present divalent anion, the negative charge also increasing.

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Structure of 3-Methoxy-6α,17β-dihydroxyestra-1,3,5(10)-trien-7-one Oxime

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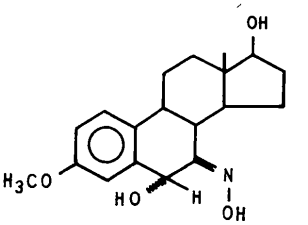
Abstract. $C_{19}H_{25}NO_4$, $M_r = 331.41$, monoclinic, $P2_1$, $a = 14.950$ (2), $b = 9.248$ (1), $c = 12.597$ (1) Å, $\beta = 100.98$ (1)°, $V = 1709.7$ (5) Å^3, $Z = 4$, $D_x = 1.283$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.53$ cm^{-1}, $F(000) = 708$, $T = 293$ (2) K, $R = 0.046$ for 2400 observed reflections. The asymmetric unit contains two molecules, which differ in the conformation of the *B* rings and in the orientations of the C(3) methoxy groups and C(7)=N—OH moieties. The molecules are held together by a three-dimensional network of hydrogen bonds.

Introduction. So far, preparation of *B*-seco estrone derivatives has been almost exclusively achieved by total syntheses (Jhingran, Gupta, Ray, Agarwal, Singh & Anand, 1983, 1986). In our recent research, directed towards a partial synthesis of some novel *B*-seco estrone derivatives (as potential anti-estrogens), the title compound (I) was prepared as a crucial intermediate. The compound was further subjected to the Beckmann fragmentation reaction, in accordance with our previous work (Miljković & Petrović, 1977), in order to bring about the formation of the corresponding *B*-seco derivative. However, as numerous attempts were unsuccessful, it became obvious that it was necessary to determine the exact geometry of the 7-oximino function (*syn* or *anti*) to overcome synthetic difficulties.



(I)

Experimental. A crystal of dimensions 0.50 × 0.36 × 0.22 mm was mounted on a CAD-4 diffractometer equipped with a graphite monochromator. Cell constants were refined by a least-squares fit for 20 centred reflections in the range $16.3 < \theta < 19.4°$. Intensities of 2663 reflections were measured of

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which 2400 were unique and observed; systematic absences $0k0$, $k = 2n + 1$; ω–2θ scan in the range $1.4 < \theta < 33.3°$ with h 0 to 16, k 0 to 10, l −13 to 13. Standard reflections ($3\bar{1}1$, 200, 020, 002) were measured every 120 min. Total loss or gain in intensity was 0.2%. Data were corrected for Lp effects and for absorption (minimum and maximum correction factors 0.9228 and 0.9986). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986), yielding all non-H atoms. Blocked full-matrix least-squares refinement with *SHELX*76 (Sheldrick, 1976) minimized $\sum w(\Delta F)^2$ for 217 parameters, where $w = 1.142/[\sigma(F_o)^2 + 18.9 \times 10^{-4} F_o^2]$, using 2400 reflections with $F_o > 2\sigma(F_o)$. Final $R = 0.046$, $wR = 0.050$, $S = 1.09$; minimum and maximum $\Delta\rho = \pm 0.23$ e Å^{-3}; $(\Delta/\sigma)_{max} = 0.27$. Positions of H atoms bound to C atoms were generated, while those linked to O atoms were located in a difference Fourier map. Their positions were not refined; they were included in the structure-factor calculations with a common isotropic temperature factor [$U = 0.054$ (3) Å^2]. Scattering factors were taken from *SHELX*76. Calculations were performed on an IBM 43/41 computer.

Discussion. Perspective views of the two symmetry-independent molecules *A* and *B*, computed from the final atomic coordinates listed in Table 1, are presented in Fig. 1. The bond lengths, bond angles and relevant torsion angles are given in Table 2. The corresponding bond distances and bond angles in molecules *A* and *B* are in satisfactory agreement. There are only slight variances in some bond distances and angles in rings *B*, but the differences become significant in the torsion angles, leading to the conformational differences (Fig. 2).

According to the ring-puckering coordinates and asymmetry parameters* (Duax, Weeks & Rohrer, 1976; Cremer & Pople, 1975), the *B* ring in molecule *A* exhibits a transition form between the 8β-envelope [the displacement of the C(8) atom from the least-squares plane through the remaining five atoms is −0.728 (4) Å] and 8β,9α-screw-boat [the displacements of C(8) and C(9) are −0.566 (4) and 0.247 (4) Å, respectively]. On the other hand, the conformation of ring *B* in molecule *B* becomes 6α,9α-boat, with displacements of C(6) and C(9) of 0.452 (4) and 0.608 (3) Å, respectively. Evidently, the change of usual envelope or half-chair conformation of ring *B* in these types of steroids can be directly attributed to the substituents. Namely, according to the literature (Duax, Weeks & Rohrer, 1976; Segaloff, Bruce, Flores, Borne, Baker, Duax, Strong & Rohrer, 1980; Duax, Duax, Strong & Segaloff, 1990; Stanković, Petrović, Miljković, Pejanović, Kovačević, Stefanović & Bruvo, 1992), the conformation of ring *B* in estrone derivatives corresponds, as a rule, to the 8β-envelope or 8β,9α-half-chair, but in none of the described cases is ring *B* in the boat conformation.

The conformational difference of rings *B* influences the orientation of the *A* rings. The value of the angle between the best planes of the rings *A* and *B* is 10.3 (1)° in molecule *A* and 21.7 (1)° in molecule *B*. Ring *C* adopts the chair conformation in both

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

$U_{eq} = (1/3)[(U_{11} + U_{33})\sin^{-2}\beta + U_{22} + 2U_{13}\sin^{-2}\beta\cos\beta]$.

	x	y	z	U_{eq}
Molecule *A*				
C(1)	9188 (3)	1626 (6)	4350 (4)	39 (1)
C(2)	8316 (3)	1323 (5)	4491 (3)	35 (1)
C(3)	7818 (3)	261 (5)	3883 (3)	29 (1)
C(4)	8226 (3)	−557 (5)	3168 (3)	28 (1)
C(5)	9099 (3)	−249 (5)	3033 (3)	26 (1)
C(6)	9450 (3)	−1072 (5)	2150 (3)	29 (1)
C(7)	10460 (3)	−837 (5)	2174 (3)	28 (1)
C(8)	11029 (3)	−163 (5)	3157 (3)	26 (1)
C(9)	10541 (3)	1266 (5)	3400 (3)	30 (1)
C(10)	9599 (3)	876 (5)	3607 (3)	29 (1)
C(11)	11093 (3)	2211 (6)	4273 (4)	40 (1)
C(12)	12084 (3)	2433 (5)	4121 (4)	39 (1)
C(13)	12546 (3)	990 (5)	4041 (3)	30 (1)
C(14)	12022 (3)	133 (5)	3082 (3)	28 (1)
C(15)	12652 (3)	−1126 (6)	2955 (4)	36 (1)
C(16)	13625 (3)	−449 (6)	3272 (4)	47 (1)
C(17)	13479 (3)	1078 (6)	3689 (4)	36 (1)
C(18)	12668 (3)	157 (6)	5121 (3)	41 (1)
C(19)	6467 (3)	769 (7)	4581 (4)	52 (1)
N	10865 (2)	−1156 (5)	1395 (3)	36 (1)
O(1)	6928 (2)	−53 *	3894 (2)	36 (1)
O(2)	8897 (2)	−626 (4)	1155 (2)	42 (1)
O(3)	10253 (2)	−1812 (4)	504 (2)	43 (1)
O(4)	14229 (2)	1493 (5)	4515 (3)	51 (1)
Molecule *B*				
C(1)	3615 (3)	2479 (5)	843 (4)	38 (1)
C(2)	2704 (3)	2742 (6)	774 (4)	43 (1)
C(3)	2421 (3)	3877 (5)	1349 (3)	34 (1)
C(4)	3059 (3)	4753 (5)	1983 (3)	33 (1)
C(5)	3985 (3)	4445 (5)	2071 (3)	30 (1)
C(6)	4681 (3)	5347 (6)	2794 (3)	38 (1)
C(7)	5507 (3)	5627 (5)	2277 (3)	32 (1)
C(8)	5813 (3)	4448 (5)	1581 (3)	34 (1)
C(9)	5297 (3)	3023 (5)	1682 (3)	31 (1)
C(10)	4277 (3)	3303 (5)	1510 (3)	31 (1)
C(11)	5569 (3)	1826 (6)	957 (4)	42 (1)
C(12)	6598 (5)	1586 (5)	1158 (4)	38 (1)
C(13)	7108 (3)	3005 (5)	1045 (3)	33 (1)
C(14)	6833 (3)	4135 (5)	1823 (3)	33 (1)
C(15)	7545 (3)	5345 (6)	1835 (4)	40 (1)
C(16)	8409 (3)	4539 (7)	1668 (5)	56 (2)
C(17)	8140 (3)	2940 (6)	1486 (4)	41 (1)
C(18)	6932 (4)	3478 (6)	−153 (3)	45 (1)
C(19)	1168 (3)	5230 (7)	1766 (5)	59 (2)
N	5955 (3)	6801 (5)	2378 (3)	43 (1)
O(1)	1491 (2)	4034 (4)	1223 (3)	47 (1)
O(2)	4968 (2)	4576 (5)	3806 (2)	55 (1)
O(3)	5615 (2)	7826 (5)	3043 (4)	63 (1)
O(4)	8672 (2)	2265 (5)	800 (3)	57 (1)

* Coordinate fixed to define origin for structure with non-centrosymmetric space group.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, ring-puckering coordinates and asymmetry parameters, and short van der Waals contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55284 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA0015]

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for molecules A and B*

	Molecule *A*	Molecule *B*
C(1)—C(2)	1.378 (6)	1.370 (5)
C(2)—C(3)	1.374 (5)	1.386 (6)
C(3)—C(4)	1.402 (5)	1.383 (5)
C(4)—C(5)	1.378 (6)	1.397 (5)
C(1)—C(10)	1.398 (6)	1.396 (5)
C(5)—C(10)	1.399 (5)	1.387 (6)
C(5)—C(6)	1.521 (5)	1.499 (5)
C(6)—C(7)	1.520 (5)	1.524 (6)
C(7)—C(8)	1.498 (4)	1.523 (5)
C(8)—C(9)	1.568 (6)	1.544 (6)
C(8)—C(14)	1.530 (5)	1.525 (5)
C(9)—C(10)	1.524 (6)	1.521 (5)
C(9)—C(11)	1.519 (5)	1.538 (6)
C(11)—C(12)	1.543 (6)	1.527 (5)
C(12)—C(13)	1.515 (6)	1.538 (6)
C(13)—C(14)	1.530 (5)	1.541 (5)
C(13)—C(17)	1.544 (6)	1.538 (6)
C(13)—C(18)	1.544 (5)	1.545 (4)
C(14)—C(15)	1.525 (6)	1.543 (6)
C(15)—C(16)	1.564 (5)	1.540 (6)
C(16)—C(17)	1.537 (7)	1.538 (7)
C(17)—O(4)	1.429 (5)	1.425 (6)
C(6)—O(2)	1.425 (3)	1.452 (4)
C(19)—O(1)	1.424 (5)	1.432 (6)
C(3)—O(1)	1.365 (4)	1.377 (4)
C(7)—N	1.282 (6)	1.269 (5)
N—O(3)	1.440 (4)	1.422 (6)
C(2)—C(1)—C(10)	122.2 (4)	121.6 (4)
C(1)—C(2)—C(3)	119.9 (4)	120.0 (5)
C(2)—C(3)—C(4)	119.2 (4)	120.0 (4)
C(2)—C(3)—O(1)	124.9 (4)	114.9 (4)
C(4)—C(3)—O(1)	115.9 (4)	125.1 (4)
C(3)—C(4)—C(5)	120.4 (4)	119.4 (4)
C(4)—C(5)—C(6)	117.0 (4)	119.8 (4)
C(4)—C(5)—C(10)	121.0 (4)	121.2 (4)
C(6)—C(5)—C(10)	121.7 (4)	119.0 (4)
C(5)—C(6)—C(7)	113.2 (4)	111.1 (4)
C(5)—C(6)—O(2)	106.0 (3)	108.4 (4)
C(7)—C(6)—O(2)	112.6 (3)	109.3 (4)
C(6)—C(7)—C(8)	118.8 (4)	118.8 (4)
C(6)—C(7)—N	124.3 (4)	123.9 (4)
C(8)—C(7)—N	116.9 (4)	117.4 (4)
C(7)—C(8)—C(9)	107.5 (3)	110.7 (3)
C(7)—C(8)—C(14)	115.4 (4)	114.8 (4)
C(9)—C(8)—C(14)	110.8 (3)	108.5 (3)
C(8)—C(9)—C(10)	108.3 (3)	110.2 (3)
C(8)—C(9)—C(11)	114.7 (4)	111.9 (4)
C(10)—C(9)—C(11)	113.9 (4)	114.2 (4)
C(1)—C(10)—C(5)	117.1 (4)	117.8 (4)
C(1)—C(10)—C(9)	122.4 (4)	124.7 (4)
C(5)—C(10)—C(9)	120.5 (4)	117.5 (4)
C(9)—C(11)—C(12)	112.9 (4)	112.2 (4)
C(11)—C(12)—C(13)	110.6 (4)	111.2 (4)
C(12)—C(13)—C(14)	109.7 (4)	108.8 (4)
C(12)—C(13)—C(17)	114.9 (4)	114.5 (4)
C(12)—C(13)—C(18)	111.1 (4)	109.7 (4)
C(14)—C(13)—C(17)	98.9 (3)	99.6 (3)
C(14)—C(13)—C(18)	113.2 (4)	114.4 (4)
C(17)—C(13)—C(18)	108.5 (4)	109.7 (4)
C(8)—C(14)—C(13)	113.6 (4)	112.3 (4)
C(8)—C(14)—C(15)	119.7 (4)	121.8 (4)
C(13)—C(14)—C(15)	104.2 (4)	103.4 (4)
C(14)—C(15)—C(16)	103.3 (4)	104.0 (4)
C(15)—C(16)—C(17)	105.6 (4)	106.5 (4)
C(13)—C(17)—C(16)	104.2 (4)	103.4 (4)
C(13)—C(17)—O(4)	115.6 (4)	115.8 (4)
C(16)—C(17)—O(4)	110.7 (4)	110.6 (4)
C(7)—N—O(3)	111.8 (4)	112.9 (4)
C(3)—O(1)—C(19)	118.6 (3)	116.8 (4)
O(4)—C(17)—C(13)—C(18)	−46.5 (5)	−44.6 (5)
O(4)—C(17)—C(16)—C(15)	147.6 (4)	149.6 (4)
C(2)—C(3)—O(1)—C(19)	0.0 (6)	−177.4 (4)
C(4)—C(5)—C(6)—O(2)	65.1 (5)	99.5 (5)
O(2)—C(6)—C(7)—N	−44.5 (6)	−96.3 (5)
C(6)—C(7)—N—O(3)	−2.0 (6)	1.1 (6)
O(2)—C(6)···N—O(3)	−42.3 (3)	−86.1 (4)
C(1)—C(10)···C(13)—C(18)	65.2 (4)	58.1 (4)

molecules. The five-membered ring *D* exhibits a transition form between 13β-envelope [the displacement of C(13) is 0.725 (3) Å for molecule *A* and 0.720 (3) Å for molecule *B*] and 13β,14α-half-chair [the displacements of C(13) and C(14) are 0.580 (3) and −0.178 (3) Å for molecule *A* and 0.634 (3) and −0.105 (3) Å for molecule *B*].

The 6-hydroxy group occupies an α-pseudo-axial position, while the 17-hydroxy moiety is α-pseudo-equatorial in both molecules. The different conformations of rings *B* and, consequently, the different orientations of the C(7)═N—OH moiety allow

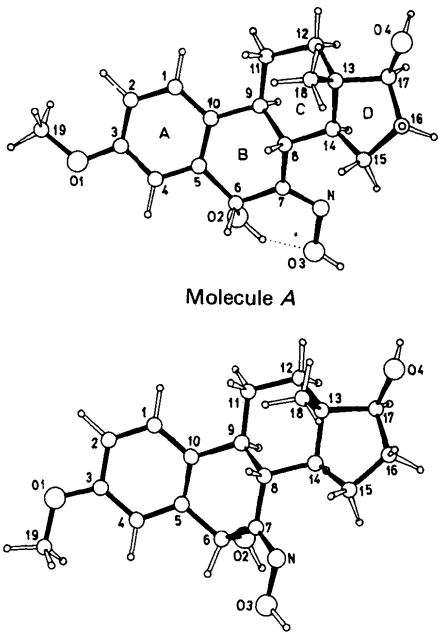

Fig. 1. A perspective view of the two symmetrically independent molecules *A* and *B*. The intramolecular hydrogen bond is indicated by a dotted line.

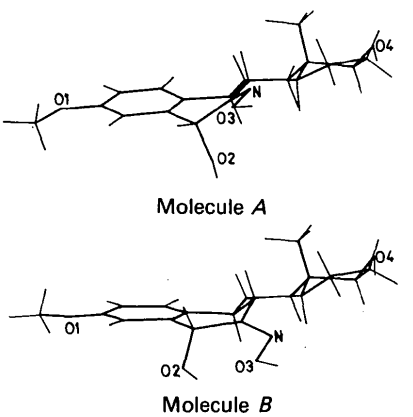

Fig. 2. The difference in conformations of the steroid skeletons for molecules *A* and *B*.

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

X—H···*Y*	*X*—H	H···*Y*	*X*···*Y*	*X*—H···*Y*	Molecule
O(2*A*)—H(O2*A*)···O(3*A*)	0.884 (5)	1.950 (5)	2.573 (5)	126.1 (5)	*x*, *y*, *z*
O(4*B*)—H(O4*B*)···O(2*A*)	0.99 (1)	1.73 (1)	2.721 (6)	174.6 (5)	*x*, *y*, *z*
O(3*A*)—H(O3*A*)···O(4*B*)	0.816 (5)	1.835 (5)	2.649 (5)	174.5 (6)	$2-x, -\frac{1}{2}+y, -z$
O(2*B*)—H(O2*B*)···O(4*A*)	0.984 (7)	1.901 (7)	2.844 (5)	159.7 (5)	$2-x, \frac{1}{2}+y, 1-z$
O(3*B*)—H(O3*B*)···O(1*A*)	0.916 (8)	1.936 (6)	2.837 (4)	167.8 (6)	$x, 1+y, z$

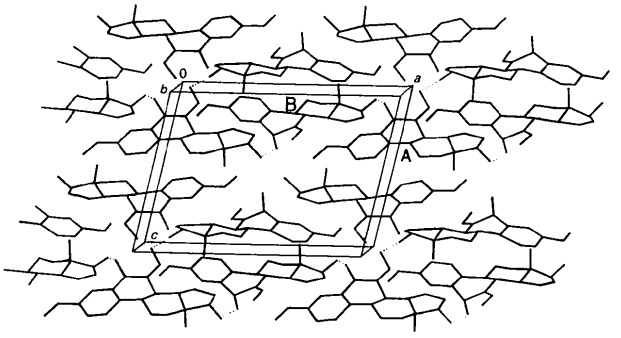

Fig. 3. The packing arrangement viewed down the *b* axis. Intramolecular hydrogen bonds are indicated by dotted lines.

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 nonbonded 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(4*B*)—H(O4*B*)···O(2*A*) hydrogen bond lie along the *a* axis. The 6α-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.

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* See deposition footnote.

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Structure of a Steriod Fungal Metabolite

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Abstract. 3α,7α,14α-Trihydroxypregn-16-en-20-one, $C_{21}H_{32}O_4$, $M_r = 348.48$, orthorhombic, $P2_12_12_1$, $a = 9.211$ (1), $b = 13.201$ (1), $c = 16.031$ (1) Å, $V = 1949.28$ (29) Å^3, $Z = 4$, $D_x = 1.187$ g cm^{-3}, λ(Cu $K\alpha$), = 1.5418 Å, $\mu = 6.07$ 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 14α-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

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