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The Crystal and Molecular Structure of the 3,5-Dinitrobenzoate Derivative of Toxisterol₂-A

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Crystals of the 3,5-dinitrobenzoate derivative of toxisterol₂-A are monoclinic, space group $P2_1$, with $a = 6.358$ (1), $b = 21.808$ (3), $c = 12.259$ (2) Å, $\beta = 102.81$ (1)°. The structure has been refined to a residual of 0.056 with 1856 independent significant reflexions measured on an automated four-circle diffractometer. In toxisterol₂-A, which is derived from ergosterol, ring *B*, a five-membered ring, is linked to ring *C via* a spiro carbon atom at the C8 position.

Introduction

Toxisterols are substances of reputed biological activity which were originally described some fifty years ago (Westerhof & Keverling Buisman, 1956, and references therein). However, only one, toxisterol₂-A (I), was properly characterized; the subscript 2 indicates that the compound is derived from ergosterol (II) rather than cholesterol (subscript 3).

(I)   (II)
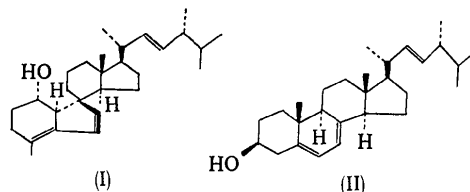
Recently the isolation, characterization and structure determination of three such compounds, toxi-

sterols$_2$-A, -B, and -C, have been reported (Barton *et al.*, 1975). The present paper reports the complete details of the X-ray crystal structure analysis of the 3,5-dinitrobenzoate derivative of toxisterol$_2$-A.

Experimental

Crystals of the 3,5-dinitrobenzoate derivative of toxisterol$_2$-A obtained from a mixture of chloroform and methanol grow as pale-yellow lathes. A crystal fragment of approximate dimensions $0.52 \times 0.35 \times 0.14$ mm parallel to a, b and c respectively and mounted along the a axis was used for the X-ray measurements. Preliminary unit-cell parameters and space-group information were obtained from precession and Weissenberg photographs taken with Cu $K\alpha$ radiation. Accu-

rate cell parameters were determined by least-squares refinement of the θ values of the Cu $K\alpha_1$ components ($\lambda = 1.5405$ Å) of 20 reflexions measured on a Hilger & Watts Y290 automated four-circle diffractometer. Intensity data were also collected on this instrument using Ni-filtered Cu radiation. The $\omega/2\theta$ step scanning technique was used with steps of $0.02°$ in ω at 1s step^{-1}. The width of scan for each reflexion as an integral number of steps was evaluated from the expression $(A + B \tan \theta)$ where A was $0.90°$ for the 183 reflexion ($\theta = 20.44°$), and B a dispersion constant ($= 0.142°$) for Cu $K\alpha$ radiation. Stationary background counts were measured at both ends of each scan for one tenth of the time taken to scan each reflexion. Three reference reflexions were measured after every 50 reflexions to monitor gradual variations in the experimental condi-

Table 1. *Atomic parameters*

Estimated standard deviations are given, where appropriate, in parentheses.

Positional ($\times 10^4$) and anisotropic thermal parameters ($U_{ij} \times 10^3$) for the non-hydrogen atoms. The expression used was
$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	3703 (15)	7347 (4)	4250 (6)	109 (6)	76 (5)	53 (4)	10 (7)	15 (7)	11 (9)
C(2)	4449 (12)	6765 (3)	4924 (6)	93 (5)	58 (4)	56 (4)	3 (6)	22 (7)	16 (7)
C(3)	5564 (10)	6922 (3)	6111 (5)	68 (4)	49 (3)	45 (3)	18 (5)	23 (5)	14 (6)
C(4)	3989 (10)	7222 (3)	6689 (5)	54 (3)	48 (3)	50 (3)	0 (5)	11 (5)	18 (5)
C(5)	2829 (11)	7742 (3)	5993 (6)	63 (4)	55 (3)	66 (4)	−4 (6)	3 (6)	10 (6)
C(6)	2152 (11)	8147 (3)	6781 (6)	70 (4)	62 (4)	71 (4)	22 (7)	15 (7)	31 (7)
C(7)	3078 (10)	8013 (3)	7837 (6)	64 (4)	46 (3)	68 (4)	−5 (6)	31 (6)	19 (6)
C(8)	4746 (9)	7497 (3)	7895 (5)	44 (3)	40 (3)	55 (3)	−13 (5)	19 (5)	6 (5)
C(9)	7042 (10)	7758 (3)	8101 (5)	58 (4)	54 (3)	55 (3)	−5 (6)	35 (5)	−26 (6)
C(10)	2654 (13)	7797 (4)	4893 (6)	85 (5)	65 (4)	67 (4)	21 (8)	−23 (7)	7 (7)
C(11)	7886 (10)	7978 (3)	9289 (5)	56 (4)	56 (3)	67 (4)	−18 (6)	25 (6)	−26 (6)
C(12)	7910 (9)	7463 (3)	10151 (5)	43 (3)	60 (3)	61 (4)	−17 (6)	12 (5)	−15 (5)
C(13)	5640 (8)	7185 (3)	10036 (5)	39 (3)	47 (3)	53 (3)	−7 (5)	25 (5)	−1 (5)
C(14)	4786 (9)	7001 (2)	8805 (5)	49 (3)	37 (3)	52 (3)	−8 (5)	30 (5)	−1 (5)
C(15)	2726 (10)	6631 (3)	8810 (5)	61 (4)	56 (3)	57 (4)	−7 (6)	10 (6)	−23 (6)
C(16)	3275 (10)	6308 (3)	9960 (5)	54 (3)	51 (3)	55 (3)	−12 (5)	22 (5)	−19 (5)
C(17)	5524 (9)	6550 (3)	10573 (5)	45 (3)	51 (3)	53 (3)	−8 (5)	28 (5)	6 (5)
C(18)	4200 (10)	7640 (3)	10500 (5)	49 (3)	59 (4)	68 (4)	−18 (6)	25 (6)	0 (5)
C(19)	1582 (18)	8327 (4)	4206 (8)	138 (9)	76 (5)	93 (6)	42 (9)	−24 (11)	64 (11)
C(20)	5854 (10)	6472 (3)	11858 (5)	61 (4)	65 (4)	54 (3)	−3 (6)	21 (6)	−1 (6)
C(21)	8025 (13)	6710 (5)	12516 (6)	87 (5)	110 (6)	59 (4)	7 (8)	11 (7)	−29 (9)
C(22)	5581 (11)	5802 (3)	12105 (5)	69 (4)	64 (4)	51 (3)	19 (6)	28 (6)	21 (7)
C(23)	4019 (11)	5553 (3)	12473 (6)	71 (4)	66 (4)	60 (4)	5 (6)	39 (6)	−4 (7)
C(24)	3706 (14)	4883 (4)	12625 (7)	105 (6)	62 (4)	76 (5)	15 (7)	41 (9)	−18 (8)
C(25)	3635 (16)	4714 (4)	13817 (8)	103 (7)	86 (6)	96 (6)	24 (10)	67 (11)	4 (10)
C(26)	5712 (21)	4882 (6)	14616 (9)	143 (10)	121 (8)	111 (8)	67 (13)	17 (14)	−43 (14)
C(27)	1618 (32)	4937 (8)	14086 (12)	251 (17)	173 (13)	120 (9)	42 (19)	122 (21)	37 (26)
C(28)	1726 (22)	4662 (5)	11750 (9)	174 (11)	91 (7)	103 (7)	−15 (12)	17 (14)	−84 (14)
C(31)	8582 (11)	5521 (3)	7276 (5)	64 (4)	45 (3)	47 (3)	−7 (5)	−1 (6)	8 (6)
C(32)	7420 (11)	5345 (3)	8063 (5)	73 (4)	47 (3)	60 (4)	−15 (6)	25 (6)	−7 (6)
C(33)	7981 (11)	4805 (3)	8657 (6)	71 (4)	41 (3)	64 (4)	0 (6)	−5 (6)	−2 (6)
C(34)	9635 (13)	4439 (3)	8513 (6)	79 (5)	53 (4)	61 (4)	1 (6)	−22 (7)	5 (7)
C(35)	10761 (11)	4621 (3)	7724 (6)	61 (4)	50 (4)	68 (4)	−19 (6)	−20 (6)	29 (6)
C(36)	10282 (10)	5153 (3)	7114 (6)	63 (4)	58 (4)	57 (4)	−14 (6)	3 (6)	13 (6)
C(37)	8091 (10)	6091 (3)	6598 (5)	56 (4)	52 (3)	50 (3)	−16 (6)	20 (6)	−3 (6)
N(38)	6731 (13)	4620 (3)	9474 (5)	111 (5)	49 (3)	65 (3)	25 (6)	24 (7)	−30 (7)
N(39)	12533 (12)	4231 (4)	7545 (6)	80 (5)	91 (5)	81 (5)	−32 (8)	10 (7)	40 (8)
O(310)	13612 (12)	4422 (3)	6927 (6)	103 (5)	112 (5)	114 (5)	−20 (8)	58 (8)	100 (8)
O(311)	12777 (12)	3738 (3)	8019 (6)	137 (6)	74 (4)	129 (5)	24 (7)	14 (8)	107 (7)
O(312)	9201 (8)	6277 (2)	5996 (4)	77 (3)	69 (3)	75 (3)	19 (5)	63 (5)	16 (5)
O(313)	6285 (7)	6351†	6731 (3)	71 (3)	42 (2)	56 (2)	6 (4)	41 (4)	25 (4)
O(314)	7318 (11)	4169 (3)	10024 (6)	112 (5)	87 (4)	118 (5)	85 (7)	34 (7)	−23 (7)
O(315)	5125 (12)	4909 (3)	9514 (5)	139 (5)	77 (4)	99 (4)	33 (6)	114 (8)	40 (8)

† This parameter was held constant.

Table 1 (cont.)

Calculated positional parameters ($\times 10^4$) for the hydrogen atoms. All hydrogen atoms were assigned an isotropic thermal parameter, $U = 0.10$ Å^2, in the expression exp ($-8\pi^2 U \sin^2 \theta/\lambda^2$).

	x	y	z
H(11)	2639	7230	3551
H(12)	4982	7547	4051
H(21)	5477	6537	4561
H(22)	3168	6501	4934
H(3)	6821	7200	6118
H(4)	2871	6906	6734
H(6)	1102	8490	6558
H(7)	2735	8221	8503
H(91)	7044	8112	7582
H(92)	8027	7431	7936
H(111)	6941	8318	9449
H(112)	9390	8134	9363
H(121)	8408	7634	10921
H(122)	8926	7133	10026
H(14)	5841	6689	8657
H(151)	2434	6326	8186
H(152)	1451	6908	8748
H(161)	3325	5854	9858
H(162)	2170	6410	10399
H(17)	6623	6285	10332
H(181)	4872	7733	11300
H(182)	4051	8027	10053
H(183)	2744	7454	10448
H(191)	1653	8266	3406
H(192)	40	8352	4262
H(193)	2340	8716	4491
H(20)	4690	6706	12105
H(211)	8130	6646	13334
H(212)	9217	6483	12281
H(213)	8148	7158	12364
H(22)	6733	5518	11970
H(23)	2924	5836	12672
H(24)	4990	4671	12455
H(25)	3552	4257	13831
H(261)	6955	4706	14344
H(262)	5853	5338	14662
H(263)	5708	4712	15374
H(271)	1594	4822	14873
H(272)	1537	5393	14005
H(273)	356	4746	13563
H(281)	1512	4213	11850
H(282)	417	4891	11849
H(283)	1963	4740	10982
H(32)	6204	5604	8198
H(34)	10018	4055	8959
H(36)	11145	5274	6559

tions during data collection. The intensity sums of the reference reflexions were used to scale the observed intensities by interpolation between groups of references; the maximum variation in the reference sum was 2·3%.

Intensity data were collected for the hkl and $hk\bar{l}$ reflexions over the range $0° \le \theta \le 70°$. A second set of data was collected for the $\bar{h}k l$ and $\bar{h}k\bar{l}$ reflexions over the range $0° \le \theta \le 30°$ to give a total of 4055 measurements. Averaging of the two data sets gave 3155 independent reflexions of which 2218 had $I \ge 3\sigma(I)$ and were thereby classified as significant. The overall agreement between the 714 reflexions measured more than once was 1·0%. Lorentz and polarization corrections were applied to all reflexions but no corrections were made for absorption [μ(Cu $K\alpha$) = 6·6 cm^{-1}].

Crystal data

The crystals are monoclinic with unit-cell dimensions, measured at room temperature (20 ± 1 °C), $a = 6·358$ (1), $b = 21·808$ (3), $c = 12·259$ (2) Å, $\beta = 102·81$ (1)°. There are two molecules of $C_{35}H_{46}O_6N_2$, formula weight 590·7, in the cell; the calculated density is 1·18 g cm^{-3}. The conditions limiting possible reflexions, $0k0 \ k = 2n$, indicate space group $P2_1$ (C_2^2, No. 4).

Solution and refinement of the structure

Initially, attempts were made to solve the structure with a weighted multisolution tangent refinement (Germain, Main & Woolfson, 1971) and a maximum of 360 normalized structure factors with $|E_\mathbf{h}| > 1·5$. The $|E_\mathbf{h}|$ were computed from the observed structure factors with the K-curve method (Karle & Karle, 1956). However, it was not possible to recognize even a partial structure from E maps computed with any of the sets of phases generated by the tangent refinement; typical values for the figures of merit were 1·00–1·25 for the absolute figure of merit and 20–22% for R_{Karle}.

The structure was eventually solved by using a Patterson space vector verification technique (Braun, Hornstra & Leenhouts, 1969) to locate the 3,5-dinitrobenzoate moiety; the model input coordinates were taken from the structure of ethyl 3,5-dinitrobenzoate (Hughes & Trotter, 1971). The remaining non-H atomic positions were obtained by the iterative Fourier synthesis technique using weighted coefficients (Sim, 1959) with the initial set of phases based on the position of the 3,5-dinitrobenzoate moiety. The value of R at this stage was 0·234.

Four cycles of full-matrix least-squares refinement with all atoms treated isotropically and using only 1856 of the significant reflexions further reduced R to 0·110. A difference Fourier synthesis showed diffuse electron density maxima, 0·2–0·4 e Å^{-3}, corresponding to most of the H atoms in the structure, but in subsequent calculations these atoms were placed in calculated positions assuming a C–H bond length of 1·0 Å. No attempt was made to refine the positional or thermal parameters (arbitrarily assessed as $U = 0·10$ Å^2) of the H atoms.

Further refinement, in which the non-H atoms were treated anisotropically, proceeded by a partial full-matrix technique. The overall scale factor was refined in each cycle but the number of atoms refined was restricted to 25 (225 parameters). Refinement was continued until all the positional parameter shifts were less than the corresponding estimated standard deviations; the maximum 'shift/e.s.d.' ratio for the thermal parameters was 1·15. The final values of R and R' [$= (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$] were 0·056 and 0·072 respectively. The weighting scheme $w = [1 - \exp(-a_1 \times \sin^2 \theta/\lambda^2)]/(a_2 + |F_o| + a_3|F_o|^2)$ with $a_1 = 20·0$, $a_2 = 30·0$ and $a_3 = 0·005$ was used to make the average values of $\sum w\Delta^2$ uniform when analysed in terms of batches of increasing $|F_o|$ and $\sin \theta/\lambda$. A final dif-

ference Fourier synthesis confirmed the correctness of the analysis and a set of structure factors computed for the 1299 reflexions not included in the refinement showed no significant discrepancies; the value of R for all 3155 reflexions was 0·105.

Throughout the structure factor calculations, the atomic scattering factors listed by Hanson, Herman, Lea & Skillman (1964) were used and all computations were performed on the CDC6600 computer at the University of London Computer Centre. The final atomic coordinates and thermal parameters are given in Table 1.* A satisfactory tensor analysis of the anisotropic thermal vibration parameters was obtained for all the non-H atoms.

Discussion

The crystal structure of the 3,5-dinitrobenzoate derivative of toxisterol$_2$-A consists of discrete molecules, one of which is shown by stereo drawings in Fig. 1(a) and (b). A schematic drawing of the molecule showing the

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31784 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Molecular geometry*

Torsion angles (°)

Ring A	C(1)—C(2)—C(3)—C(4)	64·1	
	C(2)—C(3)—C(4)—C(5)	−50·7	
	C(3)—C(4)—C(5)—C(10)	21·2	
	C(4)—C(5)—C(10)—C(1)	−2·5	
	C(5)—C(10)—C(1)—C(2)	14·0	
	C(10)-C(1)—C(2)—C(3)	−44·2	
Ring B	C(4)—C(5)—C(6)—C(7)	12·3	φ_2
	C(5) -C(6)-·C(7)— C(8)	4·7	φ_3
	C(6)—C(7)—C(8)—C(4)	−18·7	φ_4
	C(7)—C(8)—C(4)—C(5)	24·7	φ_0
	C(8)—C(4)—C(5)—C(6)	−23·4	φ_1
	$\varphi_m = 25·0°$, $\varDelta = 18·4°$		
Ring C	C(8)—C(9)—C(11)—C(12)	58·6	
	C(9)—C(11)-C(12)-C(13)	−57·0	
	C(11)-C(12)-C(13)-C(14)	52·4	
	C(12)-C(13)-C(14)-C(8)	−54·4	
	C(13)-C14)--C(8)—C(9)	53·5	
	C(14)-C(8)—C(9)—C(11)	−53·3	
Ring D	C(13)-C(14)-C(15)-C(16)	−32·2	φ_4
	C(14)-C(15)-C(16)-C(17)	4·2	φ_3
	C(15)-C(16)-C(17)-C(13)	25·9	φ_2
	C(16)-C(17)-C(13)-C(14)	−45·0	φ_1
	C(17)-C(13)-C(14)-C(15)	48·9	φ_0
	$\varphi_m = 50·1°$, $\varDelta = 25·1°$		
17β side-chain	C(13)-C(17)-C(20)-C(21)	−58·0	
	C(13)-C(17)-C(20)-C(22)	178·5	
	C(17)-C(20)-C(22)-C(23)	−110·7	
	C(20)-C(22)-C(23)-C(24)	175·0	
	C(22)-C(23)-C(24)-C(25)	122·0	
	C(22)-C(23)-C(24)-C(28)	−110·4	
	C(23)-C(24)-C(25)-C(26)	−60·8	
	C(23)-C(24)-C(25)-C(27)	70·8	

Table 2 (*cont.*)

Least-squares planes through atomic positions

Distances (Å) of the atoms from the planes, where appropriate, are given in parentheses. X, Y, Z refer to orthogonal coordinates obtained by the transformation:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a \sin \beta & 0 & 0 \\ 0 & b & 0 \\ a \cos \beta & 0 & c \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Plane (i): C(1), C(4), C(5) and C(10)
$0·8397X + 0·5433Y − 0·0034Z = 10·6115$
[C(1) 0·005, C(4) −0·005. C(5) 0·010,
C(10) −0·010, C(2) −0·298, C(3) 0·464,
C(19) 0·062, C(6) 0·134, C(7) 0·454, C(8) 0·711]

Plane (ii): C(5), C(6) and C(7)
$0·7543X + 0·6196Y − 0·2171Z = 10·2751$
[C(4) −0·310, C(8) 0·119]

Plane (iii): C(9), C(11), C(13) and C(14)
$0·7432X − 0·6651Y − 0·0725Z = −8·6700$
[C(9) 0·014, C(11) −0·013, C(13) 0·013,
C(14) −0·014, C(8) −0·671, C(12) 0·669]

Plane (iv): C(15), C(16) and C(17)
$0·4385X − 0·7432Y − 0·5054Z = −15·2708$
[C(13) −0·657, C(14) 0·110, C(20) −0·557]

Plane (v): C(31), C(37), O(312) and O(313)
$0·5257X + 0·5387Y + 0·6584Z = 14·3603$
[C(31) −0·002, C(37) 0·006, O(312) −0·002,
O(313) −0·002, C(3) 0·001, C(32) 0·157,
C(36) −0·169]

Plane (vi): C(31), C(32), C(33), C(34), C(35) and C(36)
$0·6346X + 0·5101Y + 0·5806Z = 13·9956$
[C(31) −0·002, C(32) 0·001, C(33) −0·002,
C(34) 0·004, C(35) −0·004, C(36) 0·003,
C(37) −0·004, O(312) 0·121, O(313) −0·182,
N(38) −0·016, O(314) 0·057, O(315) −0·167,
N(39) −0·014, O(310) 0·095, O(311) −0·149]

Dihedral angles between normals to planes (°)

Plane A	Plane B	Angle
(i)	(ii)	13·9
(i)	(v)	43·0
(ii)	(iii)	80·5
(iii)	(iv)	31·0
(v)	(vi)	7·8

labelling of the atoms and the intramolecular bond lengths and angles is given in Fig. 2. Further details of the molecular geometry are recorded in Table 2.

The environment about the spiro carbon atom C(8) is distorted. The magnitudes of the C(4)–C(8)–C(7) angle, 99·9 (5)°, in the five-membered ring B and the C(9)–C(8)–C(14) angle, 106·1 (5)°, in ring C, permit the angles C(4)–C(8)–C(9) and C(7)–C(8)–C(14) to open out to 112·3 (5) and 116·4 (5)° respectively, appreciably larger than the tetrahedral value. The former distortion minimizes non-bonded interactions between H(3) and the methylene H atoms at C(9), [H(3)–H(91)] = 2·66, H(3)–H(92) = 2·25 Å], while the latter distortion minimizes non-bonded interactions between H(4) and the methylene H atoms at C(15), [H(4)–H(151) = 2·25, H(4)–H(152) = 2·81 Å] and between H(7) and the C(18) methyl group [H(7)–C(18) = 2·73 Å]; the van der

Waals radii (Pauling, 1960) for the H atom and a methyl group are 1·2 and 2·0 Å respectively.

The conformations of the A, B, C and D rings are shown by the torsion angles and least-squares planes listed in Table 2. Ring A is constrained by the double bond between C(5) and C(10), 1·334 (10) Å, to adopt a distorted $2\alpha,3\beta$-half-chair conformation with C(2) and C(3) displaced by $-0\cdot298$ and $0\cdot464$ Å respectively out of the plane defined by the remaining ring atoms. The asymmetry parameters (Duax & Norton, 1975) show that rotational symmetry is dominant. An approximate C_2 axis intersects the C(2)–C(3) and C(5)–C(10) bonds with $\Delta C_2^{2-3}=6\cdot9$, $\Delta C_s^3=16\cdot7$ and $\Delta C_s^1=43\cdot1^\circ$. The ring junction between A and B is quasi-trans and the sum of the absolute values of the junction torsion angles is 44·6°.

Ring B, a five-membered ring containing a double bond between C(6) and C(7), 1·329 (9) Å, adopts a conformation midway between a $4\alpha,8\beta$-half-chair and a 4α-envelope. The pseudorotational phase parameters (Altona, Geise & Romers, 1968) are $\Delta = 18\cdot4^\circ$ and $\varphi_m = 25\cdot0^\circ$; the phase angle Δ for the idealized half-chair and envelope conformations is 0 and 36° respectively (these calculations are only strictly true for five-membered rings in which all the bond lengths are equal).

Ring C has a chair conformation with all six asymmetry parameters less than 4·5°. Mirror symmetry is dominant with an approximate C_s plane passing through C(11) and C(14); $\Delta C_s^{11}=1\cdot2$, $\Delta C_2^{2-11}=2\cdot7$ and $\Delta C_2^{8-9}=4\cdot1^\circ$. The magnitude of the C(8)–C(14)–C(13) bond angle, 118·0 (4)°, may result from the distortions about the spiro atom C(8) although values of 116·4 and 116·8° have been found in $2\alpha,3\beta$-dibromo-5α-cholestane and $2\alpha,3\beta$-dichloro-5α-cholestane (Geise & Romers, 1966). The C/D ring junction is trans; the sum of the absolute values of the endocyclic torsion angles involving the common C(13)–C(14) bond is 103·3°. Ring D has a conformation intermediate between the $13\beta,14\alpha$-half-chair and 13β-envelope conformations, in common with many other steroids containing D rings in which all the C atoms are sp^3 hybridized (Duax & Norton, 1975, and references therein). The pseudorotational parameters are $\Delta = 25\cdot1^\circ$ and $\varphi_m = 50\cdot1^\circ$.

The 17β side-chain lies approximately in the plane of the C and D rings. The H substituents at C(17) and C(20) are in an antiperiplanar conformation and C(22) is antiperiplanar to the C(13)–C(17) bond; the torsion angle C(13)–C(17)–C(20)–C(22) is 178·5°. C(21) is synclinal with respect to the C(13)–C(17) bond and the torsion angle C(13)–C(17)–C(20)–C(21) is $-58\cdot0^\circ$.
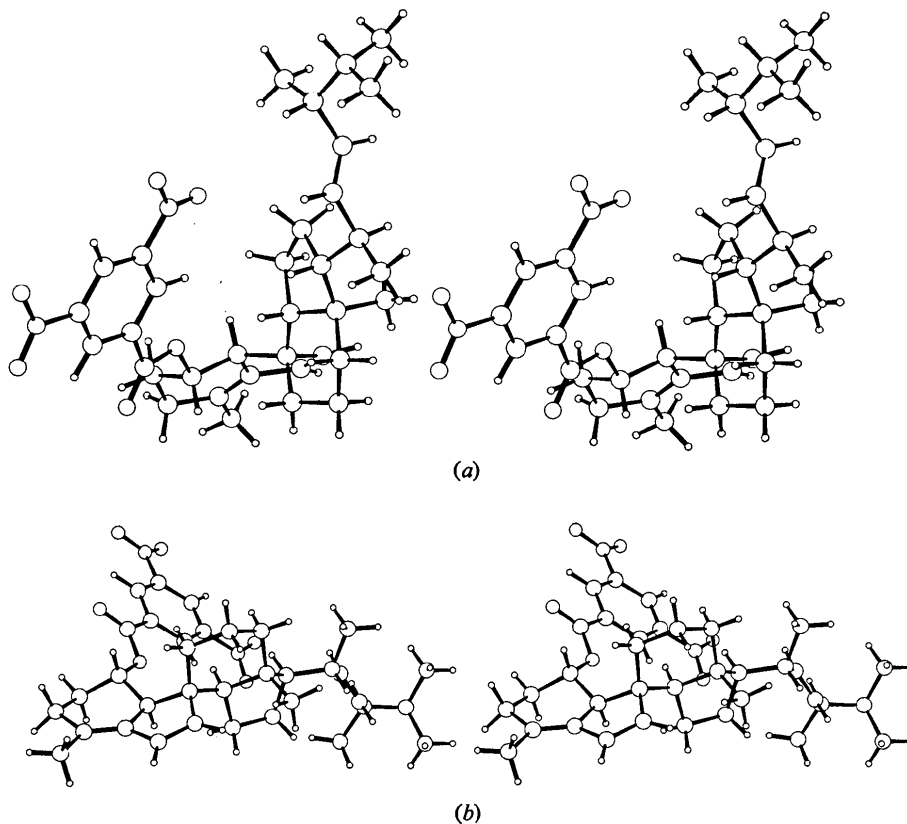

(a)

(b)

Fig. 1. Stereo drawings of the 3,5-dinitrobenzoate derivative of toxisterol$_2$-A (a) viewed along the unit-cell b axis, and (b) viewed along the bisector of the angle C(4)–C(8)–C(12).

These conformations minimize the non-bonded contacts, H(20)–H(162) 2·43, H(20)–C(18) 2·86, C(21)–C(18) 3·67, C(21)–H(121) 2·86 and C(21)–H(17) 2·79 Å. In the 3,5-dinitrobenzoxy 3β substituent the atoms

C(37), C(31), O(312) and O(313) are coplanar and this group is antiperiplanar with respect to the C(3)–C(4) bond; the torsion angle C(4)–C(3)–O(313)–O(37) = $-161\cdot3°$. O(312) is *cis* with respect to C(3) and the torsion
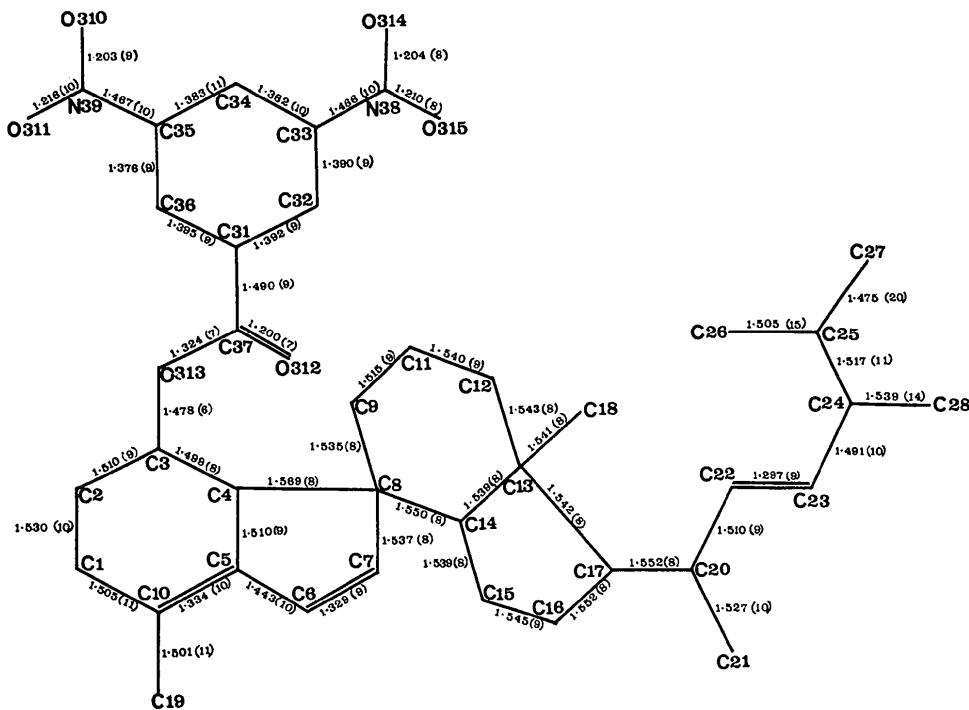
Angles not shown in figure:

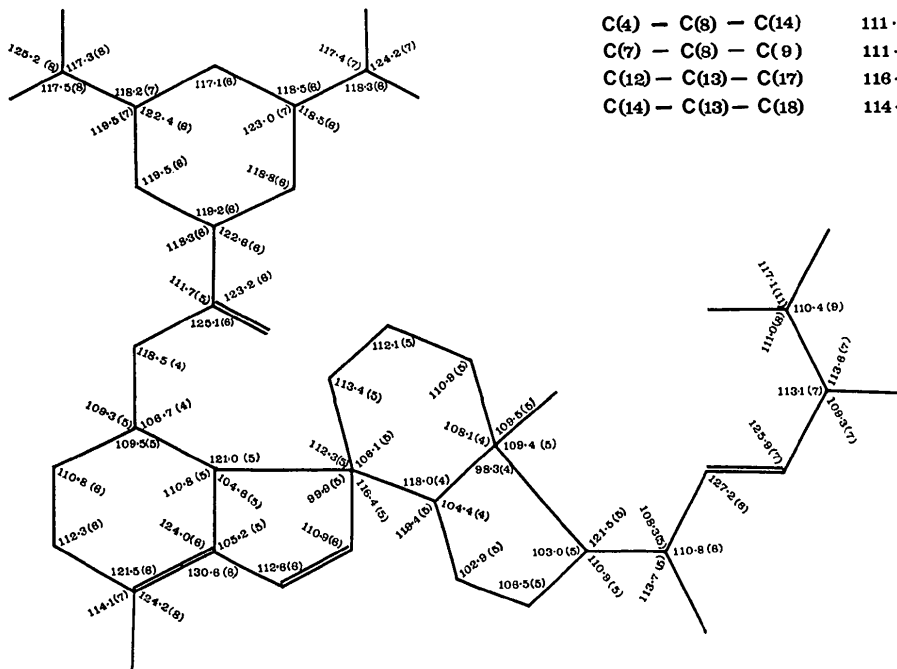|			
C(4) — C(8) — C(14)			111· 3 (4)
C(7) — C(8) — C(9)			111·0 (5)
C(12) — C(13) — C(17)			116· 5 (5)
C(14) — C(13) — C(18)			114· 8 (4)

Fig. 2. A schematic drawing of the 3,5-dinitrobenzoate derivative of toxisterol$_2$-A showing the bond lengths and angles. Estimated standard deviations are given in parentheses.
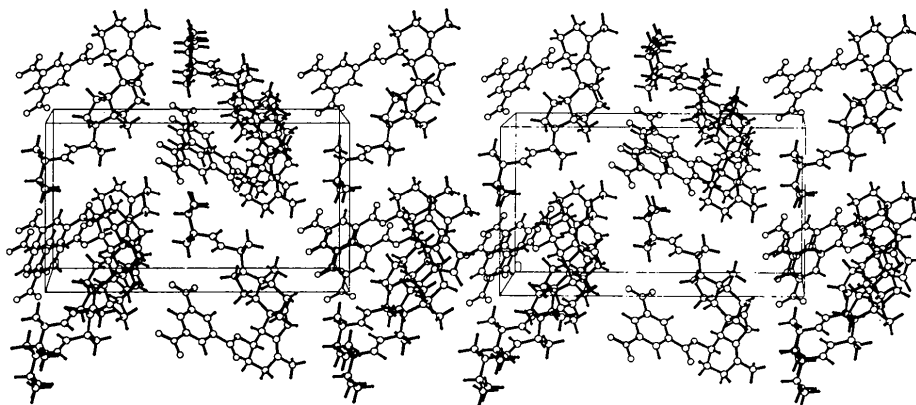
Fig. 3. The molecular packing viewed along the unit-cell a axis.

angle C(3)–O(313)–C(37)–O(312) is −1·0°. The phenyl ring is antiperiplanar to the C(3)–O(313) bond, C(3)–O(313)–C(37)–C(31) is −179·9°, and is inclined by 7·8° to the plane through C(31), C(37), O(312) and O(313); the O(312)–H(36) non-bonded separation is 2·53 Å. The nitro groups do not lie precisely in the plane of the phenyl ring but are rotated about the nitrogen–phenyl bonds thus minimizing repulsive forces between the nitro O atoms and the H atoms on the phenyl ring. The closest non-bonded contacts between the 3,5-dinitrobenzoxy substituent and the steroid skeleton are O(313)–H(14) 2·55, O(315)–H(161) 2·44, and H(32)–H(14) 2·46 Å.

The molecular packing is shown by a stereo drawing along the a axis in Fig. 3. The molecules pack in layers perpendicular to the b axis and of thickness $b/2$. There are no intermolecular contacts that are significantly shorter than the sum of the corresponding van der Waals radii.

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