

agreement with other oxetane systems (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The relatively strong *s* character of atom C(1) causes a shortening of the central C(1)—C(5) bond (1.575 Å) in comparison with the second zero bridge C(3)—C(7) (1.599 Å) in (5) and the analogous bonds of the tricyclo[3.3.0.0^{3,7}]octane system derivatives (1) to (4). Moreover, the deviation from the eclipsed conformation along this C(1)—C(5) bond of (5) is relatively large (Table 3) and, therefore, the stretching effect is reduced.

We thank Miss U. Wiesinger and Mr H. Rodewald for data collection and Mrs U. Huber-Patz for help in structural calculations. The financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- B. A. FRENZ & ASSOCIATES, INC. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
- BARNETT, B. L. & YORDY, J. D. (1975). *J. Cryst. Mol. Struct.* **5**, 113–119.
- BINGHAM, R. C., DEWAR, M. J. S. & LO, D. H. (1975). *J. Am. Chem. Soc.* **97**, 1285–1293.
- BISCHOF, P. (1976). *J. Am. Chem. Soc.* **98**, 6844–6849.
- BISCHOF, P. & FRIEDRICH, G. (1982). *J. Comput. Chem.* **3**, 486–494.
- BURLA, M. C., CAMALLI, M., CASCARANO, G., GIACOVAZZO, C., POLIDORI, G., SPAGNA, R. & VITERBO, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

- CARCELLER, E., MOYANO, A., SERRATOSA, F., FONT-ALTABA, M. & SOLANS, X. (1986). *J. Chem. Soc. Perkin Trans. 1*, pp. 2055–2067.
- COXON, J. M., O'CONNELL, M. J. & STEEL, P. J. (1986). *Aust. J. Chem.* **39**, 1537–1557.
- DEWAR, M. J. S. & THIEL, W. (1977). *J. Am. Chem. Soc.* **99**, 4899–4907.
- DEWAR, M. J. S., ZOEIBISCH, E. G., HEALY, E. F. & STEWART, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.
- FAIR, C. K. (1990). *MolEN. Structure Determination System*. Delft Instruments, Delft, The Netherlands.
- GLEITER, R., KISSLER, B. & GANTER, C. (1987). *Angew. Chem.* **99**, 1292–1294; *Angew. Chem. Int. Ed. Engl.* **26**, 1252–1254.
- GLEITER, R., SIGWART, C. & KISSLER, B. (1989). *Angew. Chem.* **101**, 1561–1563; *Angew. Chem. Int. Ed. Engl.* **28**, 1525–1526.
- GREENHOUGH, T. J. & TROTTER, J. (1980). *Acta Cryst.* **B36**, 478–480.
- HARANO, K., OKAMOTO, Y., YASUDA, M., UHEYAMA, K. & KANEMATSU, K. (1983). *J. Org. Chem.* **48**, 2728–2733.
- IRNGARTINGER, H., GOLDMANN, A., JAHN, R., NIXDORF, M., RODEWALD, H., MAIER, G., MALSCH, K. D. & EMRICH, R. (1984). *Angew. Chem.* **96**, 967–968; *Angew. Chem. Int. Ed. Engl.* **23**, 993–994.
- IRNGARTINGER, H., JAHN, R., MAIER, G. & EMRICH, R. (1987). *Angew. Chem.* **99**, 356–357; *Angew. Chem. Int. Ed. Engl.* **26**, 356–357.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LUGER, P. & BUSCHMANN, J. (1984). *J. Am. Chem. Soc.* **106**, 7118–7121.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- REICH, H. J. (1990). *PLT5.0*. Program for plotting and printing chemical structures. Univ. of Wisconsin, Madison, Wisconsin, USA.
- VOGT, B. R., SUTER, S. R. & HOOVER, J. R. E. (1968). *Tetrahedron Lett.* pp. 1609–1612.

Acta Cryst. (1993). **C49**, 62–64

Structure of Pregna-4,16-diene-7 α ,14 α -diol-3,20-dione

BY P. DASTIDAR, THERESA JOSEPH, K. M. MADYASTHA AND T. N. GURU ROW

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, India

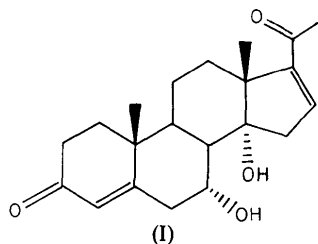
(Received 7 February 1992; accepted 22 April 1992)

Abstract. 7 α ,14 α -Dihydroxypregna-4,16-diene-3,20-dione, C₂₁H₂₈O₄, *M_r* = 344.45, orthorhombic, *P*2₁2₁2₁, *a* = 7.136 (1), *b* = 12.342 (1), *c* = 20.049 (3) Å, *V* = 1765.7 (3) Å³, *Z* = 4, *D_x* = 1.295 g cm⁻³, $\lambda(\text{Cu K}\alpha)$ = 1.5418 Å, μ = 6.7 cm⁻¹, *F*(000) = 744, *T* = 293 K, *R* = 0.048 for 1345 observations. The *A* ring may be described as in a 1 α ,2 β -half-chair conformation or a 1 α -sofa conformation. The *B* and *C* rings adopt normal chair conformations and the *D* ring has a 14 α -envelope conforma-

tion. The molecules are held together by a hydrogen bond [O(3)⋯O(7) = 2.767 Å].

Introduction. Microbial transformation has been used extensively for the introduction of functional groups into steroids in order to obtain biologically useful substances. Fermentation of pre-gna-4,16-diene-3,20-dione with the fungus *Murcor Piriformis* yielded the metabolites pre-gna-4,16-diene-7 α ,14 α -

diol-3,20-dione (I) and pregn-16-ene-3 α ,7 α ,14 α -triol-20-one. We describe the X-ray crystallographic analysis of (I).



Experimental. Plate-like single crystals were obtained from ethanol. Crystal size approximately $0.5 \times 0.4 \times 0.2$ mm. Lattice parameters refined using 25 reflections in θ range 10 – 15° . Enraf–Nonius CAD-4 diffractometer, graphite-monochromated $\text{Cu K}\alpha$ radiation. $2\theta \leq 120^\circ$, scan speed 1° min^{-1} , $\omega/2\theta$ mode. Three standard reflections (211 , 235 , 426) monitored every 100 reflections showed no significant intensity variations. 1479 unique reflections collected, $0 \leq h \leq 8$, $0 \leq k \leq 13$, $0 \leq l \leq 22$, 1345 significant [$|F_o| \geq 3\sigma(|F_o|)$]. Data not corrected for absorption or extinction. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986). The best E map gave all non-H atoms. Full-matrix least-squares program *SHELX76* (Sheldrick, 1976) used for refinement. The positional and thermal parameters of all non-H atoms were refined anisotropically. All H atoms were located in a difference Fourier map. The positional parameters and thermal parameters were not refined but their contributions to the structure-factor calculations were included in the final cycles of refinement. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, $w = 1.0/[\sigma(|F|)^2 + 0.016081|F_o|^2]$. At the end of the final cycle of refinement using F 's, $R = 0.048$, $wR = 0.056$, $S = 0.54$, $(\Delta/\sigma)_{\text{max}} = 0.001$ for 226 refinable parameters. Final difference map was featureless ($\Delta\rho \leq 0.1 \text{ e } \text{\AA}^{-3}$). Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are given in Table 1,* bond distances and angles are given in Table 2 and a *PLUTO* (Motherwell & Clegg, 1978) diagram of the title compound with atom-numbering scheme is given in Fig. 1. The A ring adopts a 1α -sofa conformation with the asymmetry param-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55405 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: L11003]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for non-H atoms of the title compound with e.s.d.'s in parentheses

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C(1)	0.4082 (5)	0.9532 (2)	0.4025 (2)	370 (9)
C(2)	0.4262 (5)	1.0612 (2)	0.3676 (2)	414 (10)
C(3)	0.2911 (5)	1.0706 (3)	0.3107 (2)	426 (10)
O(3)	0.2344 (4)	1.1600 (2)	0.2914 (1)	536 (8)
C(4)	0.2404 (5)	0.9708 (3)	0.2761 (2)	419 (10)
C(5)	0.3083 (5)	0.8733 (3)	0.2931 (2)	381 (9)
C(6)	0.2752 (5)	0.7770 (3)	0.2482 (2)	449 (10)
C(7)	0.2104 (5)	0.6766 (3)	0.2856 (2)	419 (10)
O(7)	0.0244 (4)	0.6907 (2)	0.3096 (1)	516 (9)
C(8)	0.3407 (4)	0.6518 (2)	0.3449 (2)	353 (10)
C(9)	0.3525 (4)	0.7515 (2)	0.3922 (1)	314 (8)
C(10)	0.4269 (4)	0.8547 (2)	0.3548 (2)	344 (10)
C(11)	0.4619 (5)	0.7291 (3)	0.4567 (2)	409 (10)
C(12)	0.4165 (5)	0.6220 (2)	0.4918 (2)	367 (9)
C(13)	0.4242 (4)	0.5286 (3)	0.4419 (2)	338 (9)
C(14)	0.2822 (4)	0.5534 (3)	0.3856 (2)	366 (9)
O(14)	0.1063 (3)	0.5743 (2)	0.4188 (1)	428 (7)
C(15)	0.2603 (6)	0.4413 (3)	0.3510 (2)	463 (10)
C(16)	0.2732 (5)	0.3678 (3)	0.4105 (2)	440 (10)
C(17)	0.3554 (5)	0.4166 (2)	0.4619 (2)	386 (10)
C(18)	0.6275 (5)	0.5136 (3)	0.4159 (2)	445 (11)
C(19)	0.6351 (5)	0.8426 (3)	0.3329 (2)	414 (9)
C(20)	0.3961 (5)	0.3657 (3)	0.5273 (2)	433 (10)
O(20)	0.4993 (5)	0.4088 (3)	0.5675 (1)	768 (12)
C(21)	0.3078 (6)	0.2590 (3)	0.5434 (2)	550 (11)

Table 2. Bond distances (\AA) and bond angles ($^\circ$) for non-H atoms of the title compound with e.s.d.'s in parentheses

C(1)—C(2)	1.510 (4)	C(9)—C(11)	1.535 (4)
C(1)—C(10)	1.552 (4)	C(10)—C(19)	1.556 (4)
C(2)—C(3)	1.498 (5)	C(11)—C(12)	1.532 (4)
C(3)—O(3)	1.237 (4)	C(12)—C(13)	1.527 (5)
C(3)—C(4)	1.459 (5)	C(13)—C(14)	1.547 (5)
C(4)—C(5)	1.341 (5)	C(13)—C(17)	1.520 (4)
C(5)—C(6)	1.509 (5)	C(13)—C(18)	1.552 (4)
C(5)—C(10)	1.516 (5)	C(14)—O(14)	1.444 (3)
C(6)—C(7)	1.520 (5)	C(14)—C(15)	1.555 (5)
C(7)—O(7)	1.422 (4)	C(15)—C(16)	1.501 (5)
C(7)—C(8)	1.540 (5)	C(16)—C(17)	1.330 (5)
C(8)—C(9)	1.555 (3)	C(17)—C(20)	1.482 (5)
C(8)—C(14)	1.521 (4)	C(20)—O(20)	1.214 (4)
C(9)—C(10)	1.570 (3)	C(20)—C(21)	1.495 (5)
C(2)—C(1)—C(10)	113.4 (2)	C(5)—C(10)—C(19)	108.4 (3)
C(1)—C(2)—C(3)	111.4 (2)	C(1)—C(10)—C(19)	109.3 (2)
C(2)—C(3)—C(4)	117.1 (3)	C(9)—C(11)—C(12)	115.7 (2)
C(2)—C(3)—O(3)	121.1 (3)	C(11)—C(12)—C(13)	110.0 (2)
O(3)—C(3)—C(4)	121.5 (3)	C(12)—C(13)—C(18)	110.0 (3)
C(3)—C(4)—C(5)	123.1 (3)	C(12)—C(13)—C(17)	120.1 (3)
C(4)—C(5)—C(10)	123.0 (3)	C(12)—C(13)—C(14)	107.7 (2)
C(4)—C(5)—C(6)	119.8 (3)	C(17)—C(13)—C(18)	106.3 (2)
C(6)—C(5)—C(10)	117.0 (3)	C(14)—C(13)—C(18)	112.9 (3)
C(5)—C(6)—C(7)	113.2 (3)	C(14)—C(13)—C(17)	99.2 (2)
C(6)—C(7)—C(8)	111.0 (2)	C(8)—C(14)—C(13)	111.6 (2)
C(6)—C(7)—O(7)	110.5 (2)	C(13)—C(14)—C(15)	102.4 (2)
O(7)—C(7)—C(8)	109.0 (2)	C(13)—C(14)—O(14)	105.5 (2)
C(7)—C(8)—C(14)	114.0 (2)	C(8)—C(14)—C(15)	119.8 (3)
C(7)—C(8)—C(9)	110.2 (2)	C(8)—C(14)—O(14)	110.0 (2)
C(9)—C(8)—C(14)	108.6 (2)	O(14)—C(14)—C(15)	106.0 (2)
C(8)—C(9)—C(11)	113.4 (2)	C(14)—C(15)—C(16)	100.1 (3)
C(8)—C(9)—C(10)	111.6 (2)	C(15)—C(16)—C(17)	111.6 (3)
C(10)—C(9)—C(11)	112.1 (2)	C(13)—C(17)—C(16)	110.4 (2)
C(5)—C(10)—C(9)	108.8 (2)	C(16)—C(17)—C(20)	125.4 (2)
C(1)—C(10)—C(9)	108.1 (2)	C(13)—C(17)—C(20)	123.7 (2)
C(1)—C(10)—C(5)	109.6 (2)	C(17)—C(20)—C(21)	118.7 (3)
C(9)—C(10)—C(19)	112.3 (2)	C(17)—C(20)—O(20)	121.3 (3)
		O(20)—C(20)—C(21)	119.8 (3)

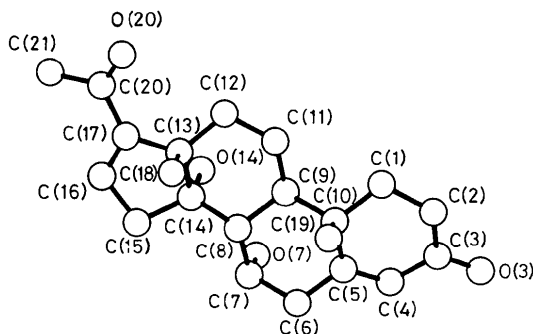


Fig. 1. A *PLUTO* diagram of the title compound showing the atom-numbering scheme.

eters $\Delta C_2(1,2) = 15.5$, $\Delta C_s(1) = 10.6^\circ$ with an average internal absolute torsion angle of 25.6° . The *B* and *C* rings adopt normal chair conformations with average endocyclic absolute torsion angles of 52.8 and 54.4° , respectively. The *D* ring adopts an approximate 14α -envelope conformation with the asymmetry parameters $\Delta C_s(13) = 23.5$ (32.5), $\Delta C_s(14) = 5.2$ (1.4) and $\Delta C_2(13,14) = 12.7^\circ$ (22.7), the values in parentheses being the ideal values for a 14α -envelope conformation (Duax & Norton, 1975). The X-ray structure of the title compound shows that the *BC* and *CD* ring junctions are *trans* [$H(8)-C(8)-C(9)-H(9) = 167.0$ (2) and $C(18)-C(13)-C(14)-O(14) = -175.0$ (2) $^\circ$]. The progesterone side-chain orientation is normally restricted with respect to the *D* ring; the torsion angle $C(16)-C(17)-C(20)-O(20)$ in 84 structures having a 20-one substitution is observed to be between 0 and -41° , *i.e.* synperiplanar to the $C(16)-C(17)$ bond (Duax, Griffin, Rohrer & Weeks, 1980). In this structure, the carbonyl at $C(20)$ is

antiperiplanar to the unsaturated $C(16)-C(17)$ bond [$C(16)-C(17)-C(20)-O(20) = 167.1$ (3) $^\circ$] as has been observed in five other 16-en-20-one structures (Khazheeva, Simonov, Kamernitskii, Pavlova-Grishina & Skorova, 1982; Duax, Langs, Strong & Osawa, 1979; Surcouf, 1979; Duax, Weeks & Strong, 1979; Dastidar, Joseph, Madyastha & Guru Row, 1991). The molecules are stabilized in the crystal lattice by hydrogen bonding [$O(3)\cdots O(7) = 2.767$, $O(3)\cdots H(O7) = 1.895$ Å, $O(3)\cdots H(O7)-O(7) = 173.2^\circ$].

The University Grant Commission, India, is thanked for financial support.

References

- DASTIDAR, P., JOSEPH, T., MADYASTHA, K. M. & GURU ROW, T. N. (1991). Unpublished communication.
- DUAX, W. L., GRIFFIN, J. F., ROHRER, D. C. & WEEKS, C. M. (1980). *Lipids*, **15**, 783–792.
- DUAX, W. L., LANGS, D., STRONG, P. D. & OSAWA, Y. (1979). *Cryst. Struct. Commun.* **8**, 565–568.
- DUAX, W. L. & NORTON, D. A. (1975). Editors. *Atlas of Steroid Structure*, Vol. I. New York: Plenum.
- DUAX, W. L., WEEKS, C. M. & STRONG, P. D. (1979). *Cryst. Struct. Commun.* **8**, 659–662.
- KHAZHEEVA, Z. I., SIMONOV, V. I., KAMERNITSKII, A. V., PAVLOVA-GRISHINA, N. S. & SKOROVA, A. V. (1982). *Kristallografiya*, **27**, 905–907.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- SURCOUF, E. (1979). *Acta Cryst.* **B35**, 2744–2746.

Acta Cryst. (1993). **C49**, 64–68

Structure of 1,8-Bis(hydroxymethyl)naphthalene

BY GEORGE D. BENNETT,* LAWRENCE J. FITZGERALD AND ROGER E. GERKIN†

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

(Received 12 February 1992; accepted 8 June 1992)

Abstract. 1,8-Naphthalenedimethanol, $C_{12}H_{12}O_2$, $M_r = 188.24$, monoclinic, $P2_1/n$, $a = 8.549$ (4), $b = 4.856$ (3), $c = 22.604$ (4) Å, $\beta = 94.24$ (3) $^\circ$, $V =$

935.8 (7) Å³, $Z = 4$, $D_x = 1.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.84$ cm⁻¹, $F(000) = 400$, $T = 295$ K, $R = 0.042$ for 1455 unique reflections having $I > 3\sigma_I$. In the title structure the exterior angles at ring atoms $C(1)$, $C(8)$ and $C(9)$ deviate significantly from 120° as a result of the steric interactions of the hydroxymethyl substituents. The ten C atoms com-

* OSU Summer Undergraduate Research Participant from Wittenberg University.

† Corresponding author.