Conformation of the oleate chains in crystals of cholesteryl oleate at 123 K[1]

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Abstract At 123 K, crystals of cholesteryl *cis*-9-octadecenoate (cholesteryl oleate, $C_{45}H_{78}O_2$) are monoclinic, space group $P2_1$ with unit cell dimensions a = 12.356(2), b = 8.980(3), c = 18.382(2) Å, β = 85.49(2)°, and have two molecules in the unit cell. The crystal structure including all H atoms has been determined from 3812 independent X-ray reflections with sin $\theta/\lambda < 0.61$ Å^{-1} and refined to give R_w = 0.08. At 123 K, the crystal structure consists of an antiparallel efficient packing of cholesteryl ring systems to form layers that are very similar to those observed in the room temperature structure. The oleate chains that protrude from these layers have a somewhat different packing arrangement from the room temperature structure because they have undergone a conformational change. At 123 K, the oleate chains are well ordered and are almost fully extended except for a kink at the *cis* double bond. The oleate chains at 123 K are 1.7 Å longer than at 295 K due in part to an uncoiling whereby their helical character is lost. On cooling, there is a substantial change in the unit cell β-angle from obtuse (93.3°) to acute (85.5°) which involves a shearing motion of 2.5 Å between adjacent molecular layers. Cell dimension measurements at 10 temperatures in the range 295 K to 123 K show that much of the change occurs in two narrow ranges centered at 262 K and 215 K.—**Gao, Q., and B. M. Craven.** Conformation of the oleate chains in crystals of cholesteryl oleate at 123 K. *J. Lipid Res.* 1986. **27:** 1214–1221.

Supplementary key words chain conformation • unsaturated fatty acids • cholesteryl ester

The crystal structures of long chain fatty acid esters of cholesterol such as cholesteryl oleate (**Fig. 1**) are of interest because the long chains usually have irregular conformations and packing arrangements that might be indicative of their behavior in noncrystalline lipid assemblies. In the crystal structure of cholesteryl oleate at 295 K (1), the cholesteryl ring systems pack together in an efficient interlocking manner to form layers (**Fig. 2, Fig. 3**). Very similar layers are found in a family of crystal structures which includes cholesteryl iodide (2), hexanoate (3), octanoate (4), and linolelaidate (5). At higher temperatures, the cholesteryl layer packing seems to be important for preserving the integrity of these crystal structures. Thus, in cholesteryl oleate at 295 K, the observed atomic thermal parameters indicate that the cholesteryl carbon atoms have considerably smaller mean square (m.s.) amplitudes of vibration (~0.2 Å^2) than the oleate carbon atoms (~0.4 Å^2). In cholesteryl oleate at 295 K, the observed electron density along the oleate chain is diffuse, so that while the chain could be traced without invoking disorder, it is possible that conformational disordering is present. The oleate chain at 295 K was found to have an extended conformation, except for a kink region of six atoms around the *cis* double bond. The chains pack with each other side by side (Fig. 2), but because of their irregular shape, there is no regular subcell structure such as occurs in the crystal structure of oleic acid (6).

The aims in determining the crystal structure of cholesteryl oleate at reduced temperature were, first, to obtain more detailed results unaffected by uncertainties due to atomic thermal vibration and disorder, and second, to study the effect of cooling on the conformation and packing of the oleate chains. Our efforts were prompted by previous work on the crystal structure of cholesteryl palmitoleate at room temperature (7) and reduced temperature (8), which showed that cooling produces significant changes affecting both the shape and size of the volume available for the palmitoleate chains. Consequently, chains that are disordered at room temperature become ordered on cooling and adopt a different conformation.

In our studies, we were alerted to electron diffraction data for cholesteryl oleate (D. L. Dorset, private communication) indicating that microcrystals have a structure similar to that reported here except for a doubling of the c-axis repeat. Our much larger crystals did not exhibit this structure by X-ray diffraction either at 295 K or 123 K.

EXPERIMENTAL

Cholesteryl oleate supplied by P-L Biochemicals, Inc., Milwaukee, WI, was recrystallized from acetone at 272

Abbreviations: m.s., mean square; e.s.d., estimated standard deviation.

[1] See NAPS document no. 04430 for 37 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only $12.85 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each of 10 pages of material thereafter, $1.50 for microfiche postage.

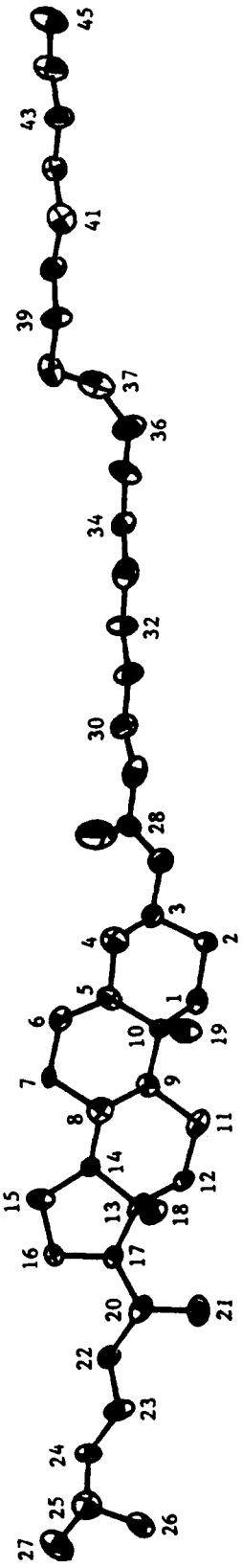


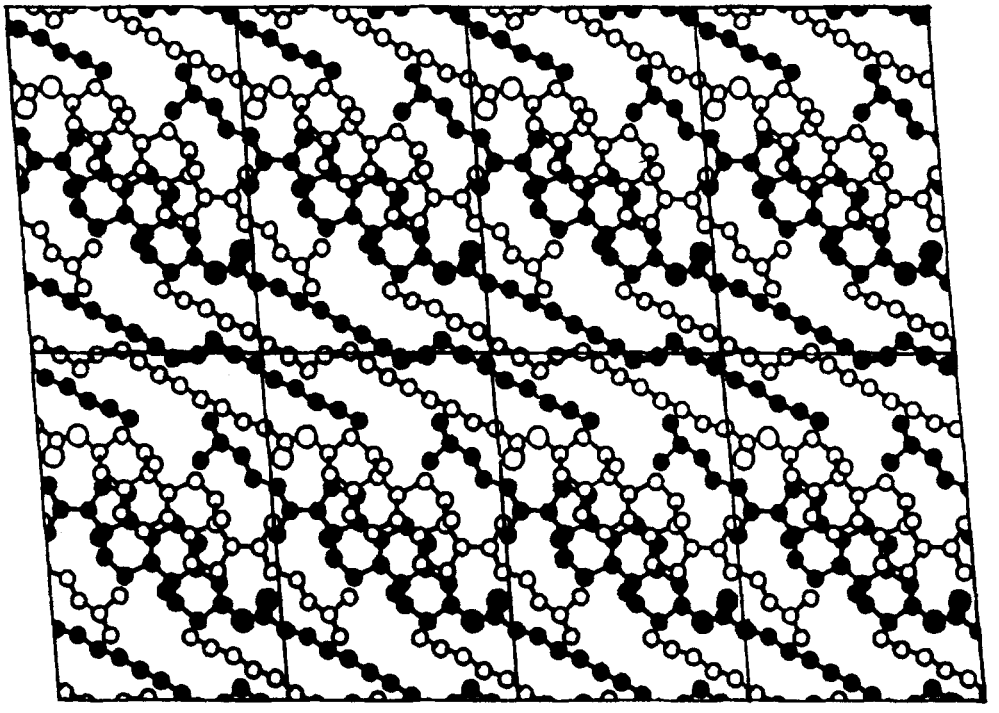
Fig. 1. Cholesteryl oleate molecule at 123 K. Thermal motion is represented as the ellipsoidal envelope with 50% probability of enclosing each atom center (19).

K in an atmosphere of nitrogen. The crystal used for preliminary X-ray photographs and subsequent data collection was a thin plate $0.24 \times 1.10 \times 0.08$ mm^3 exhibiting {001} and elongated on b. Data were collected using an Enraf-Nonius CAD-4 diffractometer with Nb-filtered MoKα radiation ($\lambda = 0.7107$ Å). The crystal was mounted with b close to the diffractometer ϕ-axis. During slow cooling (27 hr) in a stream of dry nitrogen gas, unit cell parameters were derived at ten temperatures (295 K to 123 K), by least squares fitting of $\sin^2\theta$ for reflections measured at $\pm\theta$. At intermediate temperatures, measurements were for 25 reflections ($8° < \theta < 11°$) while at 123 K, they were for 56 reflections ($15° < \theta < 20°$). Integrated intensities were measured by $\theta/2\theta$ scans for reflections $\sin\theta/\lambda < 0.61$ ÅA^{-1} ($d_{min} = 0.82$ Å). Intensity profiles for 4430 reflections were collected. After data reduction, 3812 independent reflections survived, of which there were 1723 reflections with $I > 3\ \sigma(I)$ where $\sigma^2(I) = \sigma^2 + (0.02I)^2$ and σ^2 is the variance due to counting statistics. Reflections significantly above background were estimated by the Lehmann-Larsen method (9), except in the low angle region ($\theta < 7°$) where the method of Nelmes (10) was applied to individual reflections. No corrections for X-ray absorption were applied.

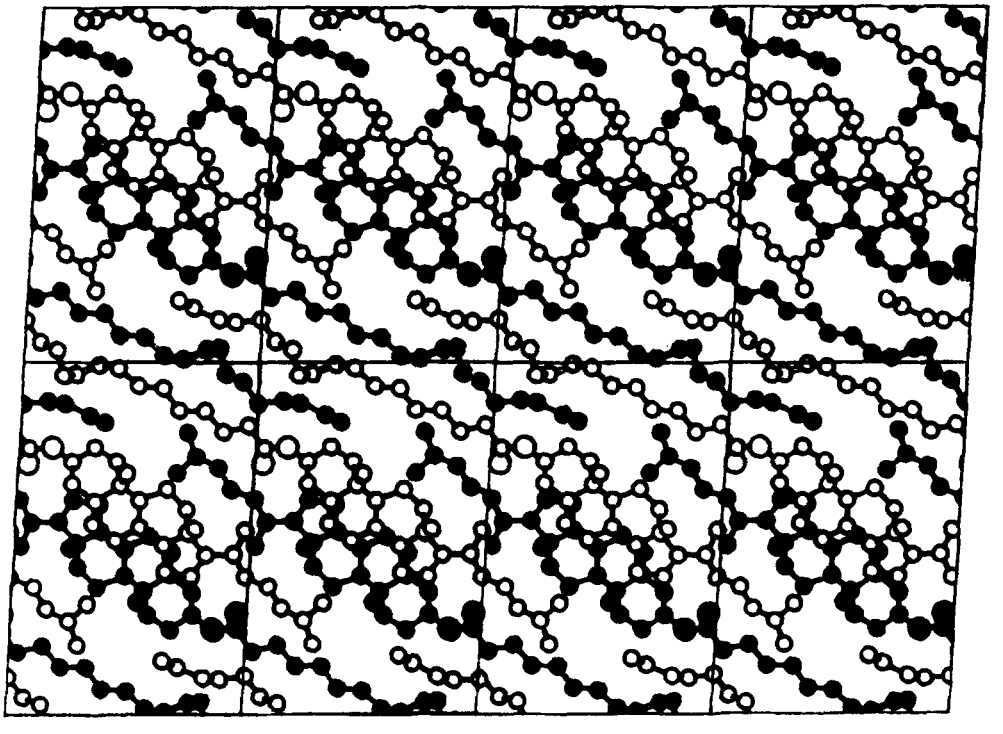
The structure determination was carried out with alternating cycles of Fourier and block-diagonal least squares refinement, beginning with room temperature positional parameters for 27 atoms C(1) through C(23), C(28), C(29), O and O(3) and assuming all thermal parameters to be B = 3.0 Å^2. The initial structure factor calculation gave R = 0.57.[2] At R = 0.16, all H atoms were located in two cycles of difference Fourier syntheses. They were subsequently included in the refinement with fixed positional parameters and assumed isotropic thermal parameters B = 6.0 Å^2. Final least squares refinement was carried out with all 3812 reflections in order to minimize the residual $\Sigma w\Delta^2$ with $w = \sigma^{-2}(F_o)$, $\Delta = |F_{obs}| - |F_{calc}|$ and $\sigma^2(F_o) = \sigma^2(F_o^2)/4F_o^2$ except for reflections with $F_o^2 < \sigma^2(F_o^2)$ where $\sigma^2(F_o) = \sigma(F_o^2)/4$ (11). Atomic scattering factors were those of Cromer and Waber (12) for C and O, and Stewart, Davidson and Simpson (13) for H. Damping factors 0.5 were applied to all parameter shifts. The largest parameter shifts in the final cycle were less than 0.25 σ. The refinement gave convergence with R = 0.20 and $R_w = 0.08$ for all reflections and $R = R_w = 0.07$ for 1723 reflections with $I > 3\ \sigma(I)$. Final atom parameters for C and O atoms are in **Table 1.**[3]

[2] $R = \Sigma|\Delta|/\Sigma|F|$, $R_w = \{\Sigma w\Delta^2/\Sigma wF_o^2\}^{1/2}$, where $w = 1/\sigma(F_o)^2$ and $\Delta = |F_o| - |F_c|$.

[3] Tables of structure factors $|F_o|$, $|F_c|$, $\sigma(F)$, the H atom positional parameters, bond lengths and angles for the molecular framework can be obtained as described in footnote 1.



at 123 K



at 295 K

Fig. 2. The crystal structure of cholesteryl oleate. Crystal axes are directed with *a* from the left to the right, *c* from the top to the bottom, and *b* out of the page.; above, at 123 K; below, at 295 K.

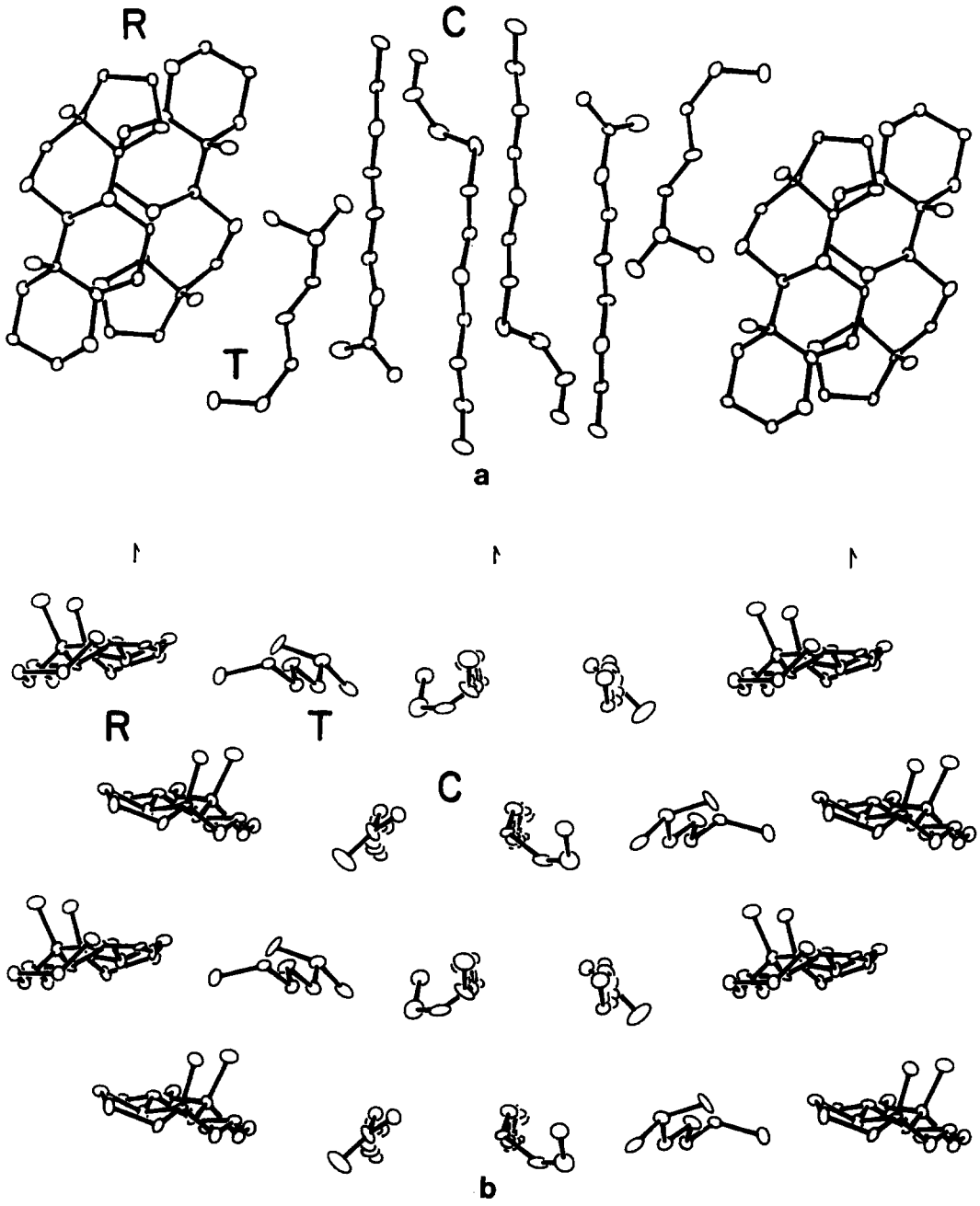


Fig. 3. Projections of a selected region of the crystal structure at 123K near the center of Fig. 2. Atoms are shown as 50% probability thermal ellipsoids (19). Molecular fragments are labelled R: tetracyclic ring system; T: tail, C(20)–C(27); C: oleate chain. (a) Projection down *b*, the same view as in Fig. 2. (b) Projection down [301], the molecular long axes.

RESULTS AND DISCUSSION

The molecular structure

At 123 K, there is no indication of disorder in the crystal structure. All atoms are clearly resolved in the electron density distribution. As can be seen in Fig. 1, the C atoms of the oleate chain have mean square (m.s.) amplitudes of thermal vibration which are only slightly greater in magnitude than for the other atoms. Compared with values at 295 K, m.s. amplitudes are generally reduced by at least one-fifth.

The C–C and C–O bond lengths and angles have been determined with estimated standard deviations (e.s.d.) ranging from 0.012 to 0.014 Å and from 0.4 to 1.1°. Bond lengths and angles agree[4] with the more accurate

[4] An exception is the C(14)–C(15) bond length, which is 1.595(13) Å in the oleate structure and 1.521(4) Å in the acetate structure.

TABLE 1. Atomic positional and thermal parameters for non-hydrogen atoms[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	5417(7)	1511(12)	7158(5)	34(6)	27(8)	31(6)	0(6)	4(5)	4(6)
C(2)	6349(7)	1807(13)	7660(5)	26(6)	38(8)	27(6)	7(6)	−6(5)	5(6)
C(3)	7402(7)	1833(13)	7189(5)	26(6)	36(8)	30(6)	−2(6)	1(5)	−2(6)
C(4)	7394(8)	2982(13)	6575(5)	45(7)	30(8)	41(7)	−7(7)	−7(5)	4(6)
C(5)	6434(7)	2779(12)	6132(5)	40(6)	14(7)	26(6)	14(6)	−8(5)	−6(5)
C(6)	6611(7)	2753(12)	5417(5)	30(6)	11(6)	34(6)	3(6)	4(5)	−8(5)
C(7)	5729(6)	2584(13)	4890(4)	18(5)	44(8)	14(5)	1(6)	5(4)	−1(6)
C(8)	4599(7)	2856(12)	5282(5)	36(6)	14(6)	41(7)	7(6)	−1(5)	1(6)
C(9)	4508(7)	2038(11)	6012(5)	32(6)	11(6)	27(5)	0(5)	−3(4)	13(5)
C(10)	5357(6)	2641(13)	6535(5)	18(5)	33(8)	24(6)	4(6)	−3(4)	−3(6)
C(11)	3297(7)	2062(12)	6371(5)	28(6)	17(7)	44(7)	−1(6)	8(5)	−2(6)
C(12)	2747(7)	1555(13)	5830(5)	17(5)	43(8)	31(6)	−12(6)	1(4)	0(6)
C(13)	2563(6)	2464(11)	5124(5)	12(5)	9(7)	40(6)	1(5)	9(4)	3(5)
C(14)	3739(6)	2274(13)	4807(5)	17(5)	38(8)	21(6)	−3(6)	0(4)	−5(6)
C(15)	3731(7)	2972(12)	4009(5)	31(6)	22(7)	39(7)	12(6)	−13(5)	3(6)
C(16)	2626(7)	2460(13)	3798(5)	28(6)	51(9)	19(6)	0(7)	0(4)	−1(6)
C(17)	1947(7)	1854(12)	4492(5)	22(5)	35(8)	26(6)	−13(6)	4(4)	5(6)
C(18)	2257(8)	4052(13)	5271(6)	25(6)	33(8)	50(8)	5(6)	−1(5)	−6(6)
C(19)	5024(8)	4171(13)	6828(6)	42(7)	32(8)	52(8)	2(7)	−17(6)	−6(7)
C(20)	733(7)	2186(12)	4478(5)	30(6)	20(7)	45(7)	8(6)	8(5)	−1(6)
C(21)	66(8)	1761(14)	5162(5)	49(7)	52(9)	35(7)	−5(7)	10(5)	−13(7)
C(22)	255(7)	1490(13)	3780(5)	24(6)	30(7)	34(6)	2(6)	0(5)	−4(6)
C(23)	−784(7)	2167(13)	3546(5)	25(6)	31(8)	58(8)	9(6)	−12(5)	−17(7)
C(24)	−1207(7)	1457(13)	2894(5)	26(6)	30(7)	37(6)	−2(6)	−10(5)	1(6)
C(25)	−2077(8)	2306(13)	2535(6)	48(7)	30(8)	50(7)	−9(7)	−5(5)	−9(7)
C(26)	−3018(8)	2809(15)	3042(5)	53(7)	66(10)	32(7)	30(8)	−12(5)	−34(7)
C(27)	−2456(9)	1395(14)	1903(6)	74(8)	39(9)	43(7)	−13(7)	−17(6)	22(7)
C(28)	9230(7)	1646(14)	7502(5)	31(6)	54(9)	26(6)	18(7)	−8(5)	−18(7)
C(29)	10103(8)	2334(13)	7926(6)	43(7)	34(8)	49(7)	−6(7)	12(5)	−1(7)
C(30)	11009(8)	1311(13)	8095(5)	32(6)	33(8)	46(7)	3(6)	−3(5)	−12(6)
C(31)	11866(7)	2095(14)	8492(5)	26(6)	39(8)	55(7)	−12(6)	−10(5)	7(7)
C(32)	12765(8)	1093(12)	8730(5)	32(6)	24(8)	50(7)	−8(6)	−18(5)	−1(6)
C(33)	13633(8)	1889(14)	9112(6)	46(7)	39(9)	50(7)	10(7)	7(5)	3(7)
C(34)	14505(7)	909(12)	9411(5)	27(6)	27(7)	41(7)	4(6)	0(5)	−3(6)
C(35)	15376(8)	1827(14)	9772(5)	55(7)	43(9)	39(7)	9(7)	−24(5)	2(7)
C(36)	16101(8)	790(15)	10115(6)	33(7)	64(11)	71(9)	−9(7)	−12(6)	−14(8)
C(37)	17207(9)	773(13)	10006(6)	68(8)	22(8)	61(9)	13(7)	−28(7)	−4(7)
C(38)	17947(8)	1688(12)	9572(5)	65(8)	16(7)	33(6)	−20(7)	2(5)	−4(6)
C(39)	18802(7)	2460(13)	9976(5)	30(6)	30(8)	51(7)	7(7)	−14(5)	−3(6)
C(40)	19705(7)	1492(13)	10268(5)	30(6)	35(8)	43(7)	−2(6)	0(5)	−4(7)
C(41)	20483(8)	2389(13)	10696(6)	58(7)	15(7)	46(7)	0(7)	−3(5)	0(6)
C(42)	21429(8)	1419(13)	10946(5)	39(6)	32(8)	34(6)	0(7)	0(5)	0(6)
C(43)	22257(7)	2297(14)	11342(5)	34(6)	53(9)	46(7)	−8(7)	−12(5)	1(7)
C(44)	23206(8)	1394(14)	11559(6)	58(8)	42(9)	53(8)	−22(7)	−25(6)	30(7)
C(45)	24052(9)	2390(15)	11860(6)	68(8)	51(10)	57(8)	5(8)	−31(6)	10(8)
O	9438(6)	711(11)	7047(4)	63(6)	84(8)	87(7)	35(6)	−27(5)	−50(6)
O(3)	8275(5)	2233(8)	7652(3)	33(4)	41(5)	39(4)	2(4)	−2(3)	−4(4)

[a] Positional parameters are fractional coordinates ($\times 10^4$) with respect to the crystal axes. Anisotropic temperature factors ($Å^2 \times 10^3$) are defined by the expression $T = \exp(-2\pi^2 \Sigma_i \Sigma_j h_i h_j a_i^* a_j^* U_{ij})$. Estimated standard deviations given in parentheses refer to the least significant digit.

values obtained for cholesteryl acetate at 123 K (14) and for the ester chains, they agree with those obtained for cholesteryl linolelaidate at 123 K (5).

The most interesting feature of the molecular structure is the conformation of the oleate chain which is quite different at 123 K and 295 K (**Fig. 4**). At 295 K, the section between the ester group and the double bond has a slight left-handed helical twist, while the section beyond the double bond has a right-handed irregular coiling. At 123 K, both these sections are stretched into almost fully extended conformations having bond torsion angles nearly 180° (**Table 2**). This stretching leads to an increase of 1.7 Å in the chain length as measured by the distance C(28)...C(45), which is 18.9 Å at 295 K and 20.6 Å at 123 K. The chain conformation can be represented approximately by the torsion angle sequences ..tttsCggtst̄..[5] at 295 K and ...tttsCsgttt... at 123 K. Thus the kink section around the double bond extends for six bonds at 295 K, but only for four at 123 K. Although the kinking at 123 K is more localized and simpler in its nature, the effect

[5] t = *trans*; g = (+)-*gauche*; s = (+)-*skew*; s̄ = (−)-*skew*; C = *cis*-double bond. Each sequence begins at the ester end of the chain.

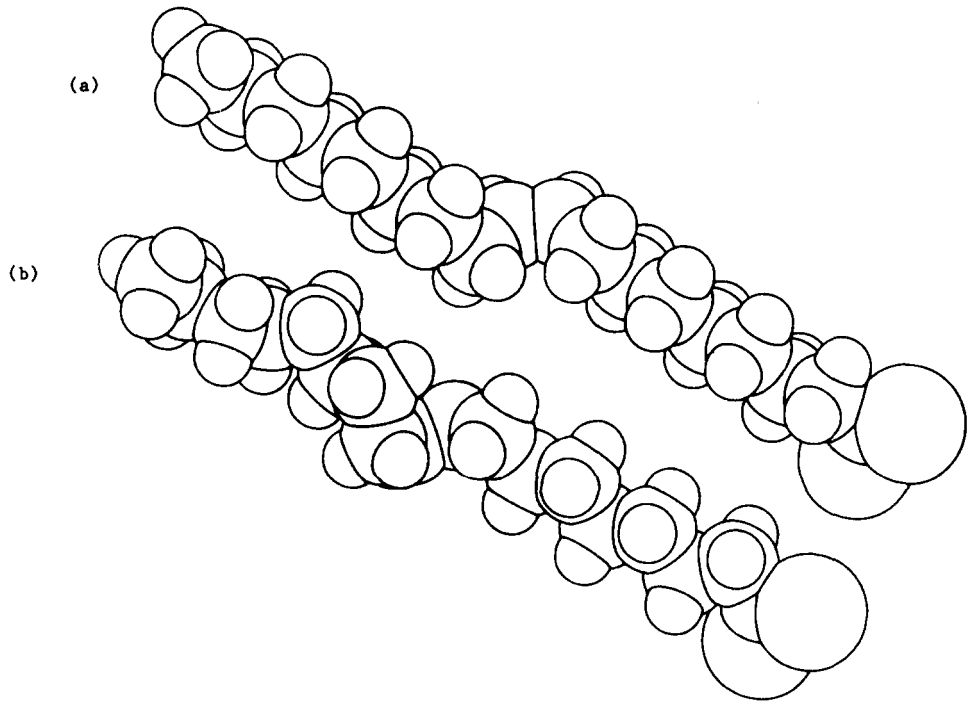


Fig. 4. The oleate chains (a) at 123 K and (b) at 295 K. Spheres of decreasing radii represent O, C, and H atoms. The chains are drawn in projection down *b*, using computer program PLUTO (20).

on the overall shape of the chain is greater than at 295 K. This can be seen primarily in the perpendicular separation between the skewed best least squares lines through the atoms of the two *trans*-sections of the chain [C(30) through C(35) and C(40) through C(44)]. This distance increases from 0.5 Å at 295 K to 1.60 Å at 123 K. The bending of the chain, as measured by the angle between the directions of these lines, is small at both 295 K (0°) and 123 K (1°). The dihedral angle between the best least squares planes[6] through the C atoms of the two chain segments is also not greatly different (24° at 295 K, 7° at 123 K).

TABLE 2. Torsion angles at 123 K and 295 K

Torsion Angle	123 K	295 K
(a) The oleate chain		
O(3)–C(28)–C(29)–C(30)	149.3(9)	−169
C(28)–C(29)–C(30)–C(31)	177.8(9)	176
C(29)–C(30)–C(31)–C(32)	175.6(9)	165
C(30)–C(31)–C(32)–C(33)	178.7(9)	179
C(31)–C(32)–C(33)–C(34)	175.6(9)	176
C(32)–C(33)–C(34)–C(35)	178.3(9)	169
C(33)–C(34)–C(35)–C(36)	173.5(9)	167
C(34)–C(35)–C(36)–C(37)	127.6(12)	113
C(35)–C(36)–C(37)–C(38)	0.9(21)	36
C(36)–C(37)–C(38)–C(39)	123.1(13)	70
C(37)–C(38)–C(39)–C(40)	70.1(12)	62
C(38)–C(39)–C(40)–C(41)	−177.2(9)	162
C(39)–C(40)–C(41)–C(42)	−176.5(8)	−139
C(40)–C(41)–C(42)–C(43)	177.0(9)	177
C(41)–C(42)–C(43)–C(44)	−177.4(9)	−173
C(42)–C(43)–C(44)–C(45)	172.7(9)	137
(b) Other torsion angles, 123 K		
C(2)–C(3)–O(3)–C(28)	146.2(8)	
C(4)–C(3)–O(3)–C(28)	−92.0(10)	
C(13)–C(17)–C(20)–C(22)	179.0(8)	
C(13)–C(17)–C(20)–C(21)	−53.7(12)	
C(17)–C(20)–C(22)–C(23)	−158.3(8)	
C(20)–C(22)–C(23)–C(24)	−179.1(8)	
C(22)–C(23)–C(24)–C(25)	−166.0(8)	
C(23)–C(24)–C(25)–C(26)	−50.9(12)	
C(23)–C(24)–C(25)–C(27)	−177.3(9)	

As can be seen from the values of the torsion angles (Table 2), the configuration at the oleate *cis*-double bond at 123 K is planar within experimental error [τ = 0.9(21)°]. For the bonds C(35)–C(36) and C(37)–C(38) adjacent to the *cis* double bond, the torsion angles are similar [128(1)° and 123(1)°]. They are consistent with crystal structural data tabulated by Matuscelli (15) and Sundaralingam (16) which indicate that the preferred conformation at C–C bonds adjacent to an unconjugated C=C bond is in the range ±(90° through 130°), that is, (±)-*skew*. In crystal structures of cholesteryl esters that contain alkenoate chains with isolated *cis*-double bonds (17), all nine of such chains are observed to have at least one of the two C–C–C=C torsion angles in the *skew* range.

[6] The root mean square displacement of atoms from the planes through atoms C(30) to C(35) and C(40) to C(44) is 0.09 Å and 0.06 Å, respectively, at 295 K, and 0.02 Å and 0.03 Å, respectively, at 123 K.

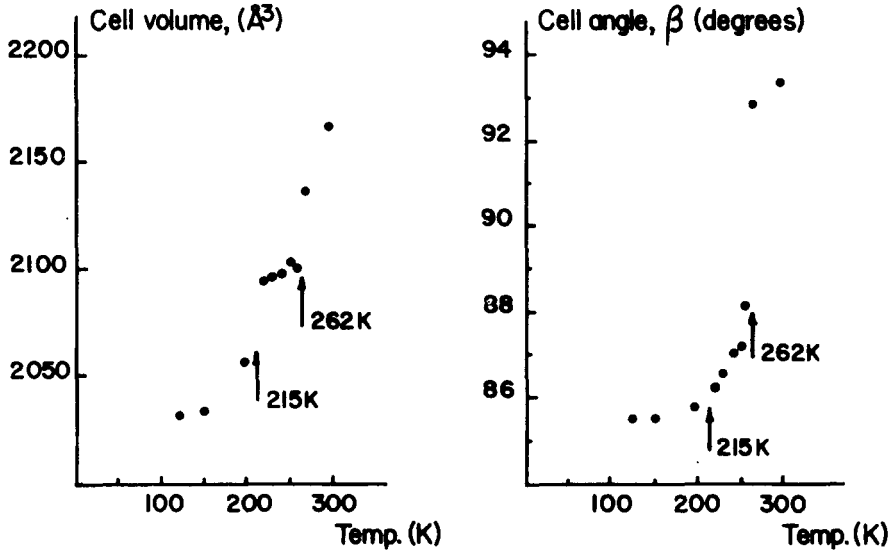


Fig. 5. Changes in the unit cell volume and β angle at ten temperatures in cholesteryl oleate.

Five of the chains, including cholesteryl oleate at 123 K, have the conformation ..sCs.. or ..$\bar{s}$C$\bar{s}$... . The conformation ...sC$\bar{s}$... has not been observed in a cholesteryl ester chain, but it does occur in the crystal structure of oleic acid (6). It should be noted that the conformations ...tttsCsttt... and ...tttsC$\bar{s}$ttt... both correspond to a bent or boomerang-shaped chain, as in the crystal structure of oleic acid. In order to have a chain which is almost straight except for a kink, as in cholesteryl oleate at 123 K, the configuration at one or more additional nearby C–C bonds must be twisted from *trans*.

The molecular packing

The crystal structure of cholesteryl oleate is similar at 123 K and 295 K (Figs. 2, 3). At both temperatures, the molecules are packed in antiparallel array to form so-called type II monolayers (18). This involves an efficient packing of the cholesteryl moieties with interlocking of the projecting methyl groups C(18), C(19) and C(21). The layers, which extend from left to right and out of the page in Fig. 2, are of thickness d_{001} = 18.76 Å at 295 K and 18.33 Å at 123 K. The molecules are aligned end to end along the crystal lattice vector [301]. The repeat distance [301], which is a measure of the molecular length, including van der Waals radii, is 41.37 Å at 295 K and 42.65 Å at 123 K. The tilt of the molecules, as measured by the angle between [301] and the *a*-axis, is 27.0° at 295 K and 25.5° at 123 K. The shortest intermolecular C...C distance is 3.59 ÅA between C(27) and C(37).

Although cooling causes a small decrease in all three unit cell dimensions, the major effect (**Fig. 5**) is the change in unit cell β-angle from obtuse (93.3° at 295 K) to acute (85.49° at 123 K). The resulting change in c cosβ is 2.53 Å, which represents a substantial shearing motion between adjacent monolayers. The orientation matrix for the crystal showed that during cooling the direction of c* remained fixed with respect to the diffractometer, while the direction of a* changed. Thus the shearing motion occurs without changing the orientation of the layers. It is surprising that, on warming, these structural changes appeared to be reversible without causing damage to the crystal. Much of the change occurs within narrow temperature ranges at 262 K and 215 K. This would suggest that the ordering and conformational change in the oleate chains occurs in two stages. The nature of these structural transitions has not been studied in detail. However, the remarkable change of almost 5° in β-angle occurs within the temperature range at which the crystal could be maintained (±1 K). Thus at 262 ± 1 K, the orientation of the crystal on the diffractometer could not be determined.

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REFERENCES

1. Craven, B. M., and N. G. Guerina. 1979. The crystal structure of cholesteryl oleate. *Chem. Phys. Lipids.* **24:** 91–98.
2. Carlisle, C. H., and D. Crowfoot. 1945. The crystal structure of cholesteryl iodide. *Proc. Roy. Soc.* **A184:** 64–83.
3. Park, Y. J., and B. M. Craven. 1981. The crystal and molecular structure of cholesteryl hexanoate at room temperature and low temperature. *J. Korean Chem. Soc.* **25:** 131–139.

4. Craven, B. M., and N. G. Guerina. 1979. The crystal structure of cholesteryl octanoate. *Chem. Phys. Lipids.* **24:** 157–166.
5. Craven, B. M., and P. Sawzik. 1983. Conformation and packing of unsaturated chains in cholesteryl linolelaidate at 123 K. *J. Lipid Res.* **24:** 784–789.
6. Abrahamsson, S., and I. Ryderstedt-Nahringbauer. 1962. The crystal structure of the low-melting form of oleic acid. *Acta Crystallogr.* **15:** 1261–1268.
7. Sawzik, P., and B. M. Craven. 1982. The structure of cholesteryl palmitoleate at 295 K. *Acta Crystallogr.* **B38:** 1777–1781.
8. Craven, B. M., and P. Sawzik. 1984. Conformational changes in cholesteryl palmitoleate in the crystal structure at low temperature. *J. Lipid Res.* **25:** 857–864.
9. Lehmann, M. S., and F. K. Larsen. 1974. A method for location of the peaks in step-scan-measured Bragg reflexions. *Acta Crystallogr.* **A30:** 580–584.
10. Nelmes, R. J. 1975. Removal of the white radiation background from data collected with β-filtered MoKα and AgKα X-rays. *Acta Crystallogr.* **A31:** 273–279.
11. Rees, B. 1977. Assessment of accuracy. *Isr. J. Chem.* **16:** 180–186.
12. Cromer, D. T., and J. T. Waber. 1965. Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18:** 104–109.
13. Stewart, R. F., E. R. Davidson, and W. T. Simpson. 1965. Coherent X-ray scattering for the hydrogen atom in the hydrogen molecule. *J. Chem. Phys.* **42:** 3175–3187.
14. Sawzik, P., and B. M. Craven. 1979. The crystal structure of cholesteryl acetate at 123 K. *Acta Crystallogr.* **B35:** 895–901.
15. Matuscelli, E. 1969. The crystal and molecular structure of the low temperature stable modification of octa-*trans*-2,*trans*-5-diene-1,8-dioic acid. *Acta Crystallogr.* **B25:** 2540–2548.
16. Sundaralingam, M. 1972. Molecular structures and conformations of the phospholipids and sphingomyelins. *Ann. NY Acad. Sci.* **195:** 324–355.
17. Sawzik, P., and B. M. Craven. 1984. Conformation and packing of unsaturated chains in crystals of cholesteryl nervonate at 123 K. *J. Lipid Res.* **25:** 851–856.
18. Craven, B. M. 1986. Cholesterol crystal structures: adducts and esters. *In* Handbook of Lipid Research, Vol. 4. D. M. Small, editor. Plenum Press, New York. 149–152.
19. Johnson, C. K. 1976. ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
20. Motherwell, W. D. S., and W. Clegg. 1978. PLUTO. Program for Plotting Molecular and Crystal Structures. University of Cambridge, England.