Crystal and Molecular Structure of (23*R*)-23-Hydroxy-3α,5α-cycloergost-7-en-6-one

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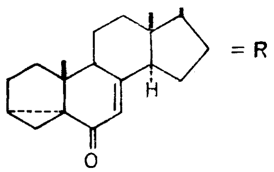
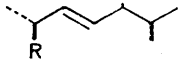
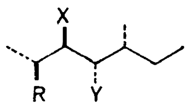
The title compound (III) crystallises in the monoclinic space group $P2_1$, with cell dimensions a = 8·048, b = 20·122, c = 7·641 Å, β = 93·92°, and Z = 2. The structure has been solved by direct methods, and refined to R 0·0845 for 1777 significant reflections, measured on a diffractometer. The configuration at C(23) is *R*, thus confirming the previous assignment. The conformation of the steroid nucleus is of some interest; whereas the BC and CD ring junctions are *trans*, AB is *cis* due to the C(3)–C(4)–C(5) cyclopropane ring. Rings A and B, and to a small extent, C, are subject to steric strains due to both the bicyclo[3.1.0]hexane ring A and the enone group in ring B. This is reflected in abnormal values for some bond lengths, angles, and dihedral angles.

INVESTIGATIONS of iodoacetoxylation and related electrophilic additions across the 22,23-bond of 3α,5α-cycloergosta-7,22-dien-6-one (I) have shown that the reactions are stereo- and regio-selective.[1] In the course of this work it became necessary to assign the stereochemistry of the acetate (II). Thus, in parallel with the chemical studies, an *X*-ray crystallographic analysis has been performed on the derived alcohol (III). Our results are in complete agreement with the stereochemical assignments of Barton *et al.*,[1] on the basis of both their chemical work and measurements of molecular rotation differences.





(I)



	X	Y
(II)	H	OAc
(III)	H	OH

A preliminary account of this work has been published.[2]

EXPERIMENTAL

Crystal Data.—Crystals of (III) were rectangular plates. $C_{28}H_{44}O_2$, M = 412·0. Monoclinic, a = 8·048(3), b = 20·122(5), c = 7·641(3) Å, β = 93·92(5)°, U = 1234·5 Å,[3] D_m = 1·11 (by flotation), Z = 2, D_c = 1·10(2), $F(000)$ = 488·0. Space group $P2_1$ (No. 4, C_2^2), from systematic absences: 0*k*0, $k = 2n$, and known optical activity. Cu-K_α radiation, λ(mean) = 1·54178 Å; μ(Cu-K_α) = 5·17 cm^{-1}.

Cell dimensions were obtained from measurements of 2θ values on a diffractometer. Intensity data were collected for a crystal of dimensions *ca.* 0·40 × 0·10 × 0·40 mm, mounted about the a^* axis, by use of a General Electric XRD 6 diffractometer, equipped with a manual goniometer, pulse-height analyser, and scintillation counter. Nickel-filtered copper radiation was used and the stationary-crystal–stationary-counter technique was employed.[3] There was no detectable crystal decomposition during the period of measurement. The intensities of 1889 independent reflections were measured, up to 2θ 120°, of which 1777 were considered to be above the 2·58σ significance level.

No correction was applied for absorption as its effects were considered to be negligible.

Structure Solution and Refinement.—The structure was

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[1] D. H. R. Barton, J. P. Poyser, and P. G. Sammes, *J.C.S. Perkin I*, 1972, 53.

[2] D. H. R. Barton, J. P. Poyser, P. G. Sammes, M. B. Hursthouse, and S. Neidle, *Chem. Comm.*, 1971, 715.

[3] R. Bonnett, M. B. Hursthouse, and S. Neidle, *J.C.S. Perkin II*, 1972, 902.

solved by direct statistical methods,[4] based on those of Karle and Karle.[5]

The data were put on an absolute scale and normalised structure factors (E values) were computed. The origin-defining phases, together with three symbolic ones, were chosen from the 196 reflections with $E > 1{\cdot}5$ (Table 1).

TABLE 1

h	E_h	Phase (millicycles)
6,0,3	3·39	0 Origin-defining
0,1,7	2·97	0
7,0,0	2·29	0
2,6,5	3·40	a (125,375) defines enantimorph
6,4,$\bar{3}$	2·29	b (125, 375, 625, 875)
5,2,$\bar{4}$	2·12	c (125, 375, 625, 875)

Application of the symbolic-addition procedure gave 75 reflections in terms of the three symbols. Subsequent tangent refinement on the 32 possible starting sets gave sets of phases with R_K values [5] ranging from 0·20 to 0·28. An E map was then computed from the set with the lowest value. This revealed 22 chemically sensible atomic positions, including the whole of the steroidal skeleton.

Least-squares refinement on this part-structure gave R 0·39. A difference-Fourier synthesis calculated from the resulting phases enabled the positions of the remaining eight atoms to be determined. Assignment of correct scattering factors to all 30 atoms, followed by four cycles of full-matrix least-squares isotropic refinement, gave R 0·168. Conversion of the temperature factors to their anisotropic (U_{ij}) equivalents, followed by five cycles of block-diagonal refinement, further reduced R to 0·131. Several of the side-chain atoms, notably C(26), C(27), and C(29), showed very considerable anisotropic motion, with U_{ij} values ranging up to 0·33. However, examination of difference-Fourier maps showed no evidence of any packing disorder for these atoms. The position of all the hydrogen atoms except those bonded to C(26), C(27), and C(29), were revealed in the difference-Fourier maps, in their expected positions. Inclusion of these in a structure-factor calculation, with each assigned an isotropic temperature factor 0·006 Å^2 greater than that of the atom to which it was bonded, followed by five cycles of refinement on the non-hydrogen parameters, gave R 0·0866. At this stage, an analysis of the observed and calculated structure factors over ranges of (F_0) and $\sin^2\theta$ suggested a Hughes-type weighting scheme [6] to be appropriate, with F^* set at 50·0. After 4 more cycles of refinement, R was 0·0845, for the 1777 observed reflections, and all parameter shifts were $< 0{\cdot}1\ \sigma$. Refinement was thus judged to be complete.

The final positional and thermal parameters for the atoms are listed in Tables 2—4. Supplementary Publication No. SUP 20650 (7 pp., 1 microfiche), lists the final observed and calculated structure factors.*

Atomic scattering factors were taken from ref. 7. All calculations were performed on the University of London CDC 6600 computer, by use of the 'X-Ray' computing system,[8] except where otherwise stated.

TABLE 2

Final positional parameters for the non-hydrogen atoms ($\times 10^4$), as fractions of the unit cell edges, with standard deviations in parentheses

Atom	x	y	z
C(1)	7173(12)	3272(6)	2361(13)
C(2)	6510(16)	3981(6)	2552(16)
C(3)	5136(13)	3952(6)	3840(14)
C(4)	5586(13)	3575(6)	5471(13)
C(5)	4650(11)	3210(5)	3908(10)
C(6)	2907(11)	3042(4)	4121(11)
C(7)	2085(10)	2606(4)	2699(11)
C(8)	2847(10)	2472(4)	1244(10)
C(9)	4628(10)	2658	939(10)
C(10)	5698(10)	2808(4)	2751(11)
C(11)	5514(10)	2174(5)	−239(11)
C(12)	4468(10)	1899(5)	−1830(11)
C(13)	2778(9)	1619(4)	−1253(10)
C(14)	1910(9)	2191(5)	−364(10)
C(15)	121(11)	1956(6)	−211(12)
C(16)	−252(11)	1534(5)	−1803(13)
C(17)	1460(10)	1451(4)	−2795(10)
C(18)	3071(12)	1011(5)	−56(11)
C(19)	6334(12)	2149(5)	3620(13)
C(20)	1559(10)	782(5)	−3739(10)
C(21)	3283(12)	692(6)	−4591(13)
C(22)	133(12)	743(5)	−5201(11)
C(23)	−97(11)	43(5)	−5968(11)
C(24)	−1207(12)	57(5)	−7718(10)
C(25)	−1235(14)	−659(6)	−8645(13)
C(26)	358(19)	−977(11)	−8808(26)
C(27)	−2188(28)	−556(8)	−10480(16)
O(28)	−790(11)	−357(4)	−4680(9)
C(29)	−3014(24)	277(7)	−7365(27)
O(30)	2062(8)	3259(4)	5259(8)

TABLE 3

Final anisotropic thermal parameters * for the non-hydrogen atoms ($\times 10^3$), with standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{12}	U_{23}
C(1)	56(6)	77(7)	71(6)	−21(6)	0(5)	−15(6)
C(2)	101(9)	75(8)	89(8)	−33(7)	10(7)	−16(7)
C(3)	70(7)	65(7)	79(7)	−6(6)	−2(5)	−20(6)
C(4)	77(7)	91(8)	59(6)	−9(6)	−1(5)	−26(6)
C(5)	57(5)	52(5)	40(5)	1(5)	0(4)	−7(4)
C(6)	60(5)	45(5)	40(5)	6(4)	−2(4)	5(4)
C(7)	43(5)	49(5)	45(5)	3(4)	3(4)	−3(4)
C(8)	45(4)	40(5)	42(5)	1(4)	−5(4)	−2(4)
C(9)	45(5)	49(5)	36(5)	0(4)	−5(3)	−3(4)
C(10)	49(5)	52(5)	46(5)	−6(4)	−10(4)	−6(4)
C(11)	41(5)	75(7)	51(5)	−7(5)	6(4)	−20(5)
C(12)	43(5)	72(6)	52(5)	−12(5)	12(4)	−18(5)
C(13)	36(4)	47(5)	36(4)	5(4)	−3(3)	−4(4)
C(14)	38(4)	57(5)	38(4)	1(4)	1(3)	−8(4)
C(15)	34(4)	99(8)	56(5)	−3(5)	0(4)	−21(6)
C(16)	43(5)	73(7)	67(6)	−3(5)	0(4)	−25(6)
C(17)	43(5)	49(5)	39(4)	−2(4)	−6(4)	0(4)
C(18)	68(6)	60(6)	42(5)	4(5)	−6(4)	3(4)
C(19)	68(6)	57(6)	69(4)	8(5)	−13(5)	−1(5)
C(20)	47(5)	51(5)	41(4)	−1(4)	−6(4)	−4(4)
C(21)	65(6)	75(7)	59(6)	2(6)	−1(5)	−19(6)
C(22)	59(5)	59(5)	44(5)	−5(5)	−13(4)	−5(5)
C(23)	64(6)	54(5)	43(5)	−1(5)	−15(4)	−7(4)
C(24)	76(6)	62(6)	32(4)	−21(5)	−12(4)	−2(4)
C(25)	89(8)	91(8)	47(5)	−28(7)	−2(5)	−10(6)
C(26)	82(10)	226(21)	228(20)	−4(12)	18(11)	−168(18)
C(27)	328(26)	112(12)	48(7)	−72(15)	−49(11)	−22(8)
O(28)	162(8)	64(5)	45(4)	−34(5)	−9(4)	6(4)
C(29)	211(19)	99(11)	236(20)	92(12)	−174(17)	−98(13)
O(30)	64(4)	76(5)	46(3)	12(4)	7(3)	−9(3)

U_{ij} Values are defined by the expression $\exp[-2\pi^2(\sum_i\sum_j U_{ij}h_ih_ja_i^*a_j^*)]$, in Å^2.

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue.

[4] (*a*) A modified version of the PHASEM program was used, M. G. B. Drew, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1969, *B*, **25**, 261; S. Neidle, D. Rogers, and M. B. Hursthouse, *J.C.S. Perkin II*, 1972, 760.

[5] I. L. Karle and J. Karle, *Acta Cryst.*, 1966, **21**, 261.

[6] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[7] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[8] A revision of 'X-Ray '67,' 'Program System for X-ray Crystallography,' ed. J. M. Stewart, University of Maryland Technical Report, 67 58, 1967.

TABLE 4

Observed, but unrefined hydrogen atom positions, as fractions of the unit-cell edges ($\times 10^3$)

Atom	*x*	*y*	*z*
H(1,1)	784	325	120
H(2,1)	800	325	340
H(3,2)	720	425	280
H(4,2)	620	425	140
H(5,3)	420	432	376
H(6,4)	700	337	540
H(7,4)	496	360	644
H(8,7)	64	253	296
H(9,9)	448	323	20
H(10,11)	664	233	−56
H(11,11)	584	177	48
H(12,12)	480	142	−260
H(13,12)	428	233	−248
H(14,14)	184	258	−128
H(15,15)	24	167	56
H(16,15)	−116	212	−16
H(17,16)	−80	217	−316
H(18,16)	−80	117	−200
H(19,17)	136	188	−356
H(20,18)	216	90	24
H(21,18)	328	110	92
H(22,18)	380	75	−60
H(23,19)	740	192	−664
H(24,19)	536	190	−600
H(25,19)	632	242	−616
H(26,20)	152	38	−292
H(27,21)	376	33	−540
H(28,21)	328	95	−508
H(29,21)	388	63	−380
H(30,22)	40	112	−620
H(31,22)	−80	82	−480
H(32,23)	80	−38	−536
H(33,24)	−40	25	−860
H(34,25)	−248	−92	−820
H(35,28)	−80	−92	−460

Mean C–H 1·00(20) Å. Each hydrogen atom was assigned a temperature factor 0·006 Å^2 greater than the isotropic temperature factor of the atom to which it was bonded. The digits after the comma in each atom designator number refer to the atom to which each hydrogen atom is bonded. The hydrogens attached to atoms C(26), C(27), and C(29), could not be located (see text).

DISCUSSION

The structure of (23*R*)-23-hydroxy-3α,5α-cycloergost-7-en-6-one (III) is shown in Figure 1.[9] Tables 5—7 give the intramolecular bond lengths, angles, and dihedral angles; the standard deviations quoted are doubtless underestimates because of the block-diagonal approximation used in the refinement.

The molecule has the angular methyl carbon atoms C(18) and C(19) both β to the steroid nucleus, and the hydroxy-group at C(23) is α (*i.e.* with an *R* configuration). This confirms the configurational assignments of Barton *et al.*[1] Both the BC and CD ring junctions are *trans*, whereas the AB is *cis*, a necessary consequence of the bicyclic nature of ring A, with the cyclopropane ring β. The detailed geometry of the molecule will be discussed further.

The mean $C(sp^3)$–$C(sp^3)$ bonds are 1·545 Å; however there are a number of significant departures from this mean (apart from the terminal bonds in the side-chain, whose atoms are severely affected by large thermal motions). The range of values is from **1·483** [C(3)–C(4)] to **1·609** Å [C(9)–C(10)]. Similar variations have been noted, *e.g.*, in the structure of a derivative of beyeran-3α-ol,[10] a strained diterpene [with a range of 1·501—1·594 Å for $C(sp^3)$–$C(3p^3)$ bonds], and in two crystalline modifications of 2,4-dibromoestradiol[11] (with a range of 1·501—1·567 Å). It is likely that these abnormalities are due to steric strains in the molecule.

TABLE 5

Intramolecular bonded distances (Å), with estimated standard deviations in parentheses

C(1)–C(2)	1·534(17)	C(12)–C(13)	1·564(12)
C(1)–C(10)	1·555(13)	C(13)–C(14)	1·530(12)
C(2)–C(3)	1·531(17)	C(13)–C(17)	1·567(10)
C(3)–C(4)	1·483(15)	C(13)–C(18)	1·536(12)
C(3)–C(5)	1·545(15)	C(14)–C(15)	1·528(12)
C(4)–C(5)	1·551(13)	C(15)–C(16)	1·559(14)
C(5)–C(6)	1·463(12)	C(16)–C(17)	1·587(12)
C(5)–C(10)	1·500(12)	C(17)–C(20)	1·531(12)
C(6)–C(7)	1·512(12)	C(20)–C(21)	1·583(13)
C(6)–O(30)	1·221(11)	C(20)–C(22)	1·548(12)
C(7)–C(8)	1·334(12)	C(22)–C(23)	1·531(14)
C(8)–C(9)	1·515(11)	C(23)–C(24)	1·557(12)
C(8)–C(14)	1·507(11)	C(23)–O(28)	1·415(12)
C(9)–C(10)	1·608(11)	C(24)–C(25)	1·605(15)
C(9)–C(11)	1·534(11)	C(24)–C(29)	1·561(22)
C(10)–C(19)	1·554(13)	C(25)–C(26)	1·446(20)
C(11)–C(12)	1·533(12)	C(25)–C(27)	1·565(17)

TABLE 6

Valence angles (deg.), with estimated standard deviations in parentheses

C(2)–C(1)–C(10)	105·4(8)	C(11)–C(12)–C(13)	110·3(7)
C(1)–C(2)–C(3)	107·3(9)	C(12)–C(13)–C(14)	106·6(7)
C(2)–C(3)–C(4)	114·5(9)	C(12)–C(13)–C(17)	115·0(6)
C(2)–C(3)–C(5)	104·7(9)	C(12)–C(13)–C(18)	110·7(7)
C(4)–C(3)–C(5)	61·6(7)	C(14)–C(13)–C(17)	101·0(6)
C(3)–C(4)–C(5)	61·2(7)	C(14)–C(13)–C(18)	113·0(7)
C(3)–C(5)–C(4)	57·2(7)	C(17)–C(13)–C(18)	110·1(7)
C(3)–C(5)–C(10)	110·3(8)	C(8)–C(14)–C(13)	115·2(6)
C(4)–C(5)–C(10)	116·5(8)	C(8)–C(14)–C(15)	118·4(7)
C(3)–C(5)–C(6)	118·4(8)	C(13)–C(14)–C(15)	105·2(7)
C(4)–C(5)–C(6)	116·3(8)	C(14)–C(15)–C(16)	103·5(7)
C(6)–C(5)–C(10)	121·5(8)	C(15)–C(16)–C(17)	106·9(7)
C(5)–C(6)–C(7)	115·5(7)	C(13)–C(17)–C(16)	102·6(6)
C(5)–C(6)–O(30)	125·5(8)	C(13)–C(17)–C(20)	119·3(7)
C(7)–C(6)–O(30)	118·8(8)	C(16)–C(17)–C(20)	111·7(7)
C(6)–C(7)–C(8)	120·8(8)	C(17)–C(20)–C(21)	111·7(7)
C(7)–C(8)–C(9)	124·9(7)	C(17)–C(20)–C(22)	109·0(7)
C(7)–C(8)–C(14)	121·5(7)	C(21)–C(20)–C(22)	108·9(7)
C(9)–C(8)–C(14)	113·2(7)	C(20)–C(22)–C(23)	112·8(8)
C(8)–C(9)–C(10)	111·8(6)	C(22)–C(23)–C(24)	111·0(8)
C(8)–C(9)–C(11)	114·6(5)	C(22)–C(23)–O(28)	107·5(7)
C(10)–C(9)–C(11)	112·5(6)	C(24)–C(23)–O(28)	112·2(8)
C(1)–C(10)–C(5)	104·9(8)	C(23)–C(24)–C(25)	110·7(8)
C(1)–C(10)–C(9)	108·6(7)	C(23)–C(24)–C(29)	110·1(10)
C(1)–C(10)–C(19)	111·1(7)	C(25)–C(24)–C(29)	110·2(9)
C(5)–C(10)–C(9)	108·7(6)	C(24)–C(25)–C(26)	116·7(11)
C(5)–C(10)–C(19)	113·0(7)	C(24)–C(25)–C(27)	105·5(9)
C(9)–C(10)–C(19)	110·4(6)	C(26)–C(25)–C(27)	111·4(13)
C(9)–C(11)–C(12)	116·2(7)		

Ring A is an example of the rare bicyclo[3.1.0]hexane system, and can be termed the *i*-steroid part of the molecule. The structures of two other similar steroids have recently been solved, *viz.*, *i*-cholesterol bromoacetate and chloroacetate,[12] and it is instructive to

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[10] J. R. Hanson, G. M. McLaughlin, and G. A. Sim, *J.C.S. Perkin II*, 1972, 1124.

[11] V. Cody, F. DeJarnette, W. Duax, and D. A. Norton, *Acta Cryst.*, 1971, *B*, **27**, 2458.

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TABLE 7

Dihedral angles ω(*ijkl*), in degrees, where ω(*ijkl*) is the angle between the projection of bond *i*–*j* and projection of bond *k*–*l* on the plane perpendicular to bond *j*–*k*. The angle is defined as positive if when viewed along *j*–*k* axis, atom *i* has to be rotated clockwise to eclipse atom *l*

i	*j*	*k*	*l*	ω(*ijkl*)
C(10)	C(1)	C(2)	C(3)	27·2
C(2)	C(1)	C(10)	C(5)	−25·8
C(2)	C(1)	C(10)	C(9)	90·2
C(2)	C(1)	C(10)	C(19)	−148·2
C(1)	C(2)	C(3)	C(4)	47·6
C(1)	C(2)	C(3)	C(5)	−17·5
C(2)	C(3)	C(4)	C(5)	−94·1
C(2)	C(3)	C(5)	C(4)	110·2
C(2)	C(3)	C(5)	C(6)	−145·3
C(2)	C(3)	C(5)	C(10)	1·1
C(4)	C(3)	C(5)	C(6)	104·6
C(4)	C(3)	C(5)	C(10)	−109·1
C(3)	C(4)	C(5)	C(6)	−108·2
C(3)	C(4)	C(5)	C(10)	98·1
C(3)	C(5)	C(6)	C(7)	122·8
C(3)	C(5)	C(6)	O(30)	−51·7
C(4)	C(5)	C(6)	C(7)	−172·0
C(4)	C(5)	C(6)	O(30)	13·5
C(10)	C(5)	C(6)	C(7)	−19·7
C(10)	C(5)	C(6)	O(30)	165·8
C(3)	C(5)	C(10)	C(1)	15·4
C(3)	C(5)	C(10)	C(9)	−100·6
C(3)	C(5)	C(10)	C(19)	136·5
C(4)	C(5)	C(10)	C(1)	−47·2
C(4)	C(5)	C(10)	C(9)	−163·2
C(4)	C(5)	C(10)	C(19)	73·9
C(6)	C(5)	C(10)	C(1)	160·5
C(6)	C(5)	C(10)	C(9)	44·5
C(6)	C(5)	C(10)	C(19)	−78·4
C(5)	C(6)	C(7)	C(8)	−9·2
O(30)	C(6)	C(7)	C(8)	165·8
C(6)	C(7)	C(8)	C(9)	7·7
C(6)	C(7)	C(8)	C(14)	−164·4
C(7)	C(8)	C(9)	C(10)	19·4
C(7)	C(8)	C(9)	C(11)	148·8
C(14)	C(8)	C(9)	C(10)	−168·0
C(14)	C(8)	C(9)	C(11)	−38·6
C(7)	C(8)	C(14)	C(11)	−135·5
C(7)	C(8)	C(14)	C(15)	−9·7
C(9)	C(8)	C(14)	C(13)	51·6
C(9)	C(8)	C(14)	C(15)	177·4
C(8)	C(9)	C(10)	C(1)	−155·7
C(8)	C(9)	C(10)	C(5)	−42·1
C(8)	C(9)	C(10)	C(19)	82·3
C(11)	C(9)	C(10)	C(1)	73·7
C(11)	C(9)	C(10)	C(5)	−172·7
C(11)	C(9)	C(10)	C(19)	−48·3
C(8)	C(9)	C(11)	C(12)	40·0
C(10)	C(9)	C(11)	C(12)	169·0
C(9)	C(11)	C(12)	C(13)	−50·2
C(11)	C(12)	C(13)	C(14)	57·7
C(11)	C(12)	C(13)	C(17)	168·7
C(11)	C(12)	C(13)	C(18)	−65·7
C(12)	C(13)	C(14)	C(8)	−60·7
C(12)	C(13)	C(14)	C(15)	167·0
C(17)	C(13)	C(14)	C(8)	178·8
C(17)	C(13)	C(14)	C(15)	46·5
C(18)	C(13)	C(14)	C(8)	61·2
C(18)	C(13)	C(14)	C(15)	−71·1
C(12)	C(13)	C(17)	C(16)	−153·1
C(12)	C(13)	C(17)	C(20)	83·0
C(14)	C(13)	C(17)	C(16)	−38·7
C(14)	C(13)	C(17)	C(20)	−162·7
C(18)	C(13)	C(17)	C(16)	81·0
C(18)	C(13)	C(17)	C(20)	−43·0
C(8)	C(14)	C(15)	C(16)	−165·1
C(13)	C(14)	C(15)	C(16)	−34·6
C(14)	C(15)	C(16)	C(17)	9·1
C(15)	C(16)	C(17)	C(13)	18·5
C(15)	C(16)	C(17)	C(20)	147·4
C(13)	C(17)	C(20)	C(21)	−59·3
C(13)	C(17)	C(20)	C(22)	−179·7
C(16)	C(17)	C(20)	C(21)	−178·7
C(16)	C(17)	C(20)	C(22)	60·9
C(17)	C(20)	C(22)	C(23)	−168·2
C(21)	C(20)	C(22)	C(23)	69·8
C(20)	C(22)	C(23)	C(24)	−165·4
C(20)	C(22)	C(23)	O(28)	71·4
C(22)	C(23)	C(24)	C(25)	172·2
C(22)	C(23)	C(24)	C(29)	−65·7
O(28)	C(23)	C(24)	C(25)	−67·6
O(28)	C(23)	C(24)	C(29)	54·5
C(23)	C(24)	C(25)	C(26)	−48·8
C(23)	C(24)	C(25)	C(27)	−172·9
C(29)	C(24)	C(25)	C(26)	−170·6
C(29)	C(24)	C(25)	C(27)	65·1

compare the geometry of ring A here with that observed in these compounds, as well as with the bicyclo[3.1.0]-hexane system in laurinterol acetate[13] and suprasterol.[14] In *i*-cholesterol chloroacetate, the cyclopropane ring has its expected[15] near-C_3 geometry, with mean bond lengths 1·514 Å; the angles C(2)–C(3)–C(4) and C(4)–C(5)–C(10) are almost equal (mean 116·4°), as are the angles C(2)–C(3)–C(5) and C(3)–C(5)–C(10) (108·2°). Laurinterol acetate also has the cyclopropane bonds equivalent in length (mean 1·50 Å); however, in this compound there are large differences between the previously mentioned pairs of bond angles, of *ca.* 8° in each case. The deviations have been attributed to steric overcrowding. The structure of suprasterol was not determined with much accuracy, and it is not possible to draw any quantitative conclusions regarding the bicyclo-part of the molecule, apart from the probable normality of the cyclopropane-ring geometry.

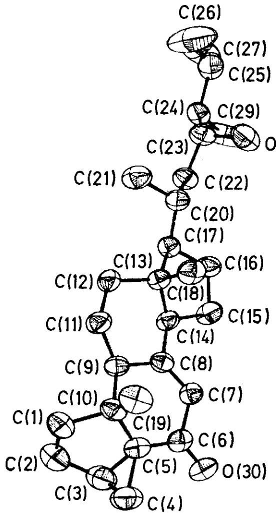

FIGURE 1 A single molecule of (III) showing the atom numbering system. The thermal ellipsoids are scaled to include 50% probability

(III) Shows considerable abnormalities both with

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[13] A. F. Cameron, G. Ferguson, and J. M. Robertson, *J. Chem. Soc.* (*B*), 1969, 692.

[14] C. P. Saunderson, *Acta Cryst.*, 1965, **19**, 187.

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respect to the cyclopropane bond lengths, and the angles made with the C(1)–C(2)–C(3)–C(5)–C(10) cyclopentane ring. The two extremes in bond length, C(3)–C(4) and C(4)–C(5), differ by 0·068 Å, which is significant at more than the 2·5σ level. Angle C(2)–C(3)–C(5) is less than C(3)–C(5)–C(10) by 5·6°. The cyclopentane ring has an envelope shape with C(1) 0·421 Å out of the C(2)–C(3)–C(5)–C(10) plane [plane (*A*1) of Table 8]. This parallels the situation in laurinterol acetate, with the corresponding atom 0·50 Å out of plane, but contrasts with *i*-cholesterol chloroacetate, where C(1) deviates by only 0·049 Å. The six atoms of ring A are thus in a boat conformation. These differences between (III) and the *i*-cholesterol are doubtless due to the increased ring-strain induced by the 7-en-6-one system in ring B of the former. Whereas a saturated ring B would be expected to be in a chair form, as indeed is observed in the *i*-cholesterol, in (III), the unsaturated system produces a very much distorted chair [plane (*B*2)]. This steric strain is further illustrated by the marked deviation of a number of angles from their normal tetrahedral values, *e.g.* C(6)–C(5)–C(10) is splayed out to 121·5°.

TABLE 8

Least-squares planes

(*a*) Deviations (Å) of atoms from the planes. Atoms not included in the calculation of a plane are italicized

Plane (*A*1): *C(1)* ***0·421***, C(2) 0·002, C(3) 0·001, C(4) 1·229, C(5) 0·001, C(10) 0·001

Plane (*A*2): C(3) 0·000, C(4) 0·000, C(5) 0·000

Plane (*B*1): C(5) −0·012, C(6) −0·041, C(7) −0·090, C(8) 0·076, O(30) 0·066

Plane (*B*2): C(5) −0·013, C(6) 0·013, *C(7)* ***−0·089***, C(8) −0·013, C(9) 0·012, *C(10)* ***0·556***

Plane (*C*1): *C(8)* ***−0·531***, C(9) −0·071, C(11) 0·071, *C(12)* ***0·667***, C(13) −0·071, C(14) 0·072

Plane (*C*2): C(8) 0·072, C(9) −0·071, C(11) −0·533, C(12) 0·068, C(13) −0·070, *C(14)* ***0·639***

Plane (*D*1): *C(13)* ***−0·485***, *C(14)* ***0·236***, C(15) 0·000, C(16) 0·000, C(17) 0·000

Plane (*D*2): *C(13)* ***−0·668***, C(14) 0·036, C(15) −0·055, C(16) 0·054, C(17) −0·035

(*b*) Equations of the planes, in direct space, in the form: $px + qy + rz = s$.

Plane	p	q	r	s
(*A*1)	5·11	−2·68	5·47	9·13
(*A*2)	7·25	−5·04	−3·17	−2·65
(*B*1)	−1·91	16·77	−3·68	−0·62
(*B*2)	−2·20	17·14	−3·26	−0·04
(*C*1)	0·26	12·29	−6·05	−3·16
(*C*2)	−3·03	14·42	−4·28	−2·18
(*D*1)	−1·23	16·84	−3·93	−0·57
(*D*2)	−1·93	15·88	−4·18	−0·96

The angle between planes (*A*1) and (*A*2) is 70°.

The B-ring may be compared with that in ecdysone.[16] This molecule bears a similarity to (III) in that both have the AB ring junction *trans*-fused, and both have the 7-en-6-one system. Ring B in ecdysone is in a half-chair conformation with C(10) as the out-of-plane atom. This is also found for (III) [plane (*B*2)], and parallels observations for a number of enone-type ring A molecules, such as 4-chlorocortisone.[17] It is apparent on examination of various parameters for the enone groups in (III) that there is some strain in ring B; thus, plane (*B*1) (Table 8) shows the group as a whole to be not particularly planar, and examination of various dihedral angles reveals the extent of the buckling (Table 7). The carbon–carbon double bond, for example, does not have coplanar substituents: the C(6)–C(7)–C(8)–C(14) dihedral angle is −164·4°. The two chromophores are at an angle of 14·2° to each other; indeed it appears that the two double bonds are relatively unconjugated since the C(sp^2)–C(sp^2) single-bond C(6)–C(7) is 1·512 Å, compared with an expected value of 1·434[4b,18] to 1·470 Å.[17]

Ring C, as expected is in a chair conformation [planes (*C*1) and (*C*2)], albeit rather flattened. This is best shown when the ring dihedral values are compared with the 'standard' ring-C values suggested for unstrained steroids,[19] as well as those found for *i*-cholesterol chloroacetate and an estradiol-urea complex[20] (Table 9). This flattening and distortion can be attributed to the influence of the ring-B enone system.

The D-ring can be considered as a half-chair [plane (*D*1)], although plane (*D*2) suggests that it approximates to a C(13) envelope. The ring can be described by the parameters ϕ_m 46·7° and Δ 11°, where ϕ_m is the maximum attainable torsion angle, and Δ gives the exact point of the five-membered ring on its pseudo-rotation circuit.[21]

TABLE 9

Dihedral angles (deg.) for the bonds in ring C, subtended in each case by the two adjacent ring bonds. For sign convention, see Table 8

	C(8)–C(9)	C(9)–C(11)	C(11)–C(12)	C(12)–C(13)	C(13)–C(14)	C(14)–C(8)
(III)	−38·6	40·0	−50·2	57·7	−50·7	51·6
'Standard' ring C[a]	−58	56	−56	58	−59	58
i-Cholesterol chloroacetate[b]	−56·5	56·9	−55·6	51·5	−56·5	59·7
Estradiol–urea complex[c]	−53·6	53·3	−54·2	54·1	−57·7	57·6

[a] Ref. 19. [b] Ref. 12. [c] Ref. 20.

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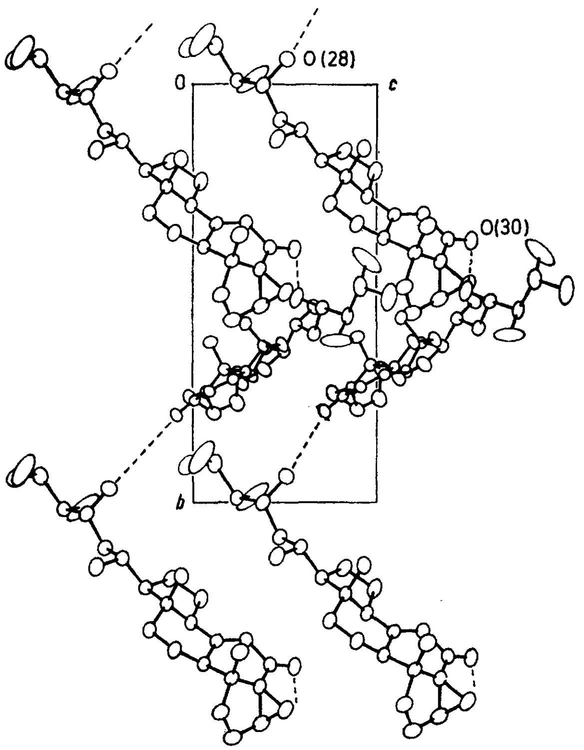

FIGURE 2 (100) Projection of the crystal structure; dashed lines represent hydrogen bonds

As observed in other studies,[12,16-21] the D-ring shape is insensitive to strains in ring A and B.

The side-chain adopts a fully extended zig-zag conformation, with all substituents reasonably well staggered with respect to each other, as expected.[22,23] The large values found for the thermal parameters of atoms C(26), C(27), and C(29) imply some considerable degree of motion, although, as previously stated, there was no observed crystallographic disorder. This contrasts with the crystal structure of *i*-cholesterol chloroacetate,[12] in which C(26) and C(27) were clearly observed to have a reasonably well-defined orientational disorder. The packing of molecules of (III) in the crystal lattice (Figure 2), with hydrogen bonds between O(28) of one molecule and O(30) of another, related by the symmetry operation $(-x, y - \frac{1}{2}, 2 - z)$, presumably imparts some degree of rigidity to the side-chain. This hydrogen bond is of length 2·989 Å.

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