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Structure of 11 α -Hydroxycon-1,4,18-trienine-3-one

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Abstract. C₂₁H₂₇NO₂, $M_r = 325.5$, orthorhombic, $P2_12_12_1$, $a = 7.516$ (2), $b = 13.430$ (2), $c = 18.047$ (2) Å, $U = 1821.79$ Å³, $Z = 4$, $D_x = 1.186$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.56$ mm⁻¹, $F(000) = 704$, $T = 293$ K, final $R = 0.04$ for 1892 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(17) displaced from their respective planes by 0.643 (3) and 0.482 (3) Å. The ring system *A/B* shows quasi-*trans* fusion, whilst ring systems *B/C* and *C/D* are *trans* fused about 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 a steroidal skeleton with nitrogen incorporated as part of the ring system or in the side chain. As part of our crystallographic studies on these compounds we report here the structure of 11 α -hydroxycon-1,4,18-trienine-3-one, a compound having an N atom present in ring *E* (Fig. 1). The compound was isolated from the bark of the plant *Holarrhena antidysentrica* (Bhutani, Ali, Sharma, Vaid & 1988). The *Holarrhena* alkaloids are important in herbal medicine as anthelmintics and antidysentrics. Earlier we have reported the crystal structure of 11 α -hydroxycon-1,4-dienine-3-one monohydrate (Radhakrishnan, Viswamitra, Bhutani & Ali, 1988).

Experimental. Crystals were grown from acetone solution by evaporation. The cell parameters were refined from accurately determined 2θ values of 25 reflections ($4.1 < \theta < 38.7^\circ$) on a CAD-4 diffractometer. Intensity data were collected with Ni-filtered

Cu K α radiation using a crystal of dimensions $0.76 \times 0.61 \times 1.38$ mm up to $(\sin\theta)/\lambda = 0.627$ Å⁻¹ using ω - 2θ scan. Lorentz, polarization and absorption corrections (North, Phillips & Mathews, 1968) were applied; the transmission factor varied from 91.1 to 99.2%. 2460 reflections were measured for $0 \leq h \leq 9$, $0 \leq k \leq 16$, $0 \leq l \leq 22$ of which 1892 had $I \geq 3\sigma(I)$. Three strong reflections monitored periodically showed that the crystal was stable to X-rays.

The structure was solved by direct methods using MULTAN11/82 (Main *et al.*, 1982). An *E* map computed with the best set of phases ($CFOM = 2.797$) revealed the positions of 23 of the 24 non-H atoms. The position of the last atom was located using a weighted Fourier map. Successive difference Fourier maps revealed the positions of 24 H atoms, and two 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 0.04 and $wR = 0.04$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where

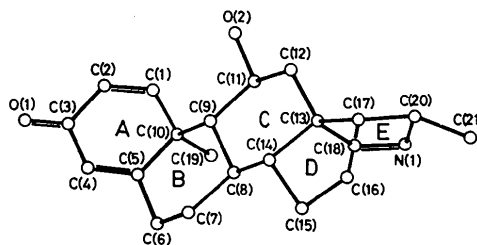


Fig. 1. Perspective view of 11 α -hydroxycon-1,4,18-trienine-3-one showing the numbering scheme.

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: $\frac{1}{3}(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3))$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
O(1)	0.8396 (3)	0.7507 (3)	0.7183 (2)	6.60 (7)
O(2)	0.3977 (2)	0.6713 (1)	1.0005 (1)	3.12 (4)
N(1)	-0.2821 (3)	0.5528 (2)	1.0029 (1)	3.37 (5)
C(1)	0.5254 (4)	0.7529 (3)	0.8649 (2)	3.61 (6)
C(2)	0.6778 (4)	0.7672 (3)	0.8295 (2)	3.83 (6)
C(3)	0.6994 (4)	0.7378 (3)	0.7523 (2)	4.38 (7)
C(4)	0.5462 (5)	0.6919 (3)	0.7170 (2)	4.24 (7)
C(5)	0.3900 (4)	0.6784 (3)	0.7515 (2)	3.52 (6)
C(6)	0.2384 (5)	0.6287 (3)	0.7122 (2)	4.56 (8)
C(7)	0.1729 (5)	0.5405 (3)	0.7562 (2)	4.35 (7)
C(8)	0.1259 (4)	0.5692 (2)	0.8358 (2)	3.22 (6)
C(9)	0.2902 (4)	0.6162 (2)	0.8759 (2)	2.81 (5)
C(10)	0.3602 (4)	0.7099 (2)	0.8315 (2)	3.10 (6)
C(11)	0.2466 (4)	0.6378 (2)	0.9588 (1)	2.64 (5)
C(12)	0.1672 (4)	0.5470 (2)	0.9981 (2)	3.04 (5)
C(13)	0.0042 (4)	0.5065 (2)	0.9583 (2)	2.83 (5)
C(14)	0.0579 (4)	0.4803 (2)	0.8788 (2)	3.24 (6)
C(15)	-0.1060 (5)	0.4239 (3)	0.8508 (2)	4.15 (7)
C(16)	-0.1544 (5)	0.3586 (3)	0.9169 (2)	4.88 (8)
C(17)	-0.0899 (4)	0.4122 (2)	0.9882 (2)	3.67 (6)
C(18)	-0.1514 (4)	0.5793 (2)	0.9628 (2)	2.88 (5)
C(19)	0.2215 (5)	0.7966 (2)	0.8324 (2)	3.92 (7)
C(20)	-0.2373 (4)	0.4556 (2)	1.0376 (2)	3.91 (6)
C(21)	-0.4024 (5)	0.3926 (3)	1.0512 (3)	6.22 (9)

$w = 1/\sigma^2(F_o)$. The residual electron density in the final difference Fourier map was between 0.213 and -0.151 e Å⁻³. The maximum shift/e.s.d. for non-H atoms is 0.16. 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).

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, bond angles and endocyclic torsion angles are given in Table 2.

Although the bond lengths C(6)–C(7), C(9)–C(10) and C(8)–C(14) show significant deviations (Table 2), the mean value of the C(sp³)–C(sp³) bonds [1.539 (5) Å] is comparable with an accepted mean of 1.533 Å (Sutton, 1965). Some of the bond angles [C(10)–C(9)–C(11), C(12)–C(13)–C(17) and C(8)–C(14)–C(15)] show considerable deviations (Table 2) from the ideal tetrahedral value: such variations are common in steroids, resulting from strain in the system. The bond lengths C(1)–C(2), C(4)–C(5), C(3)–O(1) and N(1)–C(18) are indicative of localized double bonds.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44912 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å), bond angles (°) and endocyclic torsional angles (°) of non-H atoms

Numbers in parentheses are estimated standard deviations in the least significant digits.

O(1)–C(3)	1.231 (4)	C(8)–C(14)	1.513 (4)
O(2)–C(11)	1.434 (3)	C(9)–C(10)	1.582 (5)
N(1)–C(18)	1.271 (4)	C(9)–C(11)	1.559 (4)
N(1)–C(20)	1.486 (5)	C(10)–C(19)	1.563 (4)
C(1)–C(2)	1.326 (4)	C(11)–C(12)	1.531 (4)
C(1)–C(10)	1.496 (4)	C(12)–C(13)	1.520 (4)
C(2)–C(3)	1.458 (5)	C(13)–C(14)	1.533 (5)
C(3)–C(4)	1.453 (5)	C(13)–C(17)	1.547 (5)
C(4)–C(5)	1.341 (4)	C(13)–C(18)	1.526 (4)
C(5)–C(6)	1.498 (5)	C(14)–C(15)	1.532 (4)
C(5)–C(10)	1.521 (4)	C(15)–C(16)	1.526 (5)
C(6)–C(7)	1.508 (6)	C(16)–C(17)	1.552 (5)
C(7)–C(8)	1.529 (4)	C(17)–C(20)	1.536 (4)
C(8)–C(9)	1.564 (4)	C(20)–C(21)	1.522 (6)
C(18)–N(1)–C(20)	108.0 (2)	C(9)–C(10)–C(19)	111.4 (2)
C(2)–C(1)–C(10)	125.3 (3)	O(2)–C(11)–C(9)	113.3 (3)
C(1)–C(2)–C(3)	121.2 (3)	O(2)–C(11)–C(12)	108.4 (3)
O(1)–C(3)–C(2)	122.2 (4)	C(9)–C(11)–C(12)	112.3 (3)
O(1)–C(3)–C(4)	121.3 (3)	C(11)–C(12)–C(13)	112.4 (2)
C(2)–C(3)–C(4)	116.5 (3)	C(12)–C(13)–C(14)	108.2 (2)
C(3)–C(4)–C(5)	123.2 (3)	C(12)–C(13)–C(17)	119.8 (2)
C(4)–C(5)–C(6)	120.4 (3)	C(12)–C(13)–C(18)	111.2 (2)
C(4)–C(5)–C(10)	122.1 (3)	C(14)–C(13)–C(17)	105.0 (2)
C(6)–C(5)–C(10)	117.4 (3)	C(14)–C(13)–C(18)	113.5 (2)
C(5)–C(6)–C(7)	110.4 (3)	C(17)–C(13)–C(18)	99.0 (2)
C(6)–C(7)–C(8)	111.8 (3)	C(8)–C(14)–C(13)	112.8 (2)
C(7)–C(8)–C(9)	110.8 (2)	C(8)–C(14)–C(15)	119.5 (3)
C(7)–C(8)–C(14)	111.1 (3)	C(13)–C(14)–C(15)	102.1 (2)
C(9)–C(8)–C(14)	110.4 (2)	C(14)–C(15)–C(16)	102.7 (3)
C(8)–C(9)–C(10)	110.4 (2)	C(15)–C(16)–C(17)	107.9 (3)
C(8)–C(9)–C(11)	110.7 (2)	C(13)–C(17)–C(16)	103.5 (3)
C(10)–C(9)–C(11)	114.1 (2)	C(13)–C(17)–C(20)	102.8 (2)
C(1)–C(10)–C(5)	111.6 (2)	C(16)–C(17)–C(20)	115.6 (3)
C(1)–C(10)–C(9)	112.2 (2)	N(1)–C(18)–C(13)	116.3 (2)
C(1)–C(10)–C(19)	105.2 (2)	N(1)–C(20)–C(17)	104.7 (2)
C(5)–C(10)–C(9)	108.0 (2)	N(1)–C(20)–C(21)	111.8 (3)
C(5)–C(10)–C(19)	108.4 (2)	C(17)–C(20)–C(21)	118.1 (3)

Ring B		Ring D	
9–10–5–6	52.9 (4)	17–13–14–15	41.1 (3)
10–5–6–7	-53.9 (4)	13–14–15–16	-41.9 (3)
5–6–7–8	54.0 (4)	14–15–16–17	27.9 (3)
6–7–8–9	-57.8 (3)	15–16–17–13	-2.9 (3)
7–8–9–10	57.1 (3)	16–17–13–14	-23.5 (3)
8–9–10–5	-52.5 (3)		

Ring C		Ring E	
13–12–11–9	-54.8 (3)	N(1)–20–17–13	29.9 (3)
12–11–9–8	50.7 (3)	20–17–13–18	-26.7 (3)
11–9–8–14	-52.1 (3)	17–13–18–N(1)	16.4 (3)
9–8–14–13	58.4 (3)	13–18–N(1)–20	2.5 (3)
8–14–13–12	-60.3 (3)	18–N(1)–20–17	-20.8 (3)
14–13–12–11	57.5 (3)		

Ring A is essentially planar, a feature found in relatively few steroids (Duax, Norton, Pokrywiecki & Eger, 1971; Peck, Langs, Eger & Duax, 1974; Radhakrishnan *et al.*, 1988). This ring makes an angle of 30° with the least-squares plane through the atoms of rings B, C and D. The endocyclic torsion angles vary from 0.3 (5) to 3.3 (4)°; bond angles at the sp² C atoms range from 116.3 (3) to 125.3 (3)°.

Ring B is in a normal chair conformation with the best rotational axis bisecting C(5)–C(10) and C(7)–C(8), and with the asymmetry parameter $\Delta C_2[C(5)–C(10)] = 2.4^\circ$ (Duax & Norton, 1975). Ring C is also a chair with the best rotational axis bisecting C(9)–C(11) and C(13)–C(14), with $\Delta C_2[C(9)–C(11)] = 2.1^\circ$.

Ring *D* is an envelope with a phase angle of pseudorotation $\Delta = 29.3^\circ$ and maximum angle of torsion $\varphi = 43.3^\circ$ (Altona, Geise & Romers, 1968). The asymmetry parameter $\Delta C_s[C(14)]$, which indicates distortion from the mirror symmetry bisecting C(16)–C(17), is 3.2° . Ring *E*, which contains the lone

N atom in this structure, shows a C(17) envelope conformation with $\Delta C_s[C(17)] = 0.6^\circ$, $\Delta = 24.2^\circ$ and $\varphi = 30.6^\circ$.

Fig. 2 shows Newman projections along the bonds involved in ring fusion. Atoms H(8) and H(9) as well as C(18) and H(14) have antiperiplanar configurations. The torsion angles of Table 2 show that rings *B* and *C* are slightly flattened with respect to the established average for steroids (Geise, Altona & Romers, 1967). This may be ascribed to the presence of unsaturated rings *A* and *E* in the present structure.

In the extended structure there is one hydrogen bond between the hydroxyl group and the N atom [O(2)–H(O)···N(1) = 2.896 Å]. The overall shape of the molecule is curved towards the α side. The torsion 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 67.9° .

Except for the absence of the methyl group at N(1) and the double bond N(1)–C(18) the present compound has the same atomic connectivity as 11 α -hydroxycon-1,4-dienine-3-one monohydrate (Radhakrishnan *et al.*, 1988). We note that there are significant differences in some of the torsion angles of these two compounds. In particular ring *E* is a C(17) envelope instead of the C(20) envelope of the earlier structure.

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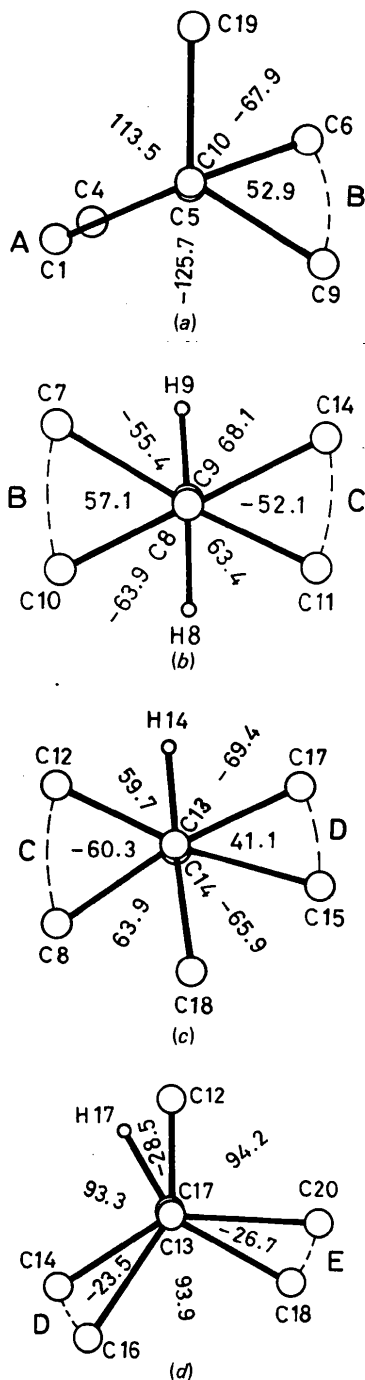


Fig. 2. Newman projections along (a) C(5)–C(10), (b) C(8)–C(9), (c) C(13)–C(14) and (d) C(13)–C(17) (angles in $^\circ$).