

- GREEN, A. L. (1967). *J. Pharm. Pharmacol.* **19**, 207–208.
- GROL, C. J., DYKSTRA, D., SCHUNSELAAR, W., WESTERINK, B. H. C. & MARTIN, A. R. (1982). *J. Med. Chem.* **25**, 5–9.
- HALLBERG, A., HINTERMEISTER, N. M., MARTIN, A. R., BATES, R. B. & ORTEGA, R. B. (1984). *Acta Cryst.* **C40**, 2110–2112.
- HALLBERG, A. & MARTIN, A. R. (1983). *Synth. Commun.* **13**, 467–470.
- HARBET, C. A., PLATTNER, J. J., WELCH, W. M., WEISSMAN, A. & KOE, B. K. (1980). *Mol. Pharmacol.* **17**, 38–42.
- HORN, A. S. & SNYDER, S. H. (1971). *Proc. Natl Acad. Sci. USA*, **68**, 2325–2328.
- HUMBER, L. G., BRUDERLEIN, F. T. & VOITH, K. (1975). *Mol. Pharmacol.* **11**, 833–840.
- JANSSEN, P. A. J. (1970). *Chemical and Pharmacological Classification of Neuroleptics*. In *Modern Problems in Pharmacopsychiatry*, Vol. 5, *The Neuroleptics*, edited by D. BOBON, P. A. J. JANSSEN & J. BOBON, pp. 33–44. Basel: S. Karger.
- JOHNSON, C. K. (1976). *ORTEP*–3rd revision. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KAISER, C. & SETLER, P. E. (1981). In *Burger's Medicinal Chemistry*, edited by M. E. WOLFF, Part III, 4th ed. New York: Wiley-Interscience.
- KAISER, C., WARREN, R. J. & ZIRKLE, C. L. (1974). *J. Med. Chem.* **17**, 131–133.
- KRAMER, T., DORT, M., HALLBERG, A., HINTERMEISTER, N. M., SVENSSON, A. & NELSON, D. L. (1984). Unpublished.
- McDOWELL, J. J. H. (1969). *Acta Cryst.* **B25**, 2175–2181.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MALREAU, J. P. & PULLMAN, B. (1964). *Theor. Chim. Acta*, **2**, 293–301.
- MARTIN, A. R., KIM, S. H., YAMAMURA, H. I. & HORN, A. S. (1980). *J. Med. Chem.* **23**, 938–941.
- MARTIN, A. R., PARADKAR, V. M., PENG, G. W., SPETH, R. C., YAMAMURA, H. I. & HORN, A. S. (1980). *J. Med. Chem.* **23**, 865–873.
- MURTHY, K. S. & ZOGRAPHI, G. (1970). *J. Pharm. Sci.* **59**, 1281–1285.
- OLSON, G. L., CHEUNG, H.-C., MORGAN, K. D., BLOUNT, J. F., TODARO, L., BERGER, L., DAVIDSON, A. B. & BOFF, E. (1981). *J. Med. Chem.* **24**, 1026–1034.
- RODGERS, J. R., HORN, A. S. & KENNARD, O. (1976). *J. Pharm. Pharmacol.* **28**, 246–247.
- ZOGRAPHI, G. & MUNSHI, M. V. (1970). *J. Pharm. Sci.* **59**, 819–822.

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Structure of (25*R*)-3β-Hydroxy-5α-spirostan-12-one Monohydrate (Hecogenin), C₂₇H₄₂O₄·H₂O*

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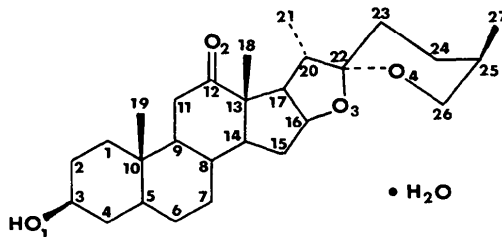
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Abstract. $M_r = 448.6$, orthorhombic, $P2_12_12_1$, $a = 7.815$ (2), $b = 9.582$ (1), $c = 32.839$ (4) Å, $V = 2459.1$ (5) Å³, $Z = 4$, $D_x = 1.21$ Mg m⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.656$ mm⁻¹, $F(000) = 984$, $T = 293$ K, $R = 0.044$ for 1807 observed reflections. The six-membered rings have chair conformations. The substituents at C(3) and C(25) are equatorial. The five-membered rings adopt a conformation intermediate between half-chair and β -envelope. The structure consists of sheets of molecules parallel to the ac plane, linked by hydrogen bonds *via* a molecule of water.

Introduction. The naturally occurring sapogenin, 3β-hydroxy-5α-spirostan-12-one monohydrate (hecogenin) (1) was isolated from tubers of the plant *Polianthes tuberosa* by chromatography. Hecogenin has been suggested as a promising raw material for the partial synthesis of cortisone (Djerassi, Ringold & Rosenkranz,

1951). As yet, no structural study of hecogenin has been reported. It was of interest to determine the crystal structure of (1) in order to ascertain its conformation and molecular geometry.



(1)

Experimental. Colourless crystal 0.13 × 0.34 × 0.30 mm. Nicolet R3 four-circle diffractometer. Lattice parameters from 25 machine-centred reflections with $14.9 < 2\theta < 28.5^\circ$. 1999 reflections with $3 < 2\theta < 115^\circ$, 1807 independent with $I > 2.5\sigma(I)$, index range h

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O(1)	3910 (4)	6693 (3)	-2244 (1)	55 (1)
O(2)	-86 (4)	5364 (5)	230 (1)	99 (2)
O(3)	5103 (3)	4291 (3)	1170 (1)	44 (1)
O(4)	3527 (3)	5326 (2)	1688 (1)	42 (1)
C(1)	1829 (4)	5835 (4)	-1239 (1)	45 (1)
C(2)	2120 (5)	5884 (4)	-1706 (1)	49 (1)
C(3)	3689 (4)	6727 (4)	-1809 (1)	42 (1)
C(4)	5251 (5)	6190 (4)	-1588 (1)	45 (1)
C(5)	4951 (4)	6159 (4)	-1126 (1)	38 (1)
C(6)	6559 (4)	5754 (4)	-891 (1)	46 (1)
C(7)	6267 (4)	5918 (4)	-434 (1)	45 (1)
C(8)	4694 (4)	5128 (4)	-283 (1)	37 (1)
C(9)	3105 (4)	5478 (4)	-538 (1)	39 (1)
C(10)	3384 (4)	5269 (3)	-1001 (1)	34 (1)
C(11)	1491 (5)	4839 (5)	-370 (1)	62 (1)
C(12)	1246 (4)	4979 (4)	83 (1)	49 (1)
C(13)	2791 (4)	4596 (3)	339 (1)	38 (1)
C(14)	4314 (4)	5435 (4)	164 (1)	36 (1)
C(15)	5698 (4)	5218 (4)	488 (1)	47 (1)
C(16)	4686 (4)	5355 (4)	880 (1)	41 (1)
C(17)	2787 (4)	5128 (3)	780 (1)	34 (1)
C(18)	3079 (5)	3019 (4)	310 (1)	50 (1)
C(19)	3630 (5)	3710 (4)	-1100 (1)	48 (1)
C(20)	2130 (4)	4194 (3)	1130 (1)	41 (1)
C(21)	427 (4)	4641 (4)	1315 (1)	51 (1)
C(22)	3663 (4)	4145 (3)	1423 (1)	41 (1)
C(23)	3844 (5)	2822 (4)	1674 (1)	51 (1)
C(24)	5392 (5)	2919 (4)	1964 (1)	56 (1)
C(25)	5237 (5)	4225 (4)	2220 (1)	53 (1)
C(26)	5016 (5)	5475 (4)	1950 (1)	50 (1)
C(27)	6835 (6)	4429 (6)	2490 (1)	74 (2)
O(5)	3968 (4)	4045 (3)	-2655 (1)	69 (1)

0–8, *k* 0–10, *l* 0–35, θ - 2θ scan mode, variable scan speed, scan width 1.0° (θ). Two standard reflections monitored every 50 measurements. Lp correction, absorption ignored, $R_{int} = 0.028$. Direct methods using *SHELXTL* (Sheldrick, 1981) gave structure. Least-squares refinement of all non-H atoms treated anisotropically; H atoms riding on the bonded C with fixed isotropic temperature factor, $U = 0.06 \text{ \AA}^2$; H atoms bonded to oxygen refined; $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + 0.00308(F_o)^2]^{-1}$. $(\Delta/\sigma)_{max} = 0.8$. Residual electron density within $\pm 0.2 \text{ e \AA}^{-3}$. Isotropic extinction parameter $X = 0.012$. Final $R = 0.044$, $wR = 0.067$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are in Table 1.* The appropriate atomic numbering scheme for (1) is shown in Fig. 1. The bond lengths and angles for non-H atoms are listed in Table 2. The average e.s.d. in the bond lengths is 0.005 \AA and in angles 0.3° .

In all essential details, the molecular geometry of (1), in terms of the bond lengths and angles, shows normal values. However, some of the individual distances are somewhat different from their expected values. The

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and H-bonding details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39688 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

E.s.d.'s are given in parentheses.

O(1)–C(3)	1.442 (4)	O(2)–C(12)	1.205 (5)
O(3)–C(16)	1.432 (4)	O(3)–C(22)	1.407 (4)
O(4)–C(22)	1.431 (4)	O(4)–C(26)	1.454 (4)
C(1)–C(2)	1.552 (4)	C(1)–C(10)	1.544 (5)
C(2)–C(3)	1.507 (5)	C(3)–C(4)	1.510 (5)
C(4)–C(5)	1.535 (4)	C(5)–C(6)	1.524 (5)
C(5)–C(10)	1.547 (4)	C(6)–C(7)	1.527 (4)
C(7)–C(8)	1.526 (5)	C(8)–C(9)	1.535 (4)
C(8)–C(14)	1.525 (4)	C(9)–C(10)	1.548 (4)
C(9)–C(11)	1.507 (5)	C(10)–C(19)	1.541 (5)
C(11)–C(12)	1.507 (5)	C(12)–C(13)	1.516 (5)
C(13)–C(14)	1.547 (5)	C(13)–C(17)	1.537 (4)
C(13)–C(18)	1.531 (5)	C(14)–C(15)	1.533 (4)
C(15)–C(16)	1.517 (4)	C(16)–C(17)	1.535 (4)
C(17)–C(20)	1.545 (4)	C(20)–C(21)	1.524 (5)
C(20)–C(22)	1.537 (5)	C(22)–C(23)	1.518 (5)
C(23)–C(24)	1.542 (6)	C(24)–C(25)	1.512 (6)
C(25)–C(26)	1.500 (5)	C(25)–C(27)	1.544 (6)
C(16)–O(3)–C(22)	106.4 (2)	C(22)–O(4)–C(26)	112.2 (3)
C(2)–C(1)–C(10)	113.3 (3)	C(1)–C(2)–C(3)	110.9 (3)
O(1)–C(3)–C(2)	107.9 (3)	O(1)–C(3)–C(4)	111.8 (3)
C(2)–C(3)–C(4)	111.6 (3)	C(3)–C(4)–C(5)	110.9 (3)
C(4)–C(5)–C(6)	112.2 (3)	C(4)–C(5)–C(10)	113.2 (3)
C(6)–C(5)–C(10)	112.2 (3)	C(5)–C(6)–C(7)	110.3 (3)
C(6)–C(7)–C(8)	112.9 (3)	C(7)–C(8)–C(9)	111.5 (3)
C(7)–C(8)–C(14)	112.0 (3)	C(9)–C(8)–C(14)	109.0 (3)
C(8)–C(9)–C(10)	113.2 (3)	C(8)–C(9)–C(11)	112.9 (3)
C(10)–C(9)–C(11)	115.2 (3)	C(1)–C(10)–C(5)	107.2 (3)
C(1)–C(10)–C(9)	109.9 (3)	C(5)–C(10)–C(9)	107.5 (2)
C(1)–C(10)–C(19)	109.4 (3)	C(5)–C(10)–C(19)	112.3 (3)
C(9)–C(10)–C(19)	110.5 (3)	C(9)–C(11)–C(12)	115.6 (3)
O(2)–C(12)–C(11)	122.1 (3)	O(2)–C(12)–C(13)	122.8 (3)
C(11)–C(12)–C(13)	115.1 (3)	C(12)–C(13)–C(14)	106.4 (3)
C(12)–C(13)–C(17)	116.1 (3)	C(14)–C(13)–C(17)	100.4 (2)
C(12)–C(13)–C(18)	108.8 (3)	C(14)–C(13)–C(18)	112.2 (3)
C(17)–C(13)–C(18)	112.6 (3)	C(8)–C(14)–C(13)	114.1 (3)
C(8)–C(14)–C(15)	120.3 (3)	C(13)–C(14)–C(15)	102.4 (3)
C(14)–C(15)–C(16)	102.1 (3)	O(3)–C(16)–C(15)	112.5 (3)
O(3)–C(16)–C(17)	105.1 (3)	C(15)–C(16)–C(17)	108.1 (3)
C(13)–C(17)–C(16)	104.3 (2)	C(13)–C(17)–C(20)	120.7 (3)
C(16)–C(17)–C(20)	104.2 (2)	C(17)–C(20)–C(21)	115.0 (3)
C(17)–C(20)–C(22)	103.0 (3)	C(21)–C(20)–C(22)	116.1 (3)
O(3)–C(22)–O(4)	109.9 (3)	O(3)–C(22)–C(20)	104.5 (2)
O(4)–C(22)–C(20)	107.3 (3)	O(3)–C(22)–C(23)	109.3 (3)
O(4)–C(22)–C(23)	109.7 (3)	C(20)–C(22)–C(23)	115.9 (3)
C(22)–C(23)–C(24)	110.9 (3)	C(23)–C(24)–C(25)	109.3 (3)
C(24)–C(25)–C(26)	110.0 (3)	C(24)–C(25)–C(27)	111.1 (4)
C(26)–C(25)–C(27)	109.4 (4)	O(4)–C(26)–C(25)	111.3 (3)

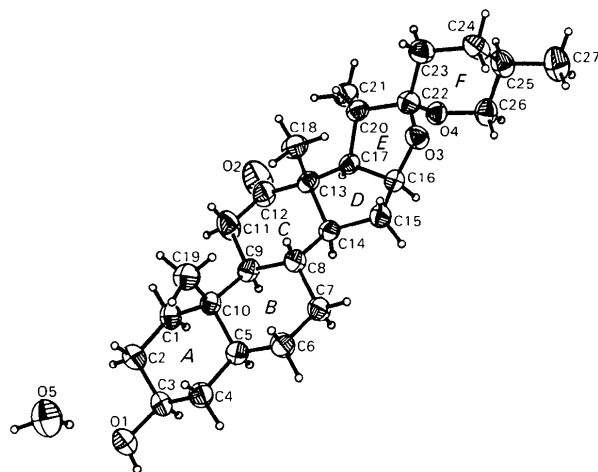


Fig. 1. The molecular conformation of (1), showing the atom numbering. The thermal ellipsoids are drawn at 50% probability level.

C(2)–C(3) and C(3)–C(4) bond distances are significantly shorter than the expected value of 1.533 Å for a C–C bond length in *n*-hydrocarbons (Bartell, 1959). The C(22)–O(3) bond adjacent to the *F* ring with a length of 1.407 (4) Å is shorter than C(16)–O(3) with length 1.432 (4) Å, probably due to the presence of two electronegative atoms, O(3) and O(4), with non-bonded electrons adjacent to C(22).

The stereochemistry of (1) is as follows: C(5)– α H *trans* to C(10)– β CH₃; C(8)– β H *trans* to both C(9)– α H and C(14)– α H; C(9)– α H *trans* to C(10)– β CH₃; C(17)– α H *cis* to both C(16)– α H and C(20)– α CH₃ and *trans* to C(13)– β CH₃.

The *A/B*, *B/C* and *C/D* ring junctions are *trans*; the *D/E* ring junction is *cis*. Rings *A*, *B*, *C* and *F* all exist in chair conformations. The average values for the endocyclic torsion angles are 55.5 (4), 55.2 (4), 52.2 (4) and 57.2 (4)°, in agreement with that obtained for cyclohexane (Kahn, Fourme, André & Renaud, 1973). The substituents at C(3) and C(25) are equatorial.

The conformation of both five-membered rings may be described by the parameters Δ and φ_m (Altona, Geise & Romers, 1968). The *D* and *E* rings have Δ and φ_m values of 12.5 (6), 47.9 (6)° and 15.7 (6), 42.9 (7)°, respectively, indicating in both cases a conformation intermediate between half-chair and β -envelope. These values are similar to those of 3 α ,6 α -dihydroxy-5 β -cholan-24-oic acid (Hall, Maslen & Cooper, 1974) ($\Delta = 14.3^\circ$ and $\varphi_m = 44.8^\circ$) and sodium 3 α ,7 α ,12 α -trihydroxy-5 β -cholan-24-oate monohydrate (Cobledick & Einstein, 1980) ($\Delta = 14.3^\circ$ and $\varphi_m = 46.6^\circ$).

The molecular arrangement, consisting of layers of molecules perpendicular to **b**, is shown in Fig. 2. Two distinct types of hydrogen-bonding sequences create a rigid three-dimensional network of molecules. The first type connects the end of one molecule to the beginning of another by means of a water molecule forming spirals consisting of two hydrogen bonds [–O(4)⋯H(5B)–O(5)–H(5A)⋯O(1)–], which run parallel to **c**

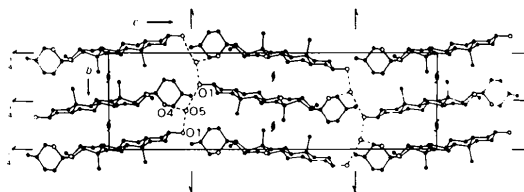


Fig. 2. The packing arrangement as viewed along **a**. Hydrogen bonds are shown by broken lines.

along the screw axes located at the edges and the centre of the unit cell (at $0,0,\frac{1}{4}$; $0,\frac{1}{2},\frac{1}{4}$ and $0,1,\frac{1}{4}$). The second type is a head-to-tail linking of adjacent layers from the C(3) hydroxy group to O(4) *via* the water molecule. Details of the hydrogen-bonding scheme have been deposited.*

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* See deposition footnote.

References

- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
 BARTELL, L. S. (1959). *J. Am. Chem. Soc.* **81**, 3497–3498.
 COBBLEDICK, R. E. & EINSTEIN, F. W. B. (1980). *Acta Cryst.* **B36**, 287–292.
 DJERASSI, C., RINGOLD, H. J. & ROSENKRANZ, G. (1951). *J. Am. Chem. Soc.* **73**, 5513–5514.
 HALL, S. R., MASLEN, E. N. & COOPER, A. (1974). *Acta Cryst.* **B30**, 1441–1447.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KAHN, R., FOURME, R., ANDRÉ, D. & RENAUD, M. (1973). *Acta Cryst.* **B29**, 131–138.
 SHELDRICK, G. M. (1981). *SHELXTL*, revision 3. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Federal Republic of Germany.

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3-Methyl-2(3H)-benzothiazolone, C₈H₇NOS

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Abstract. $M_r = 165.22$, orthorhombic, *Pbca*, $a = 16.941$ (4), $b = 10.816$ (2), $c = 8.424$ (2) Å, $V = 1544$ (1) Å³, $Z = 8$, $D_x = 1.422$ g cm⁻³, $\lambda(\text{Mo } K\alpha) =$

0.71073 Å, $\mu = 3.5$ cm⁻¹, $F(000) = 688$, $T = 297$ (1) K, $R = 0.038$ for 938 unique observed reflections. The five-membered heterocycle is flat and essentially coplanar with the fused benzene ring. Bond lengths and angles are all in accord with similar

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