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3α-Acetylthio-5α-androstan-17-one

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Abstract. $C_{21}H_{32}O_2S$, monoclinic, $C2$, $a = 14{\cdot}725$ (8), $b = 5{\cdot}900$ (3), $c = 22{\cdot}119$ (10) Å, $\beta = 92{\cdot}28$ (3)°, $Z = 4$, $D_c = 1{\cdot}206$ Mg m^{-3}, Cu $K\alpha$ radiation (carbon monochromator), $\mu = 1{\cdot}464$ mm^{-1}, $\lambda = 1{\cdot}54051$ Å. The structure was solved by an application of the Patterson function and the tangent formula and refined by a large-block least-squares procedure to $R = 0{\cdot}04$ for 1452 reflections. The molecular configuration assigned from NMR data, with the S atom adopting the axial (3α) position, was confirmed.

Introduction. Thioacetates of triterpenes are found in unusual concentrations in the urine of young children who also exhibit inexplicably high blood pressure (Edwards & Trafford, 1968). The molecular configurations of these triterpenes have been established by ^{1}H NMR with reference to the thioacetates of the androsterones (Edwards, 1978). The configuration of these thioacetates, however, has not been established by X-ray crystallography and in order to confirm the NMR assignments we have determined the X-ray crystal structure of one of the reference compounds, 3α-acetylthio-5α-androstan-17-one. The crystals were provided by R. W. H. Edwards, Institute of Child Health, London, England.

The crystal system and approximate cell dimensions were determined from Weissenberg photographs. Systematic extinctions $h + k = 2n$ indicated that the space group was either $C2$, Cm or $C2/m$, of which $C2$ was chosen since the material was an optically active natural product. The cell dimensions were refined from the circle angles of 12 general reflections with the Bragg angle 2θ in the range 60–65°, and 1542 unique reflections were measured on a Picker FACS-1 four-circle diffractometer. Of these, 1452 had $I > 3\sigma(I)$. The data were reduced to a standard scale by the routine procedure (Cameron & Cordes, 1979) and were corrected for Lorentz and polarization factors, but not for absorption or extinction.

The positions of the S atom and the two C atoms bonded to it were established from a Patterson function. The positions of the three atoms were used to find approximate phases for the ten reflections with the largest E's. The phases of these ten reflections were used in a tangent refinement (Karle & Hauptman, 1958) to establish the phases of the reflections with the 50 largest E's. The resultant E map clearly showed all the non-hydrogen atoms. After several cycles of full-matrix least-squares refinement [$\sum w(\Delta F)^2 = \text{minimum}$] with isotropic temperature factors on all atoms R was 0·13. One cycle of large-block least-squares refinement with anisotropic temperature factors reduced R to 0·09. The H atoms were located on a Fourier difference synthesis calculated at this stage. Refinement continued with isotropic temperature factors for the H atoms and converged with $R = 0{\cdot}042$ ($wR = 0{\cdot}047$). The weights were calculated (Sheldrick, 1976) from $w = (\sigma^2|F_o| + 0{\cdot}0154F_o^2)^{-1}$, where σ is the standard deviation for each reflection and was derived from the diffractometer counting statistics.

The scattering factors used were taken from *International Tables for X-ray Crystallography* (1974) and

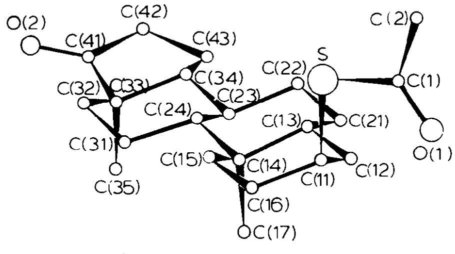

Fig. 1. The unique molecule.

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Table 1. *Atomic parameters* (× 10^4, *except* × 10^3 *for hydrogen*)

	x	y	z		x	y	z
S	−1312 (1)	354 (0)	866 (0)	H(121)	0 (9)	368 (26)	76 (5)
O(1)	−1443 (3)	2221 (6)	−203 (1)	H(122)	−27 (16)	593 (4)	113 (9)
C(1)	−1356 (2)	473 (8)	68 (1)	H(13)	12 (10)	172 (4)	168 (7)
C(2)	−1300 (3)	−1795 (8)	−235 (2)	H(151)	−165 (8)	358 (21)	257 (4)
C(11)	−1292 (2)	3375 (6)	1050 (1)	H(152)	−132 (13)	139 (4)	219 (7)
C(12)	−315 (2)	4240 (6)	1126 (1)	H(161)	−242 (5)	299 (25)	160 (9)
C(13)	157 (2)	3407 (6)	1711 (1)	H(162)	−195 (11)	548 (7)	165 (10)
C(14)	−359 (2)	4096 (5)	2279 (1)	H(171)	−85 (9)	709 (32)	267 (6)
C(15)	−1324 (2)	3092 (6)	2201 (1)	H(172)	16 (7)	754 (30)	242 (7)
C(16)	−1824 (2)	3818 (7)	1615 (1)	H(173)	−69 (10)	717 (32)	195 (4)
C(17)	−414 (2)	6657 (6)	2347 (1)	H(211)	142 (8)	355 (19)	137 (3)
C(21)	1153 (2)	4116 (7)	1750 (1)	H(212)	115 (14)	582 (4)	174 (7)
C(22)	1633 (2)	3137 (7)	2308 (1)	H(221)	227 (3)	369 (18)	235 (6)
C(23)	1157 (2)	3738 (5)	2889 (1)	H(222)	165 (7)	145 (5)	224 (7)
C(24)	140 (2)	2993 (5)	2834 (1)	H(231)	120 (14)	541 (6)	298 (9)
C(31)	−337 (2)	3343 (7)	3436 (1)	H(24)	13 (14)	132 (5)	273 (9)
C(32)	166 (2)	2301 (7)	3986 (1)	H(311)	−44 (9)	498 (7)	354 (7)
C(33)	1133 (2)	3140 (7)	4029 (1)	H(312)	−95 (4)	257 (23)	340 (9)
C(34)	1587 (2)	2583 (6)	3431 (1)	H(321)	13 (14)	63 (7)	389 (8)
C(35)	1176 (3)	5674 (9)	4192 (1)	H(322)	−15 (10)	257 (25)	437 (4)
C(41)	1777 (2)	2016 (8)	4488 (1)	H(34)	149 (11)	93 (6)	335 (7)
C(42)	2703 (2)	1867 (9)	4233 (1)	H(351)	89 (9)	590 (32)	459 (4)
C(43)	2610 (2)	2894 (8)	3595 (1)	H(352)	82 (9)	658 (29)	388 (6)
O(2)	1579 (2)	1388 (8)	4987 (1)	H(353)	181 (5)	629 (30)	422 (7)
H(21)	−101 (7)	−133 (20)	−63 (3)	H(421)	320 (7)	260 (25)	448 (6)
H(22)	−80 (5)	−147 (22)	10 (4)	H(422)	287 (12)	24 (13)	417 (10)
H(23)	−136 (8)	−350 (3)	−25 (5)	H(431)	293 (10)	210 (23)	326 (6)
H(11)	−156 (12)	413 (39)	68 (6)	H(432)	279 (12)	453 (10)	359 (7)

were corrected for the anomalous dispersion. The atomic parameters are listed in Table 1; Table 2 gives the interatomic distances and interbond angles.* The molecule is shown in Fig. 1 and the packing diagram in Fig. 2.

Discussion. The unit cell of the crystal is constructed from isolated units. The configuration of the molecule was confirmed to be correctly a 3α,5α system. The structure was refined in both enantiomeric forms, and the final R factors were $R_1 = 0{\cdot}042$, $wR_1 = 0{\cdot}047$; $R_2 = 0{\cdot}057$, $wR_2 = 0{\cdot}050$, so that Fig. 1 shows the absolute configuration of the molecule.

Within the four rings of the steroid, the C–C bond lengths are as expected. The two bonds adjacent to ring *D*, *i.e.* C(23)–C(34) and C(32)–C(33), are noticeably shorter than the average. The same effect was found in the structures of 3-oxo-5α-androstan-17β-ol toluene-*p*-sulphonate, determined at 103 K (de Graaff & Romers, 1974) and androsterone itself (High & Kraut, 1966). The structures of 5β-androstane-3α,17β-diol and, to a lesser extent, epiandrosterone (Weeks, Cooper, Norton, Hauptman & Fisher, 1971) also exhibit this shortening. Table 3 gives the torsion angles within the four rings.*

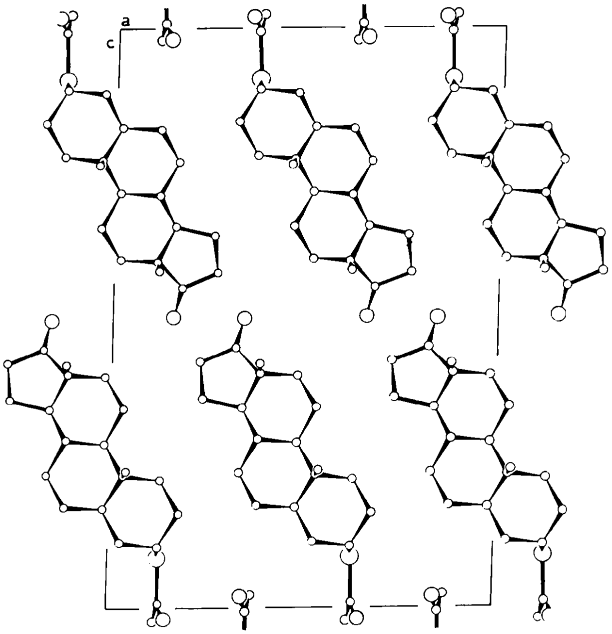

Fig. 2. The packing of molecules in the unit cell.

Rings *A*, *B* and *C* are each conventional chairs, with mean angles of twist of 54 (4), 57 (1) and 56 (4)° for rings *A*, *B* and *C* respectively. Ring *D* is an 'envelope' with C(43) 0·53 (1) Å out of the plane of the other four atoms. The mean deviation of these four atoms from the least-squares best plane is 0·12 (3) Å.

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* Lists of structure factors, thermal parameters and a full table of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34557 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

S–C(1)	1·764 (3)	C(22)–C(23)	1·530 (4)
S–C(11)	1·828 (3)	C(23)–C(24)	1·561 (4)
O(1)–C(1)	1·197 (5)	C(23)–C(34)	1·498 (4)
C(1)–C(2)	1·500 (5)	C(24)–C(31)	1·546 (4)
C(11)–C(12)	1·529 (4)	C(31)–C(32)	1·528 (5)
C(11)–C(16)	1·525 (5)	C(32)–C(33)	1·506 (5)
C(12)–C(13)	1·525 (4)	C(33)–C(34)	1·541 (5)
C(13)–C(14)	1·548 (4)	C(33)–C(35)	1·539 (5)
C(13)–C(21)	1·524 (4)	C(33)–C(41)	1·514 (5)
C(14)–C(15)	1·543 (4)	C(34)–C(43)	1·546 (5)
C(14)–C(17)	1·521 (4)	C(41)–C(42)	1·498 (5)
C(14)–C(24)	1·549 (4)	C(41)–O(2)	1·211 (5)
C(15)–C(16)	1·526 (4)	C(42)–C(43)	1·537 (5)
C(21)–C(22)	1·512 (5)		

C(1)–S–C(11)	100·6 (1)	C(22)–C(23)–C(34)	112·0 (2)
S–C(1)–O(1)	122·3 (3)	C(24)–C(23)–C(34)	108·0 (2)
S–C(1)–C(2)	114·2 (3)	C(14)–C(24)–C(23)	111·6 (2)
O(1)–C(1)–C(2)	123·4 (3)	C(14)–C(24)–C(31)	114·2 (2)
S–C(11)–C(12)	110·9 (2)	C(23)–C(24)–C(31)	111·2 (2)
S–C(11)–C(16)	110·2 (2)	C(24)–C(31)–C(32)	114·2 (2)
C(12)–C(11)–C(16)	111·3 (3)	C(31)–C(32)–C(33)	110·2 (3)
C(11)–C(12)–C(13)	112·5 (2)	C(32)–C(33)–C(34)	108·5 (3)
C(12)–C(13)–C(14)	112·4 (2)	C(32)–C(33)–C(35)	111·4 (3)
C(12)–C(13)–C(21)	111·4 (2)	C(32)–C(33)–C(41)	117·7 (3)
C(14)–C(13)–C(21)	112·6 (2)	C(34)–C(33)–C(35)	113·1 (3)
C(13)–C(14)–C(15)	106·8 (2)	C(34)–C(33)–C(41)	101·5 (3)
C(13)–C(14)–C(17)	111·8 (2)	C(35)–C(33)–C(41)	104·5 (3)
C(13)–C(14)–C(24)	107·4 (2)	C(23)–C(34)–C(33)	113·9 (2)
C(15)–C(14)–C(17)	109·9 (2)	C(23)–C(34)–C(43)	120·7 (3)
C(15)–C(14)–C(24)	109·5 (2)	C(33)–C(34)–C(43)	103·1 (3)
C(17)–C(14)–C(24)	111·4 (2)	C(33)–C(41)–C(42)	109·2 (3)
C(14)–C(15)–C(16)	113·5 (2)	C(33)–C(41)–O(2)	125·3 (3)
C(11)–C(16)–C(15)	113·7 (3)	C(42)–C(41)–O(2)	125·5 (4)
C(13)–C(21)–C(22)	111·0 (3)	C(41)–C(42)–C(43)	105·9 (3)
C(21)–C(22)–C(23)	112·5 (3)	C(34)–C(43)–C(42)	102·6 (3)
C(22)–C(23)–C(24)	109·7 (2)		

Table 3. *Selected torsion angles* (°)

E.s.d.'s are not greater than 0·7°.

Ring *A*	
C(11)–C(12)–C(13)–C(14)	−57·5
C(12)–C(13)–C(14)–C(15)	58·0
C(13)–C(14)–C(15)–C(16)	−55·9
C(14)–C(15)–C(16)–C(11)	53·2
C(15)–C(16)–C(11)–C(12)	−48·2
C(16)–C(11)–C(12)–C(13)	50·4
Mean	54 (4)
Ring *B*	
C(14)–C(13)–C(21)–C(22)	56·9
C(13)–C(21)–C(22)–C(23)	−54·9
C(21)–C(22)–C(23)–C(24)	55·0
C(22)–C(23)–C(24)–C(14)	−57·4
C(23)–C(24)–C(14)–C(13)	58·0
C(24)–C(14)–C(13)–C(21)	−57·8
Mean	57 (1)
Ring *C*	
C(23)–C(24)–C(31)–C(32)	−51·4
C(24)–C(31)–C(32)–C(33)	54·0
C(31)–C(32)–C(33)–C(34)	−56·3
C(32)–C(33)–C(34)–C(23)	62·5
C(33)–C(34)–C(23)–C(24)	−59·4
C(34)–C(23)–C(24)–C(31)	52·0
Mean	56 (4)
Ring *D*	
C(34)–C(33)–C(41)–C(42)	25·7
C(33)–C(41)–C(42)–C(43)	−1·1
C(41)–C(42)–C(43)–C(34)	−23·9
C(42)–C(43)–C(34)–C(33)	39·9
C(43)–C(34)–C(33)–C(41)	−40·3

This appears to be the first X-ray determination of the structure of an acetothiol. The C(1)–S bond length of 1·764 (3) Å compares favourably with that determined by electron diffraction for thioacetic acid (CH_3.CO.SH), 1·78 (2) Å (Gordy, 1946), and with that observed in thiphenamil hydrochloride, 1·780 (4) Å (Guy & Hamor, 1974). The C(11)–S bond length of 1·828 (3) Å also compares favourably with the corresponding S–C bond [1·814 (4) Å] found in thiphenamil hydrochloride. The difference in length of 0·064 Å between the C(1)–S and C(11)–S bonds in the title compound can be attributed to the difference in covalent radii between an sp^2 and an sp^3 C atom (Coulson, 1963), and to the electrostatic attractions between the slightly positive C atom of the carbonyl group and the electronegative S. The S atom is in an axial position with S–H transannular contacts of S--H(13) 2·85 (1), and S--H(152) 3·00 (1) Å. The van der Waals contact S--H is about 3·05 Å (Evans, 1966), so that S--H(13) is somewhat short. This short contact does not appear to be very significant, since the torsion angles for ring *A* are only slightly distorted. The C(15)–C(16)–C(11)–C(12) torsion angle of −48° is the smallest observed within the rings and it reflects the repulsion of the S atom away from H(13) (Fig. 1).

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