Plecostonol, a New *ent*-Kaurene Diterpenoid from *Plectranthus coesta* Buch-Ham.†

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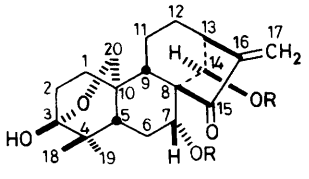
Plecostonol, a new diterpenoid having a rare 3,20-epoxy-*ent*-kaurene skeleton, has been isolated from *Plectranthus coesta* Buch-Ham, and assigned the structure *ent*-3β,20β-epoxy-3α,7β,14α-trihydroxy-kaur-16-ene-15-one (**1**) on the basis of its spectral properties and an *X*-ray crystallographic determination.

In the course of our work on plant pest control agents, we collected *Plectranthus coesta* Buch-Ham (Labiatae), a shrub from the Purandar area of Maharashtra, India which has not so far been chemically investigated. Here we report the isolation and identification of a novel type of diterpenoid hemiketal, plecostonol (**1**), possessing a rare 3,20-epoxy-*ent*-kaurene type skeleton, along with β-sitosterol and triterpenoid acids, *viz.* ursolic and oleanolic acids. Novelrabdosin[1] isolated from *Rabdosia nervosa* is the only other example of a 3,20-epoxy-*ent*-kaurene skeleton reported recently in the literature.

An acetone extract of the shade dried plant afforded, on repeated chromatography, a pure crystalline compound, plecostonol (**1**) (0.016%), $C_{20}H_{28}O_5$ (M^+, 348), m.p. 246—248 °C.‡ The presence of a five-membered ketone group conjugated with the α-methylene group of (**1**) is indicated by the following spectral data: $\lambda_{max.}$ 232 nm; $\nu_{max.}$ 1 720 and 1 650 cm^{-1}; ^1H n.m.r. (Table 1) δ 5.28 and 5.93 (each 1 H, s); ^{13}C n.m.r. (Table 2) δ 116.7 (t), 148.9 (s) (>C=CH_2), and 206.7 (s) (ketone). Compound (**1**) also shows a strong absorption in the i.r. spectrum (3 460—3 340) due to hydroxy groups. On acetylation, (**1**) gave the diacetate (**2**) [singlets at δ 1.97 (3 H) and 2.04 (3 H)] and treatment with dimethyl sulphate yielded the dimethyl ether (**3**) [singlet at δ 3.40 (6 H)]. Absorptions at $\nu_{max.}$



(**1**) R = H
(**2**) R = Ac
(**3**) R = Me

3 370 and 3 450 cm^{-1} in (**2**) and (**3**), respectively suggested that out of the five oxygen atoms in (**1**), at least three are in hydroxyl groups. From the above, it was deduced that plecostonol had the 15-oxo-*ent*-kaur-16-ene as its basic skeleton.

The ^1H n.m.r. spectrum of (**1**) exhibited only two methyl signals (δ 1.09, s, 6 H) and two double doublets assignable to the $-OCH_2\overset{|}{C}-$ group: δ 3.7 (1 H, *J* 7.5 and 3.75 Hz) and 4.28 (1 H, *J* 7.5 and 2.5 Hz); the ^{13}C n.m.r. spectrum showed signals at δ 67.7 (t) ($OCH_2\overset{|}{C}-$) and 97.4 (s) (HOCO–). These spectral data reveal a partial structure $HO\overset{|}{C}OCH_2\overset{|}{C}-$ in plecostonol. The ^1H n.m.r. data of the derivatives (**2**) and (**3**) (Table 2) are in accord with this. The foregoing evidence suggests the presence of either a 3,20- or a 7,20-epoxy system in (**1**). The dd splitting pattern of C*H*OAc in (**2**) (Figure 1) (δ 5.12, 1 H, dd, *J* 13 and 5.5 Hz) appears to be characteristic of 7-H^2 and so supports the existence of a 3,20-epoxy ring. A 1 H singlet at δ 5.47 in (**2**) could be ascribed to 14-H_β.[3] The above facts suggest *ent*-3β,20β-3α,7,14β-trihydroxykaur-16-en-15-one as the gross structure for plecostonol. Since a suitable crystal could be obtained for *X*-ray analysis we were able to assign the complete stereo structure as *ent*-3β,20β-epoxy-3α,7β,14α-trihydroxykaur-16-en-15-one (**1**).

Experimental

Optical rotations and u.v. spectra were taken for solutions in methanol. I.r. spectra were recorded in Nujol mulls and ^1H and ^{13}C n.m.r. spectra, unless otherwise stated, in deuteriated chloroform with $SiMe_4$ as internal standard. Mass spectra were determined at 70 eV using a direct inlet system.

Isolation of Plecostonol (**1**).—The whole shade-dried plant of *P.coesta* (roots, stem, leaves, and flowers) was powdered and the powdered material (3.5 kg) was extracted with acetone (3 × 10 l) at room temperature. The acetone was removed at 40 °C/25 mmHg in a rotavapour and the dark extract (98 g) was chromatographed over a silica gel column (72 × 6.8 cm). The column was eluted successively with benzene [to give fraction A(12.0 g)], benzene–acetone (90:10) [to give fraction B (28.5 g)], acetone [to give fraction C (44.0 g)], and methanol [to give fraction D (16.0 g)]. Fraction B was rechromatographed on silica gel. Benzene eluted β-sitosterol (0.5 g, m.p. 142 °C). Benzene–acetone (99:1) gave ursolic acid [8 g, m.p. (acetyl methyl ester) 252 °C] and oleanolic acid [0.2 g, m.p. (acetyl methyl ester) 212—215 °C]. Fraction C was rechromatographed on silica gel with benzene–acetone (70—50:30—50) to give a crude solid (12.2 g) which was rechromatographed to give a white solid (7.35 g) with benzene–acetone (90—80:10—20). The white solid on flash chromatography (3 batches) on a silica gel column (t.l.c. grade, 8 cm × 3 cm) with ethyl acetate as eluant gave, in the initial fraction, pure white solid, *plecostonol* (**1**) (0.575 g), m.p. 246—248 °C (from methanol); $[\alpha]_D$ −178.72° (*c* 0.094, MeOH) (Found: C, 68.6; H, 8.0. $C_{20}H_{28}O_5$ requires C, 68.94; H, 8.10%); $\lambda_{max.}$(MeOH) 232 nm (ε 6 645); $\nu_{max.}$(Nujol) 3 460, 3 340, 2 930, 2 870, 1 720, 1 650, 980, and 920 cm^{-1}; δ_H [80 MHz; $(CD_3)_2CO$] 1.09 (6 H, s), 2.93 (1 H, br), 3.70 (1 H, dd, *J* 7.5

† N. C. L. Communication No. 3871
‡ When kept, the crystals of plecostonol become translucent, probably owing to loss of methanol trapped in the crystals as shown by *X*-ray studies.

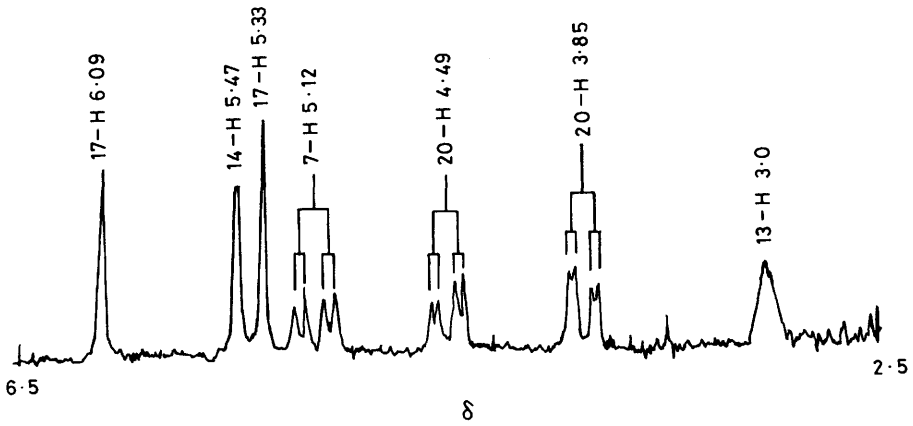


Figure 1. ^{1}H N.m.r. spectrum (δ 2.5—6.5) of plecostonyl diacetate (**2**)

Table 1. ^{1}H N.m.r. data of compounds (**1**)—(**3**)

	δ p.p.m. (splitting pattern)		
Proton	1	2	3
Gem Me	1.09 (6 H) (s)	1.02 (3 H) (s) 1.05 (3 H) (s)	1.03 (3 H) (s) 1.07 (3 H) (s)
13-H	2.93 (br)	3.00 (br)	3.03 (br)
CH_2O	3.7 (1 H) (dd, *J* 7.5 and 3.75 Hz)	3.85 (1 H) (dd, *J* 15 and 3.75 Hz)	3.76 (1 H) (m)
	4.28 (1 H) (dd, *J* 7.5 and 2.5 Hz)	4.49 (1 H) (dd, *J* 15 and 5 Hz)	4.25 (1 H) (m, C-20)
CHOR (7-H)	4.73 (d, *J* 5 Hz)	5.12 (*J* 13 and 5.5 Hz)	4.25 (1 H) (m, 7-H)
CHOR (14-H)	5.43 (s)	5.47 (s)	5.1 (s)
$=CH_2$	5.28 (1 H) (s) 5.93 (1 H) (s)	5.33 (1 H) (s) 6.09 (1 H) (s)	5.37 (1 H) (s) 6.08 (1 H) (s)

and 3.75 Hz), 4.28 (1 H, dd, *J* 7.5 and 2.5 Hz), 4.37 (s), 4.73 (1 H, d, *J* 5 Hz), 5.28 (1 H, s), 5.43 (1 H, s), and 5.93 (1 H, s); *m/z* (%) 348 (M^+ 26), 330 (54), 317 (48), 312 (59), 302 (43), 290 (27.5), 284 (66), 257 (69), 243 (57.5), and 215 (100).

Plecostonyl Diacetate (**2**).—A mixture of (**1**) (0.1 g), fused sodium acetate (1.6 g), and acetic anhydride (23 ml) was heated on a steam-bath for 3 h. The mixture was poured onto ice–water and extracted with diethyl ether. The ether extract was repeatedly washed with water, dried (Na_2SO_4), and evaporated to give a crude product which on chromatography over silica gel afforded (**2**) (60 mg), m.p. 255—258 °C (from methanol); $[\alpha]_D$ −68.7° (*c* 0.052, MeOH) (Found: C, 65.95; H, 7.4. $C_{24}H_{32}O_7$ requires C, 66.5; H, 7.46%) $\nu_{max.}$(Nujol) 3 370, 2 940, 1 745, 1 720, 1 655, 1 465, 970, and 900 cm^{-1}; δ_H (80 MHz, $CDCl_3$, expanded scale, 1 div. = 3 Hz) 1.02 (3 H, s), 1.05 (3 H, s), 1.97 (3 H, s), 2.04 (3 H, s), 3.00 (1 H, br), 3.85 (1 H, dd, *J* 15 and 3.75 Hz), 4.49 (1 H, dd, *J* 15 and 5 Hz), 5.05 and 5.20 (1 H, AB system, *J* 13 and 5.5 Hz), 5.33 (1 H, s), 5.47 (1 H, s), and 6.09 (1 H, s); *m/z* (%) 432 (M^+ 6), 372 (27), 344 (15), 330 (57), 329 (39), 312 (100), 294 (16), 284 (98.5), 269 (49), and 243 (43).

Plecostonyl Dimethyl Ether (**3**).—A mixture of (**1**) (0.2 g), potassium carbonate (12 g), dimethyl sulphate (8 ml), and acetone (20 ml) was refluxed for 6 h; it was then filtered and evaporated. The residue was heated with water (5 ml) on steam-bath for 0.5 h, cooled, and extracted with diethyl ether. The ether extract was washed with water and aqueous $NaHCO_3$,

Table 2. ^{13}C N.m.r. spectrum of plecostonol (**1**)[a]

Carbon atom	δ p.p.m.	Multiplicity	Carbon atom	δ p.p.m.	Multiplicity
1	34.2[c]	t	11	18.0	t
2	29.4[d]	t	12	34.5[c]	t
3	97.4	s	13	45.6	d
4	30.5	s	14	75.6	d
5	47.8[b]	d	15	206.7	s
6	30.3[d]	t	16	148.9	s
7	72.1	d	17	116.7	t
8	60.1	s	18	27.0	q
9	48.1[b]	d	19	19.1	q
10	40.1	s	20	67.7	t

[a] The ^{13}C n.m.r. spectrum was obtained for a $CDCl_3$ solution with Bruker WH-90 spectrometer. Chemical shifts are expressed in p.p.m. relative to internal Me_4Si. [b–d] Assignments with the same sign may be interchanged.

Table 3. Fractional atomic co-ordinates (× 10^4) with their standard deviations in parentheses.

	x	*y*	*z*
C(1)	3 984(8)	−3 175(8)	6 217(7)
C(2)	5 342(8)	−3 220(9)	5 890(8)
C(3)	6 081(7)	−2 139(8)	6 209(6)
C(4)	5 567(7)	−948(8)	5 856(6)
C(5)	4 092(8)	−1 005(8)	5 947(5)
C(6)	3 467(8)	243(8)	6 086(6)
C(7)	2 053(7)	132(7)	6 126(6)
C(8)	1 662(8)	−595(8)	6 866(5)
C(9)	2 223(7)	−1 891(8)	6 789(5)
C(10)	3 698(7)	−1 950(8)	6 585(5)
C(11)	1 780(8)	−2 712(8)	7 482(6)
C(12)	1 706(10)	−2 132(10)	8 318(6)
C(13)	1 104(9)	−863(9)	8 272(6)
C(14)	1 973(9)	−69(9)	7 718(6)
C(15)	203(7)	−799(7)	6 933(5)
C(16)	−111(7)	−896(7)	7 810(5)
C(17)	−1 349(8)	−1 030(7)	8 084(5)
C(18)	5 885(10)	−810(10)	4 953(6)
C(19)	6 208(8)	106(8)	6 305(6)
C(20)	4 593(7)	−1 826(7)	7 333(5)
C(21)	−819(10)	1 448(10)	4 549(6)
O(1)	7 378(4)	−2 355(5)	6 083(3)
O(2)	5 897(4)	−2 127(5)	7 087(3)
O(3)	1 454(5)	1 311(5)	6 124(4)
O(4)	1 517(5)	1 151(5)	7 732(4)
O(5)	−503(5)	−881(5)	6 349(3)
O(6)	297(8)	2 129(9)	4 700(5)

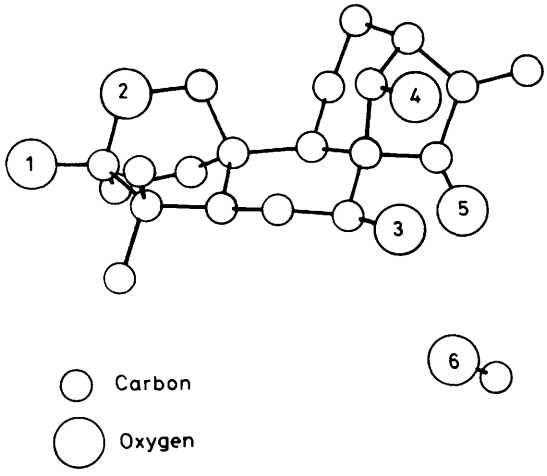


Figure 2. A perspective view of the molecule of plecostonol (**1**)

Table 4. Intramolecular bond lengths (Å) and angles (°) and their standard deviations in parentheses

C(1)–C(2)	1.52(1)	C(1)–C(10)	1.52(1)
C(2)–C(3)	1.52(1)	C(3)–C(4)	1.54(1)
C(3)–O(1)	1.395(9)	C(3)–O(2)	1.45(1)
C(4)–C(5)	1.55(1)	C(4)–C(18)	1.53(1)
C(4)–C(19)	1.54(1)	C(5)–C(6)	1.55(1)
C(5)–C(10)	1.54(1)	C(6)–C(7)	1.49(1)
C(7)–C(8)	1.51(1)	C(7)–O(3)	1.46(1)
C(8)–C(9)	1.56(1)	C(8)–C(14)	1.55(1)
C(8)–C(15)	1.55(1)	C(9)–C(10)	1.58(1)
C(9)–C(11)	1.53(1)	C(10)–C(20)	1.55(1)
C(11)–C(12)	1.52(1)	C(12)–C(13)	1.55(1)
C(13)–C(14)	1.56(1)	C(13)–C(16)	1.48(1)
C(14)–O(4)	1.44(1)	C(15)–C(16)	1.48(1)
C(15)–O(5)	1.214(9)	C(16)–C(17)	1.38(1)
C(20)–O(2)	1.463(9)	C(21)–O(6)	1.41(1)

C(2)–C(1)–C(10)	110.7(8)	C(1)–C(2)–C(3)	109.1(8)
C(2)–C(3)–C(4)	111.9(7)	C(2)–C(3)–O(1)	107.9(7)
C(2)–C(3)–O(2)	106.3(7)	C(4)–C(3)–O(1)	115.6(7)
C(4)–C(3)–O(2)	108.5(7)	O(1)–C(3)–O(2)	106.1(6)
C(3)–C(4)–C(5)	106.0(7)	C(3)–C(4)–C(18)	112.0(7)
C(3)–C(4)–C(19)	108.9(7)	C(5)–C(4)–C(18)	108.4(7)
C(5)–C(4)–C(19)	114.8(7)	C(18)–C(4)–C(19)	107.0(7)
C(4)–C(5)–C(6)	113.4(7)	C(4)–C(5)–C(10)	111.1(7)
C(6)–C(5)–C(10)	113.5(7)	C(5)–C(6)–C(7)	110.6(7)
C(6)–C(7)–C(8)	110.4(7)	C(6)–C(7)–O(3)	110.8(7)
C(8)–C(7)–O(3)	111.5(7)	C(7)–C(8)–C(9)	109.1(7)
C(7)–C(8)–C(14)	117.6(7)	C(7)–C(8)–C(15)	113.7(7)
C(9)–C(8)–C(14)	110.0(7)	C(9)–C(8)–C(15)	103.9(6)
C(14)–C(8)–C(15)	101.5(7)	C(8)–C(9)–C(10)	115.0(7)
C(8)–C(9)–C(11)	112.2(7)	C(10)–C(9)–C(11)	115.4(7)
C(1)–C(10)–C(5)	106.9(7)	C(1)–C(10)–C(9)	108.3(7)
C(1)–C(10)–C(20)	105.9(7)	C(5)–C(10)–C(9)	112.2(7)
C(5)–C(10)–C(20)	108.3(7)	C(9)–C(10)–C(20)	114.7(7)
C(9)–C(11)–C(12)	115.6(8)	C(11)–C(12)–C(13)	111.4(8)
C(12)–C(13)–C(14)	107.9(8)	C(12)–C(13)–C(16)	110.6(8)
C(14)–C(13)–C(16)	102.6(7)	C(8)–C(14)–C(13)	100.8(7)
C(8)–C(14)–O(4)	107.5(7)	C(13)–C(14)–O(4)	109.4(7)
C(8)–C(15)–C(16)	107.4(6)	C(8)–C(15)–O(5)	123.8(7)
C(16)–C(15)–O(5)	128.8(7)	C(13)–C(16)–C(15)	107.7(7)
C(13)–C(16)–C(17)	130.0(8)	C(15)–C(16)–C(17)	122.2(7)
C(10)–C(20)–O(2)	109.0(6)	C(3)–O(2)–O(20)	113.6(6)

dried (Na_2SO_4), and evaporated and the residue purified by chromatography to give (**3**) (35 mg), m.p. 87—90 °C (from methanol); $[\alpha]_D$ −152.22° (*c* 0.094, MeOH) (Found: C, 69.5; H,

Table 5. Some important torsion angles

Ring A		
	C(10)–C(1)–C(2)–C(3)	13(1)°
	C(1)–C(2)–C(3)–C(4)	−67(1)
	C(2)–C(3)–C(4)–C(5)	47.1(9)
	C(3)–C(4)–C(5)–C(10)	19.1(9)
	C(4)–C(5)–C(10)–C(1)	−70.2(9)
	C(5)–C(10)–C(1)–C(2)	50(1)
Ring A1		
	C(10)–C(1)–C(2)–C(3)	13(1)
	C(1)–C(2)–C(3)–O(2)	51.4(9)
	C(2)–C(3)–O(2)–C(20)	−69.4(8)
	C(3)–O(2)–C(20)–C(10)	15.5(8)
	O(2)–C(20)–C(10)–C(1)	49.7(8)
	C(20)–C(10)–C(1)–C(2)	−65.0(9)
Ring A2		
	C(3)–C(4)–C(5)–C(10)	19.1(9)
	C(4)–C(5)–C(10)–C(20)	43.6(9)
	C(5)–C(10)–C(20)–O(2)	−64.7(8)
	C(10)–C(20)–O(2)–C(3)	15.5(8)
	C(20)–O(2)–C(3)–C(4)	51.1(8)
	O(2)–C(3)–C(4)–C(5)	−69.8(8)
Ring B		
	C(5)–C(6)–C(7)–C(8)	65.1(9)
	C(6)–C(7)–C(8)–C(9)	−62.0(9)
	C(7)–C(8)–C(9)–C(10)	50.0(9)
	C(8)–C(9)–C(10)–C(5)	−40.8(9)
	C(9)–C(10)–C(5)–C(6)	42.0(9)
	C(10)–C(5)–C(6)–C(7)	−54.9(9)
Ring C		
	C(8)–C(9)–C(11)–C(12)	−39(1)
	C(9)–C(11)–C(12)–C(13)	43(1)
	C(11)–C(12)–C(13)–C(14)	−61(1)
	C(12)–C(13)–C(14)–C(8)	73.0(9)
	C(13)–C(14)–C(8)–C(9)	−69.6(8)
	C(14)–C(8)–C(9)–C(11)	54.2(9)
Ring D		
	C(8)–C(14)–C(13)–C(16)	−43.8(8)
	C(14)–C(13)–C(16)–C(15)	30.3(9)
	C(13)–C(16)–C(15)–C(8)	−4.8(9)
	C(16)–C(15)–C(8)–C(14)	−22.8(8)
	C(15)–C(8)–C(14)–C(13)	40.0(8)
Ring E		
	C(8)–C(9)–C(11)–C(12)	−39(1)
	C(9)–C(11)–C(12)–C(13)	43(1)
	C(11)–C(12)–C(13)–C(16)	50(1)
	C(12)–C(13)–C(16)–C(15)	−84.6(9)
	C(13)–C(16)–C(15)–C(8)	−4.8(9)
	C(16)–C(15)–C(8)–C(9)	91.4(7)
	C(15)–C(8)–C(9)–C(11)	−53.8(8)

8.1. $C_{22}H_{32}O_5$ requires C, 70.19; H, 8.57%), $\nu_{max.}$(Nujol) 3 450, 2 950, 2 870, 1 735, 1 653, 1 470, 1 390, and 990 cm^{-1}; δ_H (80 Hz, $CDCl_3$) 1.03 (3 H, s), 1.07 (3 H, s), 3.03 (1 H, br), 3.40 (6 H, s), 3.76 (1 H, m), 4.25 (2 H, m), 5.1 (1 H, br), 5.37 (1 H, s), and 6.08 (1 H, s); *m/z* (%) 376 (M^+, 2), 362 (48), 330 (63), 317 (78), 312 (59), 302 (18.5), 299 (28), 293 (20), 287 (24), 284 (46), and 257 (100).

Crystallographic Structure Determination of Plecostonol (**1**).—*Crystal Data.* $C_{20}H_{28}O_5 \cdot CH_3OH$, M = 378.5. Orthorhombic, space group $P2_12_12_1$ (D_2^4; No. 19), a = 10.472(1), b = 11.132(1), c = 16.405(2) Å, U = 1 912.4 Å^3, D_c = 1.315 g

cm^{-3}, $Z = 4$, $F(000) = 816.0$. Monochromatic Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 0.11$ cm^{-1}. Data collection was done on the crystal (dimensions 0.40 × 0.30 mm), enclosed in a Lindemann capillary.

Structure determination. A unique data set was measured within the limit of $2\theta_{max.} = 47°$ using a CAD4F-11M four circle diffractometer in the conventional ω—2θ scan. 1 652 Independent reflections were obtained, 1 245 of which with $I > 3\sigma(I)$ were considered 'observed' and were used in the least squares refinement without absorption correction. The structure was solved by direct methods using MULTAN-78.[4] A full matrix least-squares refinement[5] was used with anisotropic temperature factors for the non-hydrogen atoms. The hydrogen atoms were located on the basis of stereochemical considerations (verified by difference Fourier synthesis) but were not refined. The final R value at convergence was 0.063. A Cruickshank type[6] weighting scheme was employed with $a = 4.0$, $b = 1.0$ and $c = 0.03$. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[7] Tables of thermal parameters and hydrogen coordinates are available as a supplementary publication [SUP no. 56449 (5 pp.)]. Copies of the structure factors are available from the Editorial office.*

Discussion

The atomic co-ordinates for the non-hydrogen atoms are given in Table 3. A perspective view of the molecule is shown in Figure 2, Table 4 gives bond lengths and angles and Table 5 gives torsion angles for the rings.

Rings A, A-1 and A-2 have slightly distorted tub boat conformations.[8] Rings B and C have considerably distorted chair conformations.[9] The five-membered ring D assumes a slightly distorted envelope conformation with C(14) as its flap. The seven membered ring consisting of atoms C(8), C(9), C(11), C(12), C(13), C(16), and C(15) assumes a boat conformation.[10] The sums of torsion angles for rings B and C, a measure of the degree of distortion, are 314.8 and 339.8°, respectively, comparable with 335° for a normal cyclohexane ring.[11] That there is considerable strain in the structure can be seen from the values of tetrahedral C–C–C valence angles varying from 101—105°, the greatest difference being in the five-membered ring.

The crystal structure is stabilized by intermolecular hydrogen bonds. The hydrogen attached to O(1) (x,y,z) participates in the hydrogen bond with carbonyl oxygen O(5) ($1 + x,y,z$), O(1) · · · O(5) = 2.79 Å. The atom O(1) also forms a hydrogen bond with O(4) ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), involving HO(4) attached to O(4). [O(1) · · · O(4) = 2.81 Å].

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