Tsuboyama, S., Tsuboyama, K., Higashi, I. & Yanagita, M. (1970). *Tetrahedron Lett.* pp. 1367–1370.

Tsuboyama, K., Tsuboyama, S., Sakurai, T., Kobayashi, K., Sato, K., Togashi, Y., Yonemura, H. & Yanagita, M. (1981). *Rikagaku Kenkyusho Hokoku*, **57**, 113–130.

Acta Cryst. (1994). C**50**, 312–314

17*α*-Benzyl-3*β*,17*β*-dihydroxy-5-androstene

Slobodanka Stanković

Institute of Physics, Faculty of Sciences,
University of Novi Sad, 21000 Novi Sad,
Trg D. Obradovića 4, Serbia

Dušan Miljković, Ljubica Medić-Mijačević and
Katarina Gaši

Institute of Chemistry, Faculty of Sciences,
University of Novi Sad, Novi Sad, Serbia

Christiane Courseille

Laboratoire de Cristallographie et de Physique
Cristalline, Faculté des Sciences, Université de
Bordeaux I, Talence, France

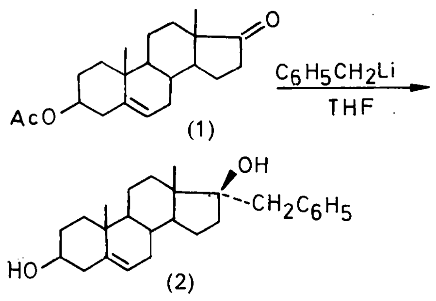
(*Received* 12 *February* 1993; *accepted* 16 *July* 1993)

Abstract

The asymmetric unit of the title compound, 17*α*-benzyl-5-androst-5-ene-3*β*,17*β*-diol, $C_{26}H_{36}O_2$, contains two molecules, which differ slightly in the conformation of the *D* ring. Of the four OH groups in the two symmetry-independent molecules, *A* and *B*, three participate in O—H···O hydrogen bonding. Crystal packing involves molecules of *A* forming helix-like chains along the *b* axis, with hydrophobic loops occupied by one part of the *B* molecules; their other parts are involved in hydrogen-bonded bridges to the neighbouring chains.

Comment

Our previous reports (Miljković & Gaši, 1982; Miljković, Gaši, Kindjer, Stanković, Ribar & Argay, 1985) describe synthetic procedures for 3*β*,17*β*-dihydroxy-17*α*-picolyl-5-androstene and its 5*α*-analogues as intermediates in multistep syntheses of 21,27-hisnorsolanidine and 21,27-hisnordemissidine. Now, as a part of a broader project aiming at the synthesis of novel antiandrogenic compounds, the synthesis of 17*α*-benzyl-3*β*,17*β*-dihydroxy-5-androstene was performed in a way analogous to the previously described synthesis of 3*β*,17*β*-dihydroxy-17*α*-picolyl-5-androstene. Stereospecific addition of benzyllithium to the 17-carbonyl group of dehydroepiandrosterone acetate (1) afforded a satisfactory yield (61.20%) of the title compound (2). Its structure was deduced on the basis of chemical and spectroscopic evidence.



In this paper the detailed structure of compound (2) is described, as the final proof of the proposed stereochemistry at C(17). The structure was solved by the use of direct methods. Since the starting material was synthesized from natural estrone, the absolute stereochemistry of which is known (Fieser & Fieser, 1967), for the purposes of the X-ray structure refinement it was assumed that the same enantiomer occurs in the crystalline state.

A perspective view of the two symmetry-independent molecules *A* and *B*, computed from the final atomic coordinates listed in Table 1, is shown in Fig. 1. Selected bond lengths, bond angles and torsion angles, given in Table 2, show that there is no significant difference between the two symmetry-independent molecules, including their conformations (shown in Fig. 2). Ring-puckering parameters (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976), listed in Table 3, define the conformation of the rings. Rings *A* and *C* have chair conformations in both molecules; ring *B* is in an 8*β*,9*α*-half-chair conformation [the distances of C(8) and C(9) from the best plane of the remaining four atoms are −0.313 (6) and 0.420 (6) Å, respectively, for molecule *A*, and −0.393 (7) and 0.313 (7) Å, respectively, for molecule *B*]. Ring *D* in molecule *A* exhibits a 13*β*-envelope conformation [the distance of C(13) from the best plane of the remaining four atoms is −0.676 (7) Å], while in molecule *B* it adopts a transition form between a 13*β*-envelope [distance of C(13) is −0.666 (1) Å] and a 13*β*,14*α*-half-chair conformation [distances of C(13) and C(14) are −0.514 (1) and 0.191 (7) Å, respectively]. The non-bonded torsion angle C(19)—C(10)···C(13)—C(18) is 10.6 (6)° in molecule *A* and 12.2 (5)° in molecule *B*. The non-bonded O(1)···O(2) distances are 11.176 (6) and

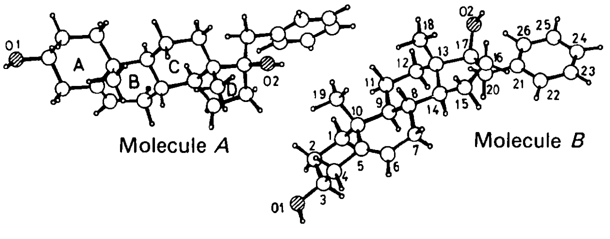


Fig. 1. A perspective view of two symmetry-independent molecules *A* and *B*.

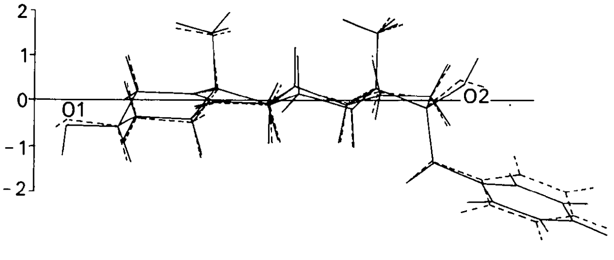


Fig. 2. Superimposed fit of molecule *A* (solid) and molecule *B* (dashed) viewed perpendicular to the C(8)—C(14) bond. The scale is in Å.

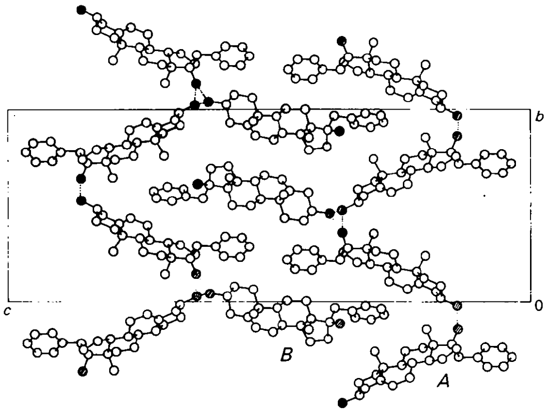


Fig. 3. The packing arrangement viewed along the *a* axis. Hydrogen bonds are indicated by dotted lines.

11.123 (6) Å in molecules *A* and *B*, respectively. In both molecules the orientation of the OH group in position 3 is equatorial. The OH group in position 17 is β oriented, while the benzyl moiety is α oriented.

Apart from the slight difference in the conformation of the *D* rings, the only significant difference between the two symmetry-independent molecules is in the arrangement of the hydrogen bonds. Namely, both O atoms from molecule *A* are involved in the intermolecular O—H···O hydrogen bonds, while molecule *B* participates in hydrogen bonding *via* O(1) only. Each of the three O atoms acts simultaneously as a donor and an acceptor forming a triangle, while O(2) from molecule *B* remains free. The packing arrangement is shown in Fig. 3. Molecules of the *A* type form helix-like chains along the *b* axis, while molecules of the *B* type are hydrogen bonded *via* their O(1) atoms to both O(1) and O(2) of the *A*···*A* intermolecular hydrogen bonds. At the same time the rest of the *B* molecule is situated in the hydrophobic loop of the nearest parallel helix, in which the phenyl ring has rather short van der Waals C···H contacts [2.693 (9)–2.829 (9) Å] with the neighbouring atoms. The spatial arrangement resembles steroid–protein receptor interactions.

Experimental

Crystal data

$C_{26}H_{36}O_2$
M_r = 380.56
Orthorhombic
$P2_12_12_1$
a = 6.691 (1) Å
b = 15.657 (1) Å
c = 42.657 Å
V = 4468.8 Å^3
Z = 8
D_x = 1.13 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.542 Å
Cell parameters from 25 reflections
θ = 10.1-26.3°
μ = 0.501 mm^{-1}
T = 293 K
Prism
0.350 × 0.075 × 0.025 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-θ scans
Absorption correction: spherical
$T_{\min}$ = 0.96, $T_{\max}$ = 0.99
3768 measured reflections
3768 independent reflections
1736 observed reflections [$I > 6\sigma(I)$]

$\theta_{\max}$ = 60°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 48$
3 standard reflections
frequency: 180 min
intensity variation: none

Refinement

Refinement on F
R = 0.051
wR = 0.046
S = 5.66
1728 reflections
530 parameters
$w = 2.0109/[\sigma^2(F_o) + 0.000304F_o^2]$

$(\Delta/\sigma)_{\max}$ = 0.107
$\Delta\rho_{\max}$ = 0.069 e Å^{-3}
$\Delta\rho_{\min}$ = −0.065 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

H atoms were generated and refined as riding groups (overall isotropic temperature factors were refined for different CH types), except those attached to O atoms, whose positions were found in the ΔF map and refined isotropically. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Software used to prepare material for publication: *CSU* (Vicković, 1988).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.0047 (12)	−0.3794 (5)	0.2968 (2)	0.053 (2)
C(2)	0.0241 (12)	−0.4188 (5)	0.3299 (2)	0.055 (2)
C(3)	0.1843 (13)	−0.4849 (5)	0.3295 (2)	0.051 (3)

C(4)	0.3845 (11)	−0.4477 (5)	0.3198 (2)	0.049 (2)
C(5)	0.3624 (11)	−0.4075 (5)	0.2877 (2)	0.042 (2)
C(6)	0.4886 (13)	−0.4332 (5)	0.2651 (2)	0.052 (2)
C(7)	0.4894 (11)	−0.3975 (4)	0.2322 (1)	0.045 (2)
C(8)	0.3589 (10)	−0.3186 (4)	0.2284 (1)	0.034 (2)
C(9)	0.1621 (11)	−0.3297 (4)	0.2469 (1)	0.038 (2)
C(10)	0.1999 (12)	−0.3445 (5)	0.2827 (2)	0.043 (2)
C(11)	0.0146 (12)	−0.2568 (4)	0.2404 (1)	0.046 (2)
C(12)	−0.0209 (11)	−0.2404 (4)	0.2053 (1)	0.038 (2)
C(13)	0.1772 (11)	−0.2259 (5)	0.1879 (1)	0.039 (2)
C(14)	0.3070 (12)	−0.3056 (5)	0.1936 (2)	0.040 (2)
C(15)	0.4760 (11)	−0.2967 (5)	0.1696 (2)	0.054 (2)
C(16)	0.3885 (10)	−0.2447 (5)	0.1423 (2)	0.046 (2)
C(17)	0.1738 (11)	−0.2241 (5)	0.1515 (2)	0.041 (2)
C(18)	0.2764 (12)	−0.1434 (4)	0.2002 (1)	0.050 (2)
C(19)	0.2604 (14)	−0.2603 (4)	0.2999 (2)	0.068 (3)
C(20)	0.0190 (12)	−0.2865 (5)	0.1373 (1)	0.052 (2)
C(21)	0.0058 (14)	−0.2854 (5)	0.1018 (2)	0.049 (3)
C(22)	0.1290 (15)	−0.3371 (5)	0.0833 (2)	0.075 (3)
C(23)	0.1136 (19)	−0.3325 (7)	0.0508 (3)	0.102 (5)
C(24)	−0.0263 (21)	−0.2844 (8)	0.0367 (2)	0.107 (5)
C(25)	−0.1460 (16)	−0.2327 (6)	0.0548 (2)	0.089 (4)
C(26)	−0.1316 (14)	−0.2348 (6)	0.0868 (2)	0.070 (3)
O(1)	0.2063 (9)	−0.5250 (3)	0.3601 (1)	0.065 (2)
O(2)	0.1132 (8)	−0.1403 (3)	0.1400 (1)	0.052 (2)
O(1*A*)	0.0839 (10)	0.0427 (4)	0.6150 (1)	0.070 (2)
O(2*A*)	0.3922 (11)	−0.1114 (5)	0.3651 (1)	0.074 (2)
C(1*A*)	0.2314 (14)	0.0653 (4)	0.5311 (1)	0.061 (3)
C(2*A*)	0.2327 (13)	0.0811 (4)	0.5666 (1)	0.064 (3)
C(3*A*)	0.0721 (13)	0.0289 (5)	0.5818 (2)	0.055 (3)
C(4*A*)	0.0999 (14)	−0.0661 (5)	0.5747 (1)	0.058 (3)
C(5*A*)	0.1071 (13)	−0.0796 (5)	0.5396 (2)	0.049 (2)
C(6*A*)	−0.0193 (14)	−0.1350 (5)	0.5258 (2)	0.053 (3)
C(7*A*)	−0.0232 (13)	−0.1572 (5)	0.4913 (1)	0.056 (3)
C(8*A*)	0.1629 (12)	−0.1250 (4)	0.4748 (1)	0.043 (2)
C(9*A*)	0.2150 (12)	−0.0342 (5)	0.4851 (1)	0.042 (2)
C(10*A*)	0.2537 (12)	−0.0284 (5)	0.5207 (1)	0.041 (2)
C(11*A*)	0.3827 (13)	0.0066 (5)	0.4656 (1)	0.061 (3)
C(12*A*)	0.3427 (12)	0.0011 (5)	0.4302 (1)	0.055 (2)
C(13*A*)	0.3035	−0.0916	0.4202	0.043
C(14*A*)	0.1268 (12)	−0.1254 (5)	0.4391 (1)	0.042 (2)
C(15*A*)	0.0680 (12)	−0.2090 (4)	0.4231 (1)	0.052 (2)
C(16*A*)	0.1138 (14)	−0.1942 (4)	0.3881 (2)	0.060 (3)
C(17*A*)	0.2236 (12)	−0.1070 (5)	0.3862 (2)	0.050 (2)
C(18*A*)	0.4952 (13)	−0.1442 (5)	0.4245 (2)	0.076 (3)
C(19*A*)	0.4699 (12)	−0.0601 (5)	0.5296 (2)	0.069 (3)
C(20*A*)	0.0886 (13)	−0.0332 (5)	0.3743 (1)	0.052 (2)
C(21*A*)	0.0122 (14)	−0.0463 (5)	0.3411 (2)	0.047 (2)
C(22*A*)	0.1240 (13)	−0.0221 (5)	0.3155 (2)	0.057 (3)
C(23*A*)	0.0555 (15)	−0.0337 (5)	0.2853 (2)	0.057 (3)
C(24*A*)	−0.1266 (16)	−0.0698 (5)	0.2803 (2)	0.063 (3)
C(25*A*)	−0.2418 (14)	−0.0931 (6)	0.3055 (2)	0.080 (3)
C(26*A*)	−0.1740 (14)	−0.0793 (6)	0.3361 (2)	0.070 (3)

Table 2. *Selected geometric parameters* (Å, °)

C(17)—C(13)	1.553 (9)	C(17*A*)—C(13*A*)	1.564 (7)
C(17)—C(16)	1.524 (9)	C(17*A*)—C(16*A*)	1.553 (10)
C(17)—C(20)	1.547 (10)	C(17*A*)—C(20*A*)	1.552 (10)
C(17)—O(2)	1.458 (8)	C(17*A*)—O(2*A*)	1.445 (9)
C(3)—O(1)	1.456 (8)	C(3*A*)—O(1*A*)	1.435 (9)
C(13)—C(17)—O(2)	110.9 (6)	C(13*A*)—C(17*A*)—O(2*A*)	108.5 (6)
C(16)—C(17)—O(2)	111.5 (6)	C(16*A*)—C(17*A*)—O(2*A*)	111.1 (7)
C(20)—C(17)—O(2)	104.5 (6)	C(20*A*)—C(17*A*)—O(2*A*)	106.6 (6)
C(16)—C(17)—C(20)	113.4 (6)	C(16*A*)—C(17*A*)—C(20*A*)	113.4 (6)
C(2)—C(3)—O(1)	111.2 (7)	C(2*A*)—C(3*A*)—O(1*A*)	107.8 (6)

C(12)—C(13)—C(17)—O(2)	82.1 (7)
C(12*A*)—C(13*A*)—C(17*A*)—O(2*A*)	85.8 (6)
C(18)—C(13)—C(17)—O(2)	−43.8 (7)
C(18*A*)—C(13*A*)—C(17*A*)—O(2*A*)	−38.6 (7)
C(15)—C(16)—C(17)—O(2)	145.4 (6)
C(15*A*)—C(16*A*)—C(17*A*)—O(2*A*)	136.6 (6)
C(15)—C(16)—C(17)—C(20)	−97.0 (7)
C(15*A*)—C(16*A*)—C(17*A*)—C(20*A*)	−103.3 (7)
C(16)—C(17)—C(20)—C(21)	−63.8 (9)
C(16*A*)—C(17*A*)—C(20*A*)—C(21*A*)	−62.5 (9)
O(2)—C(17)—C(20)—C(21)	57.8 (8)
O(2*A*)—C(17*A*)—C(20*A*)—C(21*A*)	60.0 (8)
C(1)—C(2)—C(3)—O(1)	−179.1 (6)
C(1*A*)—C(2*A*)—C(3*A*)—O(1*A*)	177.6 (6)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)	H(O1)	O(2)	1.015	1.818	2.798	161.3
O(2)	H(O2)	O(1*A*)	1.074	1.694	2.753	167.9
O(1*A*)	H(O1*A*)	O(1)	0.847	1.936	2.755	163.8

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71505 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1038]

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Top. Stereochem.* **9**, 271–383.

Fieser, L. F. & Fieser, M. (1967). *Steroids*, pp. 460–465. New York: Reinhold.

Miljković, D. & Gaši, K. (1982). *Bull. Soc. Chim. Beograd*, **47**, 173–181.

Miljković, D., Gaši, K., Kindjer, M., Stanković, S., Ribar, B. & Argay, Gy. (1985). *Croat. Chem. Acta*, **58**, 721–736.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Vicković, I. (1988). *CSU. Crystal Structure Utility Program*. Univ. of Zagreb, Yugoslavia.

Acta Cryst. (1994). C**50**, 314–317

3,12-Dinitro-5,10,15,20-tetraphenylporphyrin – an Example of a Twisted Intramolecular Charge-Transfer System

S. DAHAL AND M. NETHAJI

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

V. KRISHNAN

Jawaharlal Nehru Centre for Advanced Scientific Research, IISc. Campus, Bangalore 560 012, India

(*Received* 24 *October* 1992; *accepted* 23 *July* 1993)

Abstract

The porphyrin ring in the title compound, 10,19-dinitro-2,7,12,17-tetraphenyl-21,22,23,24-tetraazapentacyclo[16.2.1.$1^{3,6}$.$1^{8,11}$.$1^{13,16}$]tetracosa-1,3,5,7,9,11(23),-

Acta Crystallographica Section C
ISSN 0108-2701 ©1994