols of the $C_nC_{n+2}C_n$

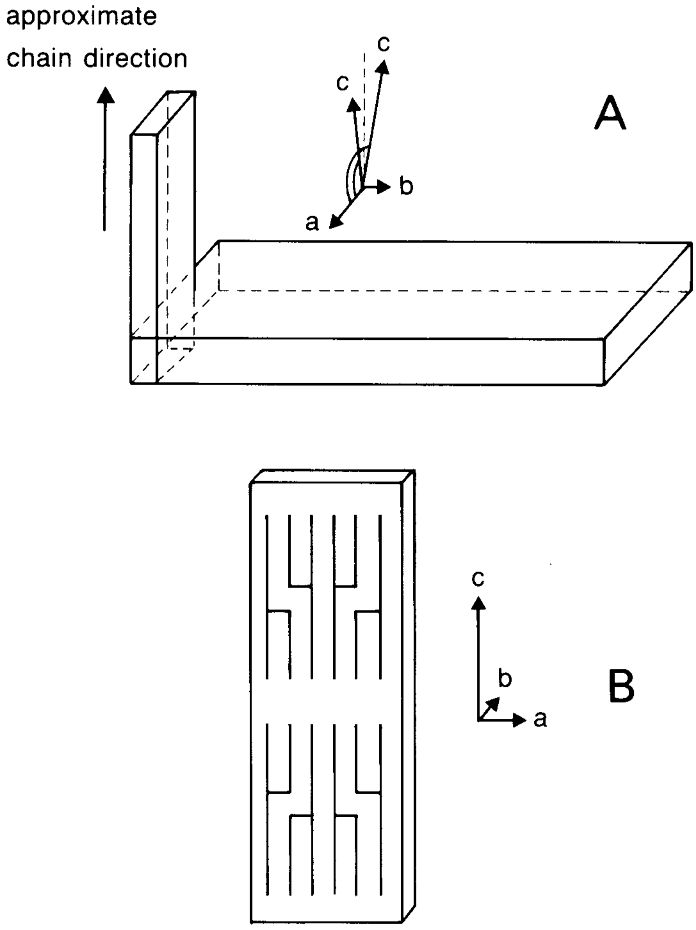

FIG. 4. (A) Crystal morphology and unit cell of β' LML in the same orientation (not on the same scale). The orientation of the two c-axes for the twins is indicated. (B) Overall impression of an arrangement of eight LML molecules in the unit cell.

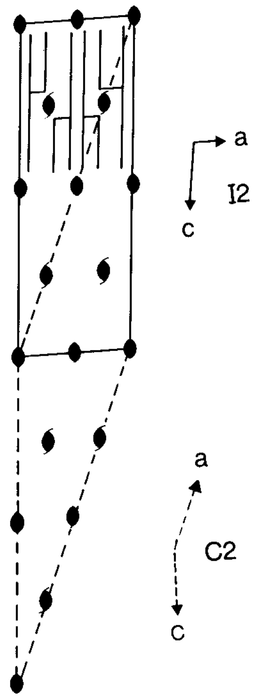

FIG. 5. The relation between the *I*2 unit cell in β' LML as indexed from the diffraction photograph and the standard setting *C*2.

series. The long spacings lie on a straight line and the melting points increase steadily with increasing chain length. These facts strongly indicate that all β' $C_nC_{n+2}C_n$ triacylglycerols have analogous structures and form a homologous series similar to those described for the β modification (7,8).

The angle between fatty acid chains and the plane through the terminal methyl groups is known as the angle of tilt, τ (1). This angle can be calculated from the increments in the long spacing as one goes from shorter to longer triacylglycerols. Each $-CH_2-CH_2-$ unit contributes 2.54 Å to the length of an alkyl chain. Going from CLC ($C_{10}C_{12}C_{10}$) to PSP ($C_{16}C_{18}C_{16}$), each fatty acid chain is lengthened by three such $-CH_2-CH_2-$ units. If the angle of tilt would be 90°, one would expect the long spacing to increase by $4 \times 3 = 12$ $-CH_2-CH_2-$ units, or 30.5 Å. The increase is, in fact, only $85.5-57.8 = 27.7$ Å. The angle of tilt calculated from this increase is $\tau = \sin^{-1}(27.7/30.5) \approx 65°$.

The melting points for a homologous series of long-chain molecules lie on a smooth curve, as in Figure 6, only if their structures consist of layers of parallel-packed alkyl chains. Only then can the methyl end planes (the "methyl terraces") of all members of the series be structurally

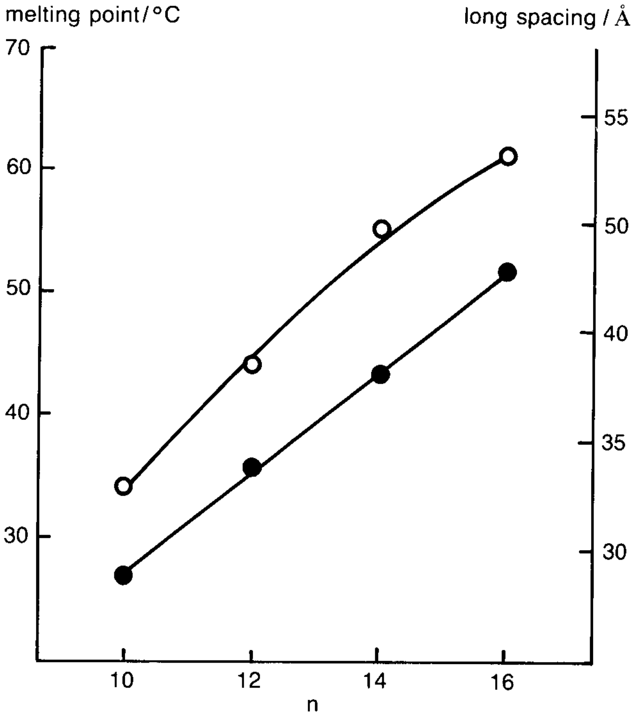

FIG. 6. Long spacings (●) and melting points (O) for four $C_nC_{n+2}C_n$-type triacylglycerols as a function of chainlength.

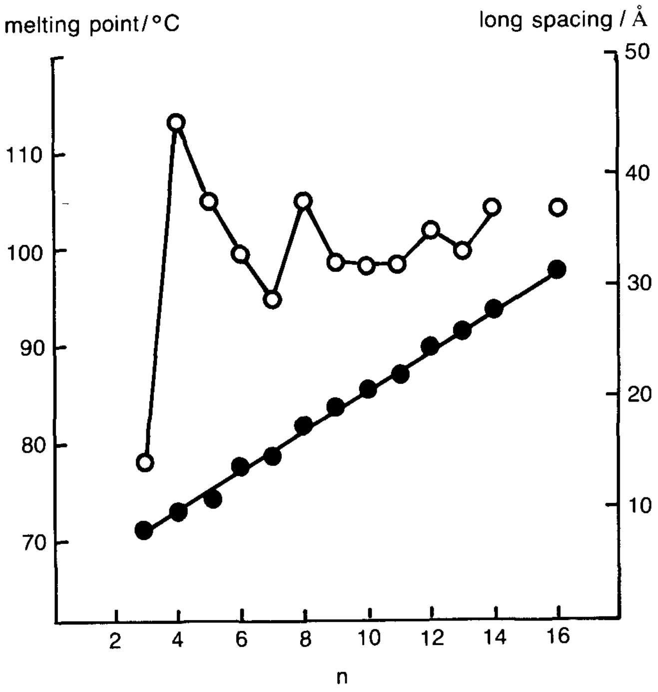

FIG. 7. Long spacings (●) and melting points (○) of aliphatic amides, $CH_3(CH_2)_{n-2}CONH_2$ (16), as a function of chainlength.

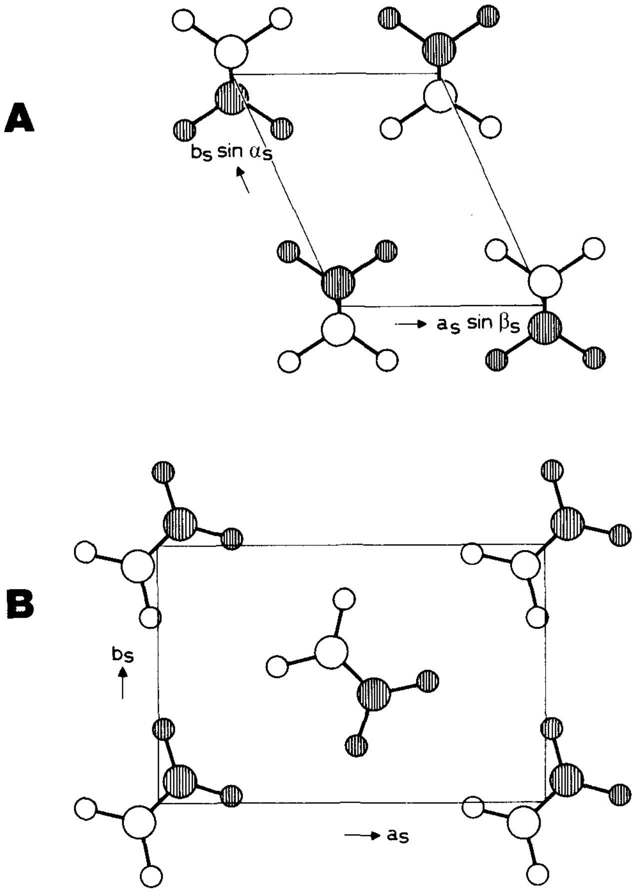

FIG. 8. The triclinic subcell packing $T_{\parallel}$ (A), and the orthorhombic subcell packing $O_\perp$ (B), projected on a plane normal to the chain axes.

identical. This is illustrated by the melting points (19) of a series of n-aliphatic amides whose alkyl chains are not all parallel within a layer (20). Their melting points are obviously not a smooth function of chainlength, even though their long spacings are a linear function of the lengths of the molecules (19; see Fig. 7). The methyl terraces in these amide structures are shaped differently for different members of the series. Consequently, their melting points, which are a function of chainlength and interactions at the methyl terrace, are not a smooth function of chainlength only.

The internal symmetry of a layer of alkyl chains that are parallel and contain repeating -CH_2-CH_2- structure elements can be described in terms of so-called subcells (21). The subcell of the β modification, for instance, is triclinic ($T_{\parallel}$) containing one -CH_2-CH_2 unit. Consequently, all zigzag planes are parallel (Fig. 8A).

Another subcell often encountered in long-chain structures is the $O_\perp$ subcell (Fig. 8B), containing two -CH_2-CH_2- units with perpendicular zigzag planes. The $O_\perp$ subcell dimensions are: a_s = 7.40 Å, b_s = 4.95 Å, c_s = 2.55 Å, and $\alpha_s = \beta_s = \gamma_s = 90°$. This $O_\perp$ subcell has similar short spacings (d_{200} = 3.7 Å, d_{110} = 4.1 Å) as the ones observed in β' triacylglycerols. There also appears to be a geometrical relationship between the $O_\perp$ subcell axes and the true unit cell axes of β' LML (see previous section): $\mathbf{a}_{LML} = 3 \cdot \mathbf{a}_s$ and $\mathbf{b}_{LML} = \mathbf{b}_s + \mathbf{c}_s$. In the a direction, the unit cell of β' LML spans three subcells and $\mathbf{a}_s$ coincides with $\mathbf{a}_{LML}$ (see Fig. 9, a_{LML} = 22.9 Å $\approx 3a_s$ = 22.2 Å). The subcell can be oriented in such a way that the b_{LML} axis coincides in direction and in length with the b_sc_s diagonal [b_{LML} = 5.7 Å $\approx \sqrt{(b_s^2 + c_s^2)} = \sqrt{(4.95^2 + 2.55^2)}$ = 5.57 Å)]. The c_s axis then makes an angle of $\sin^{-1}$ (4.95/5.57) ≈ 63° with the $a_{LML}b_{LML}$ plane, close to the observed angle of tilt, τ = 65°, derived above. The alkyl chains are perpendicular to $\mathbf{a}_s$ and thus also perpendicular to $\mathbf{a}_{LML}$. Neglecting the fact that the unit-cell angle β is not exactly 90°, the chains are consequently parallel with the $b_{LML}c_{LML}$ plane and make an angle of 90°–65° = 25° with the c_{LML} axis (Fig. 9).

All this provides evidence that an approximately orthorhombic subcell is present in the β' LML structure with the dimensions of the conventional $O_\perp$ subcell (Fig. 9). A similar relationship between $O_\perp$ subcell and the unit cell of β' tri-undecanoin was suggested by Hernqvist and Larsson (9,10). It is not likely, however, that β' LML is structured exactly as shown in Figure 9, with true $O_\perp$ subcells. In that case, the periodicity in the a direction would, for the major part of the structure (*i.e.*, neglecting the glycerol groups), be equal to one-third of the a_{LML} axis, and all reflections with $h = 3n$ would then be very weak. The diffraction patterns (Figs. 2 and 3) show that this is not the case. Therefore, it seems that β' LML contains subcells with dimensions and overall symmetry similar to those of $O_\perp$ subcells, but differing in the details regarding chain packing, *e.g.*, in the relative

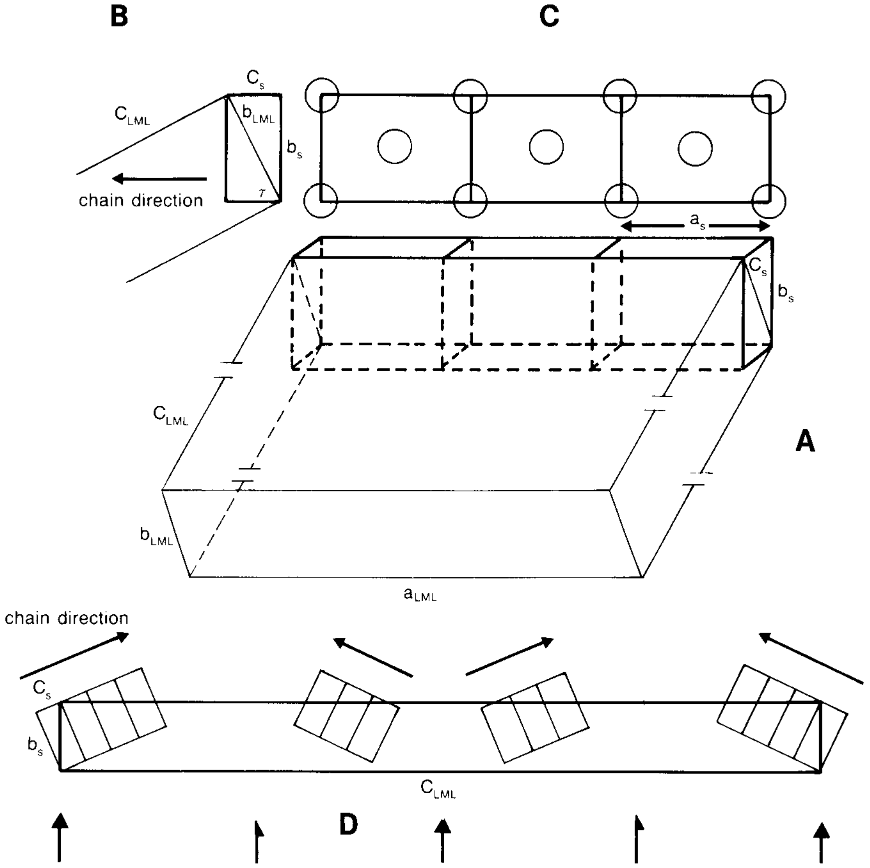

FIG. 9. Relation between the unit cell of β' LML and an $O_\perp$-like orthorhombic subcell. (A) Three orthorhombic subcells drawn in the unit cell of β' LML; the a_s and a_{LML} axes coincide, whereas the c_s and c_{LML} axes make an angle of 25° (90−τ). The b_{LML} axis coincides with the diagonal of the b_sc_s plane. (B) Projection of the *bc* plane, containing the *b* and *c* axes of both the subcell and the true LML unit cell. (C) Projection of the a_sb_s plane showing the positions of the alkyl chains, indicated by circles. (D) Projection of the $b_{LML}c_{LML}$ ($\equiv b_sc_s$) plane showing schematically the relative positions of the subcells and the directions of the alkyl chains, which are parallel to c_s.

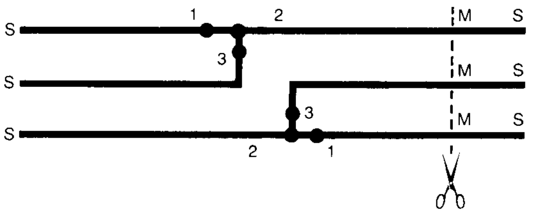

FIG. 10. Derivation of the compound SMS/MSM from β-2 SSS by one-sided shortening of the alkyl chains by four methylene groups.

orientations of the zigzag planes of the alkyl chains. Such detailed information can only be obtained from a complete crystal structure determination, which is currently under investigation.

Configuration and packing of LML molecules. Cocrystallization of binary 1:1 mixtures of triacylglycerols from a solvent can result in the formation of binary "compounds". Study of the phase behavior of such compounds may lead to conclusions about the molecular configuration in pure crystalline triacylglycerols. For example, in the β-2 crystal structure (see Fig. 1), chains 1 and 3 of each molecule are adjacent. We will refer to this as the 1,3-configuration. Figure 10 shows how a new pair of triacylglycerol molecules (SMS/MSM) is obtained when all chains at one side of a β-2 pair of SSS molecules are shortened by four -CH$_2$- groups.

The powder diffraction patterns in Figure 11 prove that a stoichiometric 1:1 mixture of SMS and MSM forms a β-2 compound, which is different from the (β-3) structures of either pure SMS or MSM, but which is practically isomorphous with the structure of β-2 PPP. Figure 12 shows that, starting from a pair of β' PSP molecules in a hypothetical 1,3-configuration, the combinations PPP/MSM, PMP/LSL and PLP/CSC can be derived by a similar chain-shortening procedure. If, on the other hand, a 1,2-configuration is assumed for PSP, one derives the combinations PSM/MPP, PSL/LMP and PSC/CLP.

1:1 Mixtures of these triacylglycerols were crystallized from solutions in chloroform, and the powder diffraction patterns were measured together with those of the individual triacylglycerols. Typical examples are shown in

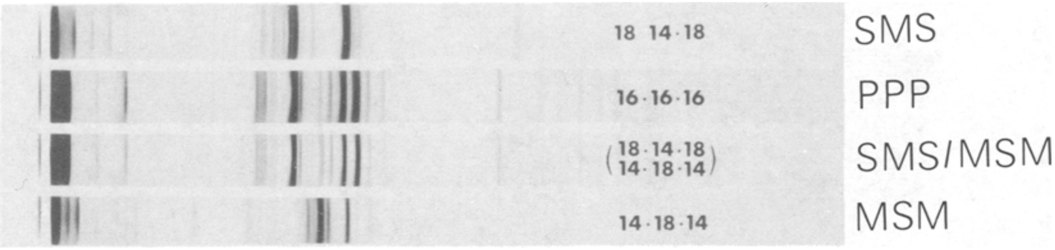

FIG. 11. Powder diffraction patterns of SMS, MSM, the SMS/MSM compound and of β′ PPP.

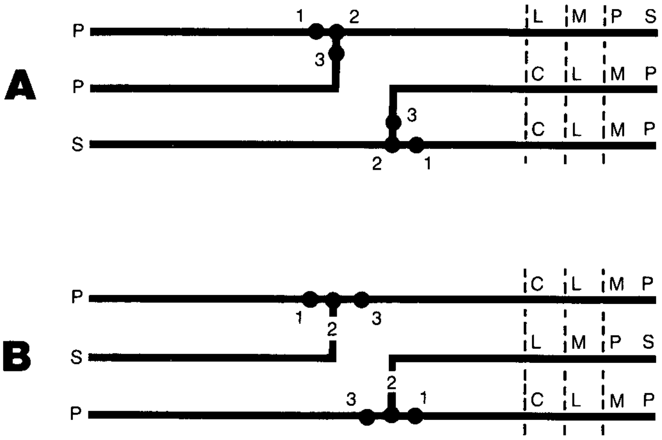

FIG. 12. Derivation of triacylglycerol combinations for potential β′ compounds, structurally related to PSP, assuming (A) initial 1,3-configuration, and (B) initial 1,2-configurations for PSP.

Figures 13 and 14. Clearly, the combinations derived from the pair of PSP molecules in the 1,3-configuration (PPP/MSM, PMP/LSL and PLP/CSC; Fig. 13) crystallize in a β structure, whereas the compounds derived from PSP in a parent 1,2-configuration (PSM/MPP, PSL/LMP and PSC/CLP; Fig. 14) crystallize in a β′ structure, which shows a large resemblance with β′ PSP itself. This provides firm evidence that in crystalline PSP (and therefore, in other members of the $C_nC_{n+2}C_n$ series, such as LML) the molecules adopt a 1,2-configuration.

It was also shown earlier that the alkyl chains make an angle of about 25° with the *ac* plane. Figure 9D shows how the two-fold axes and the two-fold screw axes of the *I*2 space group lead to alternating chain directions. A comparison of Figure 9D with Figure 5 will help visualize the positions of axes and screw axes with respect to those of the alkyl chains. The c_{LML} axis in Figure 9D corresponds with the lengths of two molecules and comprises four

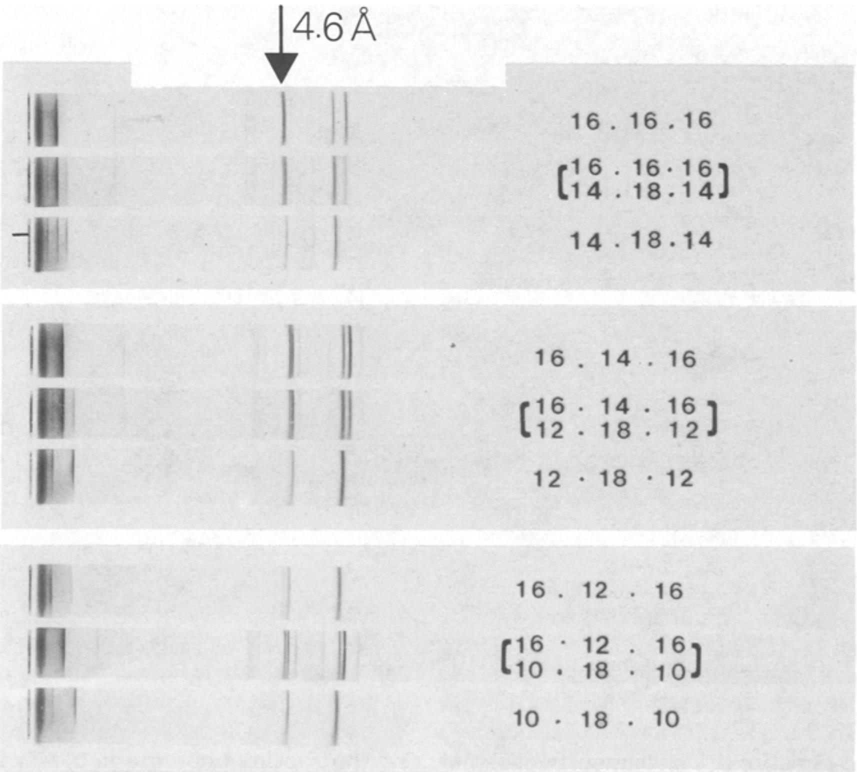

FIG. 13. X-ray powder diffraction patterns of the binary triacylglycerol mixture shown in Figure 12A, together with their pure parent components. The position of the 4.6 Å reflection typical for the β modification is indicated.

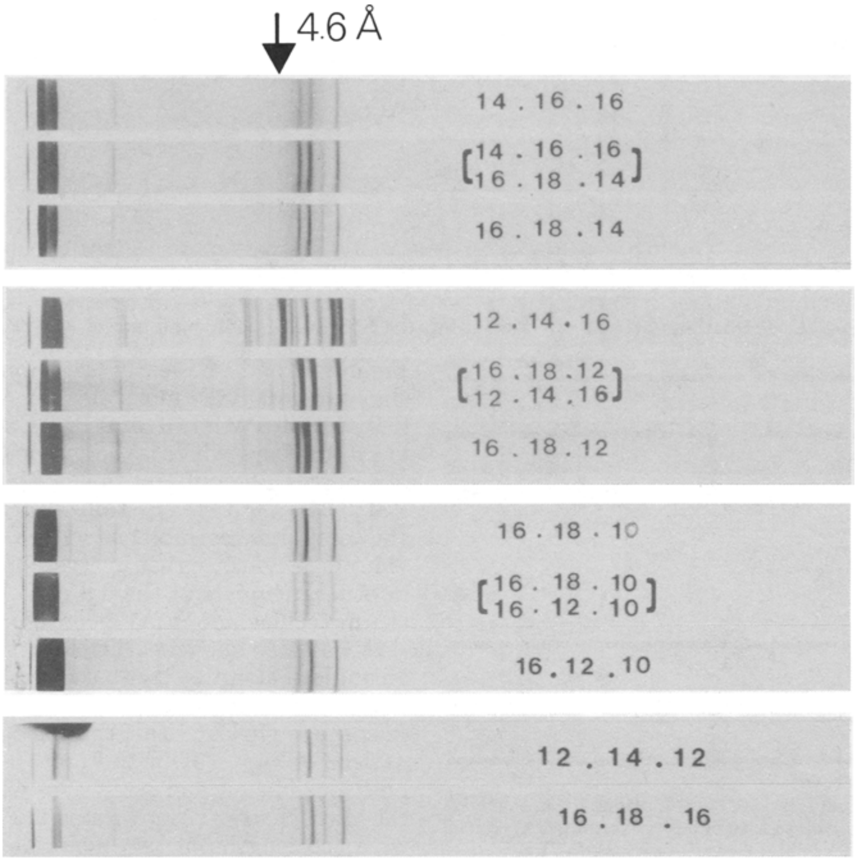

FIG. 14. X-ray powder diffraction patterns of the binary triacylglycerol mixture shown in Figure 12B, together with their pure parent components. The β-type 4.6 Å reflection is absent in the patterns of the compounds.

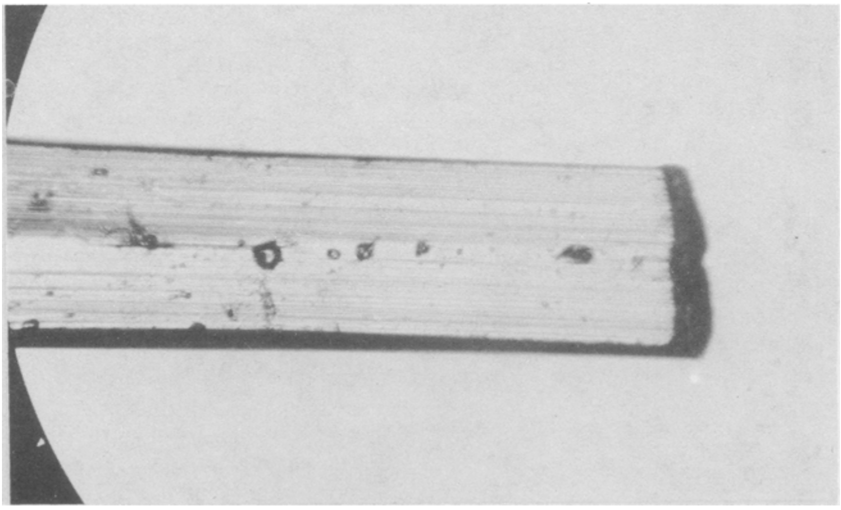

FIG. 15. Light micrograph of a β′ LML crystal.

chains in alternating directions. Consequently, it is not possible that the LML molecules in the β′ LML are straight.

Twinning. Figure 2 is a zero-level (*h0l*) Weissenberg X-ray diffraction photograph of a twinned β′ LML crystal, rotating about the *b* axis. The twinning is obvious from the double *a** axes, 2° apart and thus 89° and 91° away from the *c** axis. The same twinning is the cause of the

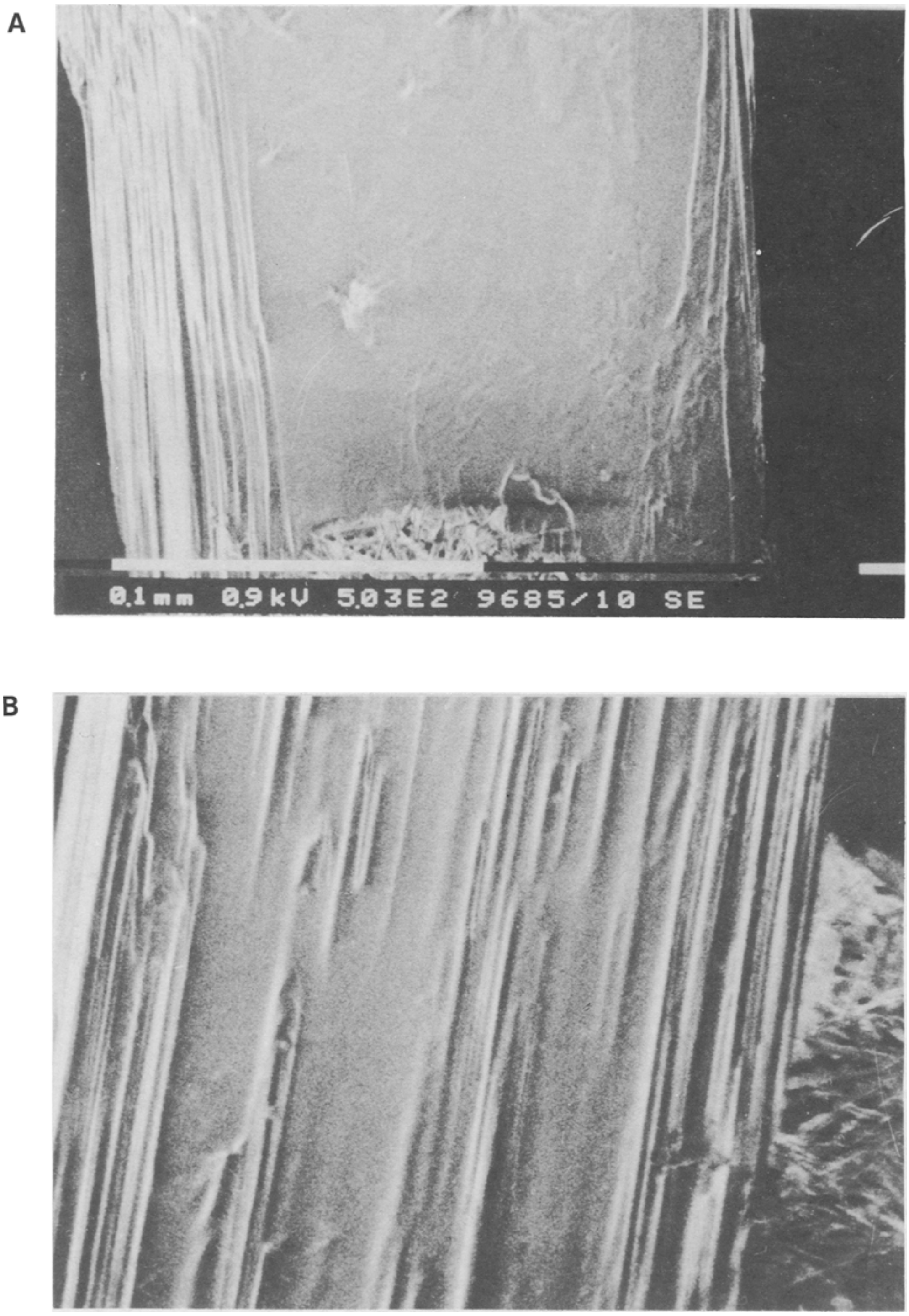

FIG. 16. Electron micrographs of a native, uncoated twinned β′ LML crystal showing its layered structure. (A) The smooth (001) face with some growth steps at the edges, and on the left-hand side, a foreshortened view of the (100) face giving a good impression of the flaky habit of the crystals. (B) Enlarged view (1050 times) of the same (100) face.

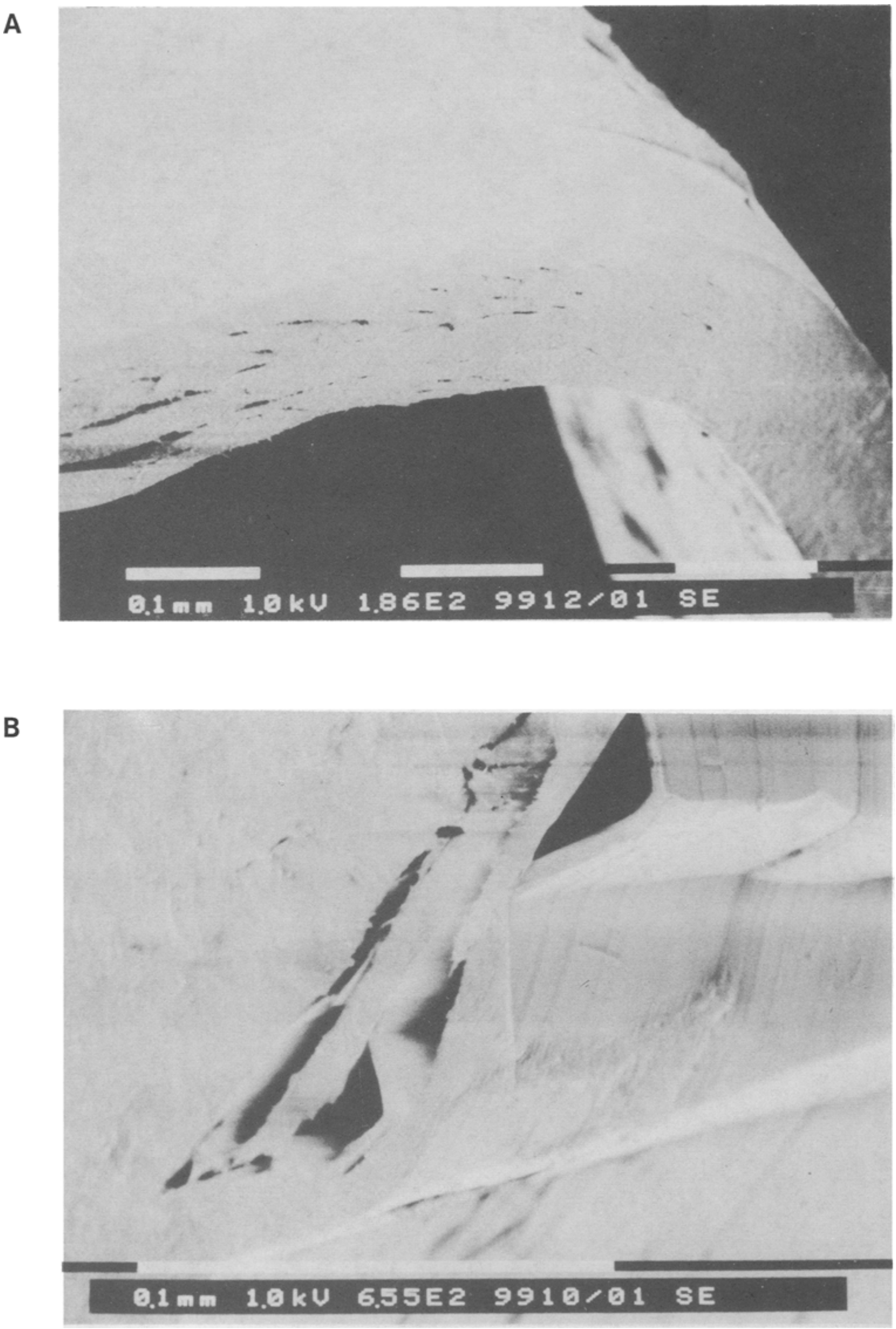

FIG. 17. Mechanical deformation of β' LML crystals. (A) Detail of rupture between layers in an irreversibly bent β' crystal. (B) Buckling of crystal layers on the inside of a bent crystal.

Inspection of the mechanical properties of a β' LML crystal showed that it can be split easily along the *ab* plane. This suggests a layered structure in the crystal. Besides, the (100) face of the crystal is not well-developed (not smooth), but it is rough, showing a distinct line pattern in the [010] direction. This line pattern is clearly visible in the electron micrograph in Figure 16A where the grooved (100) face and the much smoother (001) face are both visible. The growth steps on the (001) face prove that the crystal grows in layers, obviously because growth in the [100] and [010] directions is much faster than the surface nucleation, which initiates the deposition of a new layer of molecules. The micrographs (Fig. 16B) suggest that the crystals of β' LML consist of stacks of individual,

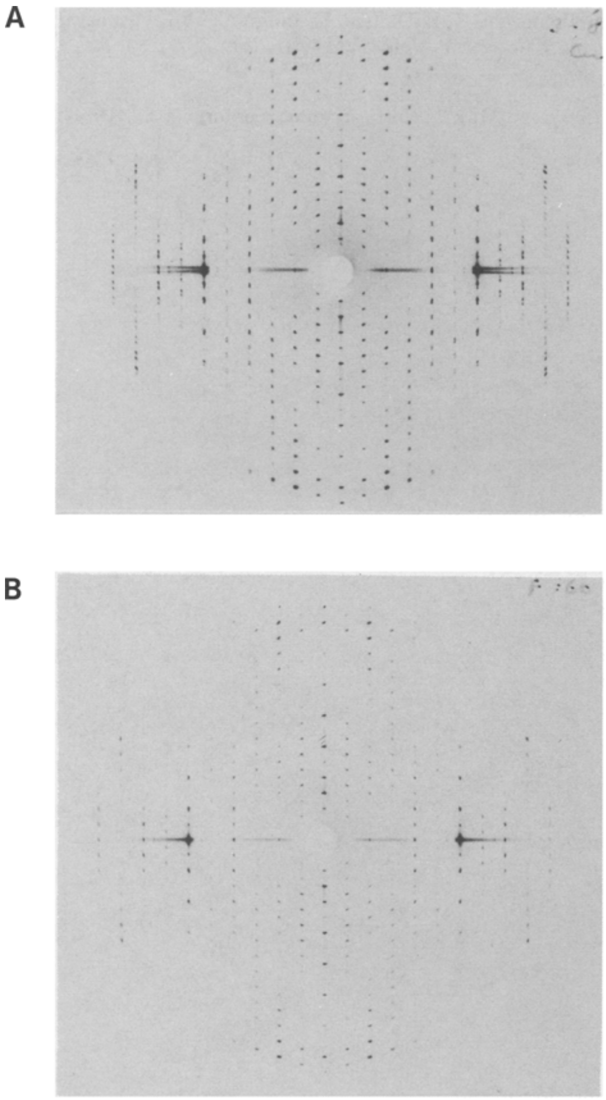

FIG. 18. (*h0l*) Precession photographs of β′ LML, illustrating the phase transition from a monoclinic twinned to a pseudo-orthorhombic single diffraction pattern effectuated by exposure to X-rays (1 kW Cu *Kα*, Ni-filtered). (A) Diffraction pattern taken some weeks after preparation of the crystal. (B) Same after 14 days exposure to *Kα* radiation.

thin mono-crystalline platelets about 1 μm thick (≈ 200 molecules).

The twinning, then, is probably the result of two different orientations of the crystalline platelets. The crystals can be described as multiple twins consisting of platelets with parallel *a* and *b* axes. Their *c* axes cannot be parallel, because β ≠ 90°. This is indicated in Figure 4 by the two *c* directions. The symmetry operation relating the two orientations of the platelets can be a two-fold twin axis parallel with **a** (*i.e.*, with the bisector of the two *a** axes of the twins) or a mirror twin plane parallel with the *ab* plane (*i.e.*, perpendicular to **c***). The remaining possibility of a two-fold twin axis parallel with **b** can be ruled out, as this does not affect the direction of the unit cell axes.

Crystal deformation. The layered texture of the β′ crystals resembles a stack of pages in a book. Bending such a stack is easy in one direction only. It appears to be possible to bend a β′ LML crystal in an analogous way. At relatively small deformations the crystal remains elastic and regains its original shape when the deformation force is relaxed. Large deformations lead to irreversible situations, leaving the crystal in a bent, ribbon-like shape (Figs. 17, A and B). The Figures show bent sections of a β′ LML crystal in detail. The crystal splits in several layers along the weakest interactions (between crystalline plates). Layered crystal sections can buckle and break away from the concave inner surface of a bent crystal. Although the overall texture of the bent crystal seems to follow its curvature, the folding and cracking of layers is quite severe on a smaller scale. This explains why the X-ray diffraction pattern deteriorates tremendously when crystals are mechanically damaged.

Effect of prolonged X-ray exposure. The monoclinic angle (β = 91°) of the individual orientations in the twinned crystals changes from 91° to 90° during prolonged X-ray exposure (Fig. 18). This subtle phase transition is completed in the course of about a ten-day exposure on a standard 1 kW Cu *Kα* X-ray generator. The resulting diffraction pattern has orthorhombic *mm* symmetry, but this is only the deceptive result of overlapping nonequivalent reflections of two monoclinic patterns. Such a phase transition under the influence of X-rays has, to the best of our knowledge, never been described in the literature.

At low temperature, the size of the monoclinic angle β changes reversibly to 93° at −140°C and is not affected by prolonged X-ray exposure. This offers better opportunities to collect a complete set of X-ray reflection data, which will be used to solve a complete three-dimensional structure. Work along these lines is in progress in cooperation with the State University at Leiden, The Netherlands.

ACKNOWLEDGMENT

We thank A.P.J. Mank for synthesizing the triacylglycerols and W.J.M. van Zeijl for making the electron micrographs.

REFERENCES

1. Chapman, D., *Chem. Rev. 62*:433 (1962).
2. Hagemann, J.W., in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker, New York, NY, 1988, pp. 9–95.
3. Wille, R.L., and E.S. Lutton, *J. Am. Oil Chem. Soc. 43*:942 (1966).
4. Larsson, K., *Arkiv Kemi 23*:1 (1964).
5. Jensen, L.H., and A.J. Mabis, *Acta Crystallogr. 21*:770 (1966).
6. Doyne, T.H., and J.T. Gordon, *J. Am. Oil Chem. Soc. 45*:333 (1968).
7. de Jong, S., and T.C. van Soest, *Acta Crystallogr. B34*:1570 (1978).
8. van Soest, T.C., S. de Jong and E.C. Roijers, *J. Am. Oil Chem. Soc. 67*:415 (1990).
9. Hernqvist, L., and K. Larsson, *Fette Seife Anstrichm. 84*:349 (1982).
10. Hernqvist, L., *Fat Sci. Technol. 90*:451 (1988).
11. Simpson, T.D., and J.W. Hagemann, *J. Am. Oil Chem. Soc. 59*:169 (1982).
12. Kellens, M., W. Meeussen, C. Riekel and H. Reynaers, *Chem. Phys. Lipids 52*:79 (1990).
13. Skoda, W., L.L. Hoekstra, T.C. van Soest, P. Bennema and M. van den Tempel, *Koll. Zeitschr. Zeitschr. Polym. 219*:149 (1967).
14. Small, D.M., *The Physical Chemistry of Lipids (Handbook of Lipid Research, Vol. 4)*, Plenum Press, New York, NY, 1986, pp. 345–394.
15. Albon, N., and A. Packer, *Nature 207*:1088 (1965).

16. *International Tables for Crystallography, Vol. A*, D. Reidel Publishing Company, Dordrecht, The Netherlands, 1983.
17. Lutton, E.S., C.B. Stewart and A.J. Fehl, *J. Am. Oil Chem. Soc. 49*:333 (1972).
18. Malkin, T., *Progr. Chem. Fats & Other Lipids 2*:1 (1954).
19. Turner, J.D., and E.C. Lingafelter, *Acta Crystallogr. 8*:549 (1955).
20. Turner, J.D., and E.C. Lingafelter, *Ibid. 8*:551 (1955).
21. Abrahamsson, S., B. Dahlén, H. Löfgren and I. Pascher, *Progr. Chem. Fats Other Lipids 16*:125 (1978).

[Received May 7, 1991; accepted September 20, 1991]