Conformation and packing of unsaturated chains in crystals of cholesteryl nervonate at 123 K[1]

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Abstract At 123 K, cholesteryl *cis*-15-tetracosenoate (cholesteryl nervonate, $C_{51}H_{90}O_2$) is monoclinic, space group $P2_1$ with $a = 12.948(5)$, $b = 8.805(5)$, $c = 42.98(5)$ Å, $\beta = 105.93(3)°$, [$\lambda(\text{CuK}\alpha = 1.5418$ Å], having two independent molecules (A) and (B) in the unit cell. The crystal structure at 123 K has been determined from 6329 reflections with $\sin\theta/\lambda < 0.54$ Å^{-1}, of which 1990 gave $I > 2\sigma(I)$. Structure refinement by Fourier methods and block diagonal least squares gave R = 0.232 for all reflections, R = 0.135 for those with $I > 2\sigma(I)$. The crystal structure consists of layers in which there is close packing of cholesteryl groups and the proximal segments of the ester chains. This layer structure occurs also in cholesteryl palmitoleate and the alkanoate esters C_9 through C_{12}. Because the nervonate chains are longer, they become aligned in the interface region between layers, but without a regular subcell structure being established. The nervonate (A)-chain is almost extended, while the (B)-chain has two bends, one in the saturated region. Both chains have complex dislocations at the *cis*-double bond.—**Sawzik, P., and B. M. Craven.** Conformation and packing of unsaturated chains in crystals of cholesteryl nervonate at 123 K. *J. Lipid Res.* 1984. **25:** 851–856.

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

The crystal structure of cholesteryl nervonate is one in a series of structure determinations of unsaturated fatty acid esters of cholesterol. The aim of this investigation is to examine the conformations of unsaturated fatty acid chains when they are close-packed in different kinds of lipid environments. Elucidation of these structures will provide useful information for models of molecular associations in less ordered lipid systems. The present structure determination was necessarily carried out at 123 K because at room temperature the details were obscured by high amplitudes of thermal motion and possibly disorder.

Cholesteryl nervonate undergoes liquid crystalline phase transformations which have been summarized by Ginsburg and Small (1) as:

$$\text{crystal} \xrightleftharpoons{310\text{ K}} \text{smectic} \xrightleftharpoons{325.5\text{ K}} \text{isotropic.}$$

The smectic-isotropic transition is reversible; however, crystals grow from the smectic phase only after undercooling. No cholesteric phase is observed for monounsaturated cholesteryl esters with chain length greater than 20 carbons.

EXPERIMENTAL

Cholesteryl nervonate was obtained from Serdary Research Labs, London, Ontario, and crystallized from a saturated acetone solution at 273 K. The crystals were thin plates elongated along the *b*-axis direction melting at 322 K. The space group, determined in a previous study (2), is $P2_1$ with four molecules in the unit cell ($C_{51}H_{90}O_2$; M = 735.3).

X-ray data were collected at 295 K and 123 K using a Nonius CAD-4 diffractometer equipped with the Enraf-Nonius Universal Low Temperature Device (dry nitrogen as the coolant), using CuKα graphite-monochromated radiation ($\lambda = 1.5418$ Å). Encasing the crystal in a bead of epoxy resin and lowering the temperature from 295 K to 123 K at a rate of 10 K/hr preserved crystal integrity during the cooling process. A crystal of dimensions 0.6 × 0.3 × 0.08 mm was mounted with the *b*-axis approximately 10° from the diffractometer Φ-axis. Unit cell parameters were determined by a least squares fit of $\sin^2\theta$ values for 48 reflections measured at $\pm\theta$ in the range $15° < 2\theta < 30°$. Cell dimensions at 123 K are: $a = 12.948(5)$, $b = 8.805(5)$, $c = 42.98(5)$ Å, $\beta = 105.93(3)°$, $V = 4712(4)$ Å^3.[2] Intensity data for 6329 independent reflections in

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

[1] See NAPS document no. 04203 for 46 pages of supplementary material, consisting of tables of structure factors, anisotropic thermal parameters, hydrogen atom positional parameters, bond distances, bond angles, and torsion angles. 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 $15.55 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 10 pages of material thereafter. $1.50 for microfiche postage.

[2] Unit cell dimensions at 295 K are: $a = 12.991(9)$, $b = 9.082(6)$, $c = 43.36(5)$Å, $\beta = 101.5(2)°$, $V = 5013$ Å^3. Intensity data for 3545 independent reflections in the range of $\sin\theta/\lambda < 0.45$ Å^{-1} were collected

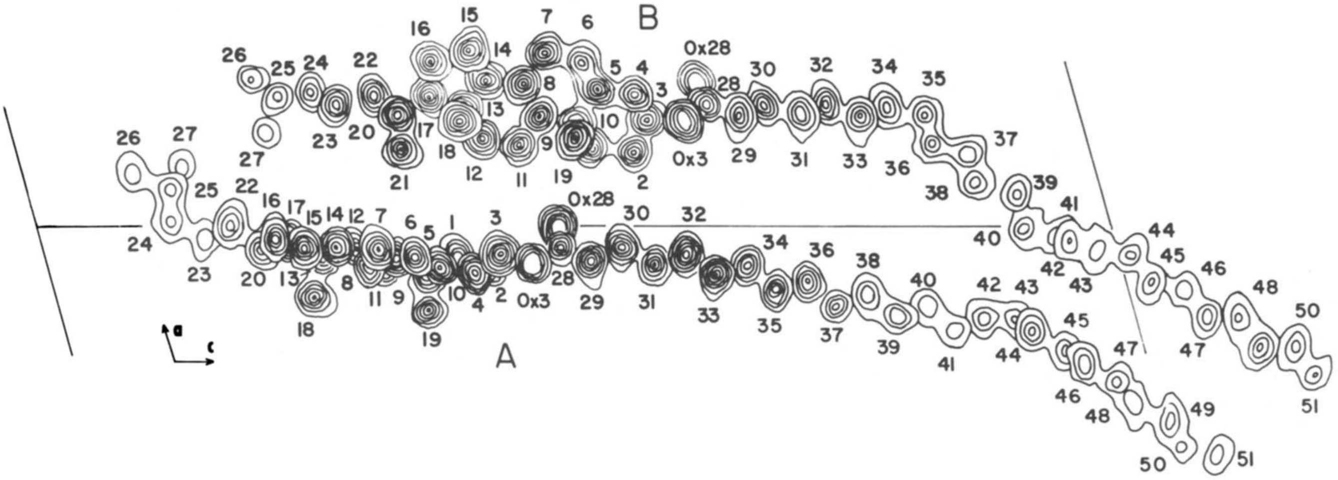

Fig. 1. The electron density and atomic numbering system for the two independent molecules (A) and (B). Shown here is a part of the unit cell depicted in Fig. 3. Contours are at intervals of 1 eÅ^{-3} and begin at 1 eÅ^{-3}.

the range of $\sin\theta/\lambda < 0.54$ Å^{-1} were collected using ω scans. There were 1990 reflections with $I > 2\sigma(I)$. Three standard reflections were collected every 100 reflections and used to put the intensity data on a uniform scale. Fluctuations in the standards were less than ±5% for all but the last 2000 reflections, mostly weak (0.42 $\text{Å}^{-1} < \sin\theta/\lambda < 0.54$ Å^{-1}), where they decreased progressively up to 15%, most likely as a result of radiation damage.

The unit cell data for cholesteryl nervonate indicated that this crystal structure was of the same type as cholesteryl palmitoleate (3, 4). Atomic coordinates for the tetracyclic ring systems [atoms C(1)–C(19)] for the two independent molecules (A, B) of cholesteryl palmitoleate were transformed into the unit cell of cholesteryl nervonate (123 K) and used as a starting model for structure determination. All remaining atoms were located with six cycles of Fourier refinement using $2\,|F_o| - |F_c|$ maps interspersed with structure factor block diagonal least squares refinement. The R-factor at this point was 0.33.

The structure refinement was carried out by atomic block diagonal least squares procedures in which the function to be minimized was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$ and $w = 1/\sigma^2(F_o)$. Only those reflections with $I > 2\sigma(I)$ were used. X-ray scattering factors were taken from Cromer and Waber (5) for C and O, and from Stewart, Davidson, and Simpson (6) for H. Atomic positional and anisotropic thermal parameters were refined for the 38 carbon atoms in the two tetracyclic ring systems. Positional and isotropic thermal parameters were refined for the remaining 68 carbon and oxygen atoms. Hydrogen atoms were included in the structure factor calculation with fixed parameters assuming C–H bond distances of 1.0 Å and standard bond angles. Isotropic thermal parameters for H-atoms were taken as $B = B_{eq}(C) + 2.0$ Å^2 where $B_{eq}(C)$ is the isotropic equivalent B-value of the carbon atom to which each hydrogen is bonded. Positional and thermal parameters for H-atoms were periodically revised during the refinement. After eight cycles the R-factor was 0.18. Seven of the temperature factors for atoms in the tetracyclic ring systems were non-positive definite and several bond distances in the fatty acid chains were judged to be unacceptable. At this point the data set was expanded to include all 6329 unique reflections (7), with e.s.d.'s as proposed by Rees (8).[3] Atomic positional and anisotropic thermal parameters for all 106 carbon and oxygen atoms were refined for the next nine cycles, converging at R = 0.232 for all reflections and R = 0.135 for those with $I > 2\sigma(I)$. All temperature factors remained positive definite and the fatty acid chains stabilized in reasonable geometries. The addition of reflections with intensities that were weak or negative did not greatly improve the final R-factor, but there was better resolution in diffuse areas of the structure (**Fig. 1**). The largest final difference density was 0.54 eÅ^{-3} located near the terminal region of the hydrocarbon chain of molecule (B). The average estimated standard deviation in the electron density was 0.16 eÅ^{-3}. Final atomic parameters are in **Table 1.**

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using ω scans. The variance in an intensity was assumed to be $\sigma^2(I) = \sigma^2 + (0.03I)^2$ where σ^2 is the variance due to counting statistics. Since there were only 326 reflections with $I > 2\sigma(I)$, efforts to determine the structure at room temperature were abandoned.

[3] It was found that the intensities measured for 27 reflections were unreliable because of significant discrepancies in ω-scans automatically carried out in both forward and reverse directions. Although $|F_o|$ and $|F_c|$ were in satisfactory agreement for some of these reflections, all were assigned large e.s.d.'s so that they were effectively excluded from the least squares refinement.

TABLE 1. Atomic positional parameters given as fractional coordinates ($\times 10^4$)

Molecule A					Molecule B				
atom	x/a	y/b	z/c	U_{eq}	atom	x/a	y/b	z/c	U_{eq}
CA1	5955 (16)	2902 (23)	1184 (4)	32 (7)	CB1	2481 (15)	4220 (26)	−353 (4)	33 (7)
CA2	6279 (14)	3370 (21)	879 (4)	20 (6)	CB2	2627 (14)	4495 (24)	−698 (5)	32 (7)
CA3	5946 (14)	4990 (22)	795 (4)	26 (6)	CB3	1566 (17)	4295 (28)	−942 (5)	47 (8)
CA4	6472 (17)	6064 (24)	1071 (4)	35 (7)	CB4	761 (15)	5524 (29)	−880 (4)	42 (7)
CA5	6262 (16)	5475 (29)	1378 (4)	42 (7)	CB5	646 (14)	5426 (25)	−541 (5)	32 (7)
CA6	5927 (19)	6552 (35)	1557 (5)	61 (9)	CB6	−317 (19)	5438 (26)	−485 (5)	48 (8)
CA7	5694 (18)	6209 (24)	1888 (5)	41 (8)	CB7	−503 (15)	5339 (23)	−166 (5)	28 (6)
CA8	6130 (15)	4643 (26)	2023 (4)	35 (6)	CB8	540 (14)	5529 (23)	126 (4)	28 (6)
CA9	5931 (15)	3475 (24)	1745 (5)	33 (7)	CB9	1456 (15)	4782 (24)	53 (5)	30 (7)
CA10	6454 (14)	3858 (21)	1474 (4)	22 (6)	CB10	1695 (15)	5407 (25)	−264 (5)	35 (7)
CA11	6187 (17)	1876 (24)	1876 (5)	34 (7)	CB11	2508 (13)	4848 (24)	337 (5)	31 (7)
CA12	5645 (18)	1456 (25)	2151 (5)	43 (8)	CB12	2255 (15)	4258 (26)	656 (5)	35 (7)
CA13	5942 (17)	2556 (25)	2432 (5)	42 (8)	CB13	1330 (15)	5116 (24)	733 (5)	33 (7)
CA14	5630 (16)	4102 (28)	2278 (5)	42 (8)	CB14	365 (14)	5002 (23)	446 (4)	26 (6)
CA15	5671 (21)	5198 (29)	2574 (5)	61 (9)	CB15	−583 (17)	5569 (25)	552 (5)	37 (7)
CA16	5358 (18)	4144 (33)	2821 (4)	57 (9)	CB16	−287 (15)	4985 (24)	919 (5)	36 (7)
CA17	5362 (17)	2551 (26)	2682 (5)	38 (7)	CB17	850 (14)	4402 (26)	1008 (4)	33 (6)
CA18	7209 (18)	2487 (28)	2604 (5)	47 (8)	CB18	1642 (16)	6853 (22)	815 (5)	30 (7)
CA19	7672 (17)	3626 (29)	1587 (4)	42 (8)	CB19	2217 (16)	6958 (23)	−220 (5)	31 (7)
CA20	5638 (19)	1324 (36)	2944 (5)	65 (10)	CB20	1475 (18)	4539 (30)	1361 (5)	58 (9)
CA21	5552 (19)	−322 (30)	2815 (5)	54 (9)	CB21	2648 (17)	4232 (27)	1441 (5)	44 (8)
CA22	4853 (26)	1406 (34)	3173 (6)	86 (13)	CB22	880 (16)	3750 (28)	1559 (4)	44 (8)
CA23	5300 (31)	467 (56)	3464 (8)	150 (19)	CB23	1259 (17)	4177 (35)	1936 (4)	56 (9)
CA24	4697 (31)	914 (49)	3728 (7)	138 (18)	CB24	673 (19)	3047 (42)	2116 (5)	83 (11)
CA25	3676 (25)	1261 (53)	3647 (7)	121 (18)	CB25	995 (19)	3455 (67)	2481 (6)	161 (24)
CA26	3205 (29)	1602 (51)	3941 (8)	141 (17)	CB26	2117 (37)	2943 (69)	2630 (11)	181 (25)
CA27	2917 (37)	−48 (60)	3483 (10)	210 (24)	CB27	272 (20)	2541 (68)	2643 (7)	172 (24)
CA28	5715 (15)	4892 (35)	218 (4)	54 (9)	CB28	1103 (16)	3860 (34)	−1509 (5)	57 (9)
CA29	6195 (16)	5580 (25)	−38 (4)	31 (7)	CB29	1450 (19)	4228 (31)	−1799 (5)	58 (9)
CA30	5723 (14)	4794 (26)	−365 (4)	34 (6)	CB30	1129 (18)	2941 (30)	−2074 (5)	55 (8)
CA31	6306 (15)	5305 (23)	−607 (4)	27 (6)	CB31	1441 (24)	3417 (31)	−2372 (6)	82 (11)
CA32	5968 (15)	4513 (22)	−937 (4)	24 (6)	CB32	1127 (21)	2135 (34)	−2639 (5)	65 (10)
CA33	6625 (16)	4938 (25)	−1157 (4)	35 (7)	CB33	1530 (22)	2576 (34)	−2929 (6)	74 (11)
CA34	6346 (16)	4048 (28)	−1475 (4)	39 (7)	CB34	1220 (29)	1244 (49)	−3200 (6)	124 (17)
CA35	7106 (19)	4381 (34)	−1680 (5)	60 (9)	CB35	1413 (30)	1620 (46)	−3530 (7)	110 (16)
CA36	6858 (21)	3324 (37)	−1977 (5)	75 (11)	CB36	2450 (21)	1628 (51)	−3508 (7)	115 (15)
CA37	7586 (19)	3714 (54)	−2205 (5)	109 (18)	CB37	2685 (20)	1959 (50)	−3826 (8)	130 (16)
CA38	7303 (28)	2436 (50)	−2510 (5)	130 (17)	CB38	3680 (29)	1356 (61)	−3823 (10)	164 (21)
CA39	7928 (23)	2241 (48)	−2728 (8)	117 (16)	CB39	4000 (26)	1586 (49)	−4154 (7)	131 (16)
CA40	7590 (25)	1388 (59)	−3043 (7)	154 (18)	CB40	5096 (29)	955 (52)	−4152 (9)	141 (18)
CA41	8389 (28)	1014 (55)	−3225 (9)	152 (20)	CB41	5306 (29)	1079 (43)	−4508 (10)	155 (20)
CA42	8015 (28)	82 (48)	−3530 (7)	133 (16)	CB42	5536 (38)	2935 (58)	−4529 (9)	192 (25)
CA43	8034 (31)	498 (48)	−3842 (8)	140 (17)	CB43	5822 (41)	3330 (54)	−4779 (10)	201 (26)
CA44	8442 (26)	2006 (48)	−3951 (7)	116 (15)	CB44	5931 (31)	2554 (80)	−5085 (9)	247 (33)
CA45	9131 (28)	1515 (60)	−4212 (8)	141 (19)	CB45	6863 (33)	2926 (63)	−5200 (9)	179 (23)
CA46	9525 (29)	3055 (44)	−4352 (6)	126 (15)	CB46	6951 (41)	2424 (66)	−5488 (9)	219 (29)
CA47	10046 (24)	2622 (61)	−4608 (7)	165 (21)	CB47	7980 (29)	2850 (53)	−5612 (7)	148 (18)
CA48	10755 (33)	3448 (49)	−4715 (8)	172 (19)	CB48	7990 (39)	2245 (60)	−5911 (8)	178 (25)
CA49	11355 (48)	3211 (39)	−5003 (10)	194 (29)	CB49	8918 (27)	2336 (35)	−6045 (7)	96 (14)
CA50	12072 (45)	2222 (45)	−5027 (12)	222 (28)	CB50	8935 (36)	1817 (48)	−6373 (8)	142 (21)
CA51	12373 (32)	2859 (56)	−5357 (8)	163 (19)	CB51	9857 (29)	1850 (75)	−6464 (8)	185 (24)
OA3	6301 (9)	5539 (16)	515 (3)	28 (4)	OB3	1712 (11)	4610 (18)	−1260 (3)	44 (5)
OA1	4965 (9)	4157 (20)	186 (3)	44 (5)	OB1	378 (13)	2993 (26)	−1492 (3)	79 (7)

Isotropic equivalent U values are $U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3 = \langle u^2 \rangle$ and are given as $Å^2 \times 10^3$. Estimated standard deviations are in parentheses.

RESULTS AND DISCUSSION

Molecular geometry

Within experimental error, bond distances and angles for the independent molecules (A) and (B) are consistent with the more accurately determined values obtained for cholesteryl laurate at 198 K (9) and cholesteryl acetate at 123 K (10). In the cholesteryl groups, the average least squares estimated standard deviation for C–C bond distances is 0.03 Å and for C–C–C bond angles 2°. In the hydrocarbon chains, these values are 0.05 Å and 3°, respectively.

The tetracyclic ring systems for molecules (A) and (B) have similar overall conformations. A best least squares fit for superposition (11) of atoms in the C(1)–C(19) fragment results in an r.m.s. displacement of 0.09 Å. The most significant difference in conformation is at the C/D ring junction. The torsion angle C(8)–C(14)–C(13)–C(18) has a value of 59(2)° in molecule (A) and 67(2)° in molecule (B). A measure of the twist in the ring system is given by the C(19)–C(10)–C(13)–C(18) torsion angle which is 7(2)° for molecule (A) and 10(2)° for (B). In related structures this value ranges from 7.9–15.0°. The length of the cholesteryl nervonate molecule, taken as the C(25)–C(51) distance, is 43.19(6) Å for molecule (A) and 43.06(6) Å for (B). In molecule (A), the C(2)–C(3)–O(3)–C(28) torsion angle has a value of 72(2)°. However for (B) this value is 148(2)°. This angle is important because it illustrates the different relationship of the alkenoate chain to cholesteryl group in molecules (A) and (B) (**Fig. 2**). The C(17) side chain has a nearly extended conformation in molecule (B) with the terminal methyl groups in a *trans*, (−)*gauche* arrangement. Molecule (A) has a strained conformation that is nearly eclipsed about the C(23)–C(24) bond and is *trans*, (+)*gauche* for the terminal methyl groups (Fig. 2).

The most interesting features of the crystal structure are the nervonate fatty acid chain conformations. The nervonate chain is 24 carbons long with a *cis*-double bond at the fifteenth carbon counting from the carbonyl group. The chains of the two molecules are quite different in conformation (Figs. 1–3). Each chain can be divided into nearly planar zigzag segments that are separated by dislocations. For molecule (A), there are two zigzag segments, C(28)–C(40) and C(45)–C(49), which are separated by the region about the *cis*-double bond, C(41)–C(42)=C(43)–C(44). Molecule (B) has three such segments; C(28)–C(33), C(37)–C(40), and C(45)–C(51) (Fig. 2). In (B), the first two segments are separated by a *gauche* twist at the C(34)–C(35) bond and the second two segments by the *cis*-double bond region. The relationship of the planar zigzag segments to one another determines the overall shape of the chain. Parameters that describe this relationship are bending (angle between best least squares lines through atoms of adjacent segments), kinking (perpendicular separation of these skewed lines), and twisting (angle between best least squares planes through atoms of adjacent segments). The nervonate (A) chain is nearly extended, with the first section slightly bowed, due to the alternation of (+) and (−) almost *trans* torsion angles about the first six bonds. There is a *gauche* twist near the end of the chain at the C(48)–C(49) bond. Least squares lines through the two planar zigzag segments [C(28)–C(40) and C(45)–C(49)] of molecule (A) make a bend of 144° and have a kink of 0.6 Å. The twist is 150°. In molecule (B) the first segment [C(28)–C(33)] is related to the second [C(37)–C(40)] by a bend angle of 135° and a kink separation of 0.7 Å. The chain is severely twisted with an angle of 90° between least squares planes through the adjacent segments. The terminal segment [C(45)–C(51)] of the (B) chain begins after the *cis*-double bond and is almost parallel to the previous segment with a bend

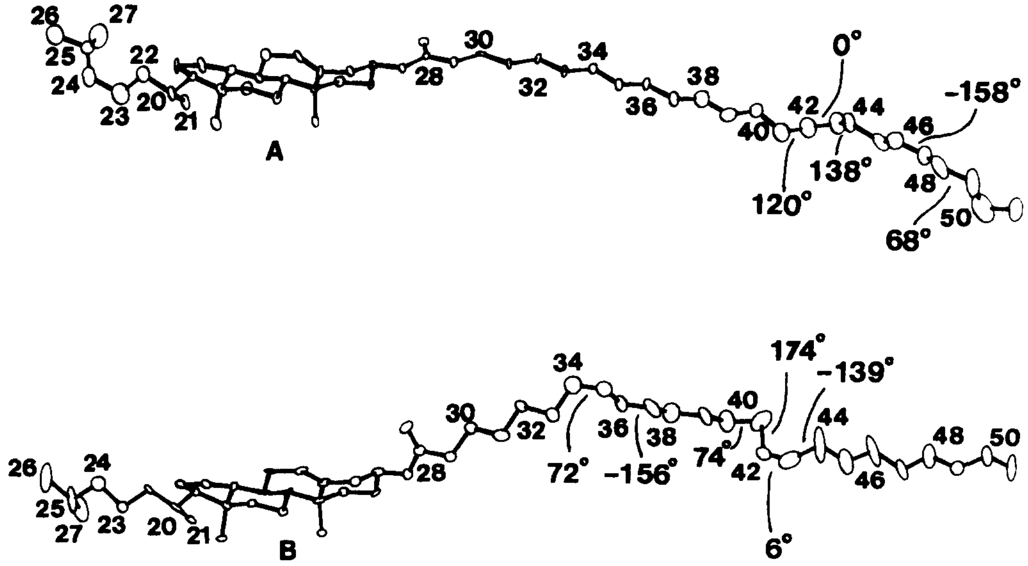

Fig. 2. Molecules (A) and (B) in their observed configuration with their tetracyclic ring systems in the same orientation. Atoms are represented as 25% probability envelopes. Selected torsion angles are given for the nervonate chains.

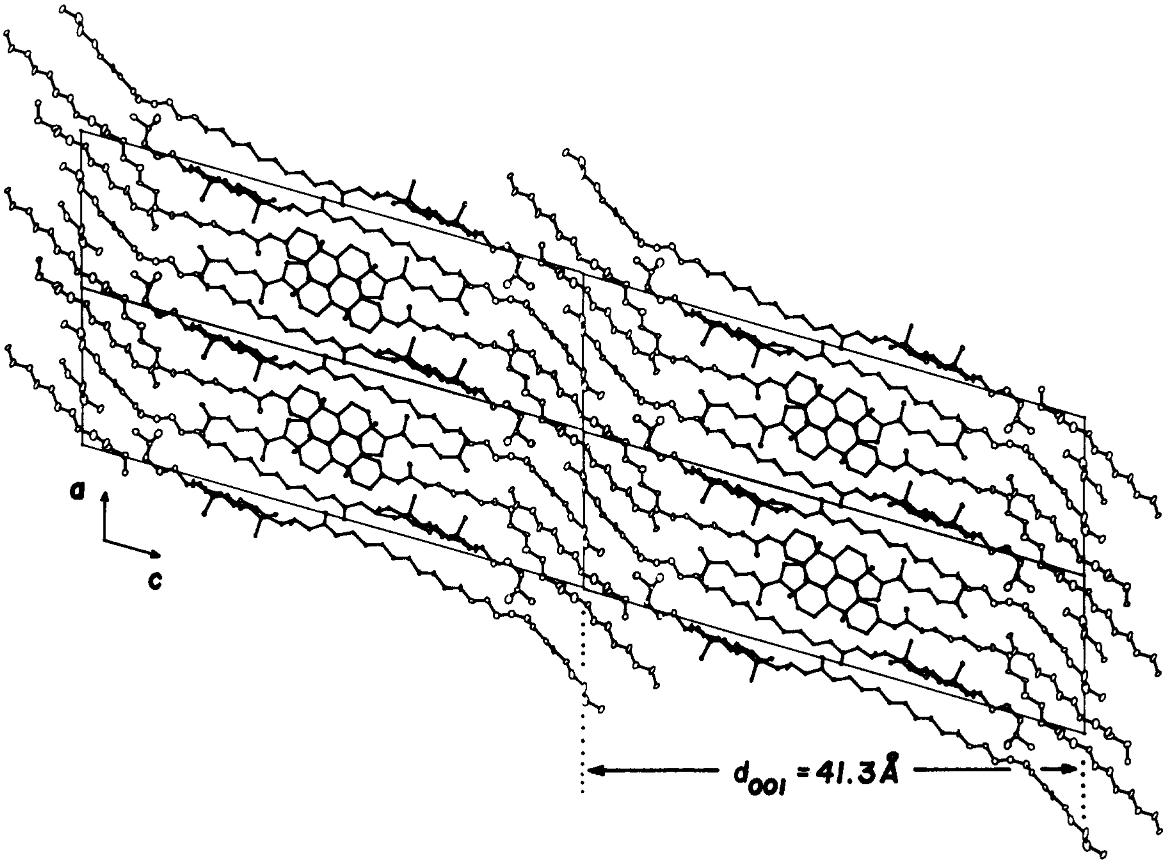

Fig. 3. The crystal structure of cholesteryl nervonate in projection down the *b*-axis. The two molecules are (A) (ring system viewed on edge) and (B). Adjacent monolayers extend vertically with the interface region occurring in vertical strips at the center and edges of the figure.

angle of 160°. The kink is 2.0 Å. Between the second and third segments there is an additional twist of 123°. Apart from the difference in overall chain conformation of (A) and (B), there are also important differences at the double bond. Beginning at the C(38)–C(39) bond of the nervonate chain, the sequence of rotations about C–C bonds for molecule (A) is (tttsCsttttgt) and for (B) it is (ttgtCs̄tttttt).[4] In the five cholesteryl alkenoate crystal structures so far determined, only two of the ester chains have simple symmetric dislocations at the ethylenic groups. They are the nervonate chain for molecule (A) (see above) and the linolelaidate chain in which the sequence of torsion angles is (· · · ttsTs̄sTs̄tt · · ·) (12). The linolelaidate chain is almost unperturbed except for a detour in the unsaturated region. The other chains are: palmitoleate (A) (295 K and 122 K), (· · · tttgsCsttt · · ·) (3, 4); molecule (B), (disordered at 295 K), (· · · ttgCsgtt · · ·) and (· · · tts̄Cs̄gtgt · · ·) (3); molecule (B) at 123 K, (· · · ttgs̄Ctgtt · · ·) (4); and oleate (· · · ttsCggts̄t · · ·) (13). In overall shape, some of the unsaturated chains like the nervonate (A)-chain are almost extended and could pack together with extended saturated chains as in the gel state of phospholipid membranes. Others are bent like a boomerang and would be better suited to more fluid phases.

Molecular packing

As noted above, cholesteryl nervonate is one of several esters with related crystal structures. They contain layers which are characterized by a central region where there is efficient packing together of both cholesteryl ring systems, the proximal section of the ester chain of molecule (A), and the C(17) tail of molecule B. Between these layers are interface regions where the fatty acid chains and C(17) tails are more loosely arranged (**Fig. 3**). The atoms in this part of the structure have high m.s. amplitudes of thermal vibration (see U_{eq} in Table 1), and the electron density is quite diffuse compared with the cholesteryl rings (Fig. 1). In cholesteryl nervonate the

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[4] Symbols are: t = *trans*, s = (+)*skew*, s̄ = (−)*skew*, g = *gauche*, ḡ = (−)*gauche*, T = double bond (*trans*), C = double bond (*cis*).

monolayers are parallel to the crystal planes (001) and have a thickness of d_{001} = 41.3 Å (Fig. 3).

It is of interest to compare the crystal structure of cholesteryl nervonate with that of cholesteryl palmitoleate (3, 4), which has the same layer structure, but shorter alkenoate chains (*cis*-9-hexadecenoate) with the double bond closer to the ester linkage. In the palmitoleate crystal structure, the ester chain of molecule (A) is nearly fully extended and is buried within the layer for almost its entire length, up to C(43). The ester chain of molecule (B) emerges at about the eighth carbon atom, C(35) almost at the double bond, C(36)=C(37). Here, the chain bends and subsequent atoms are subject to the increased thermal vibrations characteristic of the interface region. In cholesteryl nervonate, the ester chains being longer, the (A)-chain emerges from the layers at about C(43), which is the location of the double bond. As seen in Figs. 2 and 3, the chain bends and subsequent atoms have increased thermal vibrations. This is a natural flexing point for the chain, since the torsional barrier is low at bonds adjacent to a double bond (14, 15). As in the palmitoleate structure, the (B)-chain emerges from the layer at about C(35). This is prior to the double bond. Nevertheless, there is a *gauche*-conformation at the single bond C(34)–C(35), so that the chain bends and runs into the interlayer region almost parallel to the (A)-chain.

Because the nervonate chains are longer, they are better aligned in the interface region than in cholesteryl palmitoleate. However, they are not long enough for a regular subcell packing arrangement to be established.

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REFERENCES

1. Ginsburg, G. S., and D. M. Small. 1981. Physical properties of cholesteryl esters having 20 carbons or more. *Biochim. Biophys. Acta.* **664:** 98–107.
2. Sawzik, P., and B. M. Craven. 1981. Crystal data for fatty-acid esters of cholesterol and cholestanol. *J. Appl. Crystallogr.* **14:** 351–352.
3. Sawzik, P., and B. M. Craven. 1982. The structure of cholesteryl palmitoleate at 295 K. *Acta Crystallogr.* **B38:** 1777–1781.
4. Craven, B. M., and P. Sawzik. 1984. Conformational changes of cholesteryl palmitoleate in the crystal structure at low temperature. *J. Lipid Res.* **25:** 857–864.
5. Cromer, D. T., and J. T. Waber. 1965. Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18:** 104–109.
6. 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.
7. Hirshfeld, F. L., and D. Rabinovich. 1973. Treating weak reflections in least-squares calculations. *Acta Crystallogr.* **A29:** 510–513.
8. Rees, B. 1977. Assessment of accuracy. *Isr. J. Chem.* **16:** 180–186.
9. Sawzik, P., and B. M. Craven. 1980. The crystal structure of cholesteryl laurate at 198 K. *Acta Crystallogr.* **B36:** 3027–3033.
10. Sawzik, P., and B. M. Craven. 1979. The crystal structure of cholesteryl acetate at 123 K. *Acta Crystallogr.* **B35:** 895–901.
11. Nyburg, S. C. 1974. Some uses of a best molecular fit routine. *Acta Crystallogr.* **B30:** 251–253.
12. 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.
13. Craven, B. M., and N. G. Guerina. 1979. The crystal structure of cholesteryl oleate. *Chem. Phys. Lipids.* **24:** 91–98.
14. Kondo, S., E. Hirota, and Y. Morino. 1968. Microwave spectrum and rotational isomerism in butene-1. *J. Mol. Spectrosc.* **28:** 471–489.
15. Abe, A., R. L. Jernigan, and P. J. Flory. 1966. Conformational energies of n-alkanes and the random configuration of higher homologs including polymethylene. *J. Am. Chem. Soc.* **88:** 631–639.