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### (25*R*)-6β-Acetoxy-3β-bromo-5α-spirostan-23-one

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#### Abstract

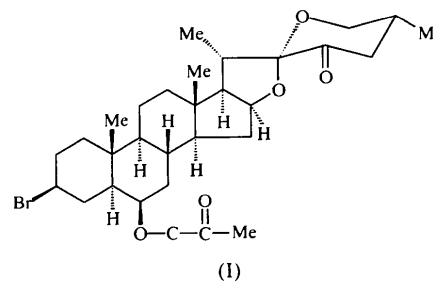
In the title compound [systematic name: (25*R*)-3β-bromo-23-oxo-5α-spirostan-6-yl acetate, C<sub>29</sub>H<sub>43</sub>BrO<sub>5</sub>], the C3—Br bond is oriented equatorially and (–)-antiperiplanar with respect to the C4—C5 bond. The six-membered *B*, *C* and *F* rings have chair conformations, as is usual in this type of compound. The five-membered *D* ring adopts a 14α-envelope conformation and the *E* ring adopts a C22β,O3α-half-chair conformation. The *A/B*, *B/C* and *C/D* ring junctions are *trans*.

#### Comment

In connection with our studies on the synthesis and characterization of bioactive steroids, we need, for reference purposes, the detailed molecular geometry of (25*R*)-

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6β-acetoxy-3β-bromo-5α-spirostan-23-one, (I), which is being used extensively as a starting material for the synthesis of different spirostanoic analogues of brasino-steroids. The title compound was obtained by treatment of an acetic acid solution of the previously reported steroid (25*R*)-5α-spirostan-2α,3α,6β-triol triacetate (Iglesias-Arteaga *et al.*, 1998).



The absolute configuration, determined from refinement of the Flack (1983) parameter in the X-ray analysis, confirmed that predicted beforehand from the synthesis route. The molecular structure of the title compound with the atomic numbering scheme is shown in Fig. 1. The C3—Br bond is oriented equatorially and (–)-antiperiplanar with respect to the C4—C5 bond. The presence of the Br atom does not disturb the chair conformation in ring *A* of the steroidal nucleus. Ring *A* has a highly symmetrical chair conformation with all asymmetry parameters below 2.70 (9°) (Duax *et al.*, 1976). Mirror symmetry is dominant, with asymmetry parameters  $\Delta C_5(C3) = 0.6$  (7),  $\Delta C_5(C5) = 1.2$  (8) and  $\Delta C_2(C4-C5) = 2.70$  (9°). The average of the torsion angles is 56.50 (9°). Rings *B*, *C* and *F* have chair conformations, as expected (Pfeiffer *et al.*, 1985). Ring *D* has a 14α-envelope conformation (Altona *et al.*, 1968). Ring *E* has a C22β,O3α-half-chair conformation. The *A/B*, *B/C* and *C/D* ring junctions are *trans*. Bond distances and valence angles are close to expected values (Honda *et al.*, 1996). The packing of the molecules is assumed to be dictated by van der Waals interactions and by intramolecular and intermolecular C—H...O hydrogen bonds (Taylor & Kennard, 1982).

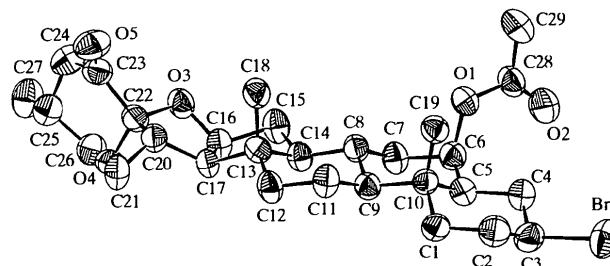


Fig. 1. Plot showing the atomic numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms and H atoms have been omitted for clarity.

## Experimental

The title compound was synthesized from an acetic acid solution of (25*R*)-5 $\alpha$ -spirostan-2 $\alpha$ ,3 $\alpha$ ,6 $\beta$ -triol triacetate with boron trifluoride ethyl etherate and sodium nitrite, followed by chromatography on alumina. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate-hexane solution (1:1).

### Crystal data

C<sub>29</sub>H<sub>43</sub>BrO<sub>5</sub>  
*M<sub>r</sub>* = 551.54  
 Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 9.2654 (12) Å  
*b* = 10.6629 (14) Å  
*c* = 27.703 (4) Å  
*V* = 2737.0 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.339 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

### Data collection

Siemens *P4* four-circle diffractometer  
 2 $\theta$ / $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.389, *T<sub>max</sub>* = 0.721  
 3629 measured reflections  
 3200 independent reflections (plus 210 Friedel-related reflections)

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.061  
*wR*(*F*<sup>2</sup>) = 0.142  
*S* = 1.097  
 3410 reflections  
 322 parameters  
 H-atom parameters constrained  
*w* = 1/[ $\sigma^2(F_o^2) + (0.0633P)^2 + 5.3297P$ ]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 ( $\Delta/\sigma$ )<sub>max</sub> < 0.001

Cu *K* $\alpha$  radiation  
 $\lambda$  = 1.54178 Å  
 Cell parameters from 46 reflections  
 $\theta$  = 6.45–55.80°  
 $\mu$  = 2.332 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism  
 0.40 × 0.26 × 0.14 mm  
 Colourless

2651 reflections with *F* > 2 $\sigma$ (*F*)  
*R<sub>int</sub>* = 0.037  
 $\theta$ <sub>max</sub> = 69.17°  
*h* = -1 → 9  
*k* = -1 → 12  
*l* = -1 → 33  
 3 standard reflections every 100 reflections  
 intensity decay: < 1.0%

$\Delta\rho$ <sub>max</sub> = 0.457 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = -0.756 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97* (Sheldrick, 1997*a*)  
 Extinction coefficient: 0.0030 (3)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: Flack (1983)  
 Flack parameter = -0.05 (5)

Table 1. Selected geometric parameters (Å, °)

Br—C3	1.972 (8)	O3—C22	1.420 (7)
O1—C6	1.464 (9)	O4—C22	1.441 (8)
O1—C28	1.345 (7)	O4—C26	1.442 (9)
O2—C28	1.192 (10)	O5—C23	1.225 (9)
O3—C16	1.445 (8)		
C6—O1—C28	118.2 (6)	O3—C22—C20	106.1 (5)
C16—O3—C22	105.3 (5)	O3—C22—C23	107.2 (5)
C22—O4—C26	112.8 (5)	O4—C22—C20	106.8 (5)
Br—C3—C2	109.0 (5)	O4—C22—C23	109.4 (5)
Br—C3—C4	109.8 (5)	O5—C23—C22	119.9 (7)
O1—C6—C5	110.6 (6)	O5—C23—C24	122.7 (7)
O1—C6—C7	107.6 (5)	O4—C26—C25	111.4 (6)

O3—C16—C15	114.8 (5)	O1—C28—O2	124.6 (7)
O3—C16—C17	105.5 (5)	O1—C28—C29	110.9 (7)
O3—C22—O4	109.7 (6)	O2—C28—C29	124.5 (6)

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
C1—H1 <i>B</i> ...O5'	0.97	2.57	3.405 (9)	145
C6—H6...O2	0.98	2.34	2.731 (8)	103
C15—H15 <i>B</i> ...O5''	0.97	2.59	3.529 (9)	163
C19—H19 <i>B</i> ...O1	0.96	2.53	2.972 (8)	108
C20—H20...O5	0.98	2.50	2.846 (9)	100
C26—H26 <i>B</i> ...O3	0.97	2.48	2.839 (9)	102

Symmetry codes: (i) 2 - *x*, *y* -  $\frac{1}{2}$ ,  $\frac{1}{2}$  - *z*; (ii) 1 - *x*, *y* -  $\frac{1}{2}$ ,  $\frac{1}{2}$  - *z*.

The title structure was solved by direct methods and Fourier synthesis. Non-H atoms were refined anisotropically by full-matrix least-squares techniques. H atoms were calculated geometrically and included in the refinement, but were restrained to ride on their parent atoms. The isotropic displacement parameters of the H atoms were fixed at 1.3*U*<sub>eq</sub> of their parent atoms.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *PLATON* (Spek, 1990), *PARST* (Nardelli, 1983, 1995) and *PARSTCIF* (Nardelli, 1991)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1383). Services for accessing these data are described at the back of the journal.

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## *N*<sup>6</sup>-Anisoyladenosine monohydrate

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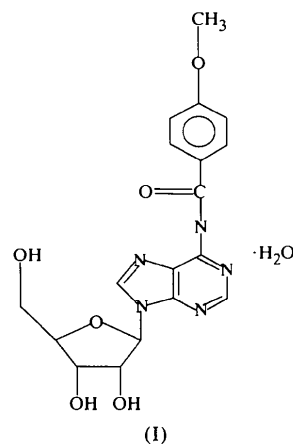
(Received 28 May 1998; accepted 19 November 1998)

### Abstract

The title compound,  $C_{18}H_{19}N_5O_6 \cdot H_2O$ , has a *syn* conformation about the glycosidic bond. Its furanose ring shows a *C2'-endo-C3'-exo* twist conformation and *trans-gauche* geometry about the  $C4'-C5'$  bond. The angle between the adenine base and the phenyl ring of the anisoyl group is  $22.9^\circ$ . Adenine and anisoyl groups stack along the *b* axis at a separation of 3.4 Å.

### Comment

The investigation of the title compound, (I), was carried out to study the effect of modifications of the base on



the nucleoside conformation as part of our studies on modified nucleosides (Padiyar & Seshadri, 1996). The conformation of the adenine base with respect to the ribose is *syn* with  $\chi_{CN} = -68.1(2)^\circ$ . This *syn* conformation is not accompanied by the  $N3-O5'$  intramolecular hydrogen bond characteristically seen in several 2'- and 2',5'-nucleotide structures (Padiyar & Seshadri, 1998; Krishnan & Seshadri, 1993, 1994). The furanose ring shows a *C2'-endo-C3'-exo* twist conformation which is evident from the pseudorotation angle  $P = 174.3^\circ$ . The maximum amplitude of pucker is  $39.4^\circ$  (Altona & Sundaralingam, 1972; Saenger, 1984). The torsion angles  $\varphi_{oo}(O5'-C5'-C4'-O4')$  and  $\varphi_{oc}(O5'-C5'-C4'-C3')$  are  $173.1(2)$  and  $-69.2(2)^\circ$ , respectively. They indicate that the conformation about the  $C4'-C5'$  bond is *trans-gauche*. The angle between the adenine base and the phenyl ring of the anisoyl group is  $22.9^\circ$  and these stack at a separation of 3.4 Å along the *b* axis. This column of nucleosides repeats along the *c* axis. An

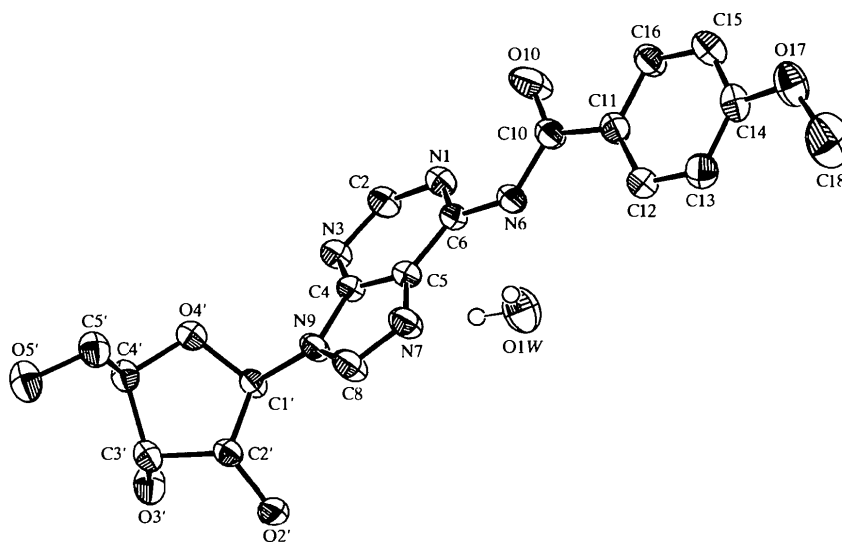


Fig. 1. Molecular structure of (I) showing 50% probability displacement ellipsoids.