We thank the DGICYT (Project PB94-0598, Madrid, Spain) for financial support.

---

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.

---

## References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dondoni, A., Franco, S., Junquera, F., Merchan, F. L., Merino, P. & Tejero, T. (1994). *Synth. Commun.* **24**, 2537–2550.
Franco, S., Merchan, F. L., Merino, P. & Tejero, T. (1995). *Synth. Commun.* **25**, 2275–2284.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1992). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spevak, W., Dasgupta, F., Hobbs, C. J. & Nagy, J. O. (1996). *J. Org. Chem.* **61**, 3417–3422, and references therein.

---

*Acta Cryst.* (1997). **C53**, 1705–1706

# (25*R*)-5*β*-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*

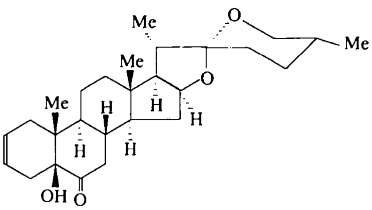
(*Received 10 October 1996; accepted 29 April 1997*)

## 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*α*,5*β* 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*β*,14*α* half-chair conformation and the *E* ring a C22*β*,O3*α* 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*)-5*β*-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*)-3*β*-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*α*,5*β* half-chair conformation; a $C_2$ axis intercepts the C2—C3 and C5—C10 bonds with asymmetric parameters (Duax, Weeks & Rohrer, 1976) $\Delta C_2(\text{C2—C3}) = 8\,(1)$, $\Delta C_s(\text{C3}) = 13\,(1)$ and $\Delta C_s(\text{C1}) = 37\,(1)°$. 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*β*,14*α* half-chair conformation (Altona, Geise & Romers, 1968). The *E* ring has a C22*β*,O3*α* 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

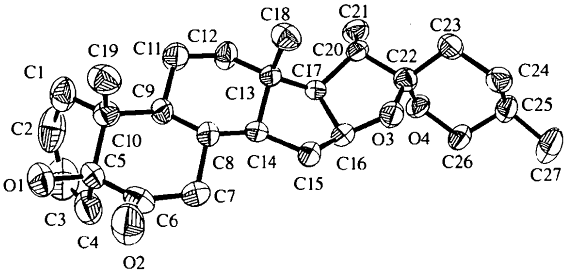


Fig. 1. Plot showing the atomic numbering scheme of (I). Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms have been omitted for clarity.

© 1997 International Union of Crystallography
Printed in Great Britain – all rights reserved

group and O2 of the carbonyl group. The packing of the molecules is assumed to be mainly dictated by van der Waals forces. The closest intermolecular contact between non-H atoms is 3.64 (1) Å for C21···C26.

## Experimental

The title compound was synthesized from (25*R*)-3β-hydroxyspirost-5-ene (diosgenin). Acetylation, epoxidation and oxidation with Jones' reagent are the early steps of the procedure (Schwartz *et al.*, 1984). The ketone was stirred with methanol and sodium carbonate under reflux for 30 min. The resulting compound was tosylated and dehydrotosylated to give the alkene. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

*Crystal data*

$C_{27}H_{40}O_4$
$M_r = 428.59$
Monoclinic
$P2_1$
$a = 11.667\,(2)$ Å
$b = 7.182\,(4)$ Å
$c = 14.337\,(3)$ Å
$\beta = 97.61\,(2)°$
$V = 1190.8\,(7)$ Å$^3$
$Z = 2$
$D_x = 1.195$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 5$–15°
$\mu = 0.078$ mm$^{-1}$
$T = 293\,(2)$ K
Prismatic
0.4 × 0.4 × 0.1 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: empirical *via* $\psi$ scan (Sheldrick, 1990)
$T_{\min} = 0.971$, $T_{\max} = 0.999$
4172 measured reflections
4026 independent reflections
1432 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.059$
$\theta_{\max} = 29.98°$
$h = -16 \rightarrow 16$
$k = -1 \rightarrow 10$
$l = 0 \rightarrow 20$
2 standard reflections every 200 reflections frequency: 60 min intensity decay: 3.1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.333$
$S = 0.986$
4023 reflections
285 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1344P)^2 + 2.2491P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.031$
$\Delta\rho_{\max} = 0.238$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.252$ e Å$^{-3}$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)

Extinction coefficient: 0.008 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: this X-ray analysis does not determine the absolute stereochemistry, which was known from chemical studies; 16 Friedel pairs were used in the refinement (Flack, 1983)
Flack parameter = −2 (5)

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

| | | | |
|---|---|---|---|
| C1—C2 | 1.48 (2) | C5—C6 | 1.536 (14) |
| C1—C10 | 1.529 (13) | C5—C10 | 1.564 (13) |
| C2—C3 | 1.33 (2) | C6—O2 | 1.214 (12) |
| C3—C4 | 1.47 (2) | C9—C10 | 1.562 (11) |
| C4—C5 | 1.518 (14) | C10—C19 | 1.510 (12) |
| C5—O1 | 1.418 (10) | | |
| C2—C1—C10 | 115.0 (11) | O1—C5—C10 | 108.2 (8) |
| C3—C2—C1 | 123.9 (14) | C19—C10—C1 | 108.8 (9) |
| C2—C3—C4 | 121.8 (13) | C19—C10—C5 | 110.5 (7) |
| C3—C4—C5 | 114.2 (12) | C1—C10—C5 | 106.1 (7) |
| O1—C5—C4 | 108.3 (8) | | |
| C10—C1—C2—C3 | 22.5 (18) | C3—C4—C5—C10 | −40.0 (12) |
| C1—C2—C3—C4 | −3 (2) | C2—C1—C10—C5 | −46.3 (11) |
| C2—C3—C4—C5 | 11.9 (19) | C4—C5—C10—C1 | 56.1 (10) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···O2 | 0.94 (10) | 2.25 (11) | 2.622 (12) | 103 (8) |

All H-atom positions were calculated and refined as a riding model, except for the hydroxy H1 atom on O1 which was located on a difference Fourier map and refined freely.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *Express*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

The X-ray diffraction experiments were carried out at the Diffraction National Laboratory (LANADI), La Plata, Argentina.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1242). Services for accessing these data are described at the back of the journal.

## References

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.
Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel & N. Allinger, pp. 271–383. New York: John Wiley.
Enraf–Nonius (1993). *CAD-4 Express Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Grove, M. D., Spencer, G. F. & Rohwedder, W. K. (1979). *Nature (London)*, **281**, 216–217.
Pfeiffer, D., Kutschabsky, L., Kretschmer, R. G., Collect, F. & Adam, G. (1985). *Z. Chem.* **25**, 183–184.
Schwartz, R., Juhász, A. & Coltea, P. (1984). *Rev. Chim.* **9/10**, 755–759.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.