N(3)—O(2)—C(11) torsion angle of 162·7°]. Such a configuration rules out the possibility of a direct transfer of the proton to the carbonyl O(1) during the nucleophilic attack on C(11) [C(11)—O(1) = 5·13 Å].

The torsion angle N(3)—O(2)—C(11)—C(12) is 167·8°. The geometry of the valine residue agrees well with normal values for bond distances and angles. The torsion angles of the residue are $\omega = 175{\cdot}4°$, $\varphi = -61{\cdot}3°$ and $\psi = -39{\cdot}0°$, the last two values agreeing well with those of an α_R helix. Bond distances of the benzyloxycarbonyl group (the protecting group of the amine function) are similar to those found in other compounds (Sacerdoti & Gilli, 1974; Itoh, Yamane, Ashida, Sugihara, Imanishi & Higashimura, 1976).

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Cholesteryl Chloroformate

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Abstract. $C_{28}H_{45}ClO_2$; $M_r = 449{\cdot}12$, monoclinic, space group $P2_1$, $a = 12{\cdot}836\ (2)$, $b = 9{\cdot}417\ (2)$, $c = 12{\cdot}327\ (2)$ Å, $\beta = 113{\cdot}47\ (1)°$, $Z = 2$, $V = 1367{\cdot}8\ (1)$ Å^3, $D_c = 1{\cdot}091$, $D_o = 1{\cdot}094$ g cm^{-3}. A three-dimensional data set was collected at room temperature with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) on a Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator to a maximum 2θ value of 100°, by the θ–2θ scan technique. The structure was solved using a Patterson rotation–translation search technique. The coordinates and the anisotropic temperature factors of the non-hydrogen atoms were refined by full-matrix least-squares methods to a final R value of 0·059 based on F. The bond lengths within the steroid nucleus are normal, but the tail region and ester group have shortened bond lengths as a result of high thermal vibration. The torsional angles in the tail are normal for this type of compound.

Introduction. Although the conformation of the nucleus of cholesterol has been well established by a number of structure determinations (Burki & Nowacki, 1956; Carlisle & Crowfoot, 1945; Craven, 1976; Craven & DeTitta, 1976; Chandross & Bordner, 1977) there are still several reasons for solving the structures of cholesterol derivatives. Cholesterol esters are important constituents of pathological conditions such as atherosclerosis, and the factors that determine their mode of crystallization and packing may be useful in understanding their deposition in arteries. In addition, the

allowable tail conformations will help define permissible interactions with membrane constituents such as phospholipids.

Cholesteryl chloroformate (Eastman 9761, $C_{27}H_{45}OCOCl$) was recrystallized from acetone. Unit-cell dimensions were obtained by a least-squares fit of 15 reflections. Systematic absences indicated the space group $P2_1$. Using our usual data collection and preliminary processing procedures (Chandross & Bordner, 1974), 1523 reflections were collected of which 1443 were considered non-zero. All intensities with a value less than 2σ were set equal to zero with zero weight. The density was measured by the flotation technique in $KI–HgCl_2$ solution.

The preliminary processing was routine and included the usual corrections. Atomic scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1962). The scattering factor for Cl is that given by Cromer & Mann (1967). The scattering factor for H is that given by Stewart, Davidson & Simpson (1965). Both anomalous dispersion components were applied to Cl (*International Tables for X-ray Crystallography*, 1962). No corrections were made for absorption.

Normalized structure factors, $|E|$, (Karle & Karle, 1966) were calculated using an overall temperature factor of 6·69 Å^2. All of the observable data were used, and the symmetry effects on the average distribution of the intensity data were corrected for by the method of Wilson (1950).

Attempts to determine the structure with the subprograms *MULTAN* (Germain, Main & Woolfson, 1971) failed. The phase problem was finally solved with the rotation–translation programs *ROTRAN* (Craven, 1976). The molecule was initially oriented using as the search fragment the coordinates of the 17 atom steroid nucleus found in our determination of the structure of cholesteryl *p*-toluenesulfonate (Chandross & Bordner, 1977). Using $|E| \geq 1·0$ in this search we obtained two peaks, corresponding to two potentially correct orientations. It was clear from the Patterson synthesis that the plane of the molecule was approximately perpendicular to the *b* axis of the unit cell. By comparing the two possible orientations obtained from the search program with the density distribution on the Patterson section $v = 0$, the correct orientation was readily apparent. The translation was determined by using the translation function program to locate the vector between molecules related by the screw axis. The remaining non-hydrogen atoms were located by doing several cycles of difference Fourier syntheses.

Least-squares refinement was started with full-matrix isotropic refinement, and continued with the non-hydrogen coordinates in one matrix and the scale factor, secondary extinction factor (Larson, 1967) and anisotropic temperature factors in a second matrix. The methylene H atoms were then introduced by calculation (with a C—H bond distance of 1·0 Å) and the methyl H atoms were found by a combination of difference Fourier maps and calculation. Refinement

Table 2. *Bond distances* (Å)

C(1)–C(2)	1·529 (11)	C(13)–C(14)	1·535 (10)
C(1)–C(10)	1·543 (11)	C(13)–C(17)	1·549 (10)
C(2)–C(3)	1·513 (12)	C(13)–C(18)	1·514 (12)
C(3)–C(4)	1·486 (13)	C(14)–C(15)	1·529 (9)
C(3)–O(1)	1·477 (21)	C(15)–C(16)	1·546 (11)
C(4)–C(5)	1·494 (11)	C(16)–C(17)	1·554 (10)
C(5)–C(6)	1·343 (11)	C(17)–C(20)	1·548 (10)
C(5)–C(10)	1·520 (11)	C(20)–C(21)	1·511 (11)
C(6)–C(7)	1·508 (11)	C(20)–C(22)	1·518 (10)
C(7)–C(8)	1·531 (10)	C(22)–C(23)	1·537 (11)
C(8)–C(9)	1·507 (10)	C(23)–C(24)	1·511 (11)
C(8)–C(14)	1·519 (10)	C(24)–C(25)	1·523 (13)
C(9)–C(10)	1·583 (10)	C(25)–C(26)	1·429 (20)
C(9)–C(11)	1·537 (10)	C(25)–C(27)	1·503 (14)
C(10)–C(19)	1·516 (12)	C(28)–O(1)	1·228 (19)
C(11)–C(12)	1·501 (10)	C(28)–O(2)	1·151 (24)
C(12)–C(13)	1·515 (10)	C(28)–Cl	1·733 (17)

Table 1. *Heavy-atom coordinates* ($\times 10^4$) *and their standard deviations*

	x	*y*	*z*		*x*	*y*	*z*
C(1)	2759 (5)	3196 (9)	1609 (6)	C(17)	8186 (5)	3436 (8)	5731 (6)
C(2)	1500 (6)	3491 (10)	877 (6)	C(18)	7285 (6)	5567 (10)	4461 (6)
C(3)	881 (6)	3590 (10)	1693 (8)	C(19)	3438 (5)	5706 (10)	2077 (6)
C(4)	1371 (6)	4672 (10)	2640 (7)	C(20)	9356 (5)	3689 (9)	5677 (6)
C(5)	2615 (6)	4431 (9)	3305 (7)	C(21)	9393 (5)	3140 (13)	4542 (7)
C(6)	3069 (6)	4384 (9)	4492 (7)	C(22)	10305 (6)	3069 (9)	6757 (6)
C(7)	4306 (5)	4225 (10)	5296 (5)	C(23)	11500 (6)	3601 (10)	6959 (6)
C(8)	5061 (5)	4447 (9)	4612 (6)	C(24)	12410 (6)	2977 (9)	8058 (6)
C(9)	4567 (5)	3699 (10)	3435 (5)	C(25)	13623 (8)	3353 (15)	8244 (7)
C(10)	3352 (6)	4279 (9)	2604 (6)	C(26)	13864 (9)	4839 (15)	8398 (10)
C(11)	5408 (5)	3659 (10)	2831 (5)	C(27)	14445 (6)	2456 (13)	9217 (8)
C(12)	6588 (5)	3191 (10)	3609 (6)	C(28)	−1091 (11)	3233 (20)	892 (16)
C(13)	7103 (5)	4045 (9)	4741 (6)	O(1)	−302 (6)	4035 (9)	996 (6)
C(14)	6258 (5)	3920 (8)	5334 (5)	O(2)	−957 (9)	2031 (16)	1059 (16)
C(15)	6907 (6)	4520 (9)	6575 (6)	Cl	−2396 (2)	3999	64 (2)
C(16)	8150 (5)	4065 (9)	6881 (6)				

continued with the hydrogen parameters in a third matrix, and concluded with all the heavy-atom parameters in a single matrix and the hydrogen atoms in a second matrix. Weights throughout the refinement were assigned on the basis of counting statistics. The secondary extinction factor at the conclusion of the refinement was $3\cdot3 \times 10^{-6}$.

The final R index, $\sum||F_o| - |F_c||/\sum|F_o|$ was 5·9%, and the goodness of fit, $[\sum w(F_o^2 - F_c^2)^2/(m-s)]^{1/2}$ (where m is the number of observations and s is the number of parameters refined), was 2·9. Both data-fit criteria were based on non-zero reflections. The final positional coordinates for the non-hydrogen atoms with their standard deviations (calculated from the least-squares residuals and the inverse matrix of the final least-squares cycle) are given in Table 1, the bond distances and angles are given in Tables 2 and 3 and a stereoview of the molecule is shown in Fig. 1.*

Discussion. The steroid nucleus is normal, with no unusual bond distances or angles. The bond lengths in the tail show the apparent shortening which is characteristic of cholesterol, and is caused by the high thermal vibrations in this region. In this case, it is especially pronounced in the C(25)–C(26) bond (1·43 Å). It is interesting that the shortening of C(25)–C(27) is not nearly as extreme. The thermal vibrations of the chloroformate group are also extremely large [the isotropic B value of O(2) is 13·8 Å^2] and highly anisotropic, resulting in an extremely short C=O bond distance.

* Lists of structure factors, anisotropic temperature factors and hydrogen parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33571 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°)

C(10)–C(1)–C(2)	114·9 (0·7)	C(14)–C(13)–C(12)	105·0 (0·6)
C(3)–C(2)–C(1)	109·3 (0·6)	C(17)–C(13)–C(12)	117·1 (0·7)
C(4)–C(3)–C(2)	113·2 (0·7)	C(18)–C(13)–C(12)	110·0 (0·6)
O(1)–C(3)–C(2)	108·8 (0·7)	C(17)–C(13)–C(14)	100·3 (0·5)
O(1)–C(3)–C(4)	106·2 (0·7)	C(18)–C(13)–C(14)	112·6 (0·7)
C(5)–C(4)–C(3)	110·7 (0·7)	C(18)–C(13)–C(17)	111·0 (0·6)
C(6)–C(5)–C(4)	120·5 (0·7)	C(13)–C(14)–C(8)	115·9 (0·5)
C(10)–C(5)–C(4)	118·2 (0·6)	C(15)–C(14)–C(8)	119·2 (0·6)
C(10)–C(5)–C(6)	121·2 (0·7)	C(15)–C(14)–C(13)	103·9 (0·6)
C(7)–C(6)–C(5)	127·2 (0·8)	C(16)–C(15)–C(14)	103·9 (0·6)
C(8)–C(7)–C(6)	110·9 (0·6)	C(17)–C(16)–C(15)	106·6 (0·5)
C(9)–C(8)–C(7)	110·5 (0·6)	C(16)–C(17)–C(13)	103·5 (0·6)
C(14)–C(8)–C(7)	110·2 (0·5)	C(20)–C(17)–C(13)	119·4 (0·6)
C(14)–C(8)–C(9)	110·6 (0·6)	C(20)–C(17)–C(16)	111·2 (0·6)
C(10)–C(9)–C(8)	113·0 (0·6)	C(21)–C(20)–C(17)	112·1 (0·6)
C(11)–C(9)–C(8)	111·7 (0·6)	C(22)–C(20)–C(21)	111·7 (0·7)
C(11)–C(9)–C(10)	113·3 (0·5)	C(23)–C(22)–C(20)	114·7 (0·6)
C(5)–C(10)–C(1)	107·0 (0·6)	C(24)–C(23)–C(22)	112·6 (0·7)
C(9)–C(10)–C(1)	109·5 (0·6)	C(25)–C(24)–C(23)	115·1 (0·7)
C(19)–C(10)–C(1)	110·0 (0·6)	C(26)–C(25)–C(24)	113·7 (1·0)
C(9)–C(10)–C(5)	109·9 (0·5)	C(27)–C(25)–C(24)	109·9 (0·9)
C(19)–C(10)–C(5)	109·2 (0·7)	C(27)–C(25)–C(26)	113·5 (0·9)
C(19)–C(10)–C(9)	111·2 (0·6)	O(2)–C(28)–O(1)	121·8 (1·6)
C(12)–C(11)–C(9)	115·0 (0·5)	Cl–C(28)–O(1)	123·7 (1·2)
C(13)–C(12)–C(11)	113·0 (0·7)		

The steroid atoms O(1) and C(3) lie within the plane defined by Cl–O(2)–C(28), with the torsion angle about C(28)–O(1) being 178·8°. As a result, the chloroformate group is essentially perpendicular to the plane of the steroid nucleus with a dihedral angle between the two planes of 87·0°.

The torsion angles within the tail of the molecule are presented in Table 4. If the C(17)–C(25) distance is taken as a measure of the extension of the tail, this structure is almost fully extended (6·4 *vs* 6·9 Å for the fully extended structure). This is by virtue of the antiperiplanar conformation about C(22)–C(23) and about C(23)–C(24), which have rotational variability. It would appear that no generalizations can be made at this time concerning the most probable configuration of the tail, and its conformation will be determined by

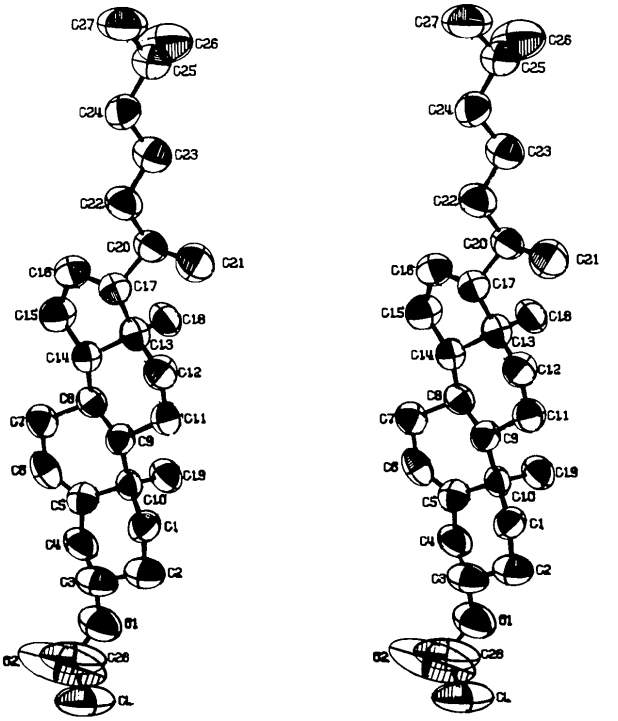

Fig. 1. Stereoscopic view (Johnson, 1965) of cholesteryl chloroformate.

Table 4. *Torsional angles* (°) *in the tail region*

φ is the torsion angle about the A–B bond in which the two atoms required to define the angle are those attached to either end of the bond.

C(13)–C(17)–C(20)–C(22)	176·7
C(13)–C(17)–C(20)–C(21)	−57·7
C(21)–C(20)–C(22)–C(23)	69·6
C(20)–C(22)–C(23)–C(24)	179·0
C(22)–C(23)–C(24)–C(25)	175·0
C(23)–C(24)–C(25)–C(26)	63·8
C(23)–C(24)–C(25)–C(27)	−168·9

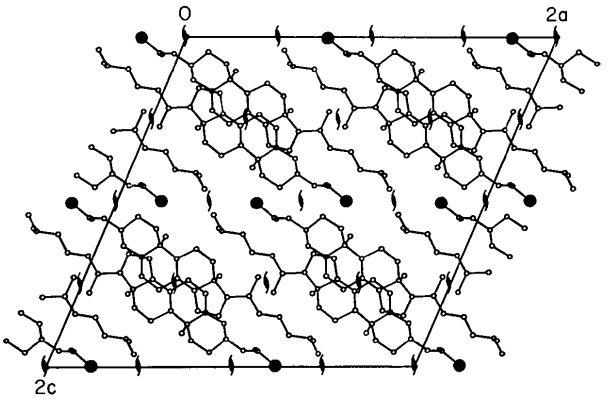

Fig. 2. Partial packing diagram of cholesteryl chloroformate.

local packing conditions. It has now been found in an extended configuration in this structure, in cholesteryl iodide (Carlisle & Crowfoot, 1945) and in 7-bromocholesteryl chloride (Burki & Nowacki, 1956) and in a relatively contracted state caused by the synclinal conformation about C(22)–C(23) [*i.e.* cholesteryl myristate molecule *A* (Craven & DeTitta, 1976) and cholesterol monohydrate molecule *A* (Craven, 1976)]. The conformation about C(23)–C(24) will of course have less of an effect upon the total length of the tail.

A packing diagram is shown in Fig. 2. The plane of the rings is parallel to the *ac* plane with the entire molecule oriented parallel to the [$\bar{1}$02] direction. Viewed down the screw axis, there is some overlap of the *B*, *C*, and *D* rings in a manner similar to the *B* form of cholesteryl iodide (Carlisle & Crowfoot, 1945). A search for intermolecular contacts found no close encounters of any kind. This appears to be one of the few reported cases of a steroid-type structure stabilized entirely by weak van der Waals forces.

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The Structure of Pyridinium 1-Amino-4-bromo-9,10-dioxoanthracene-2-sulphonate

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Abstract. $C_{19}H_{13}BrN_2O_5S$, triclinic, $P\bar{1}$, $a = 12{\cdot}493$ (3), $b = 9{\cdot}784$ (3), $c = 7{\cdot}895$ (1) Å, $\alpha = 101{\cdot}38$ (2), $\beta = 85{\cdot}14$ (2), $\gamma = 108{\cdot}61$ (2)°; $Z = 2$; $V = 895{\cdot}94$ Å^3; $D_m = 1{\cdot}692$, $D_x = 1{\cdot}719$ g cm^{-3}; $\mu r = 0{\cdot}6$. Diffractometer data collected with monochromatic Cu $K\alpha$ radiation consisted of 1628 independent reflexions with $I > 1{\cdot}96\sigma(I)$. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to the final R value of 0·033. The anion (excluding the SO_3 group) and the cation are both planar. They are linked in pairs by N—H···O hydrogen bonds (2·759 Å).

Introduction. A crystal structure analysis of the title compound was undertaken to solve some problems connected with the synthesis of one of the anthrapyridone dyes. The crystals were supplied by Dr J. Omąkowska from the Institute of Chemistry, University of Łódź.