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2β-Ethynyl-5β,17β-dihydroxy-3,4-bisnorandrostane 17-Acetate

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Abstract. $C_{21}H_{30}O_3$, $M=330$, orthorhombic, $P2_12_12_1$; $a=7{\cdot}570$ (1), $b=11{\cdot}043$ (3), $c=22{\cdot}815$ (7) Å, $V=1907{\cdot}2$ Å^3, $Z=4$, $d_c=1{\cdot}15$ g cm^{-3}. Final $R=0{\cdot}074$ for 1353 observed reflexions. Unusual stereochemistry is exhibited by ring *A* and the *A*/*B* ring junction.

Introduction. The system and space group were obtained from preliminary photographs. A crystal (0·2 × 0·3 × 0·9 mm) was used to measure all parameters and intensities on a Philips PW 1100 four-circle diffractometer. The unit-cell dimensions were determined by a least-squares refinement of the θ values of 50 reflexions. Data were collected to a maximum θ of 68° with graphite-monochromated Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å, ω–2θ scan, scan width 1·50°, scan speed 0·0375° s^{-1}). Of the 2037 measured reflexions, 1353 were observed with $I>2\sigma(I)$, $\sigma(I)$ being the standard deviation derived from counting statistics. Corrections were made for Lorentz and polarization effects but not for absorption. The structure was solved by the symbolic addition method (Karle & Karle, 1966) using the phase function (Riche, 1973). Refinement was carried out by full-matrix least-squares calculations (Busing, Martin & Levy, 1962) with individual anisotropic thermal factors. All the hydrogen atoms were located on a difference map. To each we assigned the equivalent thermal factor of the bonded carbon atom and their different parameters were not refined. The conventional final *R* was 0·074 with the observed reflexions (0·083 with all measured reflexions).* The scattering factors of Doyle

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30988 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

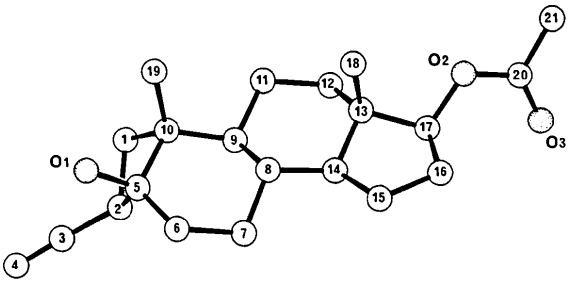
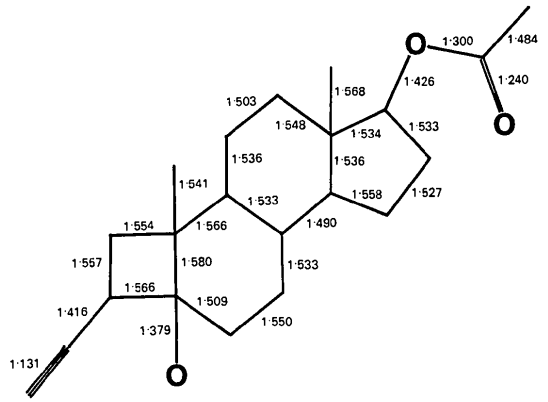


Fig. 1. A perspective view of the molecule showing the atomic numbering.

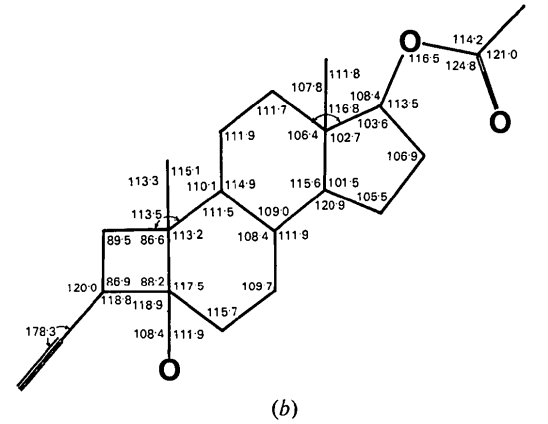
Table 1. *Positional and thermal parameters* ($\times 10^4$) *for the non-hydrogen atoms with estimated standard deviations in parentheses*

Thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

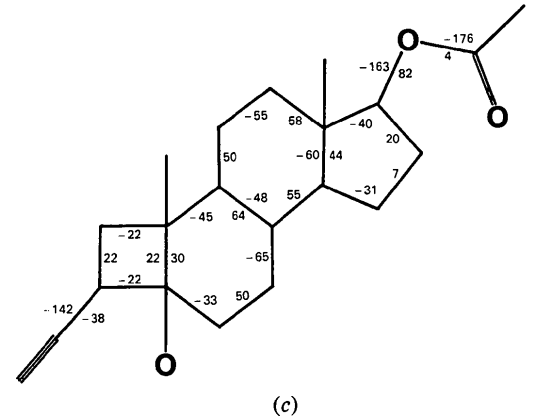
	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4296 (9)	6554 (6)	3764 (3)	199 (14)	123 (7)	29 (2)	−10 (9)	−12 (4)	15 (3)
C(2)	6057 (8)	7282 (5)	3775 (3)	213 (15)	93 (6)	21 (1)	−10 (8)	−2 (4)	−4 (3)
C(3)	6455 (10)	8100 (6)	3316 (3)	294 (18)	87 (6)	28 (2)	−34 (10)	2 (5)	5 (3)
C(4)	6814 (12)	8744 (7)	2949 (3)	411 (23)	125 (8)	31 (2)	−76 (13)	−16 (6)	21 (3)
C(5)	7027 (7)	6029 (5)	3792 (2)	167 (13)	78 (5)	21 (1)	−18 (8)	5 (4)	0 (3)
C(6)	8679 (8)	5902 (6)	4157 (3)	182 (14)	96 (7)	36 (2)	−18 (9)	19 (4)	8 (3)
C(7)	8395 (8)	5896 (6)	4830 (3)	138 (12)	124 (7)	26 (2)	−19 (9)	2 (4)	15 (3)
C(8)	6940 (7)	4989 (5)	4990 (2)	130 (12)	81 (5)	17 (1)	4 (7)	5 (3)	−1 (2)
C(9)	5196 (7)	5434 (5)	4725 (2)	126 (11)	73 (5)	21 (1)	5 (7)	7 (3)	−3 (2)
C(10)	5269 (8)	5454 (5)	4040 (3)	175 (13)	72 (5)	26 (1)	−24 (8)	−9 (4)	−3 (2)
C(11)	3546 (7)	4747 (6)	4933 (3)	133 (11)	156 (8)	16 (1)	−25 (9)	−3 (3)	5 (3)
C(12)	3483 (7)	4641 (5)	5590 (3)	94 (11)	98 (6)	37 (2)	−6 (8)	0 (4)	−3 (3)
C(13)	5187 (7)	4061 (5)	5838 (2)	139 (12)	59 (5)	26 (1)	−1 (8)	10 (3)	−6 (2)
C(14)	6726 (7)	4866 (5)	5636 (3)	127 (11)	68 (5)	29 (2)	1 (7)	1 (4)	−5 (2)
C(15)	8264 (8)	4385 (6)	6026 (3)	161 (12)	109 (7)	33 (2)	7 (9)	−12 (4)	1 (3)
C(16)	7401 (9)	3973 (6)	6597 (2)	223 (14)	103 (6)	20 (1)	−10 (9)	−5 (4)	1 (2)
C(17)	5398 (8)	4061 (5)	6507 (2)	217 (14)	74 (6)	16 (1)	−18 (9)	3 (4)	−1 (2)
C(18)	5350 (9)	2754 (5)	5576 (3)	246 (16)	70 (5)	35 (2)	−18 (9)	10 (5)	−15 (3)
C(19)	4824 (10)	4241 (5)	3740 (2)	346 (19)	119 (8)	20 (1)	−90 (10)	9 (5)	−10 (3)
C(20)	4111 (8)	3075 (6)	7297 (3)	176 (13)	70 (6)	28 (2)	6 (8)	−9 (4)	4 (3)
C(21)	3222 (10)	1969 (6)	7520 (3)	383 (21)	101 (7)	32 (2)	−35 (11)	20 (6)	−3 (3)
O(1)	7287 (6)	5645 (3)	3223 (2)	338 (12)	108 (4)	21 (1)	−16 (6)	29 (3)	−10 (2)
O(2)	4450 (6)	3052 (3)	6738 (2)	304 (11)	85 (4)	13 (1)	−39 (6)	16 (3)	−7 (1)
O(3)	4477 (6)	3926 (4)	7629 (2)	305 (12)	88 (4)	26 (1)	−16 (7)	−6 (3)	−3 (2)



(*a*)



(*b*)



(*c*)

Fig. 2. (*a*) Bond lengths (Å). (*b*) Valency angles (°) [C(10)–C(5)–O(1) 109·5, C(5)–C(10)–C(19) 112·0, C(14)–C(13)–C(18) 111·0]. (*c*) Torsional angles (°). The mean value of the standard deviation is 0·008 Å on distances and 0·5° on angles.

& Turner (1968) were taken for carbon and oxygen, those of Stewart, Davidson & Simpson (1965) for hydrogen. Atomic coordinates and thermal factors are listed in Table 1.

Discussion. The title compound has been synthesized by Guénard (1974). The structure determination of this new type of steroid was undertaken as part of a program carried out in our Institute to study the induced shift by lanthanides. In order to calculate the induced shift according to the McConnell & Robertson (1958) equation, it was necessary to know the precise geometry of the molecule. An *ORTEP* drawing (Johnson, 1965) is given in Fig. 1; bond lengths, valency and torsional angles are shown in Fig. 2. The cyclobutane ring is puckered, with a mean dihedral angle of 148,5° comparable with other puckered four-membered rings (Adman & Margulis, 1968). In this ring the ethynyl chain and the methyl group C(19) are in a pseudo-equatorial position. Ring *C* is chair-shaped while ring *B* adopts a conformation between a chair and a sofa, resulting from the *cis A*/*B* junction. Ring *D* exhibits a conformation intermediate between a C(13)β–C(14)α half-chair and a C(13)β envelope, as shown by the parameters $\Delta = 18{\cdot}4°$ and $\varphi_m = 44{\cdot}6°$ (Altona, Geise & Romers, 1968). The acetate group is coplanar with the C(13) and C(17) atoms. In the crystal only normal van der Waals contacts are observed.

We thank Dr D. Guénard for supplying the crystals and suggesting the problem.

References

ADMAN, E. & MARGULIS, T. N. (1968). *J. Amer. Chem. Soc.* **90**, 4517–4521.

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 19.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

GUÉNARD, D. (1974). Thèse Doctorat ès Sciences.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794 revised.

KARLE, I. L. & KARLE, J. (1966). *Acta Cryst.* B**21**, 849–859.

MCCONNELL, H. M. & ROBERTSON, R. E. (1958). *J. Chem. Phys.* **29**, 1361.

RICHE, C. (1973). *Acta Cryst.* A**29**, 133–137.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.