

SHORT COMMUNICATIONS

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The crystal structure of cholesteryl laurate at 298 K. By PATRICIA SAWZIK and B. M. CRAVEN, *Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA*

(Received 12 September 1978; accepted 24 October 1978)

Abstract

Cholesteryl laurate, $C_{39}H_{68}O_2$, is monoclinic, space group $P2_1$ with cell dimensions $a = 12.989$ (8), $b = 9.008$ (5), $c = 32.020$ (14) Å, $\beta = 91.36$ (5)°, and $Z = 4$ (two molecules in the asymmetric unit, A , B). Integrated intensities with $I > 2\sigma(I)$ were measured with a diffractometer for 1346 reflections at room temperature. The structure was solved using Patterson rotation and translation methods. Block-diagonal least-squares refinement gave $R = 0.104$. The C(17) cholesterol side chains and ester groups have almost fully extended conformations in both molecules A and B . The greatest conformational difference in the two molecules comes from a difference of 48° in the rotation at the ester bond. Molecular packing in the crystal structure of cholesteryl laurate is isostructural with that of cholesteryl nonanoate. The ester chains are packed with cholesteryl ring systems so as to provide a model for the molecular associations of cholesterol in biological membranes.

Introduction

The crystal structure of cholesteryl laurate is one of a series of cholesteryl ester structure determinations which we have undertaken. An independent structure determination for cholesteryl laurate has been carried out (Dahlén, 1979). Molecular packing and conformation in these structures may be relevant to less-ordered systems involving the cholesteryl esters (Guerina & Craven, 1979).

The liquid-crystalline phases of cholesteryl laurate are monotropic. The solid melts at ~364 K and the cholesteric phase is formed at 361 K on cooling. The smectic-cholesteric transition occurs at 354 K (Davis, Porter & Barrall, 1970). Two solid phases, separated by an exothermal recrystallization, are reproducibly formed when cholesteryl laurate is heated (Barrall & Johnson, 1974). However, Davis & Porter (1970) report a single solid phase when samples of cholesteryl laurate are recrystallized from n -pentanol.

Experimental

Cholesteryl laurate, from Supelco Chemical Co., Bellefonte, PA, was crystallized by slow evaporation of an n -pentanol solution at room temperature. The resulting monoclinic

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plate-like crystals melted at 363.2 K. Exploratory X-ray Weissenberg and precession photographs gave crystal data in agreement with those of Barnard & Lydon (1974) and Abrahamsson & Selin (1963). X-ray data were collected at room temperature using a Nonius CAD-4 diffractometer and Mo $K\alpha$ graphite-monochromated radiation ($\lambda = 0.7093$ Å). A crystal with dimensions $0.6 \times 0.2 \times 0.4$ mm was mounted with the b^* axis 1.5° from the diffractometer φ axis. Unit-cell parameters as determined by a least-squares fit of $\sin^2 \theta$ values for 24 reflections with $20 \leq 2\theta \leq 30^\circ$ are given in Table 1. X-ray intensities for 3584 non-symmetry-related reflections with $\sin \theta/\lambda < 0.47$ Å $^{-1}$ were collected using ω scans. Reflections with $I > 2\sigma(I)$, of which there were 1346, were used for the structure determination and refinement. The variance in an integrated intensity was assumed to be $\sigma^2(I) = \sigma^2 + (0.02I)^2$ where σ^2 is the variance due to counting statistics.

A Patterson rotation and translation method (Craven & DeTitta, 1976) was used to locate the tetracyclic ring system for each of the two independent cholesteryl laurate molecules. The remaining 42 non-hydrogen atoms of the ester groups and cholesterol C(17) side chains were found in subsequent electron density maps.

The structure refinement was carried out by a block-diagonal least-squares procedure in which the function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, and $w = 1/\sigma^2(F_o)$. The X-ray scattering factors were those of Cromer & Waber (1965) for C and O and those of Stewart, Davidson & Simpson (1965) for hydrogen. All H atoms were included with fixed parameters obtained by assuming a C–H bond length of 1.0 Å and standard bond angles. Anisotropic temperature factors were assumed only for the atoms of the tetracyclic system. Refinement converged with $R =$

Table 1. *Crystal data for cholesteryl laurate*

$C_{39}H_{68}O_2$, $M_r = 569.0$, m.p. 363.2 K
Space group $P2_1$
$a = 12.989$ (8), $b = 9.008$ (5), $c = 32.020$ (14) Å
$\beta = 91.36$ (5)°
$Z = 4$ (2 molecules/asymmetric unit)
$V = 3745$ (6) Å 3
$D_c = 1.009$, $D_m = 1.007$ Mg m $^{-3}$
$\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu(\text{Mo } K\alpha) = 0.063$ mm $^{-1}$
Crystal dimensions: $0.6 \times 0.2 \times 0.4$ mm

$\sum |A_i|/\sum |F_o| = 0.104$. Final atomic parameters are in Table 2.*

Results and discussion

Crystals of cholesteryl laurate are isostructural with cholesteryl nonanoate (Guerina & Craven, 1979) and cholesteryl decanoate (Pattabhi & Craven, 1979). In these

* Lists of temperature factors, hydrogen atom positional parameters, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34054 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structures molecules are arranged in monolayers called type I, so as to distinguish them from the monolayers of type II which occur in cholesteryl octanoate (Craven & Guerina, 1979b) and cholesteryl oleate (Craven & Guerina, 1979a). In cholesteryl laurate (Fig. 1), the monolayers are parallel to the crystal planes (001). Molecular long axes are nearly parallel to the crystal [101] direction. In the three isostructural esters, the molecular-packing arrangements are very similar in the central region of the monolayer. The change in the layer d -spacing (32.02, 30.22, 27.24 Å) in the series laurate, decanoate, nonanoate is associated with structural differences in the layer interface region. The laurate is the only structure in which both the alkanoate chains and the cholesteryl C(17) side chains have almost fully extended conformations. In these crystal structures, there is efficient cholesteryl–cholesteryl packing involving only the B mole-

Table 2. Atomic positional parameters ($\times 10^4$) for non-hydrogen atoms

Estimated standard deviations are given in parentheses.

Molecule A	x	y	z	x	y	z	
C(1)	-4823 (20)	2170 (30)	1566 (8)	C(21)	-2842 (32)	5140 (55)	3737 (12)
C(2)	-5438 (19)	1730 (34)	1179 (7)	C(22)	-1708 (26)	3454 (47)	4163 (10)
C(3)	-5152 (17)	120 (33)	1057 (7)	C(23)	-1742 (27)	4110 (47)	4582 (11)
C(4)	-5364 (20)	-852 (31)	1409 (8)	C(24)	-779 (28)	3875 (50)	4817 (11)
C(5)	-4846 (17)	-482 (31)	1823 (7)	C(25)	-883 (31)	4435 (55)	5272 (12)
C(6)	-4289 (18)	-1442 (35)	2052 (8)	C(26)	162 (44)	4331 (74)	5419 (16)
C(7)	-3748 (21)	-1073 (35)	2430 (8)	C(27)	-1763 (44)	4225 (77)	5451 (17)
C(8)	-4110 (19)	328 (37)	2648 (7)	C(28)	-5540 (19)	189 (38)	315 (8)
C(9)	-4197 (17)	1568 (32)	2310 (7)	C(29)	-6175 (20)	-393 (36)	-26 (8)
C(10)	-4973 (19)	1108 (39)	1950 (8)	C(30)	-6043 (19)	275 (35)	-448 (8)
C(11)	-4370 (20)	3082 (35)	2501 (8)	C(31)	-6852 (19)	-209 (36)	-765 (7)
C(12)	-3562 (20)	3525 (34)	2855 (8)	C(32)	-6799 (18)	561 (32)	-1195 (7)
C(13)	-3547 (16)	2419 (33)	3184 (7)	C(33)	-7701 (17)	-19 (33)	-1489 (7)
C(14)	-3318 (19)	936 (37)	2969 (8)	C(34)	-7796 (18)	755 (34)	-1895 (7)
C(15)	-3106 (22)	-249 (40)	3332 (8)	C(35)	-8758 (21)	473 (39)	-2134 (9)
C(16)	-2567 (21)	887 (41)	3638 (9)	C(36)	-8777 (22)	1405 (40)	-2536 (9)
C(17)	-2687 (21)	2525 (35)	3516 (9)	C(37)	-9703 (28)	974 (53)	-2834 (11)
C(18)	-4555 (20)	2414 (37)	3430 (8)	C(38)	-9858 (28)	2081 (57)	-3223 (12)
C(19)	-6143 (16)	1368 (33)	2098 (7)	C(39)	-10588 (44)	1499 (84)	-3521 (18)
C(20)	-2727 (27)	3686 (46)	3878 (11)	O(3)	-5762 (12)	-265 (22)	702 (5)
				O(28)	-4812 (13)	1048 (23)	281 (5)
Molecule B							
C(1)	-2848 (17)	953 (31)	-473 (7)	C(21)	-1261 (18)	811 (34)	1851 (7)
C(2)	-3306 (18)	648 (35)	-910 (8)	C(22)	589 (19)	1313 (36)	2030 (8)
C(3)	-2499 (19)	655 (33)	-1228 (8)	C(23)	588 (21)	744 (41)	2472 (9)
C(4)	-1618 (18)	-417 (34)	-1140 (7)	C(24)	1377 (23)	1579 (44)	2727 (10)
C(5)	-1234 (18)	-261 (34)	-691 (7)	C(25)	1355 (28)	1595 (54)	3196 (11)
C(6)	-211 (18)	-288 (34)	-627 (7)	C(26)	482 (27)	1697 (52)	3443 (11)
C(7)	349 (17)	-243 (33)	-205 (7)	C(27)	2420 (30)	2176 (59)	3337 (12)
C(8)	-404 (15)	-483 (28)	146 (7)	C(28)	-2674 (20)	1406 (36)	-1961 (8)
C(9)	-1428 (16)	251 (27)	52 (6)	C(29)	-3162 (21)	921 (39)	-2388 (9)
C(10)	-1974 (17)	-215 (33)	-356 (7)	C(30)	-3176 (22)	2291 (44)	-2711 (9)
C(11)	-2201 (18)	320 (35)	441 (8)	C(31)	-3818 (20)	1684 (37)	-3070 (8)
C(12)	-1629 (17)	818 (33)	851 (7)	C(32)	-3686 (23)	2823 (39)	-3399 (9)
C(13)	-644 (17)	-21 (31)	946 (8)	C(33)	-4397 (30)	2351 (59)	-3802 (12)
C(14)	61 (17)	38 (30)	540 (7)	C(34)	-4377 (43)	3550 (76)	-4150 (17)
C(15)	1071 (15)	-465 (29)	711 (6)	C(35)	-5054 (34)	3234 (58)	-4551 (13)
C(16)	1150 (18)	-36 (33)	1170 (7)	C(36)	-5354 (46)	4065 (83)	-4794 (18)
C(17)	98 (16)	656 (31)	1277 (6)	C(37)	-6275 (44)	3713 (78)	-5095 (18)
C(18)	-884 (22)	-1731 (38)	1051 (9)	C(38)	-6630 (71)	4448 (147)	-5334 (28)
C(19)	-2444 (22)	-1816 (36)	-305 (8)	C(39)	-7439 (65)	4258 (117)	-5550 (25)
C(20)	-149 (18)	438 (33)	1728 (7)	O(3)	-2907 (13)	458 (23)	-1657 (5)
				O(28)	-1838 (17)	1996 (34)	-1944 (7)

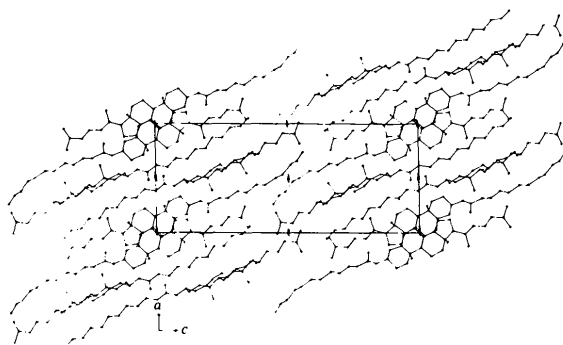


Fig. 1. The crystal structure of cholesteryl laurate in projection down the b axis. Molecules A are close to the screw axis at $(\frac{1}{2}, y, 0)$. Molecules B are close to the screw axis at $(0, y, 0)$.

cules. There is almost no laurate–laurate packing. Most importantly, the packing of the laurate A and B chains with the cholesteryl groups might be relevant to the structural arrangement when cholesterol is incorporated in phospholipid bilayers (Huang, 1977).

Bond lengths and angles for cholesteryl laurate molecules A and B are consistent with those found in cholesteryl acetate (Sawzik & Craven, 1979), and in related crystal structures (Craven & Guerina, 1979b; Guerina & Craven, 1979; Craven & DeTitta, 1976). The apparent bond distances in the terminal region of the ester chains are shortened considerably as a result of large atomic thermal vibrations.

The tetracyclic ring systems of the two independent cholesteryl laurate molecules have similar conformations. A best least-squares fit for the superposition of the C(1)–C(19) fragment from A and B molecules (Nyburg, 1974) gave an average r.m.s. displacement for corresponding atoms of 0.091 Å. Differences in the conformation at the ester linkage follow the same pattern as in the nonanoate structure (Guerina & Craven, 1979). The C(2)–C(3)–O(3)–C(28) angle is 79° in cholesteryl laurate A and 127° for B . In both laurate molecules, the ester chains are almost fully extended, with torsion angles in the bonds along the chain from

C(29)–C(30) through C(37)–C(38) of $-170, 174, -179, 174, -167, 177, 171, 171, 167^\circ$ for molecule A and $-171, -170, -177, 175, -179, 159, -161, 179, -171^\circ$ for molecule B .

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The crystal and molecular structures of magnesium di-*o*-phthalatocuprate(II) tetrahydrate and strontium di-*o*-phthalatocuprate(II) trihydrate: errata. By MARINA BIAGINI CINGI, ANNA MARIA MANOTTI LANFREDI, ANTONIO TIRIPICCHIO and MARISA TIRIPICCHIO CAMELLINI, *Istituto di Chimica Generale, Università di Parma, Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma, Italy*

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Abstract

The Mg compound, a tetrahydrate, was given by mistake as a dihydrate in the paper by Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini [*Acta Cryst.* (1978). B **34**, 406–411]. Thus the title, the formula and crystal data must be corrected to: title: The crystal and molecular

structure of magnesium di-*o*-phthalatocuprate(II) tetrahydrate; formula: $\text{Mg}[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$; crystal data: $\text{C}_{16}\text{H}_{16}\text{CuMgO}_{12}$, $M_r = 488.15$, $D_c = 1.76 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 1.283 \text{ mm}^{-1}$.

All information is given in the *Abstract*.

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