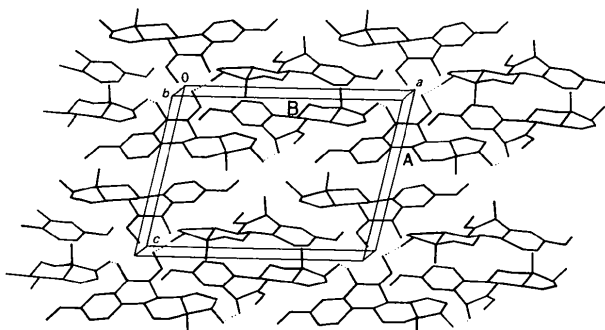


Table 3. Possible hydrogen-bond geometry (Å, °)

X—H...Y	X—H	H...Y	X—		Molecule
			X...Y	H...Y	
O(2A)—H(O2A)...O(3A)	0.884 (5)	1.950 (5)	2.573 (5)	126.1 (5)	<i>x, y, z</i>
O(4B)—H(O4B)...O(2A)	0.99 (1)	1.73 (1)	2.721 (6)	174.6 (5)	<i>x, y, z</i>
O(3A)—H(O3A)...O(4B)	0.816 (5)	1.835 (5)	2.649 (5)	174.5 (6)	2 - <i>x</i> , - $\frac{1}{2}$ + <i>y</i> , - <i>z</i>
O(2B)—H(O2B)...O(4A)	0.984 (7)	1.901 (7)	2.844 (5)	159.7 (5)	2 - <i>x</i> , $\frac{1}{2}$ + <i>y</i> , 1 - <i>z</i>
O(3B)—H(O3B)...O(1A)	0.916 (8)	1.936 (6)	2.837 (4)	167.8 (6)	<i>x</i> , 1 + <i>y</i> , <i>z</i>

Fig. 3. The packing arrangement viewed down the *b* axis. Intramolecular hydrogen bonds are indicated by dotted lines.

the rather short intramolecular O(2)—H(O2)...O(3) hydrogen bond in molecule *A* only (Table 3), forming the six-membered pseudo-ring. The non-bonded distances between O atoms of molecules *A* and *B* are also different: the most important distance for biological activity O(1)...O(4) is 10.888 (4) Å in molecule *A* and 10.972 (5) Å in molecule *B*.

The packing arrangement viewed down the *b* axis is presented in Fig. 3. Two independent molecules linked by the O(4B)—H(O4B)...O(2A) hydrogen bond lie along the *a* axis. The 6 α -hydroxy group of molecule *A* acts simultaneously as a donor of an

intramolecular hydrogen bond to O(3). These pairs are then linked to another pair of molecules by short van der Waals contacts* forming columns. The columns are linked by three other hydrogen bonds (Table 3) between the molecules from different asymmetric units.

The authors are grateful to Dr Nicholas C. Payne, University of Western Ontario, Canada, for data collection. This study was supported by the Research Foundation of Autonomous Province Vojvodina.

* See deposition footnote.

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Acta Cryst. (1993). **C49**, 273–275

Structure of a Steroid Fungal Metabolite

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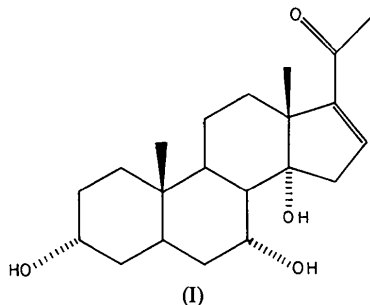
(Received 7 November 1991; accepted 6 May 1992)

Abstract. 3 α ,7 α ,14 α -Trihydroxypregn-16-en-20-one, C₂₁H₃₂O₄, *M_r* = 348.48, orthorhombic, *P*₂12₁2₁, *a* = 9.211 (1), *b* = 13.201 (1), *c* = 16.031 (1) Å, *V* = 1949.28 (29) Å³, *Z* = 4, *D_x* = 1.187 g cm⁻³, $\lambda(\text{Cu } K\alpha)$ = 1.5418 Å, μ = 6.07 cm⁻¹, *F*(000) = 760, *T* = 293 K, *R* = 0.061 for 1337 observations. The *A*, *B* and *C* rings adopt normal chair conformations with the *D* ring in a 14 α -envelope conformation. The

molecules are held together by two hydrogen bonds [O(3)...O(20) = 2.879 and O(7)...O(14) = 2.612 Å].

Introduction. The microbial transformation of steroids has been used extensively for the introduction of functional groups in order to obtain biologically useful substances. Fermentation of pregna-4,16-dien-3,20-dione with the fungus *Mucor piriformis* yielded

the metabolites 7 α ,14 α -dihydroxypregna-4,16-dien-3,20-dione and 3 α ,7 α ,14 α -trihydroxy-16-en-20-one (I). We report the X-ray crystallographic analysis of (I) in this paper.



Experimental. Plate-like single crystals of the title compound were obtained from ethanol. Crystal size approximately 0.4 × 0.2 × 0.15 mm. Lattice parameters refined using 25 reflections in θ range 10–15°. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation; $\theta \leq 60^\circ$; scan speed 1° min⁻¹; $\omega/2\theta$ mode. 3 standard reflections (253, 236, 234) monitored after every 3600 s showed no significant intensity variation. 1638 unique reflections collected ($0 \leq h \leq 10$, $0 \leq k \leq 14$, $0 \leq l \leq 18$), 1337 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. All H atoms except H(O7) were located in difference Fourier map. The positional parameters of all the other H atoms except H(11A) were refined and the thermal parameters held fixed during subsequent refinement. No crystallographic assignment of chirality was made, but the reported structure exhibits the standard stereochemistry of the steroid skeleton. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, $w = 1.0/[\sigma(|F_o|)^2 + 0.002267|F_o|^2]$. At the end of the final cycle of refinement using *F*'s, $R = 0.061$, $wR = 0.064$, $S = 1.06$, $\Delta/\sigma = 0.001$ for 318 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)

* Lists of structure factors, anisotropic thermal parameters and H-atom bond distances, angles and coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55436 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0521]

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

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

	x	y	z	U_{eq}
C(1)	0.0324 (7)	0.1399 (4)	0.0452 (4)	552 (18)
C(2)	0.1391 (8)	0.2134 (4)	0.0846 (4)	669 (22)
C(3)	0.2722 (7)	0.1609 (5)	0.1199 (4)	712 (22)
C(4)	0.3429 (7)	0.0948 (5)	0.0535 (4)	649 (21)
C(5)	0.2349 (6)	0.0203 (4)	0.0149 (3)	501 (18)
C(6)	0.3055 (6)	-0.0513 (4)	-0.0459 (4)	554 (19)
C(7)	0.2013 (6)	-0.1344 (4)	-0.0727 (3)	493 (17)
C(8)	0.0588 (6)	-0.0910 (4)	-0.1072 (3)	445 (16)
C(9)	-0.0078 (5)	-0.0093 (4)	-0.0494 (3)	451 (18)
C(10)	0.1006 (6)	0.0746 (4)	-0.0239 (3)	501 (20)
C(11)	-0.1530 (7)	0.0294 (4)	-0.0866 (4)	635 (20)
C(12)	-0.2604 (7)	-0.0529 (4)	-0.1119 (4)	617 (22)
C(13)	-0.1914 (6)	-0.1299 (4)	-0.1685 (3)	513 (18)
C(14)	-0.0538 (6)	-0.1710 (4)	-0.1238 (3)	446 (16)
C(15)	-0.0175 (6)	-0.2673 (4)	-0.1726 (4)	594 (20)
C(16)	-0.1698 (8)	-0.3050 (5)	-0.1925 (4)	625 (21)
C(17)	-0.2657 (6)	-0.2306 (5)	-0.1869 (3)	561 (21)
C(18)	-0.1526 (8)	-0.0813 (5)	-0.2539 (4)	714 (23)
C(19)	0.1425 (8)	0.1399 (4)	-0.0977 (4)	677 (22)
C(20)	-0.4213 (7)	-0.2421 (6)	-0.2031 (4)	714 (26)
C(21)	-0.4863 (9)	-0.3453 (6)	-0.2069 (5)	952 (28)
O(3)	0.2387 (5)	0.0960 (4)	0.1890 (3)	810 (18)
O(7)	0.1628 (4)	-0.1952 (3)	-0.0015 (2)	572 (13)
O(14)	-0.1026 (4)	-0.2075 (3)	-0.0433 (2)	477 (12)
O(20)	-0.4967 (6)	-0.1673 (4)	-0.2137 (3)	925 (20)

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

C(1)–C(2)	1.518 (8)	C(9)–C(11)	1.550 (7)
C(1)–C(10)	1.537 (7)	C(10)–C(19)	1.513 (7)
C(2)–C(3)	1.517 (9)	C(11)–C(12)	1.524 (8)
C(3)–C(4)	1.522 (9)	C(12)–C(13)	1.503 (7)
C(3)–O(3)	1.434 (8)	C(13)–C(14)	1.553 (7)
C(4)–C(5)	1.529 (8)	C(13)–C(17)	1.524 (8)
C(5)–C(6)	1.505 (7)	C(13)–C(18)	1.553 (8)
C(5)–C(10)	1.559 (7)	C(14)–C(15)	1.529 (7)
C(6)–C(7)	1.519 (7)	C(14)–O(14)	1.449 (6)
C(7)–C(8)	1.535 (7)	C(15)–C(16)	1.522 (9)
C(7)–O(7)	1.439 (6)	C(16)–C(17)	1.324 (9)
C(8)–C(9)	1.548 (7)	C(17)–C(20)	1.464 (8)
C(8)–C(14)	1.503 (7)	C(20)–C(21)	1.489 (11)
C(9)–C(10)	1.546 (7)	C(20)–O(20)	1.219 (9)
C(2)–C(1)–C(10)	113.1 (5)	C(1)–C(10)–C(19)	110.3 (4)
C(1)–C(2)–C(3)	112.7 (4)	C(9)–C(11)–C(12)	115.2 (4)
C(2)–C(3)–O(3)	112.7 (5)	C(11)–C(12)–C(13)	111.6 (4)
C(2)–C(3)–C(4)	110.2 (5)	C(12)–C(13)–C(18)	110.4 (4)
C(4)–C(3)–O(3)	106.8 (5)	C(12)–C(13)–C(17)	121.1 (4)
C(3)–C(4)–C(5)	111.9 (5)	C(12)–C(13)–C(14)	107.6 (4)
C(4)–C(5)–C(10)	112.4 (4)	C(17)–C(13)–C(18)	107.0 (4)
C(4)–C(5)–C(6)	112.6 (4)	C(14)–C(13)–C(18)	111.2 (4)
C(6)–C(5)–C(10)	111.9 (4)	C(14)–C(13)–C(17)	98.6 (4)
C(5)–C(6)–C(7)	111.3 (4)	C(8)–C(14)–C(13)	113.5 (4)
C(6)–C(7)–O(7)	109.5 (4)	C(13)–C(14)–O(14)	105.8 (4)
C(6)–C(7)–C(8)	111.8 (4)	C(13)–C(14)–C(15)	103.4 (4)
C(8)–C(7)–O(7)	106.4 (4)	C(8)–C(14)–O(14)	106.8 (4)
C(7)–C(8)–C(14)	113.0 (4)	C(8)–C(14)–C(15)	121.5 (4)
C(7)–C(8)–C(9)	112.5 (4)	C(15)–C(14)–O(14)	104.3 (4)
C(9)–C(8)–C(14)	108.7 (4)	C(14)–C(15)–C(16)	100.2 (4)
C(8)–C(9)–C(11)	109.9 (4)	C(15)–C(16)–C(17)	110.9 (5)
C(8)–C(9)–C(10)	113.6 (4)	C(13)–C(17)–C(16)	111.1 (5)
C(10)–C(9)–C(11)	115.0 (4)	C(16)–C(17)–C(20)	124.3 (6)
C(5)–C(10)–C(9)	106.7 (4)	C(13)–C(17)–C(20)	124.3 (5)
C(1)–C(10)–C(9)	109.1 (4)	C(17)–C(20)–O(20)	119.8 (6)
C(1)–C(10)–C(5)	107.1 (4)	C(17)–C(20)–C(21)	119.7 (6)
C(9)–C(10)–C(19)	111.4 (4)	C(21)–C(20)–O(20)	120.4 (6)
C(5)–C(10)–C(19)	111.8 (4)		

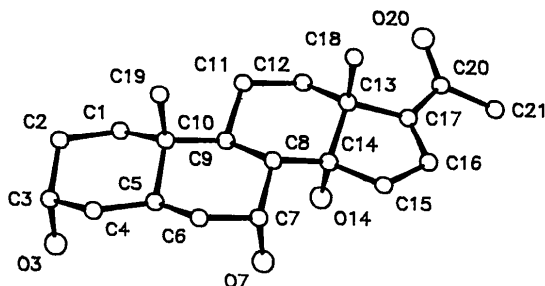


Fig. 1. A *PLUTO* diagram of the title molecule with atom-numbering scheme.

diagram of the title compound with the atomic numbering scheme is shown in Fig. 1. The *A*, *B* and *C* rings adopt normal chair conformations with average endocyclic absolute torsion angles of 55.2, 54.7 and 55.4°, respectively. The *D* ring adopts a 14 α -envelope conformation with the asymmetry parameters $\Delta C_s(13) = 23.8$ (32.5), $\Delta C_s(14) = 4.2$ (1.4), $\Delta C_2(13-14) = 13.4$ (22.7), the values in parentheses being the ideal values for a 14 α -envelope conformation (Duax & Norton, 1975). The X-ray structure of the title molecule shows that all the ring junctions adopt a *trans* configuration [$H(5)-C(5)-C(10)-C(19) = 178.3$ (4), $H(8)-C(8)-C(9)-H(9) = 173.8$ (4), $C(18)-C(13)-C(14)-O(14) = -176.1$ (4)°]. The progesterone side-chain orientation is normally restricted to a region over the *D* ring; the torsion angle $C(16)-C(17)-C(20)-O(20)$ in 84 structures having a ketone group at C(20) 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 [$C(16)-C(17)-C(20)-O(20) = 164.6$ (6)°] as has been observed in four other 16-en-20-one structures (Khazheeva, Simonov, Kamernitskii, Pavlova-Grishina & Skorova, 1982; Duax, Langs, Strong & Osawa, 1979; Surcouf, 1979; Duax, Weeks & Strong, 1979). The molecules are stabilized in the crystal lattice by hydrogen bonding [$O(3)\cdots O(20) = 2.879$, $O(3)-H(O3) = 0.813$, $H(O3)\cdots O(20) = 2.110$ Å, $O(3)-H(O3)\cdots O(20) = 161.01$ °; $O(7)\cdots O(14) = 2.612$ Å].

The University Grants Commission is thanked for financial support.

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Acta Cryst. (1993). **C49**, 275-278

Structures of Sobrerol Enantiomers and Racemates. III.

(±)-*cis*-5-Hydroxy- $\alpha,\alpha,4$ -trimethyl-3-cyclohexene-1-methanol (Racemic *cis*-Sobrerol)

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Abstract. $C_{10}H_{18}O_2$, $M_r = 170.25$, monoclinic, $P2_1/c$, $a = 16.955$ (1), $b = 9.313$ (1), $c = 13.380$ (1) Å, $\beta = 111.44$ (1)°, $V = 1966.5$ (3) Å³, $Z = 8$, $D_m = 1.148$, $D_x = 1.150$ g cm⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 0.73$ cm⁻¹, $F(000) = 752$, $T = 296$ K, $R = 0.026$ for

1318 unique reflections with $I > 3\sigma(I)$. The asymmetric unit of the crystal contains two molecules joined by $O-H\cdots O$ [2.839 (2) Å] hydrogen bonds and $C-H\cdots O$ [3.432 (3) Å] weak contacts. Enantiomeric molecules connected by $O-H\cdots O$ [2.810 (2)