bromide. The solution was poured on ice and extracted with ether; the ether layer was washed, dried, and evaporated, leaving XVIII which after recrystallization (twice) from hexane formed colorless plates (50 mg), mp 62.5–64°.

Anal. Calcd for C_8H_7BBrN: C, 46.23; H, 3.39; Br, 38.44. Found: C, 46.15; H, 3.48; Br, 38.22.

Acknowledgment. We are very grateful to Dr. N. F. Chamberlain[12] for the nmr measurements on I and XVIII, and to Dr. W. B. Smith and Mr. J. Roark[13] for the attempt to identify the protons in I by nitrogen decoupling.

The Structure of the Benzilic Acid Rearrangement Product of 3α,17β-Diacetoxy-11-hydroxy-12-oxo-5β-androst-9(11)-ene. An Unusual Structure with Three Five-Membered Rings *cis*-Fused

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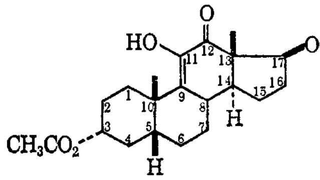
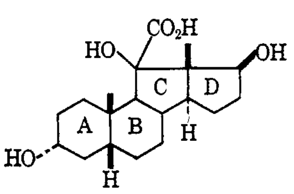
Abstract: The benzilic acid rearrangement product of 3α,17β-diacetoxy-11-hydroxy-12-oxo-5β-androst-9(11)-ene has been shown to be 3α,11α,17β-trihydroxy-11β-carboxy-13α-C-nor-5β-androstane-11β-carboxylic acid 11a,17-lactone by the results of a single-crystal X-ray analysis on a *p*-bromobenzoyl ester of the product. The heavy atom derivative crystallizes in the space group $P2_12_12_1$, with $a = 16.76 \pm 0.03$, $b = 7.05 \pm 0.01$, and $c = 19.58 \pm 0.03$ Å, and with four molecules of $C_{26}H_{31}O_5Br$ in the unit cell. The detailed conformation of the steroid derivative is discussed and compared with other related compounds. The effect of severe steric compression in the *cis*-fused five-membered rings on the rest of the molecule is noteworthy.

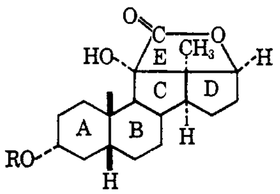
The steroid derivative 3α,17β-diacetoxy-11-hydroxy-12-oxo-5β-androst-9(11)-ene (I), when treated with base, gives a compound $C_{19}H_{28}O_4$, which can be shown to contain two hydroxyl groups and a lactone ring.[1] A benzilic acid rearrangement of I would be expected to give initially II. Lactonization of II between the carboxyl group on C(11) and the hydroxyl group at C(17) would be impossible on steric grounds with a *trans* C/D ring junction.[1] To account for the experimental facts, a retroaldol equilibrium, with epimerization at C(13 leading to a *cis* C/D ring junction prior to the benzilic acid rearrangement, was postulated and the structure IIIa was proposed for the lactone.[1] During the course of this transformation numerous keto–enol equilibria could lead to a change of stereochemistry of the B/C as well as the C/D ring junctions.



I



II



IIIa, R = H
b, R = *p*-BrC₆H₄CO

A crystal structure analysis was carried out on a *p*-bromobenzoyl ester of the rearrangement product to confirm the structural proposals and to establish the geometry of the unusual *cis*-fused five-membered ring system. A preliminary report of this work has been published.[2]

Experimental Section

A crystalline sample of the *p*-bromobenzoyl ester of the rearrangement product was kindly supplied by Dr. Paul Kurath of Abbott Laboratories, Chicago, Ill. The crystals are colorless needles, mp 250–251°.

Crystal data for $C_{26}H_{31}O_5Br$ were $M = 503.4$; orthorhombic; $a = 16.76 \pm 0.03$, $b = 7.05 \pm 0.01$, $c = 19.58 \pm 0.03$ Å; $V = 2313.5 \times 10^{-24}$ cm^3; $\rho_{\text{meas}} = 1.42$ g cm^{-3}; $Z = 4$; $\rho_{\text{calcd}} = 1.45$ g cm^{-3}; $F(000) = 1048$; systematic absences: $h00$ when $h = 2n + 1$; $0k0$, when $k = 2n + 1$; $00l$, when $l = 2n + 1$; space group $P2_12_12_1(D_2^4)$; linear absorption coefficient $\mu(\text{Cu K}\alpha) = 29.6$ cm^{-1}. The cell dimensions were determined from precession photographs using Mo Kα radiation (λ = 0.7107 Å). The density was determined by flotation in an aqueous zinc chloride solution.

Equiinclination Weissenberg photographs (Cu Kα radiation) were taken on a fine needle mounted about the *b* crystallographic axis. The levels *h*0*l* to *h*6*l* were recorded at 25°, with the X-ray generator settings at 35 kV and 20 ma. Visual estimates gave a total of 1493 independent nonzero intensity measurements. Corrections were made for Lorentz and polarization effects, but not for absorption.

Structure Determination

The coordinates of the bromine atom were readily determined from the three Harker sections of the three-

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[1] P. Kurath, *Experientia*, **22**, 657 (1966); *J. Org. Chem.*, **32**, 3626 (1967).

[2] J. S. McKechnie and I. C. Paul, *Experientia*, **23**, 612 (1967).

Table I. Final Atomic Coordinates and Final Temperature Parameters[a]

	x	y	z	B_θ (Å^2)
C(1)	0.1486(11)	−0.022(3)	0.5518(9)	4.3(0.4)
C(2)	0.1392(12)	−0.167(3)	0.4938(8)	4.5(0.4)
C(3)	0.1335(12)	−0.053(3)	0.4263(9)	4.4(0.4)
C(4)	0.0600(10)	0.084(3)	0.4242(8)	4.0(0.4)
C(5)	0.0695(11)	0.223(3)	0.4860(9)	4.4(0.4)
C(6)	0.0015(12)	0.368(3)	0.4839(10)	4.9(0.4)
C(7)	−0.0771(10)	0.269(3)	0.5020(8)	3.8(0.4)
C(8)	−0.0714(11)	0.172(3)	0.5731(8)	3.9(0.4)
C(9)	−0.0030(10)	0.026(3)	0.5703(8)	3.2(0.3)
C(10)	0.0774(11)	0.120(3)	0.5548(9)	4.0(0.4)
C(11)	−0.0184(10)	−0.097(3)	0.6339(8)	3.3(0.3)
C(12)	0.0051(11)	−0.015(3)	0.7040(9)	4.2(0.4)
C(13)	−0.1115(11)	−0.107(3)	0.6380(9)	3.9(0.4)
C(14)	−0.1452(10)	0.038(3)	0.5873(8)	3.6(0.3)
C(15)	−0.2180(12)	0.136(3)	0.6225(10)	5.1(0.4)
C(16)	−0.1905(12)	0.152(3)	0.7003(10)	5.1(0.5)
C(17)	−0.1353(13)	−0.026(3)	0.7098(9)	4.6(0.4)
C(18)	−0.1480(12)	−0.304(3)	0.6280(10)	5.7(0.5)
C(19)	0.1037(11)	0.276(3)	0.6094(10)	5.4(0.4)
C(20)	0.1442(12)	−0.149(3)	0.3092(10)	4.7(0.4)
C(21)	0.1359(12)	−0.304(3)	0.2580(9)	4.7(0.4)
C(22)	0.0926(12)	−0.465(3)	0.2733(10)	5.0(0.4)
C(23)	0.0883(12)	−0.620(3)	0.2259(10)	5.5(0.5)
C(24)	0.1352(12)	−0.589(3)	0.1669(9)	4.8(0.4)
C(25)	0.1809(12)	−0.440(3)	0.1475(10)	5.4(0.5)
C(26)	0.1834(11)	−0.286(3)	0.1964(9)	4.8(0.5)
O(3)	0.1210(7)	−0.197(2)	0.3722(6)	4.6(0.3)
O(11)	0.0210(6)	−0.271(2)	0.6263(5)	3.9(0.2)
O(12)	0.0696(9)	−0.001(2)	0.7279(7)	6.3(0.3)
O(17)	−0.0569(8)	0.038(2)	0.7413(6)	5.3(0.3)
O(20)	0.1711(8)	0.005(2)	0.2918(7)	6.5(0.3)
Br	0.1305(2)	−0.7943(4)	0.1026(1)	b

[a] Coordinates are given as fractions of the unit cell edge with estimated standard deviations in parentheses. The origin as in "International Tables for X-Ray Crystallography." The isotropic temperature parameters (B_θ) expressed as $\exp-(B_\theta \sin^2\theta/\lambda^2)$, the anisotropic thermal parameters expressed as $\exp-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}\cdot hk + b_{23}kl + b_{13}hl)$. [b] b_{11}, 0.0079(1); b_{22}, 0.0349(7); b_{33}, 0.0041(1); b_{12}, 0.0031(6); b_{13}, −0.0017(2); b_{23}, −0.0081(4).

dimensional Patterson function. The y coordinate of the bromine atom, as determined from the Patterson map, was 0.233. A Fourier synthesis, calculated with the phases of the bromine contribution to the structure factors, contained evidence of a pseudo mirror at the plane $y = {}^1/_4$. Despite this complication, the positions of nine atoms other than bromine were identified from this Fourier map, and the addition of these atoms to two cycles of structure factor and Fourier calculations gave an electron density map from which we could identify all atoms other than hydrogen. At this point, the crystallographic R factor was 0.30. Four cycles of full-matrix, least-squares refinement[3] varying the positional and isotropic thermal parameters of all atoms, followed by an adjustment of the interzonal scale factors, gave an R factor of 0.15. All observed reflections were given unit weight and the quantity minimized was $\Sigma w||F_o| - |F_c||$.[2] Introduction and refinement of anisotropic temperature parameters for the bromine atom, together with refinement of the positional and isotropic thermal parameters of all the other atoms has given a final R factor of 0.11 on 1493 observed reflexions. No attempt was made to locate hydrogen atoms.

The scattering curves used in the present analysis were those for Br, C, and O in the compilation in "International Tables for X-Ray Crystallography."[4] The curve for bromine was corrected for the real component of anomalous dispersion.[5] The final sets of atomic coordinates and thermal parameters are given in Table I. The list of h, k_o l, F_o, F_c, and α_c is deposited with the Library of Congress.[6] The final electron density map in the region of a single molecule is shown in Figure 1.

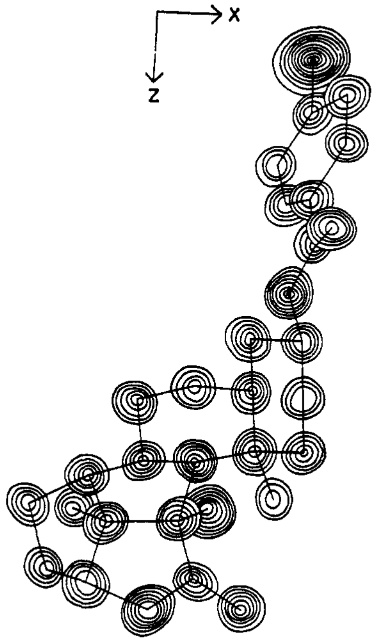

Figure 1. Superimposed contour representation of the final electron density map covering the region of a single molecule, viewed along the b axis. Contours are drawn at equal, but arbitrary intervals; the interval around the bromine atom is four times that of the other atoms.

Results and Discussion

Views of the molecule looking along the three crystallographic axes are shown in Figure 2. The structure corresponds to IIIb and verifies that the rearrangement product is 3α,11α,17β-trihydroxy-11β-carboxy-13α-C-

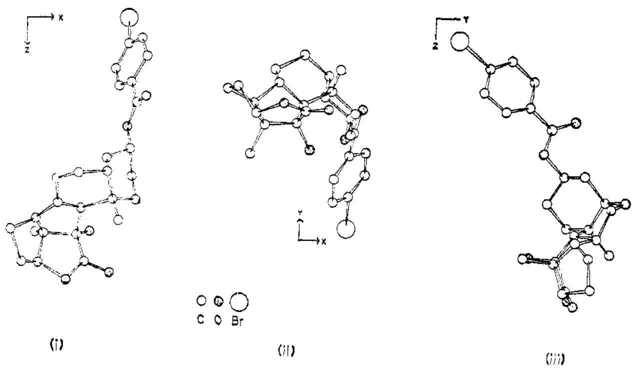

Figure 2. Views of the molecule looking along the three crystallographic axes.

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(3) Using a program written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, IUC World List of Crystallographic Computer Programs, 1962, No. 384.

(4) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, pp 201–207.

(5) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(6) These are available from American Documentation Institute, Auxiliary Publications Project, Library of Congress, Washington, D. C. 20540, Document No. 9723. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress.

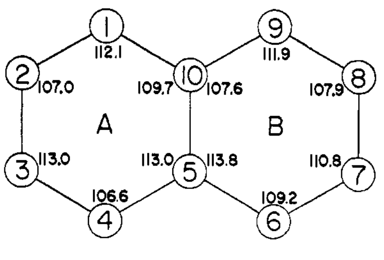


Figure 3. Diagram showing the valency angles (degrees) in rings A and B exhibiting the "reflex" effect.

nor-5β-androstane-11β-carboxylic acid 11a,17-lactone (IIIa). We find the A/B ring junction to be *cis*, the B/C *trans*, and the three five-membered rings *cis*-fused. The drawings and atomic coordinates are given to correspond to the known absolute configuration of natural steroids.[7] Bond distances and angles, uncorrected for thermal libration, are given in Tables II and III. The atom numbering used in the crystallographic discussion is shown in IV. Intramolecular contacts which define the geometry of the molecule are given in Table IV.

Table II. Final Bond Lengths and Estimated Standard Deviations in Å

C(1)–C(2)	1.54 ± 0.03	C(12)–O(12)	1.18 ± 0.02
C(1)–C(10)	1.56 ± 0.03	C(12)–O(17)	1.32 ± 0.02
C(2)–C(3)	1.55 ± 0.02	C(13)–C(14)	1.53 ± 0.02
C(3)–C(4)	1.57 ± 0.03	C(13)–C(17)	1.57 ± 0.03
C(3)–O(3)	1.48 ± 0.02	C(13)–C(18)	1.53 ± 0.03
C(4)–C(5)	1.57 ± 0.03	C(14)–C(15)	1.56 ± 0.03
C(5)–C(6)	1.53 ± 0.03	C(15)–C(16)	1.60 ± 0.03
C(5)–C(10)	1.54 ± 0.03	C(16)–C(17)	1.57 ± 0.03
C(6)–C(7)	1.53 ± 0.03	C(17)–O(17)	1.52 ± 0.02
C(7)–C(8)	1.55 ± 0.02	C(20)–C(21)	1.49 ± 0.03
C(8)–C(9)	1.54 ± 0.03	C(20)–O(3)	1.34 ± 0.02
C(8)–C(14)	1.58 ± 0.03	C(20)–O(20)	1.22 ± 0.03
C(9)–C(10)	1.53 ± 0.03	C(21)–C(22)	1.38 ± 0.03
C(9)–C(11)	1.54 ± 0.02	C(21)–C(26)	1.45 ± 0.03
C(10)–C(19)	1.60 ± 0.03	C(22)–C(23)	1.44 ± 0.03
C(11)–C(12)	1.54 ± 0.02	C(23)–C(24)	1.41 ± 0.03
C(11)–C(13)	1.56 ± 0.02	C(24)–C(25)	1.35 ± 0.03
C(11)–O(11)	1.40 ± 0.02	C(24)–Br	1.92 ± 0.02
		C(25)–C(26)	1.45 ± 0.03

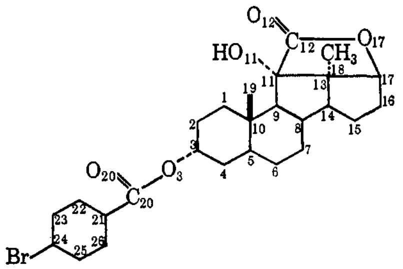
Table III. Final Bond Angles with Standard Deviations (in degrees)

C(2)C(1)C(10)	112.1 ± 1.2	C(11)C(12)O(17)	113.4 ± 0.9
C(1)C(2)C(3)	107.0 ± 1.0	O(12)C(12)O(17)	118.4 ± 1.2
C(2)C(3)C(4)	113.0 ± 0.9	C(11)C(13)C(14)	107.7 ± 1.1
C(2)C(3)O(3)	105.2 ± 1.3	C(11)C(13)C(17)	106.5 ± 1.0
C(4)C(3)O(3)	107.0 ± 0.8	C(11)C(13)C(18)	115.7 ± 1.6
C(3)C(4)C(5)	106.6 ± 1.0	C(14)C(13)C(17)	104.1 ± 1.6
C(4)C(5)C(6)	108.8 ± 1.5	C(14)C(13)C(18)	112.0 ± 1.2
C(4)C(5)C(10)	113.0 ± 0.9	C(17)C(13)C(18)	110.1 ± 1.7
C(6)C(5)C(10)	113.8 ± 1.1	C(8)C(14)C(13)	103.0 ± 1.4
C(5)C(6)C(7)	109.2 ± 1.7	C(8)C(14)C(15)	115.1 ± 1.4
C(6)C(7)C(8)	110.8 ± 1.5	C(13)C(14)C(15)	107.3 ± 1.0
C(7)C(8)C(9)	107.9 ± 1.2	C(14)C(15)C(16)	103.1 ± 1.7
C(7)C(8)C(14)	111.9 ± 1.1	C(15)C(16)C(17)	103.1 ± 1.7
C(9)C(8)C(14)	100.9 ± 0.9	C(13)C(17)C(16)	109.5 ± 1.7
C(8)C(9)C(10)	111.9 ± 1.2	C(13)C(17)O(17)	104.6 ± 1.5
C(8)C(9)C(11)	102.9 ± 1.4	C(16)C(17)O(17)	108.7 ± 1.5
C(10)C(9)C(11	123.5 ± 1.4	C(12)O(17)C(17)	111.8 ± 1.3
C(1)C(10)C(5)	109.7 ± 1.6	C(3)O(3)C(20)	116.4 ± 1.5
C(1)C(10)C(9)	113.8 ± 1.1	O(3)C(20)C(21)	114.1 ± 1.1
C(1)C(10)C(19)	104.9 ± 1.5	O(3)C(20)O(20)	126.1 ± 0.9
C(5)C(10)C(9)	107.6 ± 1.1	C(21)C(20)O(20)	119.9 ± 1.1
C(5)C(10)C(19)	106.6 ± 1.0	C(20)C(21)C(22)	120.4 ± 1.4
C(9)C(10)C(19)	114.1 ± 1.1	C(20)C(21)C(26)	116.4 ± 1.9
C(9)C(11)C(12)	117.8 ± 1.3	C(22)C(21)C(26)	122.7 ± 1.9
C(9)C(11)C(13)	103.5 ± 1.5	C(21)C(22)C(23)	120.8 ± 1.6
C(9)C(11)O(11)	109.2 ± 1.4	C(22)C(23)C(24)	112.5 ± 1.3
C(12)C(11)C(13)	103.1 ± 1.5	C(23)C(24)C(25)	131.5 ± 1.3
C(12)C(11)O(11)	107.6 ± 1.0	C(23)C(24)Br	113.4 ± 0.9
C(13)C(11)O(11)	115.9 ± 1.5	C(25)C(24)Br	115.1 ± 0.9
C(11)C(12)O(12)	128.2 ± 1.8	C(24)C(25)C(26)	114.4 ± 1.5
		C(21)C(26)C(25)	117.9 ± 1.6

Table IV. Important Intramolecular Contacts (Å)

C(2)···C(9)	3.13
C(4)···C(9)	3.08
C(4)···C(7)	3.05
C(19)···O(12)	3.09
C(18)···O(11)	2.84

The two six-membered rings, A and B, exist in the chair conformation. In ring A, the plane defined by C(1), C(3), and C(5) makes an angle of 1° 49′ with the plane through C(2), C(4), and C(10); in the ideal chair conformation these planes would be parallel. In ring B, the plane defined by C(5), C(7), and C(9) makes an angle of 1° 50′ witht he plane through C(6), C(8), and C(10). A survey[8] of X-ray results on six-membered rings in steroids indicates that the valency angles are generally 1–2° larger than tetrahedral with an accompanying decrease in dihedral angles[9] from the ideal value of 60°. Dihedral angles in rings A, B, and E are given in Table V. The valency angles in rings A and B (Figure 3) alternate about the tetrahedral value, exhibiting the "reflex-effect" described elsewhere.[10,11]



IV

One unusual feature of the present structure is the severe steric compression between atoms C(19) and O(12). Whereas Dreiding models suggest the separation would be 2.30 Å, the actual distance found is 3.09 Å. This steric repulsion is accommodated by a substantial increase of the valency angles C(9)C(10)C(19), C(10)C(9)C(11), and C(9)C(11)C(12) from the usual values, and may be the primary factor causing the alternation of valency angles in ring A; the influence of steric factors on valency angles in the six-membered rings in 5α-androstane derivatives has been recognized.[8] An interesting effect of the steric compression concerns

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(7) *Cf.* L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp 330–337.

(8) H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, 23, 439 (1967).

(9) In ref 8, the term *dihedral angle* is used to describe the projected valency angle around a single atom. In the present paper, we consider the terms *dihedral* angle and *torsional* angle synonymous; see, *e.g.*, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 6, and we routinely use the former term.

(10) B. Waegell, P. Pouzet, and G. Ourisson, *Bull. Soc. Chim. France*, 1821 (1963).

(11) L. C. G. Goaman and D. F. Grant, *Tetrahedron*, **19**, 1531 (1963).

Table V. Dihedral Angles (degrees) in Rings A, B, and E[a]

U	X	Y	V	τ
C(10)	C(1)	C(2)	C(3)	+58.9
C(1)	C(2)	C(3)	C(4)	−61.2
C(2)	C(3)	C(4)	C(5)	+59.1
C(3)	C(4)	C(5)	C(10)	−55.9
C(4)	C(5)	C(10)	C(1)	+56.0
C(5)	C(10)	C(1)	C(2)	−57.4
C(10)	C(5)	C(6)	C(7)	−56.5
C(5)	C(6)	C(7)	C(8)	+57.0
C(6)	C(7)	C(8)	C(9)	−59.4
C(7)	C(8)	C(9)	C(10)	+61.0
C(8)	C(9)	C(10)	C(5)	−58.6
C(9)	C(10)	C(5)	C(6)	+56.4
C(13)	C(11)	C(12)	O(17)	−6.5
C(11)	C(12)	O(17)	C(17)	+9.4
C(12)	O(17)	C(17)	C(13)	−8.0
O(17)	C(17)	C(13)	C(11)	+3.6
C(17)	C(13)	C(11)	C(12)	+1.1

[a] The angle is designated positive if atom U has to be rotated clockwise to eclipse atom V, when the bond is viewed down X to Y.

Table VI. Details of Planes through Various Groups of Atoms[a]

	A	B	C	D	E	F	G	H	I
C(1)	*0.00*	0.50							
C(2)	−0.53	*0.00*							
C(3)	*0.00*	0.53							
C(4)	−0.50	*0.00*							
C(5)	*0.00*	0.46	*0.00*	−0.45					
C(6)			0.46	*0.00*					
C(7)			*0.00*	−0.51					
C(8)			0.54	*0.00*					
C(9)			*0.00*	−0.52					
C(10)	−0.46	*0.00*	0.48	*0.00*					
C(11)					*0.08*	*0.00*	*−0.01*	0.07	
C(12)					*0.03*	*0.01*	−0.11	*−0.03*	
C(13)					*−0.01*	−0.21	*0.02*	*0.03*	*−0.04*
C(14)									*−0.03*
C(15)									−0.60
C(16)									*−0.01*
C(17)					*−0.08*	−0.27	*−0.02*	*−0.05*	*0.08*
O(12)					*−0.09*	*−0.01*	−0.31	−0.19	
O(17)					*0.07*	*0.00*	*0.01*	*0.04*	
Mean esd					0.06	0.01	0.02	0.04	0.03
L	0.832	0.842	0.180	0.201	−0.006	0.070	−0.085	−0.043	0.827
M	0.539	0.518	0.683	0.695	0.907	0.917	0.902	0.900	0.554
N	−0.134	−0.148	0.708	0.691	−0.420	−0.394	−0.423	−0.434	0.094
O	−0.545	0.071	−8.018	−8.350	5.914	5.534	5.824	6.052	0.749

[a] The equations of the planes are expressed as $LX + MY + NZ + O = 0$. Distances involving atoms included in the plane calculations are italicized.

the external angles at the fusion of rings B and C. In almost all steroids examined recently by X-ray methods,[12] the two external angles at the fusion of rings C and D are considerably greater than tetrahedral (the values range from 114 to 121°). At the B/C ring junction in IIIb, the overcrowding between C(19) and O(12) forces the C(10)C(9)C(11) angle to such a large value (123.5°) that the B/C ring fusion can be accommodated with a relatively normal C(7)C(8)C(14) external angle (111.9°).

In ring A, the largest deviation of dihedral angle from 60° involves the ring junction and bonds adjacent to it. This is consistent with the findings in other steroids.[8] The only other steroid containing a *cis* A/B ring junction and whose structure has been accurately determined by crystal structure analysis is 2β,3β,14α,22β,25-pentahydroxy-Δ^7-5β-cholestenone-6,[8,13] where the dihedral angles in rings A and B at the ring junction are 53.9 and 56.3°, respectively. 17β-Bromoacetoxy-9β,10α-androst-4-en-3-one[14] contains a *cis* B/C ring junction, and we calculate from the published coordinates that the ring junction dihedral angles are 60.4 and 48.3°, respectively.

Similar *cis*-fused five-membered ring systems have been proposed for anhydroplatynecine[15] and for triquinacene,[16] while preliminary details of an X-ray study on Ginkolide A[17] indicate the presence of three five-membered rings in a *cis*-fused configuration. In this latter example, one of the rings is a lactone, and another is a tetrahydrofuran. At present, no detailed structural information is available for Ginkolide A.

The five atoms of the lactone ring (E) and the oxygen atom of the carbonyl group approach planarity to a very first approximation (Table VI), the largest deviations being 0.08, −0.08, and −0.09 Å for C(11), C(17), and O(12), respectively. The atoms C(11), C(12), O(12), and O(17) are coplanar, with C(17) and C(13) lying 0.27 and 0.21 Å from the plane, paralleling the deviations (0.25 and 0.42 Å) found in D-glucurono-γ-lactone (V),[18] and providing another example of a nonplanar

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[12] D. A. Norton, G. Kartha, and C. T. Lu, *Acta Cryst.*, **16**, 89 (1963); 17, 77 (1964); H. J. Geise, C. Romers, and E. W. M. Rutten, *ibid.*, 20, 249 (1966); H. J. Geise and C. Romers, *ibid.*, **20**, 257 (1966); C. Romers, B. Hesper, E. van Heijkoop, and H. J. Geise, *ibid.*, **20**, 363 (1966); D. F. High and J. Kraut, *ibid.*, **21**, 88 (1966); W. E. Oberhänsli and J. M. Robertson, *Helv. Chim. Acta*, **50**, 53 (1967).

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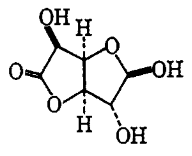
[16] R. B. Woodward, T. Fukunaga, and R. C. Kelly, *ibid.*, **86**, 3162 (1964).

[17] N. Sakabe, S. Takada, and K. Okabe, *Chem. Commun.*, 259 (1967).

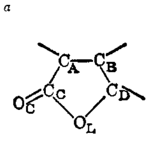
[18] G. A. Jeffrey and S. H. Kim, *ibid.*, 211 (1966); S. H. Kim, G. A. Jeffrey, R. D. Rosenstein, and P. W. R. Corfield, *Acta Cryst.*, **22**, 733 (1967).



V

lactone CC(=O)OC grouping.[19] Best plane calculations indicate that C(11), C(13), C(17), and O(17) are planar within the accuracy of the analysis (Table VI), in contrast to V and also most other γ-lactones; C(12) and O(12) lie at distances of 0.11 and 0.31 Å from this plane. In V, the carbon atom adjacent to the carbonyl group lies 0.25 Å out of the accurate plane through the other four ring atoms, whereas in IIIb, C(12), O(17), C(17), and C(13) are only approximately planar (Table VII), but C(11) lies just 0.07 Å from that best plane.

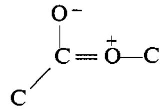
Table VII. Comparison of Dimensions in Lactone Ring with Those Found in D-Galactono-γ-lactone[20] and in D-Glucurono-γ-lactone[18, a]



	Present work	Ref 20	Ref 18
C_C–O_C	1.18	1.20	1.215
C_C–O_L	1.32	1.36	1.340
C_D–O_L	1.52	1.46	1.475
$C_AC_CO_L$	113.4	109.5	111.0
$C_AC_CO_C$	128.2	128.5	128.9
$O_LC_CO_C$	118.4	121.6	120.0
$C_CO_LC_D$	111.8	109.3	111.0
$O_LC_DC_B$	104.6	103.0	106.2
$C_DC_BC_A$	106.5	100.3	104.9
$C_BC_AC_C$	103.1	102.2	104.0

[a] Distances are in Å; angles are in degrees.

Despite the deviation of C(17) from the plane of the other four atoms of the lactone, the C(12)–O(17) bond length of 1.32 Å would indicate significant double bond character resulting from contributions of the resonance structure

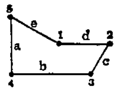


$$\overset{O^-}{\overset{|}{C}}\!=\!\overset{+}{O}\!-\!C \quad (\text{with } C/ \text{ below left})$$

Furthermore, the pattern of the bond angles in the lactone ring, with the largest values being found for C(11)-C(12)O(17) and C(12)O(17)C(17), is generally similar to that found in D-galactono-γ-lactone[20] and in V[18] (Table VII), and supports some double bond character in the C(17)O(17) bond. The internal bond angles in the lactone ring at C(11), C(13), and C(17) are generally larger than those found in most γ-lactones[19] (as exemplified by D-galactono-γ-lactone), but agree well with those found in D-glucurono-γ-lactone which implies that the increase results from the conformation imposed by the *cis*-fusion of the five-membered rings.

The conformation of the five-membered ring D (C(13), C(14), C(15), C(16), and C(17)) is best described as a distorted envelope conformation, with C(13), C(14), C(16), and C(17) lying within 0.1 Å of the best plane through these four atoms, while C(15) is 0.60 Å from this plane. The ideal envelope conformation in cyclopentane with C_s symmetry has the fifth atom lying 0.75 Å from the exact plane through the other four atoms.[21,22] The five-membered ring C (C(8), C(9), C(11), C(13), and C(14)) also adopts a distorted envelope conformation, with C(9), C(11), C(13), and C(14) being approximately planar (maximum deviations +0.07 and −0.05 Å), and with C(8) 0.67 Å from this plane. The distortions from planarity of the groups of four atoms are undoubtedly a consequence of the highly strained *cis*-fused ring system. An alternative conformational description of these two rings as distorted "half-chairs" [21] would have C(14) and C(15) lying 0.16 and −0.42 Å from the plane through C(13), C(17), and C(16) in one case, and C(8) and C(9) lying 0.47 and −0.29 Å from the plane through C(13), C(11), and C(14). Clearly, neither conformational description is fully adequate, and the rings are intermediate between the "half-chair" and "envelope" forms. The conformation of the five-membered rings can also be described in terms of the five internal dihedral angles and can be compared with the values found in a good example[23] of an ideal envelope conformation (Table VIII), where the dihedral angles are +50, −31, 0, +31, and −50° taken around the ring.

Table VIII. Comparison of the Dihedral Angles (degrees) in Rings C and D with Those Found[23] in an Ideal Envelope Conformation[a]



	Ring C	Ring D	Ref 23
a	+39.5	+36.8	+50.2
b	−17.6	−26.7	−31.1
c	−11.0	+6.3	−0.2
d	+36.1	+15.7	+31.2
e	−47.1	−31.0	−50.5
Atom 5	C(8)	C(15)	

[a] A conformation which has atom 5 lying 0.75 Å out of the plane through the other four atoms.

Another significant intramolecular steric effect involves C(18) and O(11). From an undistorted model the distance between these atoms is 2.5 Å, whereas that found in the present analysis is 2.84 Å, resulting in an increase of the bond angles C(13)C(11)O(11) and C(11)C(13)C(18) from normal values to 115.9 and 115.7°, respectively.

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(19) Most crystallographic investigations have found this group of five atoms in a lactone to be planar, *e.g.*, K. K. Cheung, K. H. Overton, and G. A. Sim, *Chem. Commun.*, 634 (1965); J. F. McConnell, A. M. Mathieson, and B. P. Schoenborn, *Tetrahedron Letters*, 445 (1962); A. M. Mathieson, *ibid.*, 81 (1963); G. A. Jeffrey, R. D. Rosenstein, and M. Vlasse, *Acta Cryst.*, 22, 725 (1967).

(20) G. A. Jeffrey, R. D. Rosenstein, and M. Vlasse, *ibid.*, 22, 725 (1967).

(21) F. V. Brutcher, Jr., and W. Bauer, Jr., *J. Am. Chem. Soc.*, **84**, 2233 (1962); F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *ibid.*, **81**, 4915 (1959).

(22) G. A. Sim, *J. Chem. Soc.*, 5974 (1965).

(23) M. G. Newton, J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., Sect. B*, 189 (1967).

The best plane through the carboxyl group, C(21), C(20), O(20), and O(3) makes an angle of 18.5° with the best plane through the six carbon atoms of the phenyl ring.

Table IX lists intermolecular contacts less than 3.70 Å and the packing of molecules looking along the *b* axis is shown in Figure 4. There is a hydrogen bond of length 2.98 Å involving O(17) in the lactone ring and O(11) in the molecule related by the screw axis along *b*. The C(11)O(11)···O(17) angle is 113.5°. The other contacts correspond closely to the sums of the appropriate van der Waals radii.

Table IX. Intermolecular Contacts Less than 3.70 Å[a]

$C(19)\cdots O(11)^{I}$	3.50	$C(19)\cdots O(17)^{IV}$	3.55
$O(20)\cdots C(23)^{I}$	3.25	$O(12)\cdots C(18)^{IV}$	3.41
$O(20)\cdots C(15)^{II}$	3.56	$O(12)\cdots O(11)^{IV}$	3.62
$O(20)\cdots C(16)^{II}$	3.35	$O(17)\cdots C(12)^{IV}$	3.44
$O(20)\cdots C(18)^{III}$	3.70	$O(17)\cdots O(11)^{IV}$	2.98
$C(16)\cdots O(12)^{IV}$	3.47	$O(17)\cdots O(12)^{IV}$	3.31
		$C(6)\cdots Br^{V}$	3.67

[a] I denotes atom related to those in Table I by x, $1 + y$, z. II denotes atom related to those in Table I by $1/2 + x$, $1/2 - y$, $1 - z$. III denotes atom related to those in Table I by $1/2 + x$, $-1/2 - y$, $1 - z$. IV denotes atom related to those in Table I by $-x$, $1/2 + y$, $1\,1/2 - z$. V denotes atom related to those in Table I by $-x$, $1\,1/2 + y$, $1/2 - z$.

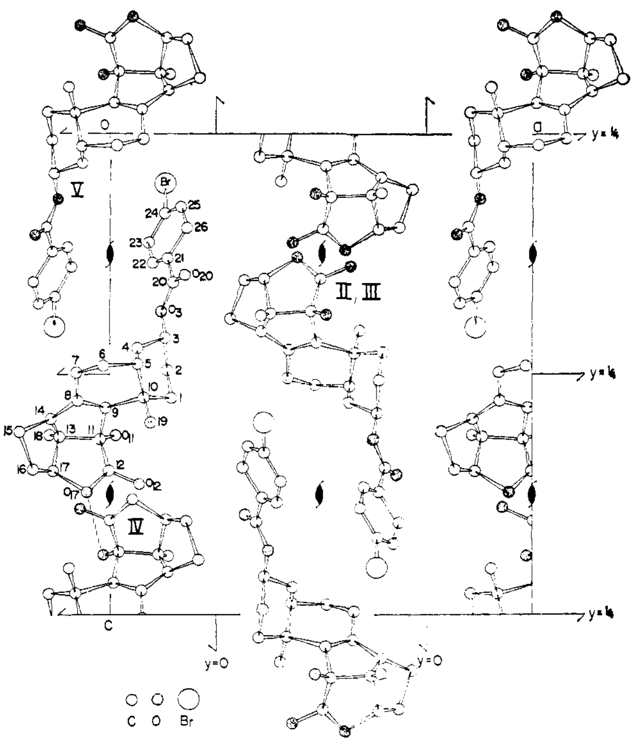

Figure 4. The packing of molecules viewed along the *b* axis. The atoms are numbered in the basic molecule and the Roman numerals describe the molecules referred to in Table IX. The hydrogen bond is marked by a discontinuous line.

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