Table 1. 3,4-*Dibromo*-2,3,4,5-*tetrahydro*-1,6-*benzodioxocin coordinates* (× 10⁴) *for non*-H *atoms and* U_{eq} *values* (Å² × 10³) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	4610 (5)	870 (18)	3521 (8)	50 (4)
C2	4229 (7)	1289 (28)	4112 (10)	41 (5)
C3	4419 (6)	5490 (30)	3312 (10)	44 (5)
O4	4955 (5)	5166 (18)	3983 (7)	50 (4)
C5	6042 (8)	4249 (29)	4023 (11)	53 (6)
C6	6508 (8)	2780 (33)	3927 (12)	61 (6)
C7	6344 (8)	794 (33)	3673 (12)	55 (6)
C8	5705 (7)	169 (32)	3574 (11)	52 (6)
C9	5235 (6)	1597 (27)	3679 (9)	36 (4)
C10	5394 (7)	3665 (28)	3875 (10)	44 (5)
C11	3639 (7)	2589 (27)	3670 (9)	38 (4)
Br12	2958 (1)	2229 (4)	4271 (1)	63 (1)
C13	3802 (6)	5002 (28)	3656 (10)	43 (5)
Br14	3093 (1)	6415 (4)	2892 (2)	74 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°)

C2–O1	1·427 (18)	C9–O1–C2	118·3 (12)
C9–O1	1·390 (17)	C11–C2–O1	107·1 (12)
C11–C2	1·559 (21)	C13–C3–O4	106·6 (12)
O4–C3	1·443 (17)	C10–O4–C3	117·0 (12)
C13–C3	1·576 (20)	C10–C5–C6	120·7 (17)
C10–O4	1·373 (19)	C7–C6–C5	120·4 (15)
C6–C5	1·394 (24)	C8–C7–C6	119·0 (17)
C10–C5	1·409 (21)	C9–C8–C7	121·3 (18)
C7–C6	1·344 (26)	C8–C9–O1	117·3 (15)
C8–C7	1·402 (21)	C10–C9–O1	122·8 (14)
C9–C8	1·387 (22)	C10–C9–C8	119·7 (14)
C10–C9	1·369 (23)	C5–C10–O4	118·4 (15)
Br12–C11	1·944 (13)	C9–C10–O4	122·9 (13)
C13–C11	1·561 (24)	C9–C10–C5	118·6 (16)
Br14–C13	1·980 (15)	Br12–C11–C2	108·5 (9)
		C13–C11–C2	110·9 (12)
		C13–C11–Br12	108·4 (11)
		C11–C13–C3	113·7 (13)
		Br14–C13–C3	105·6 (10)
		Br14–C13–C11	107·7 (10)

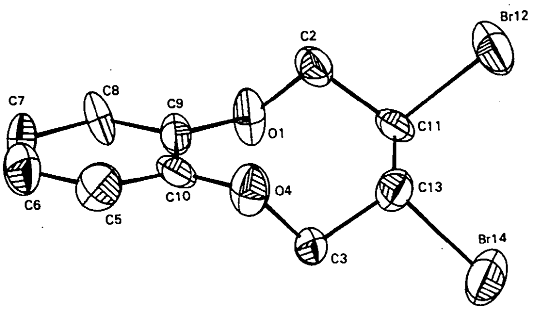

Fig. 1. 3,4-Dibromo-2,3,4,5-tetrahydro-1,6-benzodioxocin.

and C3 but at the expense of eclipsing the C–H bonds on C2 and C11 and on C3 and C13 which are staggered in the observed structure. This conformation is that found in 8,9-dimethyl-1,6-benzodithiocin (Barnes, Schroth & Moegel, 1978) where the corresponding deviations from the plane of the benzene ring are 0·808, −1·080, 0·368 and −0·837 Å, making the angle between C11–C13 and the normal to the benzene ring plane 33·8 (4)°.

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The Structure of 11α-Hydroxycon-1,4-dienine-3-one Monohydrate

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Abstract. $C_{22}H_{31}NO_2.H_2O$, $M_r = 359{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}032\,(1)$, $b = 11{\cdot}186\,(1)$, $c = 17{\cdot}980\,(1)$ Å, $U = 2017{\cdot}48$ Å³, $Z = 4$, $D_x = 1{\cdot}276$ Mg m⁻³, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}69$ mm⁻¹, $F(000) = 784$, $T = 293$ K. Final $R = 0{\cdot}05$ for 1972 unique reflections with $I \geq 3\sigma(I)$. Ring *A* is planar, and rings *B* and *C* adopt a chair conformation. Rings *D* and *E* are envelopes, with C(14) and C(20) displaced from their respective ring planes by 0·616 (2) and 0·648 (3) Å. The *A*/*B* ring junction is quasi-*trans*,

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whilst ring systems *B*/*C* and *C*/*D* are *trans* fused about the bonds C(8)—C(9) and C(13)—C(14) respectively. The *D*/*E* junction shows *cis* fusion.

Introduction. Steroidal alkaloids are a class of compounds possessing the basic or modified steroidal skeleton with nitrogen incorporated as an integral part of the ring or in the side chain. 11α-Hydroxycon-1,4-dienine-3-one is a steroidal alkaloid with the N atom in ring *E* (Fig. 1). The compound was isolated from the bark of the plant *Holarrhena anti-dysenterica* (Bhutani, Ali, Sharma, Vaid & Gupta, 1987). The *Holarrhena* alkaloids have a long history in herbal medicine as antidysentrics and anthelmintics.

Experimental. The crystals were grown from acetone solution by slow evaporation. The cell parameters were refined from accurately determined 2θ values of 24 reflections, $4{\cdot}8 < \theta < 29{\cdot}8°$, on an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected with Cu $K\alpha$ radiation using a crystal of dimensions $1{\cdot}1 \times 0{\cdot}6 \times 0{\cdot}5$ mm up to $(\sin\theta)/\lambda = 0{\cdot}627$ Å^{-1} using ω–2θ scan. Absorption correction (North, Phillips & Mathews, 1968) was applied, transmission factor varied from 96·9 to 97·2%. Lorentz and polarization corrections were also applied. 2644 reflections were measured with $0 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 22$ of which 1972 reflections had $I \ge 3\sigma(I)$. Three strong reflections monitored periodically showed that the crystal was stable to X-rays.

The structure was solved by direct methods using *MULTAN*11/82 (Main *et al.*, 1982). An *E* map computed with the best set of phases (CFOM = 2·799) revealed the positions of 23 out of 26 non-H atoms. Successive difference Fourier maps revealed the positions of the remaining three non-H atoms as well as those of 29 H atoms. The remaining three H atoms were fixed stereochemically. After the final cycle of refinement with anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms the *R* value was 0·05, $wR = 0{\cdot}061$ and *S* (goodness of fit) = 2·4. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The residual electron density in the final difference Fourier map was between +0·198 and −0·270 e Å^{-3}. The maximum shift/e.s.d. for non-H atoms is 0·08, including H atoms it is 0·29. All calculations were performed using the Enraf–Nonius (1979) *Structure Determination Package* on a PDP 11/44 computer. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

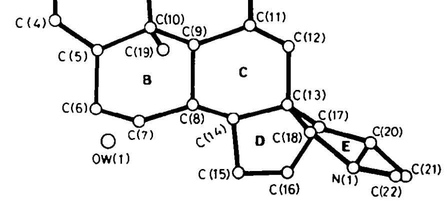

Fig. 1. The numbering scheme of 11α-hydroxycon-1,4-dienine-3-one.

Table 1. *Final fractional coordinates and equivalent isotropic temperature factors of non*-H *atoms*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	*y*	*z*	*B*(Å^2)
O(1)	0·2765 (3)	0·7509 (2)	0·8686 (1)	5·73 (5)
O(*W*1)	0·7434 (4)	1·0056 (2)	0·6007 (1)	7·25 (7)
O(3)	0·2460 (4)	1·2857 (2)	0·8331 (1)	6·53 (6)
N(1)	0·2343 (2)	1·5298 (2)	0·5571 (1)	3·14 (4)
C(1)	0·3480 (3)	1·0544 (3)	0·8284 (2)	3·81 (5)
C(2)	0·3346 (3)	0·9542 (3)	0·8673 (2)	4·01 (5)
C(3)	0·2931 (3)	0·8429 (2)	0·8326 (2)	3·93 (5)
C(4)	0·2708 (3)	0·8476 (2)	0·7534 (2)	4·12 (6)
C(5)	0·2882 (3)	0·9464 (2)	0·7126 (2)	3·86 (5)
C(6)	0·2610 (5)	0·9455 (3)	0·6304 (2)	5·97 (8)
C(7)	0·1559 (4)	1·0387 (3)	0·6120 (2)	5·03 (7)
C(8)	0·1982 (3)	1·1625 (2)	0·6386 (1)	3·29 (5)
C(9)	0·2212 (2)	1·1614 (2)	0·7246 (1)	2·79 (4)
C(10)	0·3300 (3)	1·0652 (2)	0·7460 (1)	3·41 (5)
C(11)	0·2499 (3)	1·2888 (2)	0·7537 (1)	3·58 (5)
C(12)	0·1499 (3)	1·3815 (2)	0·7267 (1)	3·59 (5)
C(13)	0·1393 (2)	1·3824 (2)	0·6418 (1)	2·88 (4)
C(14)	0·0963 (3)	1·2570 (2)	0·6185 (1)	3·30 (5)
C(15)	0·0564 (3)	1·2734 (3)	0·5376 (2)	4·59 (6)
C(16)	0·0163 (3)	1·3941 (3)	0·5373 (2)	4·27 (6)
C(17)	0·0335 (3)	1·4641 (3)	0·6070 (1)	3·58 (5)
C(18)	0·2699 (3)	1·4289 (2)	0·6062 (1)	3·45 (5)
C(19)	0·4696 (3)	1·0994 (3)	0·7151 (2)	5·75 (7)
C(20)	0·1103 (3)	1·5788 (2)	0·5885 (2)	3·70 (5)
C(21)	0·0403 (4)	1·6679 (3)	0·5380 (2)	5·73 (7)
C(22)	0·8407 (3)	0·8841 (3)	0·4487 (2)	4·67 (6)

Discussion. The numbering scheme is given in Fig. 1. The final coordinates and equivalent thermal parameters for non-H atoms are given in Table 1.* Bond lengths, valence angles and endocyclic torsion angles are given in Table 2.

The mean value of the C(sp^3)—C(sp^3) bonds [1·537 (4) Å] agrees with the accepted average (1·533 Å; Sutton, 1965), although the bonds C(9)—C(10), C(16)—C(17) and C(5)—C(6) show significant deviations (Table 2). Such variations in bond lengths are common in steroids, owing to the strains imposed by ring junctions, side chains and bond unsaturation. The bond lengths C(1)—C(2), C(4)—C(5) and C(3)—O(1) indicate their double-bond nature.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44475 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ring *A* is essentially planar, a feature found in only a few steroids (Duax, Norton, Pokrywiecki & Eger, 1971; Peck, Langs, Eger & Duax, 1974). The endocyclic torsion angles vary from 0·1 to 2·3°. The bond angles at the sp^2 C atoms range from 115·9 (2) to 125·3 (2)°. This ring makes an angle of 32° with the least-squares plane formed by C(5), C(9), C(12) and C(17).

Ring *B* shows the normal chair conformation with the best rotational axis bisecting the C(5)–C(10) and C(7)–C(8) bonds and with the asymmetry parameter ΔC_2[C(5)–C(10)] = 2·1 (3)°. Ring *C* is also in a chair conformation. The best rotational axis bisects C(9)–C(11) and C(13)–C(14), with ΔC_2[C(9)–C(11)] = 3·2 (4)°.

Table 2. *Bond lengths* (Å) *and valence angles of non*-H *atoms and observed and calculated values of torsional angles for rings* (°)

O(1)–C(3)	1·227 (3)	C(8)–C(14)	1·514 (4)
O(3)–C(11)	1·430 (3)	C(9)–C(10)	1·580 (3)
N(1)–C(18)	1·476 (3)	C(9)–C(11)	1·546 (3)
N(1)–C(20)	1·472 (4)	C(10)–C(19)	1·555 (4)
C(1)–C(2)	1·329 (5)	C(11)–C(12)	1·522 (4)
C(1)–C(10)	1·496 (4)	C(12)–C(13)	1·530 (3)
C(2)–C(3)	1·454 (5)	C(13)–C(14)	1·526 (4)
C(3)–C(4)	1·442 (4)	C(13)–C(17)	1·534 (4)
C(4)–C(5)	1·337 (4)	C(13)–C(18)	1·548 (3)
C(5)–C(6)	1·503 (4)	C(14)–C(15)	1·521 (4)
C(5)–C(10)	1·518 (4)	C(15)–C(16)	1·535 (5)
C(6)–C(7)	1·519 (5)	C(16)–C(17)	1·561 (5)
C(7)–C(8)	1·525 (4)	C(17)–C(20)	1·533 (4)
C(8)–C(9)	1·563 (3)	C(20)–C(21)	1·520 (5)

C(18)–N(1)–C(20)	105·1 (2)	C(9)–C(10)–C(19)	111·5 (2)
C(2)–C(1)–C(10)	125·3 (3)	O(3)–C(11)–C(9)	108·1 (2)
C(1)–C(2)–C(3)	121·7 (3)	O(3)–C(11)–C(12)	108·5 (2)
O(1)–C(3)–C(2)	122·0 (3)	C(9)–C(11)–C(12)	113·4 (2)
O(1)–C(3)–C(4)	122·0 (3)	C(11)–C(12)–C(13)	111·6 (3)
C(2)–C(3)–C(4)	115·9 (2)	C(12)–C(13)–C(14)	106·6 (2)
C(3)–C(4)–C(5)	123·5 (3)	C(12)–C(13)–C(17)	117·3 (3)
C(4)–C(5)–C(6)	120·7 (3)	C(12)–C(13)–C(18)	110·9 (3)
C(4)–C(5)–C(10)	122·8 (2)	C(14)–C(13)–C(17)	103·9 (2)
C(6)–C(5)–C(10)	116·4 (2)	C(14)–C(13)–C(18)	115·8 (2)
C(5)–C(6)–C(7)	109·6 (3)	C(17)–C(13)–C(18)	102·5 (2)
C(6)–C(7)–C(8)	111·3 (3)	C(8)–C(14)–C(13)	112·7 (3)
C(7)–C(8)–C(9)	110·1 (2)	C(8)–C(14)–C(15)	119·3 (2)
C(7)–C(8)–C(14)	111·8 (2)	C(13)–C(14)–C(15)	103·1 (2)
C(9)–C(8)–C(14)	109·9 (2)	C(14)–C(15)–C(16)	103·5 (2)
C(8)–C(9)–C(10)	110·4 (2)	C(15)–C(16)–C(17)	106·7 (2)
C(8)–C(9)–C(11)	110·8 (2)	C(13)–C(17)–C(16)	104·5 (2)
C(10)–C(9)–C(11)	114·7 (3)	C(13)–C(17)–C(20)	103·9 (3)
C(1)–C(10)–C(5)	110·8 (2)	C(16)–C(17)–C(20)	114·0 (2)
C(1)–C(10)–C(9)	112·4 (3)	N(1)–C(18)–C(13)	107·4 (2)
C(1)–C(10)–C(19)	105·4 (2)	N(1)–C(20)–C(17)	101·4 (2)
C(5)–C(10)–C(9)	108·0 (3)	N(1)–C(20)–C(21)	113·9 (2)
C(5)–C(10)–C(19)	108·9 (2)	C(17)–C(20)–C(21)	116·6 (2)

	Observed	Calculated	
Ring *B*			
9–10–5–6	54·1 (4)	58	
10–5–6–7	−55·9 (5)	−57	
5–6–7–8	56·4 (3)	56	
6–7–8–9	−59·2 (3)	−56	
7–8–9–10	57·7 (2)	58	
8–9–10–5	−53·2 (3)	−59	
Ring *C*		With ring *D*	Without ring *D*
13–12–11–9	−54·9 (3)	−56	−56
12–11–9–8	49·3 (3)	57·3	56
11–9–8–14	−50·5 (3)	−58	−58
9–8–14–13	59·7 (3)	58	58
8–14–13–12	−63·1 (3)	−58	−59
14–13–12–11	59·0 (3)	58	58
Ring *D*			
17–13–14–15	42·4 (3)	44·4	
13–14–15–16	−39·8 (3)	−44·4	
14–15–16–17	22·5 (3)	27·4	
15–16–17–13	3·2 (3)	0·0	
16–17–13–14	−27·7 (2)	−27·4	
Ring *E*			
N1–20–17–13	42·9 (2)	44·4	
20–17–13–18	−26·5 (2)	−27·4	
17–13–18–N1	0·9 (2)	0·0	
13–18–N1–20	26·3 (2)	27·4	
18–N1–20–17	−42·4 (2)	−44·4	

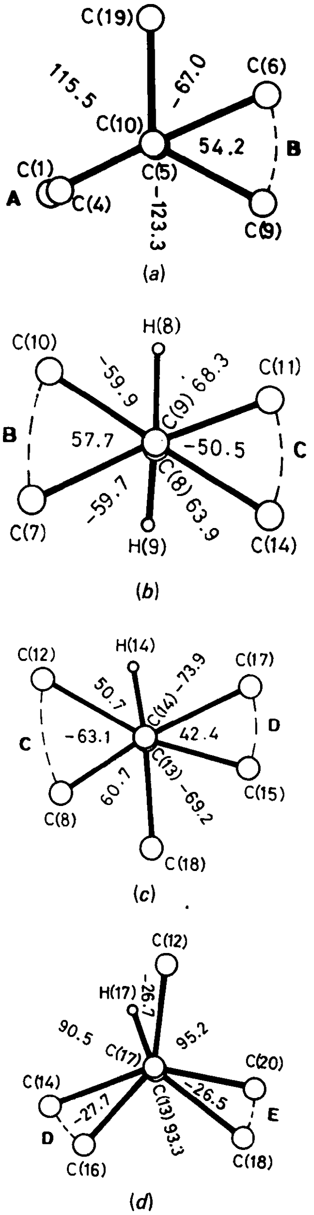

Fig. 2. Newman projections along (*a*) C(5)–C(10), (*b*) C(8)–C(9), (*c*) C(13)–C(14) and (*d*) C(13)–C(17).

Ring *D* is a distorted envelope with a phase angle of pseudorotation $\Delta = 27{\cdot}3\ (4)^\circ$ and maximum angle of torsion $\varphi = 41{\cdot}2\ (3)^\circ$ (Altona, Geise & Romers, 1968). The asymmetry parameter $\Delta C_s[C(14)] = 4{\cdot}0\ (5)^\circ$, which represents the distortion from ideal mirror symmetry bisecting the C(16)—C(17) bond. Ring *E*, which contains the lone N atom in the structure, has an ideal C(20) envelope configuration $\{\Delta C_s[C(20)] = 0{\cdot}4\ (2)^\circ,\quad \Delta = 35{\cdot}5\ (3)^\circ$ and $\varphi = 40{\cdot}4\ (5)^\circ\}$.

Fig. 2 gives Newman projections along the bonds involved in ring fusion and shows that atoms H(8) and H(9) as well as C(18) and H(14) have antiperiplanar configurations. Table 2 gives observed torsional angles for the rings, together with values calculated for appropriately substituted cyclohexane and cyclopentane rings (Geise, Altona & Romers, 1967; Altona, Geise & Romers, 1968). The differences between observed and calculated values for ring *B* are probably the result of ring *A* being planar here, rather than puckered as in the above calculations. Torsional deviations of ring *C* from the expected values reflect the strain induced by ring *E* in the present compound.

In the crystal structure the lone water molecule forms three hydrogen bonds. One of these is with the phenolic O(3) atom [O(3)—H(3)···O*W*(1) = 2·735 Å], the remaining two are with the keto O(1) atom [O*W*(1)—H(O*W*)···O(1) = 2·809 Å] and the N(1) atom [O*W*(1)—H(O*W*)···N(1) = 2·865 Å]. The hydrogen bonds from the water molecule link the steroid molecules which are symmetrically related by $1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$; $1-x$, $\frac{1}{2}+y$, $\frac{3}{3}-x$ and $\frac{1}{2}+x$, $\frac{5}{2}-y$, $1-z$.

The overall shape of the molecule is convex towards the α side, causing the vector C(10)—C(19) and ring *E* to diverge. The torsional angle C(1)—C(10)—C(13)—C(18) which gives the twist of the steroid molecule about the line joining C(10) and C(13) is 110·2 (3)°.

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Conformation and Structure of *N*-Benzyloxycarbonyl-L-arginine Hemihydrate

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Abstract. $C_{14}H_{21}N_4O_4.\frac{1}{2}H_2O$, $M_r = 318{\cdot}36$, monoclinic, $P2_1$, $a = 8{\cdot}671\ (3)$, $b = 21{\cdot}454\ (36)$, $c = 8{\cdot}733\ (2)$ Å, $\beta = 95{\cdot}86\ (2)^\circ$, $V = 1616\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}308$, D_m(flotation in $CHCl_3/CH_2Cl_2$) = 1·311 (3) Mg m^{-3}, Mo $K\alpha$ ($\lambda K\alpha_1 = 0{\cdot}70926$, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 1{\cdot}07$ cm^{-1}, $F(000) = 676$, $T = 295$ K, $R = 0{\cdot}060$, $wR = 0{\cdot}062$ for 1803 observations. There are two independent Z-Arg molecules in the cell, but the two independent molecules have very similar structures. The side-chain conformations observed in these two molecules are unusual, but are similar to that observed in one previous study.

Introduction. The interaction between the guanidyl groups of arginine residues and the dicarboxylate functionalities of γ-carboxyglutamic acid (Gla) residues in a variety of proteins including bovine prothrombin is believed to be of considerable importance

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