C1—C2—C3	108.9 (7)	C2′—C1′—C6′	107.6 (6)
C2—C3—C7	100.2 (7)	C1′—C2′—C3′	107.4 (6)
C2—C3—C4	106.4 (5)	C2′—C3′—C7′	100.5 (6)
C7—C3—C4	98.9 (7)	C2′—C3′—C4′	106.2 (5)
C8—C4—C5	104.3 (5)	C7′—C3′—C4′	98.7 (5)
C8—C4—C3	115.3 (8)	C8′—C4′—C5′	105.4 (5)
C5—C4—C3	103.1 (5)	C8′—C4′—C3′	116.6 (5)
C9—C5—C4	106.3 (5)	C5′—C4′—C3′	102.8 (5)
C9—C5—C6	116.8 (5)	C9′—C5′—C4′	105.2 (5)
C4—C5—C6	101.8 (5)	C1′—C6′—C7′	100.5 (6)
C1—C6—C7	101.7 (6)	C1′—C6′—C5′	106.4 (5)
C1—C6—C5	107.4 (5)	C7′—C6′—C5′	99.8 (6)
C7—C6—C5	99.0 (6)	C6′—C7′—C3′	94.1 (6)
C6—C7—C3	93.4 (5)	O1′—C8′—N1′	123.7 (6)
O1—C8—N1	120.9 (6)	O1′—C8′—C4′	128.3 (5)
O1—C8—C4	129.5 (6)	N1′—C8′—C4′	107.9 (5)
N1—C8—C4	109.6 (6)	O2′—C9′—N1′	123.7 (6)
O2—C9—N1	124.1 (5)	O2′—C9′—C5′	129.0 (6)
O2—C9—C5	128.3 (6)	N1′—C9′—C5′	107.2 (5)
N1—C9—C5	107.6 (5)	N1′—C10′—C11′	111.2 (5)
N1—C10—C11	114.5 (4)	N1′—C10′—C12′	104.9 (4)
N1—C10—C12	110.4 (4)	C11′—C10′—C12′	118.2 (5)
C11—C10—C12	109.2 (4)	C10′—C11′—S1′*A*	120.1 (8)
C10—C11—S1	113.5 (4)	C10′—C11′—S1′	113.8 (5)
O3—C12—O4	125.2 (5)	O3′—C12′—C10′	124.6 (6)
O3—C12—C10	125.8 (5)	O4′—C12′—C10′	110.8 (6)

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

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*A*···O1$^{\rm i}$	2.402 (8)	3.102 (8)	128.7 (6)
C3—H3···O2$^{\rm ii}$	2.454 (9)	3.323 (9)	147.5 (7)
C4′—H4′···O2$^{\rm iii}$	2.511 (8)	3.484 (8)	172.0 (6)
C13*F*′—H13*F*···O2′$^{\rm iv}$	2.38 (2)	3.289 (9)	158 (1)
C6—H6···O4$^{\rm v}$	2.482 (8)	3.286 (8)	139.1 (6)

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

One S atom of the disulfide bridge was disordered between two positions (S1′ and S1′*A* with 0.67 and 0.33 occupancies, respectively). Final refinement (Sheldrick, 1993) included (*a*) the displacement-coefficient restraints *ISOR* of 0.005 for C12′ and 0.008 for O1 to prevent these atoms becoming 'non-positive definite', and *EADP* for S1′ and S1′*A* to force these partially occupied atoms to have identical displacement coefficients, and (*b*) bond-length restraints *DFIX* of 1.810 (5) Å for C11—S1, C11′—S1′ and C11′—S1′*A*, 2.040 (5) Å for S1—S1′, and 1.520 (5) Å for C10′—C12′. The problem of disorder around the sulfur site gave rise to rather elongated ellipsoids for S1′ and S1′*A*. The highest residual electron density peak (1.14 Å) did not indicate any feature of chemical significance.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *REFINE* (incorporated in *MADNES*). Data reduction: *ABSMAD* (Karaulov, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1223). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1703–1705

Chiral Hydroxylamines. IV. 1-(*N*-Benzyl-*N*-hydroxyamino)-2:3;4:5-di-*O*-isopropylidene-α-D-mannofuranose

Pedro Merino, Francisco L. Merchan, Tomas Tejero and Santiago Franco

Departamento de Quimica Organica, Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza, E-50009 Zaragoza, Spain. E-mail: pmerino@posta.unizar.es

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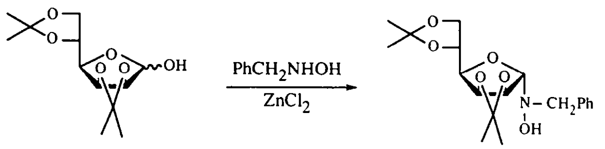
Abstract

The title compound, $C_{19}H_{27}NO_6$, was synthesized from the reaction of the known D-mannose diacetonide with *N*-benzylhydroxylamine in the presence of zinc dichloride. The absolute configuration at the anomeric center has been deduced from that of the mannose used in the synthesis. In the crystal, molecules are joined by O—H···O intermolecular hydrogen bonds.

Comment

In previous reports we have described the synthesis of nitrones by condensation of the corresponding parent carbonyl compounds with *N*-substituted hydroxylamines (Franco, Merchan, Merino & Tejero, 1995; Dondoni, Franco, Junquera, Merchan, Merino & Tejero, 1994). Application of that methodology to the protected

D-mannose diacetonide, (I), afforded the novel glycosyl hydroxylamine, (II), the structure of which is presented here. Although examples of carbohydrates bearing an amino group at the anomeric center have been described (Spevak, Dasgupta, Hobbs & Nagy, 1996) there are no reports concerning stable anomeric hydroxylamines.



(I) (II)

The crystal structure and numbering scheme of (II) are given in Fig. 1. The three five-membered rings adopt envelope conformations, with the C4, C6 and O4 atoms lying out of the planes of the other atoms of each ring by 0.491 (7), 0.523 (8) and 0.521 (6) Å, respectively, and have total puckering amplitudes (Cremer & Pople, 1975) of 0.320 (4), 0.337 (6) and 0.344 (4) Å, respectively. In addition to bond lengths and angles, Table 1 lists torsion angles between the furanose ring and the anomeric hydroxylamino group, thus allowing us to define the relative configuration of the anomeric center C1 and the conformation of the chain bonded to it. Since the starting aldofuranose, (I), belongs to the D series, the absolute configuration at C1 was assigned as *S*.

An intermolecular O1—H(O)···O2^{i} hydrogen bond [O1—H(O) 0.84 (1), H(O)···O2^{i} 2.10 (2), O1···O2^{i} 2.878 (5) Å and O1—H(O)···O2^{i} 154.5 (5)°; symmetry code: (i) $x-1, y, z$] joins the molecules along the *x* axis.

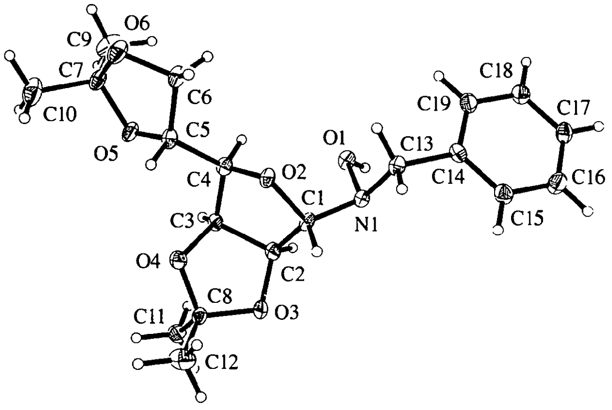


Fig. 1. Crystal structure of glycosylhydroxylamine (II) showing the atom numbering. Displacement ellipsoids are shown at the 30% probability level.

Experimental

Crystals of (II) were obtained by slow evaporation from a diethyl ether solution. The melting point is 389 K and $[\alpha]_D$ = +10.4 (c 10 g l^{-1}, chloroform).

Crystal data

$C_{19}H_{27}NO_6$
$M_r = 365.42$
Orthorhombic
$P2_12_12_1$
$a = 5.4700\,(10)$ Å
$b = 18.310\,(4)$ Å
$c = 18.880\,(4)$ Å
$V = 1890.9\,(7)$ Å^3
$Z = 4$
$D_x = 1.284$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 77 reflections
$\theta = 8.063–24.772°$
$\mu = 0.095$ mm^{-1}
$T = 173\,(2)$ K
Transparent block
0.22 × 0.16 × 0.08 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2639 measured reflections
2447 independent reflections
1925 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.129$

$\theta_{\rm max} = 25.03°$
$h = -1 \rightarrow 6$
$k = -1 \rightarrow 21$
$l = -1 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: 9.59%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.340$
$S = 1.078$
2219 reflections
240 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1276P)^2 + 1.079P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.003$
$\Delta\rho_{\rm max} = 0.367$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.321$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—O1	1.439 (5)	O4—C8	1.430 (6)
N1—C1	1.444 (6)	O4—C3	1.433 (6)
N1—C13	1.482 (6)	O5—C5	1.425 (6)
O2—C4	1.437 (6)	O5—C7	1.437 (6)
O2—C1	1.456 (5)	O6—C6	1.421 (6)
O3—C2	1.424 (6)	O6—C7	1.426 (6)
O3—C8	1.430 (6)		
O1—N1—C1	107.2 (3)	O3—C2—C3	105.4 (4)
O1—N1—C13	106.6 (3)	O3—C2—C1	111.5 (4)
C1—N1—C13	112.8 (4)	O4—C3—C2	102.2 (4)
C4—O2—C1	108.1 (3)	C4—C3—C2	104.2 (4)
C2—O3—C8	108.2 (3)	O2—C4—C3	104.7 (4)
C8—O4—C3	105.5 (3)	O5—C5—C6	102.6 (4)
C5—O5—C7	108.6 (4)	C6—C5—C4	116.0 (4)
C6—O6—C7	106.2 (4)	O6—C6—C5	103.2 (4)
N1—C1—O2	114.0 (4)	O6—C7—O5	106.3 (4)
N1—C1—C2	112.7 (4)	O4—C8—O3	104.7 (3)
O2—C1—C2	106.5 (3)		
O2—C1—C2—C3	1.8 (5)	C3—C4—C5—O5	−59.0 (5)
C3—C2—C1—N1	−123.9 (4)	O2—C1—N1—C13	56.1 (5)
O3—C2—C1—N1	122.5 (4)	C1—N1—C13—C14	169.2 (4)
O2—C4—C5—C6	68.9 (5)	N1—C13—C14—C15	94.4 (5)

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1319). Services for accessing these data are described at the back of the journal.

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(25*R*)-5β-Hydroxyspirost-2-en-6-one

Angel Dago Morales,[a] Ramón Pomés Hernández,[a] Francisco Coll Manchado,[b] María Teresa Hechavarría Fonseca,[b] Graciela Punte[c] and Gustavo Echeverría[c]

[a]*Dirección de Química, Centro Nacional de Investigaciones Científicas, Apartado 6990, Ciudad de la Habana, Cuba,* [b]*Facultad de Química, Universidad de la Habana, Ciudad de la Habana 10400, Cuba, and* [c]*PROFIMO, Departamento de Física, Facultad de Ciencias Exactas, UNLP, CC 67-(1900) La Plata, Argentina. E-mail: xray@infomed.sld.cu*

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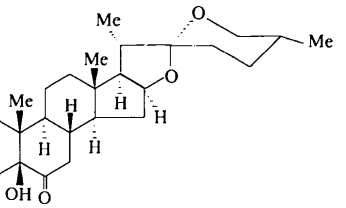
Abstract

In the title compound, $C_{27}H_{40}O_4$, the presence of a double bond between C2 and C3 forces ring *A* to adopt a $10\alpha,5\beta$ half-chair conformation. The *B*, *C* and *F* rings have chair conformations, as is usual in this type of compound. The *D* ring adopts a $13\beta,14\alpha$ half-chair conformation and the *E* ring a $C22\beta,O3\alpha$ half-chair conformation. The *A*/*B* ring junction is *cis* and the *B*/*C* and *C*/*D* ring junctions are both *trans*.

Comment

The steroidal alkenes are appropriate intermediates for introducing into the steroidal nucleus the oxygenated functions typical of many families of biologically active steroids, such as ecdysteroids and brassinosteroids. This paper reports the crystal structure of (25*R*)-5β-hydroxyspirost-2-enone, (I), used as an intermediate in the synthesis of brassinosteroids, which have been widely used as precursors of plant growth (Grove, Spencer & Rohwedder, 1979).



(I)

This X-ray analysis does not determine the absolute stereochemistry, which was known from chemical evidence. The studied compound was synthesized starting from (25*R*)-3β-hydroxyspirost-5-ene (Schwartz, Juhász & Coltea, 1984) and the synthesis only affects rings *A* and *B*; there was no change in the chiral centres.

The presence of a double bond between C2 and C3 forces ring *A* to adopt a $10\alpha,5\beta$ half-chair conformation; a C_2 axis intercepts the C2—C3 and C5—C10 bonds with asymmetric parameters (Duax, Weeks & Rohrer, 1976) ΔC_2(C2—C3) = 8 (1), ΔC_s(C3) = 13 (1) and ΔC_s(C1) = 37 (1)°. The average of the dihedral angles is 30 (1.5)°. The *B*, *C* and *F* rings, as usual in this kind of compound (Pfeiffer, Kutschabsky, Kretschmer, Collect & Adam, 1985), have chair conformations. The *F* ring has a highly symmetrical chair conformation with all asymmetry parameters below 5.3°. The *D* ring has a $13\beta,14\alpha$ half-chair conformation (Altona, Geise & Romers, 1968). The *E* ring has a $C22\beta,O3\alpha$ half-chair conformation. The *A*/*B* ring junction is *cis* and the *B*/*C* and *C*/*D* ring junctions are both *trans*. Bond distances and angles are close to expected values. The O1 atom of the hydroxyl group is synclinal to the C19 atom of the methyl group and is almost eclipsed with respect to atom O2 of the carbonyl group. There is an intramolecular hydrogen bond between the H atom of the hydroxyl

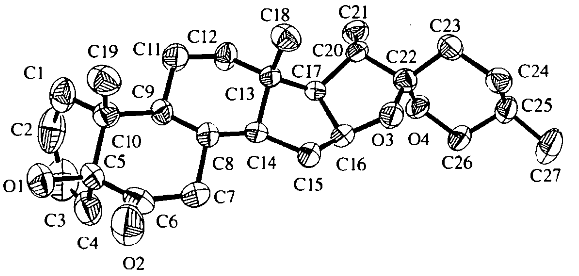


Fig. 1. Plot showing the atomic numbering scheme of (I). Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms have been omitted for clarity.

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