# Crystal and Molecular Structure of Abieslactone, (23*R*)-3α-Methoxy-5α,9β-lanosta-7,24-diene-26,23-lactone

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Crystals of the triterpene abieslactone (III), are orthorhombic, $a = 6.633(3)$. $b = 11.761(6)$, $c = 35.009(19)$ Å, $Z = 4$, space group $P2_12_12_1$. The structure was determined by direct methods from diffractometer data, and refined by least-squares methods to a final R of 0.098 for 1860 reflexions. The analysis establishes the existence of a double bond in the 7,8- and not in the 9,11-position as previously suggested. The three six-membered rings (A, B, C) adopt the chair, sofa, and twist-boat conformations respectively; the cyclopentane ring D is a half-chair while the lactone ring is planar.

THE triterpene abieslactone occurs [1] in the bark and leaves of *Abies mariesii* Masters, a fir tree of northern Japan, and also in the North American Pacific silver fir [2] [*A. amabilis* (Dougl.) Forbes] and Noble fir [*A. procera* Rehd.]. On the basis of chemical studies [3,4] the structure (I) was advanced for abieslactone, but

(I)

(II)

(III)
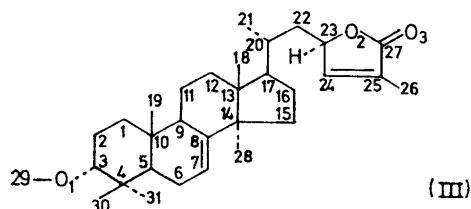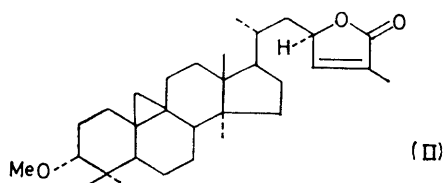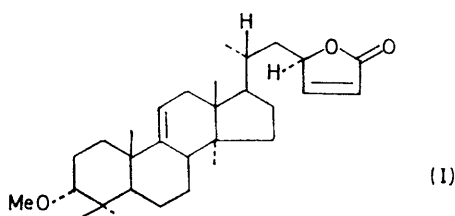
some recent chemical and crystallographic investigations [5,6] of some novel cyclopropane triterpene lactones indicated the need for possible revision of this assignment. In particular the structure and absolute stereochemistry of cyclograndisolide were established as (II), the only difference between (I) and (II) being the presence of a 9,19-cyclopropane system in (II), whereas (I) was reported to contain a $\Delta^{9,(11)}$ double bond. Com-

pounds containing the 9,19-cyclopropane system may be converted into the $\Delta^{9(11)}$ olefin with acid,[7] but application of this reaction to (II) failed to give the expected abieslactone. In parallel with further chemical investigations we have undertaken a three-dimensional X-ray analysis of abieslactone. This work has shown [8] that abieslactone contains a double bond in the 7,8-position (III; which also shows the crystallographic numbering used in this paper). We now present a full account of the crystallographic study.

EXPERIMENTAL

Crystals of abieslactone are colourless needles elongated along *a*. The Laue symmetry and space group were determined by use of oscillation and Weissenberg photographs. Cell parameters were obtained from least-squares refinement of twenty 2θ values measured on a Picker diffractometer.

Crystal Data.—$C_{31}H_{48}O_3$, $M = 478.8$. Orthorhombic, $a = 6.633(3)$, $b = 11.761(6)$, $c = 35.009(19)$ Å, $U = 2731(1)$ Å^3, $D_m = 1.13 \pm 0.03$, $Z = 4$, $D_c = 1.140$. $F(000) = 1032$. Space group $P2_12_12_1$ (D_2^4, No. 19), from absences. Cu-K_α radiation, λ(mean) $= 1.54178$ Å; μ(Cu-K_α) $= 5.56$ cm^{-1}.

Intensity data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator; the θ—2θ scan technique was employed at a speed of 2° min^{-1} in 2θ with background counting for 20 s at the scan limits. The specimen used had the dimensions *ca.* $0.30 \times 0.20 \times 0.20$ mm^3 and was mounted with *a* parallel to the φ axis of the goniostat. Of the 2011 independent reflexions with 2θ < 110° 151 had $I < 2\sigma(I)$, where $\sigma^2(I) = S + B + (dS)^2$, S is the scan count, B the background count corrected to scan time, and d is a constant included to account for instrumental instability, its value being determined as 0.02 from a study of the fluctuation of the S values of 'check' reflexions measured at regular intervals throughout the data collection period. These weak reflexions were classified as unobserved. Lorentz and polarization corrections were applied and structure amplitudes derived in the usual manner.

Structure Solution and Refinement.—Data were placed on an approximately absolute scale and $|E|$ values derived.

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[1] T. Takahashi, *J. Pharm. Soc. Japan*, 1938, **58**, 888.
[2] H. L. Hegert, N.W. Reg. Amer. Chem. Soc., Meeting, Seattle, June 1949.
[3] S. Matsunaga, J. Okada, and S. Uyeo, *Chem. Comm.*, 1965, 525.
[4] S. Uyeo, J. Okada, S. Matsunaga, and J. W. Rowe, *Tetrahedron*, 1968, **24**, 2859.

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[6] F. H. Allen and J. Trotter, *J. Chem. Soc.* (*B*), 1971, 1079.
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The $|E|$ statistics obtained are compared with the theoretical values [9] for centrosymmetric and non-centrosymmetric structures in Table 1. The structure was solved by direct

TABLE 1

$|E|$ Statistics for abieslactone

	Found	Calc. Centro.	Calc. Non-centro.
$\langle|E|\rangle$	0·854	0·798	0·886
$\langle|E^2|\rangle$	1·000	1·000	1·000
$\langle|E^2 - 1|\rangle$	0·840	0·968	0·736
$|E|>3·0$ (%)	32·50	32·00	37·00
$|E|>2·0$ (%)	3·20	5·00	1·80
$|E|>1·0$ (%)	0·20	0·30	0·01

methods using iterative application of the tangent formula; full details of the procedure used, definition of symbols, and leading references are described elsewhere.[10,11]

The 187 reflexions with $|E| > 1·60$ were used, and a Σ_2 listing computed. Some manual symbolic addition calculations were performed and three zonal reflexions (Table 2), with large $|E|$ and which entered into many Σ_2 interactions, were chosen to define the origin. The same criteria were employed in the choice of reflexions to be assigned symbolic phases (a, b, c). The manual procedure indicated that the values of a and b were close to 0 or π, and the value for c was close to $\pm\pi/2$. Since no suitable zonal reflexion of the required parity was present the enantiomorph was effectively specified by restricting the initial values of c to the range $0 < c < \pi$; the value of a was similarly restricted to lie in the range $-\pi/4 < a < \pi/4$ since the indications that $a \sim 0$ considerably outweighed those for $a \sim \pi$. The starting set, together with the final refined values of a, b, c, is listed in Table 2.

TABLE 2

Starting set of reflexions, together with final refined values for the symbolic phases

h	k	l		$\phi(h)$ initial	$\phi(h)$ final
0	9	13		$\pi/2$	Fixed for origin definition
3	0	3		$\pi/2$	
0	7	20		$\pi/2$	
1	1	1	a	125, 875 mc *	3 mc ($\sim$0)
1	6	1	b	125, 375, 625, 875 mc	-337 mc (ca. $-\pi$)
2	5	3	c	125, 375 mc	-282 mc (ca. $-\pi/2$)°

* 1000 mc = 2π = 360°.

In the tangent formula refinement procedure [10,11] the first 60 reflexions (in decreasing order of $|E|$) were refined for 7 cycles, the first 110 for the next 8 cycles, and all 187 data were included in the final 10 cycles. The values of $|E|_{min}$, t_{min}, and α_{min} [10,11] were set at 1·90, 0·25, and 2·00. This run produced a phase set with an R_{Karle} value of 0·237 which refined to 0·224 after 5 extra cycles. The strongest 40 peaks in the resultant E-map were located automatically and their interpolated co-ordinates input to a computer program (written by W. D. S. M.) which utilizes the space-group symmetry and a maximum bond-length value (1·8 Å) to assemble a unique bonded fragment(s); the assembled

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies.

[9] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Cryst.*, 1965, **19**, 713.

information is then plotted on-line. All atoms, except for the methyl carbon of the methoxy-group and one of the methyl carbons at C(4), were immediately located: of the highest 34 peaks only two were spurious.

One cycle of full-matrix least-squares refinement of these 32 atomic positions, together with isotropic thermal parameters and all weights set to unity, reduced R from 0·309 to 0·227. The two remaining methyl carbon atoms were located in an electron-density synthesis and included in the least-squares calculations. A further two cycles reduced R to 0·122. An analysis of the data indicated that fairly constant values of $w(|F_o - F_c|)^2$ over ranges of $|F_c|$ could be obtained by use of the weighting scheme due to Hughes [12] where $w = 1$ for $F_o < F^*$ and $w = F^*/F_o$ for $F_o > F^*$, with F^* set at 10·5 on an absolute scale. Anisotropic temperature factors of the form: $f = f_o \cdot \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$ were ascribed to each atom and, because of space limitations in the least-squares program (max. no. of variables 234) the molecule was split into two overlapping portions for anisotropic refinement. One complete cycle reduced R to 0·098 for the observed data and 0·102 overall. The refinement was concluded at this stage since the object of the analysis was to establish the structure and stereochemistry of the molecule. A difference electron-density synthesis indicated no peaks $>0·4$ eÅ^{-3} but no attempt was made to interpret this map in terms of hydrogen atom positions. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20620 (9 pp., 1 microfiche).† An

TABLE 3

Agreement analysis over ranges of $|F_o|$ and sin θ/λ.

Range of $|F_o|$	R	Erf *	No. of planes
0·0—3·5	0·310	1·216	142
3·5—4·8	0·170	1·031	174
4·8—6·1	0·139	1·089	157
6·1—7·4	0·129	1·221	148
7·4—8·7	0·111	1·387	158
8·7—10·1	0·079	0·932	160
10·1—12·1	0·096	1·258	153
12·1—14·4	0·084	1·232	166
14·4—17·5	0·084	1·070	146
17·5—22·6	0·071	0·975	156
22·6—33·8	0·095	1·173	150
33·8 up	0·093	1·037	150
Totals	0·098	1·141	1860
Range sin θ/λ			
0·0—0·262	0·118	1·728	278
0·262—0·330	0·100	1·348	236
0·330—0·378	0·086	1·034	225
0·378—0·416	0·068	0·932	236
0·416—0·448	0·075	0·901	209
0·448—0·476	0·087	0·941	230
0·476—0·501	0·087	0·793	212
0·501—0·524	0·107	0·981	176
0·524—0·545	0·115	0·844	58
Totals	0·098	1·141	1860

* Erf is defined as: $\{[\Sigma w(|F_o| - |F_c|)^2]/(N_o - N_v)\}^{\frac{1}{2}}$ where N_o is the number of observations, and N_v is the number of variables, in the least-squares analysis.

analysis of agreement indices over various classes of reflexions is given in Table 3, while final atomic co-ordinates

[10] F. H. Allen, J. Trotter, and D. Rogers, *J. Chem. Soc.* (*B*), 1971, 166.
[11] O. Kennard, N. W. Isaacs, W. D. S. Motherwell, J. C. Coppola, D. L. Wampler, A. C. Larson, and D. G. Watson, *Proc. Roy. Soc.*, 1971, *A*, **325**, 401.
[12] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

TABLE 4

Final fractional atomic co-ordinates

Atom	x	y	z
C(1)	−0·0325(14)	0·6794(7)	−0·1475(2)
C(2)	−0·0094(16)	0·6286(8)	−0·1889(2)
C(3)	−0·1370(15)	0·6966(8)	−0·2162(3)
C(4)	−0·0811(15)	0·8216(8)	−0·2175(3)
C(5)	−0·0706(13)	0·8732(7)	−0·1761(2)
C(6)	0·0153(16)	0·9930(7)	−0·1756(3)
C(7)	−0·0012(16)	1·0459(8)	−0·1364(3)
C(8)	−0·0211(13)	0·9821(7)	−0·1053(2)
C(9)	−0·0078(13)	0·8528(7)	−0·1049(2)
C(10)	0·0377(14)	0·8015(7)	−0·1455(2)
C(11)	−0·1850(15)	0·8048(8)	−0·0822(3)
C(12)	−0·1778(16)	0·8443(8)	−0·0384(3)
C(13)	−0·0601(11)	0·9565(6)	−0·0326(2)
C(14)	−0·0958(12)	1·0350(6)	−0·0679(2)
C(15)	0·0084(14)	1·1457(7)	−0·0547(2)
C(16)	−0·0488(13)	1·1519(7)	−0·0109(2)
C(17)	−0·1297(13)	1·0340(7)	0·0006(2)
C(18)	0·1701(14)	0·9341(7)	−0·0270(2)
C(19)	0·2720(16)	0·8057(8)	−0·1494(3)
C(20)	−0·0689(13)	0·9989(7)	0·0415(2)
C(21)	−0·1438(17)	0·8785(8)	0·0526(3)
C(22)	−0·1549(14)	1·0898(7)	0·0697(2)
C(23)	−0·0934(14)	1·0700(7)	0·1115(2)
C(24)	−0·1603(14)	1·1635(7)	0·1371(2)
C(25)	0·0010(13)	1·2119(7)	0·1535(2)
C(26)	0·0131(16)	1·3110(8)	0·1808(3)
C(27)	0·1780(14)	1·1545(8)	0·1397(2)
C(28)	−0·3211(15)	1·0623(7)	−0·0729(2)
C(29)	−0·4291(18)	0·5761(9)	−0·2117(3)
C(30)	0·1171(18)	0·8310(9)	−0·2416(3)
C(31)	−0·2440(17)	0·8884(8)	−0·2404(3)
O(1)	−0·3474(11)	0·6865(5)	−0·2052(2)
O(2)	0·1227(10)	1·0713(5)	0·1142(2)
O(3)	0·3515(11)	1·1701(5)	0·1480(2)

and thermal parameters are in Tables 4 and 5. The β_{ij} values have been converted into the more useful values U_{ij} (in Å²) in Table 5.

DISCUSSION

A perspective view of the molecular structure is given in Figure 1; the correct absolute stereochemistry,
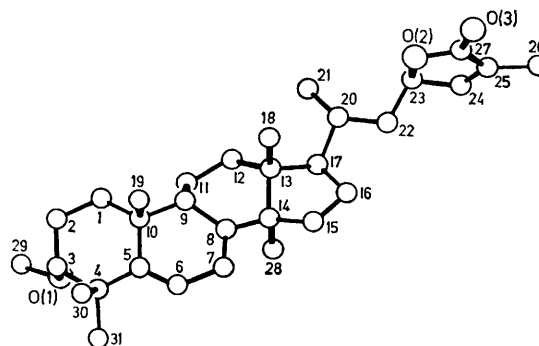

FIGURE 1 Perspective drawing of the molecular structure of abieslactone showing the absolute configuration

obtained by correlation with the known cyclo-grandisolide [5,6] is shown. The double bond is in the 7,8- and not in the suggested [3,4] 9,11-position. The chirality at position 23 is R and the compound may be identified as (23R)-3α-methoxy-5α,9β-lanosta-7,24-diene-

TABLE 5

Anisotropic thermal parameters ($U_{ij} \times 10^5$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	5878(54)	4247(46)	5278(62)	−8(45)	59(41)	584(39)
C(2)	5033(54)	5389(48)	5464(62)	47(53)	388(47)	292(41)
C(3)	3852(55)	5774(49)	5899(62)	771(49)	−612(42)	63(41)
C(4)	4906(56)	5851(53)	5216(62)	506(47)	−623(44)	−438(43)
C(5)	3379(48)	5136(42)	4719(62)	−91(38)	235(38)	−834(37)
C(6)	5568(55)	4884(48)	5091(62)	−229(49)	−729(45)	−1043(41)
C(7)	5499(56)	4590(49)	5526(62)	−1324(52)	−153(49)	−501(45)
C(8)	3963(48)	3973(42)	5029(62)	−636(43)	200(39)	−1106(37)
C(9)	3671(46)	3728(42)	5278(62)	340(44)	−1000(41)	−125(35)
C(10)	5073(52)	4240(46)	5154(62)	−356(43)	71(39)	−459(39)
C(11)	6098(59)	5585(51)	4471(62)	−1253(49)	−1094(45)	167(43)
C(12)	6337(60)	5073(55)	5650(62)	−1699(50)	−482(47)	125(45)
C(13)	3604(41)	2950(36)	5216(62)	−597(32)	35(32)	−459(31)
C(14)	4685(43)	4078(37)	4346(62)	360(35)	−106(32)	−188(31)
C(15)	7382(51)	4099(43)	6271(62)	−937(47)	−471(41)	−250(37)
C(16)	6107(48)	4071(43)	5837(62)	−798(39)	−576(36)	−21(35)
C(17)	4855(46)	3742(42)	5029(62)	−123(41)	−188(37)	−292(35)
C(18)	5035(52)	6068(47)	6085(62)	194(42)	12(39)	−334(37)
C(19)	3791(59)	6636(53)	6271(62)	585(50)	−271(44)	−250(45)
C(20)	6495(48)	5228(45)	5216(62)	316(38)	106(37)	−188(37)
C(21)	9796(61)	5732(54)	6644(62)	−700(54)	−459(49)	−1210(45)
C(22)	5811(49)	6125(43)	4471(62)	198(42)	153(39)	334(37)
C(23)	4317(51)	6979(48)	5216(62)	−198(41)	−71(39)	793(41)
C(24)	4034(50)	7330(47)	4719(62)	123(44)	−271(39)	271(39)
C(25)	4953(51)	5725(42)	4408(62)	656(45)	−153(41)	−855(35)
C(26)	8635(63)	7603(56)	6892(62)	−292(58)	118(50)	1043(47)
C(27)	4714(55)	5193(46)	5837(62)	−32(43)	−118(39)	−1252(41)
C(28)	4382(57)	7603(50)	6457(62)	1253(47)	400(43)	271(41)
C(29)	4311(70)	5725(65)	9562(62)	−648(56)	−94(54)	776(54)
C(30)	6076(70)	7729(65)	5961(62)	−1502(62)	−2506(55)	−1360(54)
C(31)	7774(61)	6167(57)	5774(62)	763(52)	−1682(51)	−1443(47)
O(1)	4291(42)	5844(39)	7265(62)	585(37)	−365(31)	1443(31)
O(2)	4705(36)	6174(32)	5774(62)	814(30)	294(28)	−25(29)
O(3)	4141(47)	8213(39)	8941(62)	−316(37)	918(34)	−400(31)

26,23-lactone,† the correct chemical representation being given in (III).

Intermolecular bonded distances and valency angles, together with their estimated standard deviations, are in Tables 6 and 7. Intra-annular torsion angles defining

Bond lengths throughout the molecule are normal. The mean of the 24 independent $C(sp^3)$–$C(sp^3)$ distances

TABLE 6

Bond lengths (Å) with estimated standard deviations in parentheses

C(1)–C(2)	1·577(10)	C(13)–C(14)	1·562(10)
C(1)–C(10)	1·511(12)	C(13)–C(17)	1·547(10)
C(2)–C(3)	1·505(13)	C(13)–C(18)	1·562(12)
C(3)–C(4)	1·517(13)	C(14)–C(15)	1·544(11)
C(3)–O(1)	1·452(12)	C(14)–C(28)	1·538(13)
C(4)–C(5)	1·574(13)	C(15)–C(16)	1·581(10)
C(4)–C(30)	1·565(15)	C(16)–C(17)	1·541(12)
C(4)–C(31)	1·558(15)	C(17)–C(20)	1·544(10)
C(5)–C(6)	1·520(12)	C(20)–C(21)	1·550(13)
C(5)–C(10)	1·542(11)	C(20)–C(22)	1·563(11)
C(6)–C(7)	1·510(14)	C(22)–C(23)	1·536(10)
C(7)–C(8)	1·331(13)	C(23)–C(24)	1·486(11)
C(8)–C(9)	1·524(12)	C(23)–O(2)	1·437(11)
C(8)–C(14)	1·530(10)	C(24)–C(25)	1·342(12)
C(9)–C(10)	1·572(10)	C(25)–C(26)	1·509(13)
C(9)–C(11)	1·526(13)	C(25)–C(27)	1·438(12)
C(10)–C(19)	1·561(14)	C(27)–O(2)	1·374(11)
C(11)–C(12)	1·604(15)	C(27)–O(3)	1·202(12)
C(12)–C(13)	1·546(12)	C(29)–O(1)	1·426(12)

the conformations of the five rings are in Table 8. The estimated standard deviations of these quantities were computed using the formula due to Huber.[13] Table 9 contains details of least-squares planes in the molecule.

The four rings of the triterpenoid nucleus are all *trans*-fused and a mean plane through this part of the molecule coincides approximately with the crystallographic *bc* plane. The nucleus is slightly convex towards the methyl groups [C(18), C(19), C(30)], and this

TABLE 7

Valency angles (deg.)

C(2)–C(1)–C(10)	112·0(6)	C(12)–C(13)–C(18)	111·5(6)
C(1)–C(2)–C(3)	109·1(7)	C(14)–C(13)–C(17)	101·6(5)
C(2)–C(3)–C(4)	113·4(8)	C(14)–C(13)–C(18)	110·3(5)
C(2)–C(3)–O(1)	109·2(7)	C(17)–C(13)–C(18)	107·2(6)
C(4)–C(3)–O(1)	108·8(7)	C(8)–C(14)–C(13)	112·8(5)
C(3)–C(4)–C(5)	110·9(7)	C(8)–C(14)–C(15)	117·0(6)
C(3)–C(4)–C(30)	106·9(7)	C(8)–C(14)–C(28)	107·6(6)
C(3)–C(4)–C(31)	109·6(7)	C(13)–C(14)–C(15)	101·1(5)
C(5)–C(4)–C(30)	115·5(7)	C(13)–C(14)–C(28)	111·1(6)
C(5)–C(4)–C(31)	108·1(7)	C(15)–C(14)–C(28)	107·1(6)
C(30)–C(4)–C(31)	105·6(8)	C(14)–C(15)–C(16)	102·8(6)
C(4)–C(5)–C(6)	112·6(7)	C(15)–C(16)–C(17)	107·2(6)
C(4)–C(5)–C(10)	116·8(6)	C(13)–C(17)–C(16)	103·2(6)
C(6)–C(5)–C(10)	108·9(7)	C(13)–C(17)–C(20)	117·5(6)
C(5)–C(6)–C(7)	111·4(7)	C(16)–C(17)–C(20)	113·2(6)
C(6)–C(7)–C(8)	121·3(7)	C(17)–C(20)–C(21)	113·1(6)
C(7)–C(8)–C(9)	124·3(7)	C(17)–C(20)–C(22)	107·9(6)
C(7)–C(8)–C(14)	120·2(7)	C(21)–C(20)–C(22)	110·4(6)
C(9)–C(8)–C(14)	114·7(6)	C(20)–C(22)–C(23)	113·6(6)
C(8)–C(9)–C(10)	112·7(6)	C(22)–C(23)–C(24)	112·5(6)
C(8)–C(9)–C(11)	109·2(6)	C(22)–C(23)–O(2)	109·1(6)
C(10)–C(9)–C(11)	118·4(7)	C(24)–C(23)–O(2)	104·5(6)
C(1)–C(10)–C(5)	110·1(6)	C(23)–C(24)–C(25)	109·6(7)
C(1)–C(10)–C(9)	110·4(6)	C(24)–C(25)–C(26)	129·9(7)
C(1)–C(10)–C(19)	109·4(7)	C(24)–C(25)–C(27)	107·9(7)
C(5)–C(10)–C(9)	109·2(6)	C(26)–C(25)–C(27)	122·2(7)
C(5)–C(10)–C(19)	112·7(6)	C(25)–C(27)–O(2)	109·6(7)
C(9)–C(10)–C(19)	105·0(7)	C(25)–C(27)–O(3)	128·9(7)
C(9)–C(11)–C(12)	111·6(7)	O(2)–C(27)–O(3)	121·5(7)
C(11)–C(12)–C(13)	112·8(7)	C(3)–O(1)–C(29)	113·4(7)
C(12)–C(13)–C(14)	108·9(6)	C(23)–O(2)–C(27)	108·5(6)
C(12)–C(13)–C(17)	116·8(6)		

is 1·549(12) Å, and only one value [C(11)–C(12) 1·604 Å] differs significantly from this. Other mean values are: $C(sp^3)$–$C(sp^2)$ 1·512(12) and $C(sp^3)$–O 1·438(10) Å, both

TABLE 8

Intra-annular torsion angles (ω°) compared with theoretical values from minimum-energy calculations

(a) Six-membered rings

Ring A			Ring B			Ring C		
Bond	$\omega_{obs.}$	$\omega_{calc.}$	Bond	$\omega_{obs.}$	$\omega_{calc.}$	Bond	$\omega_{obs.}$	$\omega_{calc.}$
1—2	−61·1(9)	−55·8	5—6	−56·1(10)	−54	8—9	37·5(9)	31
2—3	59·1(10)	55·8	6—7	21·5(13)	27	9—11	−62·9(9)	−65
3—4	−50·5(11)	−55·8	7—8	6·5(14)	0	11—12	24·7(11)	31
4—5	44·1(10)	55·8	8—9	1·4(11)	0	12—13	34·7(9)	31
5—10	−46·3(9)	−55·8	9—10	−35·9(9)	−28	13—14	−61·1(8)	−65
10—1	53·7(9)	55·8	10—5	63·3(8)	56	14—8	23·7(9)	31
	' Chair '			' Sofa '			' Twist-boat '	

(b) Five-membered rings

Ring D			Ring E		
Bond	$\omega_{obs.}$	$\omega_{calc.}$	Bond	$\omega_{obs.}$	$\omega_{calc.}$
13—14	49·3(7)	43·9	23—24	−1·3(9)	0
14—15	−38·7(7)	−34·8	24—25	0·4(9)	0
15—16	14·6(8)	12·3	25—27	0·7(10)	0
16—17	15·7(8)	15·0	27—0(2)	−1·5(9)	0
17—13	−39·7(7)	−36·4	0(2)—23	1·7(8)	0
	' Half-chair '			' Planar '	

point is further discussed later. The lactone ring E is perpendicular to the nucleus.

of which are close to the cited [14] means of 1·510 and 1·426 Å. The two double bonds in the structure are of

† This name is in accordance with IUPAC; in the arbitrary crystallographic numbering system, shown in (III) and in the Figures, the compound is a 27,23-lactone.

[13] P. Huber, Appendix to: E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, 1961, **64**, 2027.

[14] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.

TABLE 9

Equations of mean planes in the molecule, is the form $lX + mY + nZ + p = 0$ where X, Y, and Z are co-ordinates in Å. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (1):

C(6)—(9), C(14) $0.9775X + 0.1134Y + 0.1777Z - 0.4315 = 0$
  [C(6) −0.100, C(7) 0.107, C(8) 0.087, C(9) 0.002, C(14) −0.095, C(10) −0.023, C(5) −0.820]

Plane (2):

C(6)—(9) $0.9951X + 0.0325Y + 0.0931Z + 0.0798 = 0$
  [C(6) −0.012, C(7) 0.027, C(8) −0.027, C(9) 0.012, C(14) −0.378, C(10) 0.161, C(5) −0.626]

Plane (3):

C(23)—(25), $-0.0633X - 0.6441Y + 0.7618Z + 5.0967 = 0$
C(26), C(27),
O(2), O(3)
  [C(23) 0.007, C(24) 0.012, C(25) 0.011, C(26′) −0.019, C(27) −0.004, O(2) −0.028, O(3) 0.021]

Plane (4):

C(23)—(25), $-0.0564X - 0.6517Y + 0.7563Z + 5.2232 = 0$
C(27), O(2)
  [C(23) 0.009, C(24) −0.005, C(25) −0.001, C(26) −0.043, C(27) 0.007, C(2) −0.010, O(3) 0.042]

Plane (5):

C(15)—(17) $0.9265X - 0.2874Y + 0.2431Z + 4.2868 = 0$
  [C(13) 0.407, C(14) −0.379]

normal length (mean 1.337 Å) but the other geometrical features are somewhat distorted (see later).

Ring A adopts a slightly distorted chair conformation, as can be seen from Table 8 where the experimentally determined torsion angles are compared with those obtained from strain-energy minimization calculations.[15] The mean value of $|\omega|_{obs.}$ is 52.5° (cf. 55.8° for $|\omega|_{calc.}$) but there is some significant flattening about the bonds C(4)–C(5) and C(5)–C(10), with a corresponding increase in the $|\omega|$ values for the bonds on the opposite side of the ring. This distortion is due partially to the fusion of the cyclohexene ring B, but primarily to the 1,3-diaxial methyl–methyl interaction between C(19) and C(30). In the ' ideal ' chair system the vectors C(10)–C(19) and C(4)–C(30) should be parallel, in the present structure they make an angle of 27.7°, a value which is almost identical to the mean angular distortion (27.6°) for three such interactions in 3β-methoxy-21-keto-Δ¹³-serratene.[16] This angular distortion increases the methyl–methyl distance to 3.52 Å, a value which is still shorter than twice the van der Waals radius for a methyl group (r 2.0 Å).[17] It is this strong 1,3-diaxial methyl–methyl interaction, together with the weaker 1,5-inter-action C(19) · · · C(18), which gives the four-ring nucleus a slightly convex shape. For the 1,5-interaction non-parallelism of 10, 11, 14, and 9° is quoted [18] for four different molecules containing the perhydrophenanthrene skeleton. In the present structure the vectors C(10)–C(19) and C(13)–C(18) make an angle of

[15] R. Bucourt and D. Hainaut, Bull. Soc. chim. France, 1965, 1366.
[16] F. H. Allen and J. Trotter, J. Chem. Soc. (B), 1970, 721.

6.9° with each other. The mean valency angle in ring A is 112.1°, slightly larger than the predicted [15] 111.1°. As expected the intra-annular angles at the fully sub-stituted atoms C(4) and C(10) approach the tetrahedral value; the angle at C(5) is expanded to 116.8°, owing to the 1,3-interaction cited earlier, while the value at the

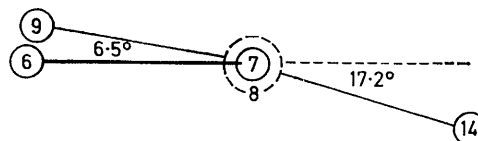

FIGURE 2   Newman projection down the double bond C(7)–C(8)
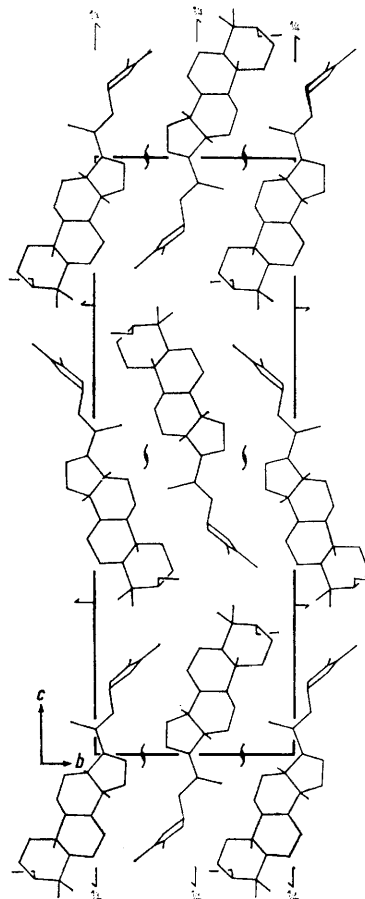

FIGURE 3   Molecular packing viewed along the a axis

unsubstituted C(2) is contracted to 109.1° to compensate for this.

The cyclohexene ring B adopts a distorted ' sofa ' or 1,2-diplanar conformation.[15] The distortion occurs at the 7,8-double-bond as can be seen from Plane (1) of Table 9, and in Figure 2, which shows the relevant Newman projection. In the ' ideal ' sofa conformation the atoms C(6)—(10) should form a plane with C(5) displaced. In the present case the best plane is that

[17] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
[18] H. J. Geise, C. Altona, and C. Romers, Tetrahedron, 1967, 23, 439.

through C(6)—(9) [Plane (2) in Table 9]; C(10) is then displaced by 0·161, and C(5) by −0·626 Å. These values compare well with those of 0·15 and −0·61 Å for the cyclohexene ring in the serratene derivative,[16] where the double bond is also under some torsional strain. As predicted [15] by the intra-annular angles at C(7) and C(8) in this ring are somewhat in excess of 120°.

The ring C adopts a 'twist-boat' conformation [19] being forced out of the energetically preferred chair form by the presence of the 7,8-double-bond, and by the fusion of the cyclopentane ring D. The agreement between the observed and the calculated torsion angles is good (Table 8). The angle C(9)–C(8)–C(14) is contracted to 114·7° and the mean angle in the ring [including that at the C(sp^2) atom] is 111·7°, close to the predicted value.[15]

The cyclopentane ring D is in the half-chair conformation with C(13) and C(14) respectively 0·407 above and 0·379 Å below the plane through C(15)—(17). Hendrickson [20] has shown that there are a number of cyclopentane conformations of equal energy corresponding to values of ω_1 between 0 and 45°. His calculated conformation for ω_1 15° corresponds closely to the values found in this investigation. In agreement with the results cited by Geise *et al.*[18] the torsion angle in this ring about the C(13)–C(14) bond falls in the range 46—50° and the intra-annular angles at C(13) and C(14) approach 100° (101·6 and 101·1°). Hendrickson [20] predicts a mean

valency angle of 104·2°; in the present structure it is 103·2°.

Ring E is planar (Table 9), so that the lactone grouping itself, C–(CO)–O–C, is also planar, as expected from the results of Mathieson and Taylor [21] who also predict that the bond length C(23)–O(2) should be *ca.* 0·1 Å longer than O(2)–C(27). Here the difference in length is 0·063 Å. The valency angles within the ring range from 104·5—109·6° and there is, therefore, some angular distortion at the C(sp^2) atoms C(24), C(25), C(27); the four extra-annular angles at C(25) and C(27) being expanded to a mean of 125·6°.

The molecular packing viewed down the *a* axis is illustrated in Figure 3. The plane of the steroid nucleus is roughly parallel to the crystallographic *bc* plane, while the lactone group is almost perpendicular to the nucleus. Intermolecular contacts correspond to van der Waals interactions, the shortest being C · · · C 3·52 and C · · · O 3·26 Å.

[19] W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Amer. Chem. Soc.*, 1961, **83**, 606.

[20] J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537; 1963, **85**, 4059.

[21] A. McL. Mathieson and J. C. Taylor, *Tetrahedron Letters*, 1961, 590.