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Structure of Methyl (4′*S*,16*S*)-3*β*-Acetoxy-17-oxospiro[5-androstene-16,3′-(4,5-dihydropyrazole)]-4′-carboxylate

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Abstract. $C_{25}H_{34}N_2O_5$, $M_r = 442{\cdot}54$, monoclinic, $P2_1$, $a = 6{\cdot}414\ (1)$, $b = 9{\cdot}729\ (2)$, $c = 19{\cdot}192\ (3)$ Å, $\beta = 91{\cdot}09\ (1)°$, $V = 1197{\cdot}4\ (4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}227\ (1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}796$ mm^{-1}, $F(000) = 476$, $T = 293$ K, final $R = 0{\cdot}035$ for 1150 independent reflections. The configurations at chiral centers 4′ and 16 (3′) were found to be both *S*, assuming the *S* configuration at 13. The bowing of ring *A* relative to the remainder of the steroid nucleus is 17·03 (2)°. The rings have the following conformations: *A* chair; *B* half chair; *C* slightly deformed chair; *D* slightly distorted envelope.

Introduction. In the course of investigations on steroidal lactones having cytostatic properties (Kocór, Kabat, Wicha & Peczyńska-Czoch, 1983), the title compound was synthesized by treatment of (*E*)-3*β*,-17*β*-dihydroxy-5-androsten-16-ylidenacetic acid with diazomethane followed by acetylation of the hydroxy group at C(3). The sequence of atoms in the dihydropyrazole ring thus formed was elucidated from the ^{1}H NMR data. However, the configuration at the new chiral centers 16 (3′) and 4′ could not be established and therefore X-ray structural analysis of the title compound was necessary.

Experimental. Crystal (0·25 × 0·36 × 0·67 mm) from methanol. CAD-4D diffractometer (Enraf–Nonius), Mo $K\alpha$ radiation. Cell constants refined from 25 reflections ($13{\cdot}3 < \theta < 20{\cdot}6°$) by *SDP* system, $\omega/2\theta$ scan, $2\theta_{\max} = 50°$. Stability controlled with two reflections, no significant decay. 2243 unique reflections measured ($hkl_{\max} = 7, 11, 22$), 751 intensities zero (too diffuse), 1150 with $I > 2\sigma_I$. Equivalent reflections averaged automatically by *SDP* system, $R_{\rm int}$ not estimated. Lorentz and polarization, no absorption correction. Space group $P2_1$. Structure solved by direct methods (*MULTAN*80; Main *et al.*, 1980). Mean atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). Non-H-atom parameters refined anisotropically for one enantiomorph by a full-matrix procedure (*XRAY*70 system; Stewart, Kundell & Baldwin, 1970) for 1150 observed *F*'s. H-atom positions found from $\Delta\rho$ maps, added and refined (damping 0·3) in the last refinement step ($B = B_{\rm eq}$ of adjacent atom + 1 Å^2, invariant). Final $R = 0{\cdot}035$ ($wR = 0{\cdot}033$, unit weights) at $\Delta/\sigma < 0{\cdot}1$. Max. and min. electron densities on final $\Delta\rho$ map 0·3 and $-0{\cdot}2$ e Å^{-3}, respectively. Programs used for calculations of secondary results were *RING* (Párkányi, 1979) and *PLALIN* (Nardelli, Musatti, Domiano & Andreetti, 1978). Computations done on PDP8/11, Cyber-73 and MERA-400 computers.

Discussion. Table 1 gives the fractional coordinates of non-hydrogen atoms.* The bond lengths and valence angles are given in Table 2. Fig. 1 presents a projection of the steroid molecule oriented at optimal viewing.

In the description of the molecular structure of the steroid under investigation the conventions applied by Duax & Norton (1975) are followed. Fig. 2 shows a view of the steroid parallel to the least-squares plane through the atoms C(1) to C(17) (rings *B, C* and *D*). The bowing angle of ring *A* with respect to this plane (*A/B–C–D*) is 17·03 (2)°.

The mean values of C—C bond lengths and C—C—C angles in saturated rings *A* and *C* are 1·536 (8) Å and 111·0 (4)°, respectively. For the unsaturated ring *B*, the mean value for single C—C bond lengths is 1·533 (7) Å with the mean angle of 111·6 (4)°. All bond lengths and angles in rings *A, B* and *C* are in agreement (within twice the e.s.d.) with the mean values for 13 Δ^5-steroid structures quoted by Duax & Norton (1975) with two exceptions: bonds C(9)—C(11) and C(13)—C(14) (ring *C*) deviate by more than 0·03 Å, being longer and shorter, respectively.

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* Lists of structure factors, hydrogen-atom positions, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42348 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ring *A* of the steroid reported here may be characterized by a chair conformation $^{10}C_3$ ($^4C_1$). The asymmetry parameters are: $\Delta C_s^3 = 5\cdot6$ (6)° and $\Delta C_2^{1,2} = 3\cdot0$ (6)°. Since the deviations of C(3) and C(10) from the least-squares plane of *A* [defined by C(1), C(2), C(4) and C(5)] are nearly symmetrical [±0·656 (6) Å], an almost ideal chair conformation with mean torsion angle of 54·6 (6)° may be assumed. The *O*-acetyl substituent at C(3) is found in the equatorial position.

The unsaturated ring *B* has the half-chair conformation $^8H_9$. The asymmetry parameter $\Delta C_2^{5,6} = 0\cdot8$ (7)°. The deviations of C(8) and C(9) from the least-squares plane of *B* [defined by C(5), C(6), C(7) and C(10)] are nearly symmetrical with respect to the $C_2^{5,6}$ symmetry axis [0·371 (5) and −0·360 (6) Å, respectively]. The mean value for non-planar torsion angles is 28·6 (7)°. Thus, the assigned half-chair conformation is very close to an ideal model of the half-chair assumed from a cyclohexene molecule.

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

Origin along *b* specified by keeping *y* of O(1) fixed.

	x	*y*	*z*	B_{eq}(Å^2)*
C(1)	1066 (8)	4506 (6)	3736 (3)	4·2 (2)
C(2)	−355 (8)	5483 (7)	4147 (3)	4·6 (2)
C(3)	−1964 (9)	6106 (6)	3642 (3)	4·4 (2)
C(4)	−3208 (7)	4992 (6)	3269 (3)	4·0 (2)
C(5)	−1849 (7)	3956 (5)	2914 (3)	3·3 (2)
C(6)	−2152 (7)	3677 (6)	2244 (3)	3·6 (2)
C(7)	−936 (8)	2599 (6)	1853 (2)	3·9 (2)
C(8)	344 (7)	1669 (5)	2319 (2)	2·9 (2)
C(9)	1434 (7)	2525 (6)	2907 (3)	3·6 (2)
C(10)	−117 (8)	3311 (6)	3372 (3)	3·7 (2)
C(11)	2932 (7)	1577 (6)	3353 (2)	3·7 (2)
C(12)	4539 (8)	807 (6)	2917 (3)	4·0 (2)
C(13)	3412 (7)	−18 (5)	2345 (2)	3·3 (2)
C(14)	2078 (7)	951 (6)	1907 (3)	3·5 (2)
C(15)	1550 (8)	156 (6)	1229 (3)	3·6 (2)
C(16)	3705 (8)	−484 (6)	1074 (3)	3·5 (2)
C(16′)	3884 (8)	−1764 (6)	612 (3)	3·7 (2)
C(17)	4832 (9)	−611 (6)	1795 (3)	4·0 (2)
C(18)	2223 (8)	−1263 (6)	2644 (3)	4·4 (2)
C(19)	−1096 (9)	2398 (6)	3921 (3)	4·4 (2)
C(20)	4986 (10)	−1218 (7)	−40 (3)	5·0 (2)
C(21)	−2977 (12)	8166 (7)	4255 (3)	5·0 (2)
C(22)	−4768 (11)	8802 (8)	4629 (3)	5·6 (3)
C(23)	1784 (8)	−2422 (6)	469 (3)	3·4 (2)
C(24)	−685 (11)	−3911 (7)	930 (4)	6·8 (3)
N(1)	4878 (7)	616 (5)	688 (3)	4·5 (2)
N(2)	5512 (8)	210 (6)	124 (3)	5·1 (2)
O(1)	6495 (6)	−1157	1876 (2)	5·2 (2)
O(2)	−3503 (6)	6890 (4)	4040 (2)	4·9 (1)
O(3)	−1379 (8)	8710 (5)	4124 (3)	6·9 (2)
O(4)	688 (6)	−2198 (5)	−25 (2)	5·6 (1)
O(5)	1314 (6)	−3240 (4)	994 (2)	4·5 (1)

* $B_{eq} = 8\pi^2 D_u{}^{1/3}$, where D_u is the determinant of the *U* matrix.

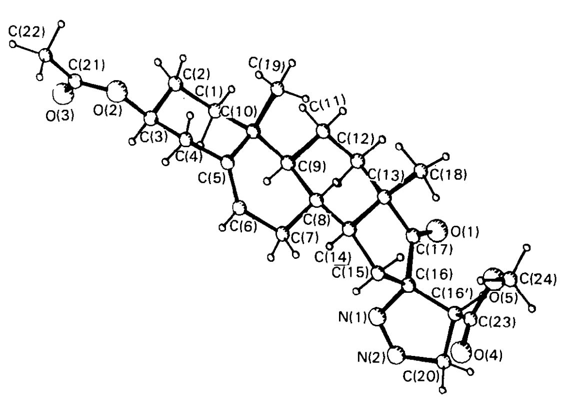

Fig. 1. Parallel projection of a single molecule oriented at optimal viewing, with crystallographic labelling of atoms.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·544 (8)	C(13)–C(17)	1·522 (7)
C(1)–C(10)	1·547 (8)	C(13)–C(18)	1·547 (8)
C(2)–C(3)	1·528 (8)	C(14)–C(15)	1·546 (7)
C(3)–C(4)	1·517 (8)	C(15)–C(16)	1·550 (7)
C(3)–O(2)	1·474 (7)	C(16)–C(16′)	1·535 (8)
C(4)–C(5)	1·504 (7)	C(16)–C(17)	1·554 (7)
C(5)–C(6)	1·324 (7)	C(16)–N(1)	1·511 (7)
C(5)–C(10)	1·538 (7)	C(16′)–C(20)	1·543 (8)
C(6)–C(7)	1·515 (8)	C(23)–C(16′)	1·512 (7)
C(7)–C(8)	1·504 (7)	C(17)–O(1)	1·199 (6)
C(8)–C(9)	1·558 (7)	C(20)–N(2)	1·462 (9)
C(8)–C(14)	1·544 (7)	C(21)–C(22)	1·501 (10)
C(9)–C(10)	1·551 (7)	C(21)–O(2)	1·348 (8)
C(9)–C(11)	1·573 (7)	C(21)–O(3)	1·184 (9)
C(10)–C(19)	1·522 (8)	C(23)–O(4)	1·190 (7)
C(11)–C(12)	1·536 (7)	C(23)–O(5)	1·323 (7)
C(12)–C(13)	1·529 (7)	C(24)–O(5)	1·442 (8)
C(13)–C(14)	1·517 (7)	N(1)–N(2)	1·228 (7)
C(2)–C(1)–C(10)	113·8 (4)	C(14)–C(13)–C(18)	114·6 (4)
C(1)–C(2)–C(3)	108·5 (5)	C(17)–C(13)–C(18)	105·4 (4)
C(2)–C(3)–C(4)	111·1 (5)	C(8)–C(14)–C(13)	113·7 (4)
C(2)–C(3)–O(2)	109·1 (5)	C(8)–C(14)–C(15)	120·6 (4)
C(4)–C(3)–O(2)	105·3 (4)	C(13)–C(14)–C(15)	105·5 (4)
C(3)–C(4)–C(5)	112·8 (4)	C(14)–C(15)–C(16)	100·4 (4)
C(4)–C(5)–C(6)	120·1 (5)	C(15)–C(16)–C(16′)	120·9 (4)
C(4)–C(5)–C(10)	115·7 (4)	C(15)–C(16)–C(17)	105·2 (4)
C(6)–C(5)–C(10)	124·3 (5)	C(15)–C(16)–N(1)	105·3 (4)
C(5)–C(6)–C(7)	123·8 (5)	C(16′)–C(16)–C(17)	114·2 (4)
C(6)–C(7)–C(8)	113·7 (4)	C(16′)–C(16)–N(1)	104·4 (4)
C(7)–C(8)–C(9)	110·0 (4)	C(17)–C(16)–N(1)	105·4 (4)
C(7)–C(8)–C(14)	111·0 (4)	C(16)–C(16′)–C(20)	103·2 (4)
C(9)–C(8)–C(14)	107·2 (4)	C(16)–C(16′)–C(23)	111·9 (4)
C(8)–C(9)–C(10)	113·4 (4)	C(20)–C(16′)–C(23)	114·7 (5)
C(8)–C(9)–C(11)	110·0 (4)	C(13)–C(17)–C(16)	108·3 (4)
C(10)–C(9)–C(11)	111·6 (4)	C(13)–C(17)–O(1)	128·4 (5)
C(1)–C(10)–C(5)	107·1 (4)	C(16)–C(17)–O(1)	123·2 (5)
C(1)–C(10)–C(9)	108·4 (4)	C(16′)–C(20)–N(2)	105·1 (5)
C(1)–C(10)–C(19)	109·3 (4)	C(22)–C(21)–O(2)	109·7 (6)
C(5)–C(10)–C(9)	109·6 (4)	C(22)–C(21)–O(3)	126·2 (6)
C(5)–C(10)–C(19)	109·3 (4)	O(2)–C(21)–O(3)	124·0 (6)
C(9)–C(10)–C(19)	112·8 (5)	C(16′)–C(23)–O(4)	125·3 (5)
C(9)–C(11)–C(12)	113·5 (4)	C(16′)–C(23)–O(5)	109·3 (4)
C(11)–C(12)–C(13)	109·5 (4)	O(4)–C(23)–O(5)	125·3 (5)
C(12)–C(13)–C(14)	109·0 (4)	C(16)–N(1)–N(2)	112·4 (5)
C(12)–C(13)–C(17)	114·6 (4)	C(20)–N(2)–N(1)	114·5 (5)
C(12)–C(13)–C(18)	112·0 (4)	C(3)–O(2)–C(21)	118·0 (5)
C(14)–C(13)–C(17)	100·9 (4)	C(23)–O(5)–C(24)	115·0 (5)

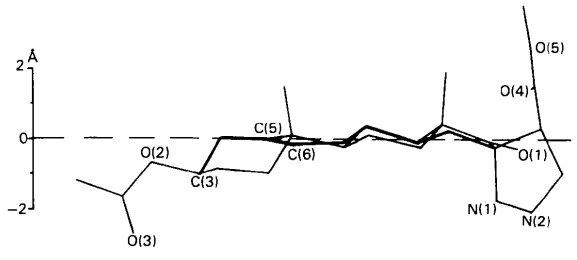

Fig. 2. A view of the steroid molecule along the least-squares plane through *B*–*C*–*D* (Duax & Norton, 1975). The trace of the plane is shown by the dashed line.

For the saturated ring *C* a slightly deformed chair conformation $^{13}C_9$ ($^4C_1$) may be assigned. The asymmetry parameters are: $\Delta C_s^9 = 4{\cdot}5\ (6)°$ and $\Delta C_2^{11,12} = 6{\cdot}1\ (5)°$. The mean value of torsion angles is 57·4 (5)°. The deviations of C(9) and C(13) from the four-atom least-squares plane through C(8), C(11), C(12) and C(14) are −0·689 (5) and 0·711 (5) Å, respectively. The distortion of the chair conformation in *C* is significantly greater than that in the *A* ring.

The five-membered ring *D* represents a slightly distorted envelope conformation $_{14}E$, as concluded from the asymmetry parameter $\Delta C_s^{14} = 2{\cdot}0\ (6)°$, and from the deviations of ring atoms from the four-atom least-squares plane, being within ±0·012 (5) Å for plane-defining atoms and −0·647 (6) Å for C(14). The O(1) carbonyl atom deviates slightly from that plane [0·099 (2) Å].

The dihedral angles at ring junctions (for convention see Duax & Norton, 1975, p. 22) are: *A/A–B* 125·3 (3)°, *A–B/B* 124·2 (2)°, *B/B–C* 136·6 (2)°, *B–C/C* 128·0 (2)°, *C/C–D* 133·8 (2)° and *C–D/D* 129·4 (2)°.

The dihydropyrazole ring *E* is nearly planar. The values of the endocyclic torsion angles are in the range 0·2–5·5 (6)° [mean value 3·7 (6)°]. The dihedral angle *D/E* is 91·8 (2)°.

The configuration at the two new chiral centers C(16) and C(16′) in *E*, formed by cyclization by diazomethane, are of particular interest. If the *S* configuration is assumed for the chiral center at C(13), the *S* configuration must be also assigned to C(16) as well as to C(16′).

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Structure of 2-(1-Adamantyl)-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silaethylene[*]

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Abstract. $C_{20}H_{42}OSi_4$, $M_r = 410{\cdot}9$, triclinic, $P\bar{1}$, $a = 6{\cdot}541\ (9)$, $b = 10{\cdot}057\ (2)$, $c = 20{\cdot}391\ (3)$ Å, $\alpha = 101{\cdot}69\ (1)$, $\beta = 90{\cdot}86\ (1)$, $\gamma = 105{\cdot}77\ (1)°$, $V = 1261\ (2)$ Å^3, $Z = 2$, D_m not determined, $D_x = 1{\cdot}082$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}70926$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}240$ mm^{-1}, $F(000) = 452$, $T = 223$ K, $R = 0{\cdot}049$, $wR = 0{\cdot}039$ for 3067 significant reflections with $I > 3\sigma(I)$. The compound is the first crystalline silene to be prepared which is stable at room temperature. The double-bond system is twisted 14·6° and the double bond, 1·764 (3) Å in length, is longer than that, 1·702 (5) Å, subsequently reported for a less sterically hindered silene.

Introduction. Interest in silenes, compounds containing an Si=C double bond, has recently intensified with the discovery of routes for preparing this long-sought but highly reactive species. [Recent reviews are given in Gusel'nikov & Nametkin (1979), Barton (1980), Coleman & Jones (1981) and Schaefer (1982).] An obvious challenge was to attempt the synthesis of a silene sufficiently stable to survive, preferably as a solid, at room temperature.

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[*] Adamantyl is tricyclo[3.3.1.1^{3,7}]decyl.

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