A STEROID STRUCTURE

WHICH REFUTES THE ISOLATION

OF C(17)-C(20) ROTATIONAL ISOMERS

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Received: 11/29/76

ABSTRACT

Isolation of two C(17)-C(20) rotamers of 20-methyl-20-(2-hydroxyethoxy)-5-pregnene-3 β ,17 α -diol has been reported. X-Ray analysis of a diacetate derivative of one of the "rotamers" shows that the actual structure is 3 β -acetoxy-17 α -(2-acetoxyethoxy)-17 α ,17 α f-dimethyl-Dhomo-5-androsten-17 β -ol (C₂₈H₄₄O₆). Thus, although this investigation refutes the existence of C(17)-C(20) rotamers, it suggests a possible new pathway for D-homo steroid synthesis.

INTRODUCTION

Facile isolation of two C(17)-C(20) rotamers of 20-methyl-20-(2hydroxyethoxy)-5-pregnene-3 β ,17 α -diol having different melting points, proton magnetic resonance spectra, and optical rotations was reported by Kohen *et al* in 1969 [1]. The ethylene ketal (Figure 1a) of 17 α hydroxypregnenolone was prepared according to Stache *et al* [2]. Following Kohen's procedure [1], methylmagnesium bromide in ether was added to (1a) in benzene and the mixture was heated under reflux for 90 hours. Both the "20 α " (mp 275-278°) and the "20 β " (mp 200-203°) isomers were isolated in amounts corresponding to the originally reported yields.

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X-Ray analysis of a diacetate derivative of the "20 β " compound was undertaken in order to verify or disprove the proposed structure.

FIGURE 1



RESULTS & DISCUSSION

X-Ray analysis demonstrates that the diacetate derivative of the "20ß" product of the reaction between methylmagnesium bromide and 3ß,17 α -dihydroxy-5-pregnene-20-one ethylene ketal (Figure 1a) is a D-homo-androstene* (1b) rather than the expected 20-methylpregnene (1c). Thus, this structure determination disproves the first reported isolation of rotamers with asymmetry due to restricted rotation about the steroidal C(17)-C(20) bond [1]. A preliminary account of these findings has been published elsewhere [3].

In view of the findings that the major reaction product has a D-homo structure, the possibility that the starting ethylene ketal (1a) might be a D-homologated compound was examined by deketalization reactions. Hydrolysis of the ketal (1a) in aqueous acetic acid at room temperature [4] or in dilute methanolic sulfuric acid under reflux [5] gave only starting 17α -hydroxypregnenolone, indicating no sign of D-homologation in the ethylene ketal formation. The mechanism of the

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The trivial name 17α -hydroxypregnenolone will also be used for 3 β , 17α -dihydroxy-5-pregnen-20-one.

The trivial name "D-homo-androstene" will be used throughout the remainder of this paper as an abbreviation for 3β -acetoxy- 17α , $17\alpha\beta$ -dimethyl-D-homo-5-androsten- 17β -ol,

unusual D-homologation during the Grignard reaction is presently under investigation.

The atomic numbering, bond distances, valency angles, and endocyclic torsion angles for the D-homo-androstene are illustrated in Figure 2. The ranges of the estimated standard deviations of the bond distances and valency angles are 0.005-0.011Å and 0.2-0.6°, respectively, and the values of these parameters agree closely with the averages reported for Δ^5 -steroids [6]. The overall conformation of the D-homoandrostene molecule is illustrated in Figure 3. The A-, C-, and Drings have chair conformations, and the B-ring has a half-chair conformation. The side chain orientations may be seen from Figure 3, and they are also described by the torsion angles given in Table I. The orientations of 3β -acetate and 3β -benzoate substituents relative to the A-ring are defined by the torsion angles C(2)-C(3)-O(3)-C(n) and C(4)-C(3)-O(3)-C(n), in which C(n) is the carbonyl carbon. These substituents are observed to fall into two conformational classes [7]. In conformer A, the O(3)-C(n) bond is trans to C(3)-C(4) and gauche to C(2)-C(3), and in conformer B, the O(3)-C(n) bond is gauche to C(3)-C(4) and trans to C(2)-C(3). The D-homo-androstene is an example of conformer A. A third conceivable conformer in which the O(3)-C(n)bond is gauche to both C(3)-C(4) and C(2)-C(3) has never been observed.

The atoms comprising the $C(17a\alpha)$ side chain lie in two approximately planar groupings which are defined in Table II and which form a dihedral angle of 78°. The best plane through each of these groups was calculated by means of least-squares, and the distances of the atoms from the planes are also given in Table II. The 17aβ-methyl carbon, C(21), also is near the plane defined by C(17a), $O(17a\alpha)$,

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C(24), and C(25). The two oxygens in the ethylene glycol molety have a gauche orientation as indicated by the O($17a\alpha$)-C(24)-C(25)-O(25) torsion angle of -63.2°. The carbonyl bond [C(26)-O(26)] in the acetate group is *cis* coplanar with the O(25)-C(25) bond. The 3β-acetate has a similar conformational feature.

TABLE I

Side Chain Torsion Angles

Atoms	Angle
38-Acetate	
$C(2)-C(3)-O(3\beta)-C(22)$	86.5°
$C(4)-C(3)-O(3\beta)-C(22)$	-153.6
$C(3)=O(3\beta)=C(22)=O(22)$ $C(3)=O(3\beta)=C(22)=C(23)$	-13.4
C(17aα) Side Chain	
C(13)-C(17a)-O(17aα)-C(24)	120.6
$C(17)-C(17a)-O(17a\alpha)-C(24)$	-119.9
$C(21)-C(17a)-O(17a\alpha)-C(24)$	-1.5
C(17a)-O(17aα)-C(24)-C(25)	173.3
0(17aα)-C(24)-C(25)-O(25)	-63.2
C(24)-C(25)-O(25)-C(26)	-80.1
C(25)-O(25)-C(26)-O(26)	-0.9
C(25)-O(25)-C(26)-C(27)	176.9

TABLE II

Planes in the $C(17a\alpha)$ Side Chain

Plane 1

Atoms	(Å)	C(17α)	0(17aα)	C(24)	C(25)	C(21) [*]	
Distances		0.04	-0.05	-0.02	0.03	0.19	
			Plane 2				
Atoms	(Å)	C(25)	C(25)	C(26)	0(26)	C(27)	
Distances		0,02	-0.02	-0.02	0.00	0.02	

*Atom not included in the plane

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(a) Bond distances $\begin{pmatrix} A \\ O \end{pmatrix}$, (b) valency angles (deg), and (c) endocyclic torsion angles (deg). A torsion angle α - β - γ - δ is positive if, when viewed down the β - γ bond, the α - β bond will eclipse the γ - δ when rotated less than 180° in a clockwise direction.

FIGURE 3

a)



b)



EXPERIMENTAL

The X-ray measurements required for single crystal structure analysis were performed on an Enraf-Nonius CAD-4 diffractometer using CuK α radiation. Crystal structure solution was by direct methods using the MULTAN computer program [8], and full-matrix least-squares calculations were used for structure refinement. Melting points were measured on a Fisher-Jones melting point apparatus and were uncorrected. Proton magnetic resonance (pmr) spectra were obtained with a Varian EM-360 spectrometer at 60 MHz using tetramethylsilane as an internal standard. Infrared (IR) spectra were run with a Perkin-Elmer 267 spectrophotometer on KBr disks. Precoated silica gel GF plates (UNIPLATE, Analteck, Inc.) were used for thin layer chromatography (TLC). Elemental analyses were performed by Instranal Laboratory, Inc., Rensselaer, New York.

Preparation of 3β , 17α -dihydroxy-5-pregnen-20-one ethylene ketal (1) [2]

A suspension of 17α -hydroxypregnenolone (6.53 g) and p-toluenesulfonic acid (0.21 g) in ethylene glycol (137 ml) was heated under 3.5 mmHg at 140-150° for 6 hr. Ethylene glycol was slowly distilled and an additional 30 ml was added at both 2 hr and 4 hr. After neutralization with 2N-NaOH and addition of water, the precipitates were collected by filtration, washed with water, and dried in vacuo to give 7.77 g of crude product. Recrystallization from methanol containing 0.1% of pyridine gave 5.70 g of crystals having the following physical properties: mp 186-190° (reported [4] mp 190°); IR 3460 (broad), 1365, 1180, 1045 cm⁻¹; pmr (CDCl₃) & 0.83 (3H, s, 18-CH₃), 1.03 (3H, s, 19-CH₃), 1.37 (3H, s, 21-CH₃); pmr (pyridine) δ 1.03 (3H, s, 18 or 19-CH₃), 1.07 (3H, s, 18 or 19-CH₃), 1.55 (3H, s, 21-CH₃).

Hydrolysis of \underline{I} to 17α -hydroxypregnenolone in acetic acid [4]

6 ml of 50% AcOH was added to 5.1 mg of I and left for 16 hr at room temperature. The product was extracted with ether and $CH_2C\ell_2$ to give 3.4 mg of crystals having an Rf identical to 17α -hydroxy-pregnenolone on TLC ($CDC\ell_3$ -acetone, 8:2), mp 271-273° (reported [9] mp 271-273°), and IR peaks at 3400, 1680, 1360, and 1065 cm⁻¹.

Hydrolysis of \underline{I} to 17α -hydroxypregnenolone in sulfuric acid [5]

576 mg of <u>I</u> was dissolved in 65 ml of MeOH and 1.4 ml of conc. H_2SO_4 in 14 ml of water. The solution was refluxed for one-half hour and then poured into water. The precipitate was filtered and washed with water to give 447 mg of crude material having an Rf identical to 17α -hydroxypregnenolone on TLC (CHC ℓ_3 -acetone, 8:2), mp 258-268°, and IR peaks at 3400, 1680, 1350, and 1065 cm⁻¹. The crude product was acetylated with pyridine and acetic anhydride at room temperature for 16 hr. The product was recrystallized from benzene-hexane to give 215 mg of 17α -hydroxypregnenolone 3-acetate [mp 230-233° (reported [9] mp 234-235°); IR 3400, 1725, 1690, 1245, 1035 cm⁻¹; pmr (CDC ℓ_3) δ 0.72 (3H, s, 18-CH₃), 1.02 (3H, s, 19-CH₃), 2.04 (3H, s, OAc), 2.27 (3H, s, 21-CH₃)].

Methyl Grignard addition to I

Following the original procedure of Kohen *et al* [1], methylmagnesium bromide in ether (2.7 M, 20 ml) was added to 1.0 g of \underline{I} in 50 ml of anhydrous benzene, and the mixture was refluxed for 90 hr. After hydrolysis with aqueous ammonium acetate, the mixture was taken up in benzene and ether. The extract was washed with water, dried over anhydrous magnesium sulfate, and condensed to give 1.1 g of crude product. It was submitted to preparative TLC using CHCl₃-EtOAc (3:7). The products were detected by UV light and eluted with ether-EtOH (4:1) giving 4 fractions: Fraction I (Rf 0.20, 10%), II (Rf 0.37, 37%), III (Rf 0.54, 7.5%), and IV (Rf 0.75, 12%).

The major product (Fraction II) after recrystallization from methanol had the following characteristics: mp 180-197°; IR 3360, 1450, 1370, 1200, 1120, 1050 cm⁻¹; pmr (CDCl₃) δ 0.98 (3H, s, 18-CH₃), 1.03 (3H, s, 19-CH₃), 1.17 (3H, s, CH₃), 1.25 (3H, s, CH₃); pmr (pyridine) δ 1.05 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.47 (3H, s, CH₂). It was acetylated with acetic anhydride and pyridine at room temperature for 16 hr. The mixture was then poured into ice-water and the precipitates were collected by filtration and recrystallized from benzene-hexane to give the diacetate [mp 162.5-165°; IR 3490, 1730, 1710, 1365, 1240, 1130 cm⁻¹; pmr (CDCl₃) δ 1.02 (3H, s, 18 or 19-CH₃), 1.03 (3H, s, 18 or 19-CH₃), 1.15 (3H, s, CH₃), 1.23 (3H, s, CH₃), 2.02 (3H, s, OAc), 2.05 (3H, s, OAc); pmr (pyridine) δ 0.98 (3H, s, 19-CH₃, Δ = +0.04 ppm), 1.33 (3H, s, 18-CH₃, Δ = -0.30 ppm), 1.38 (3H, s, CH₂), 1.40 (3H, s, CH₂), 2.05 (3H, s, OAc), 2.06 (3H, s, OAc); Anal. Calc'd. for C₂₈H₄₄O₆: C 70.56, H 9.29; Found: C 70.98, H 9.23]. These properties match those originally assigned by Kohen et al [1] to "20-methyl-20 β -(2-hydroxyethoxy)pregn-5-ene-36,17a-dio1" [Free alcohol: mp 200-203°, 32.5% yield. Diacetate: mp 166.5-167.5°, pmr at 18-CH3 δ 1.06 (in CDCl3) and δ 1.30 (in pyridine), $\Delta = -0.26$ ppm.]. On the basis of crystallographic results, this structure was reassigned as 17α , $17a\beta$ -dimethy1-17a α -(2-hydroxyethoxy)-D-homo-5-androstene- 3β , 17β -dio1 and its diacetate.

X-Ray crystal structure determination

The diacetate was recrystallized from chloroform-methanol and a needle-shaped single crystal with approximate dimensions 0.25 x 0.25 x 0.7mm was chosen for the experimental X-ray measurements which were performed on an Enraf-Nonius CAD-4 diffractometer. The systematic absences in the diffraction pattern were consistent with the orthorhombic space group P2₁2₁2₁, and the cell constants were determined by a least-squares analysis of the 20 values for 50 reflections [at 20°C; $\lambda(CuK\overline{\alpha}) = 1.54178A$]. The crystal data are: a = 9.178(1), b = 35.177(1), c = 8.288(1)A, $V = 2675A^3$, Z = 4, M = 476.66, $D_c = 1.18$, $D_m = 1.209 \cdot cm^{-3}$,

and mp 162.5-165°C.

Integrated intensities were measured for 3163 independent reflections having θ < 75° using CuK α radiation. Lorentz and polarization corrections $[(1+\cos^22\theta)/2 \sin 2\theta]$ were applied, and normalized structure factor amplitudes were computed. The structure was then solved by a straightforward application of the MULTAN program [8]. The positional and anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least-squares using the 2424 reflections for which the observed intensity was greater than twice the corresponding standard deviation. After several cycles of refinement, Fourier difference maps were computed, and the majority (39) of the hydrogen atoms were located. The remaining five hydrogens bonded to carbon atoms were placed at their geometrically expected positions. The parameters of the nonhydrogen atoms were then refined for four final cycles with the hydrogens included in the structure factor calculations but their parameters not refined. All hydrogen atoms were given iso-tropic thermal parameters of 4.0Å². The quantities $(1/\sigma_F^2)$ were used as weights where σ_F is as defined by equation H.14 of Stout and Jensen [10] using 0.06 rather than 0.01 as the instability correction. This value increases $\sigma_{\rm F}$ for reflections with small $|{\rm F}|$ and prevents them from controlling the refinement. The R index was defined as $\Sigma(||Fo| - |Fc||)/$ Its final value was 9.9% for all data and 6.8% for the data Σ Fo. used in the refinement. The final coordinates and anisotropic thermal parameters $(x10^4)$ for the nonhydrogen atoms as well as the coordinates of the hydrogen are given in Table III. The standard deviations of the refined parameters are given in parentheses, and the anisotropic thermal parameters are of the form $\exp\left[-2\pi^2(U_{22}h^2a^{*2}+2U_{12}hka^{*b^{*+}}..)\right]$.

ACKNOWLEDGEMENT

This research was supported by Grant No. CA-10906 from the National Cancer Institute, DHEW and Grant No. HD-04945 from the National Institute of Child Health and Human Development, DHEW.

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TABLE III

Atomic Positional and Thermal Parameters

ATOM	X/A	¥/8	Z/C	U11	USS	U33	012	013	U23
C(1)	0.3816(6)	0.72809(10)	0 8086165	72(3)	12/21	52/21	-2(2)	10(2)	112
C (2)	8.41971 71	0.68918(11)	0.7352(6)	86(3)	34(2)	60(2)	5(2)	7 (3)	2/2
6133	0.00775 51	0 40040(11)	REPART	66(3)	37/35	66(2)	2(2)	/(3)	= = = = = = = = = = = = = = = = = = = =
6 (0)	0 E0167 EN	C. 70707(11)	0.3344(0)	55(2)	21(2)	00(2)	4(2)	4(2)	#912
0143	0,0000(0)	0./2010(11)	4,4055(5)	64(2)	41(2)	48(2)	4(2)	3(5)	-8(5
L (3)	0,4159(4)	0.76080(11)	P.5625(5)	40(2)	41(2)	43(2)	0(1)	4(2)	-5(2
C(6)	0,4449(5)	2,79094(11)	0,4739(5)	67(2)	40(2)	37(2)	+6(2)	0(5)	-5(5
C(7)	0,4228(5)	0.82997(10)	0,5389(5)	67(2)	33(1)	33(2)	-1(2)	-1(5)	3(1
C(8)	0,4671(4)	0.83425(9)	0.7144(4)	42(2)	29(1)	34(2)	0(1)	0(1)	2(1
C(9)	0.4150(4)	0.79960(9)	0.8117(4)	38(2)	29(1)	15(2)	3(1)	0(1)	311
C(10)	0.47901 41	0.76144(10)	0.7451(5)	42(2)	33(1)	48(2)	a (+)	2121	0/1
0(11)	0.44341 51	B BB8444(10)	0 0000100	42 (2)	21/11	76/31	9(3)	4/25	5 (1
6 (12)	0 1811/ 51	D B#101(10)	1 0075614J	57(3)	21111	33161	6(2)	1161	501
C (1 3 1	0 4077/ 45	0 0 0 0 1 7 3 (10)	1,00/07/01	37(2)	37(1)	30(2)	-1(6)	2121	211
C () ()	0,40307.43	0,010/4(9)	0.9883131	34(2)	24(1)	20(6)	-111)		0(1
6(14)	0,40/0(4)	6.01124(4)	0.7886(4)	38(5)	30(1)	34(2)	0(1)	0(1)	4(1
L(15)	0.4466(5)	0.90717(10)	0.6900(5)	52(2)	34(1)	40(2)	0(S)	1(2)	7 (1
C(16)	0,3681(5)	0.94079(10)	0,7556(5)	51(2)	34(2)	49(2)	-1(2)	-4(2)	8(2
C(17)	0,4039(4)	0,94998(9)	0,9307(5)	38(2)	30(1)	52(2)	-3(1)	-3(2)	5(1
C(17A)	0,3774(4)	0,91437(9)	1,0373(5)	37(2)	33(1)	39(2)	-3(1)	0(5)	0(1
C(18)	0.6138(4)	0.87727(11)	0.9949(6)	42(2)	41(2)	57(2)	5(2)	+11(2)	-1(2
C(19)	0.6368(5)	0.75606(15)	0.7995(6)	53(2)	72121	64131	19721	-12(2)	-2212
C (20)	0.31367 51	0 08478/111	0 0257(4)	68(2)	76/21	64(3)	10(3)	6/31	3(3
C(21)	0.42521 51	0 02205(11)	1 2102(6)	42(2)	4+(3)	10(2)	2(2)	-0(2)	-8(2
14417	0 1188/ 51	0 L 36 33 (44)	1.0100(0)	DELES	41(2)	44163	2(2)		
61223	0 4550(44)		0,4102(4)	90(4)	0/(3)	110(4)	15(2)	-22141	- e (1 5
	0.4009(11)	0.54644(10)	0.3464(8)	168(7)	62(3)	89(4)	18(4)	~2(5)	-35(5
L(24)	0.1277(5)	0.91005(11)	1,1592(5)	57(2)	42(2)	46(2)	0(5)	14(2)	5(5
0(52)	-0,0254(5)	0,90823(12)	1,1004(6)	54(2)	44(2)	58(2)	-5(2)	13(2)	-5(5
C(56)	-0,0980(4)	0,97231(12)	1.0825(6)	36(2)	46(2)	78(3)	-3(2)	1(5)	-5(2
C(27)	-0.1288(6)	1,00524(15)	0,9748(9)	64(3)	67(3)	112(4)	-6(2)	-27 (3)	21(3
0(38)	0.4603(4)	0.65548(8)	0.4878(6)	85(5)	41(1)	107(3)	5(2)	(2)	-23(2
0(17AA)	0.2194(3)	0.90896(8)	1.0232(3)	36(1)	47(1)	43(1)	+1(1)	6(1)	-3(1
0(178)	0.5558(3)	0.95971(7)	0.9426(4)	42(1)	36(1)	76(2)	-9(1)	-4121	6.01
0(22)	0.25587 51	0 62588(11)	0 5405(4)	03(3)	80(3)	163751	8(2)	-11 /43	-1468
0(25)	-0 0434(3)	0 000311 21	1 0020(0)	47243	50(5)	56/31	-7/41		
0(26)		0 07307(0)	1 2343/67	4/(1)	56(1)	20(2)	-2(1)	1111	-10(7
0(20)	-0.0371(4)	0.7/37/(7)	1,2203(3)	10(2)	20151	//(2)	=3(E)	61 (6)	•17(6
		u / m	7/6	ATON	4	¥ / A	*/	8	715
ATUM	X/A	1/8	270		.,		,,	u u	
H(1A)	0.2788	0.7343	0.7789	HC	188)	0.6486	0.89	96	0,960
HIST	0.3792	0.7264	0.9308	HC	180)	0.6357	0.87	78	1.127
HIZAT	0.3658	0.6699	0.7897	HC	1941	0.6651	0.73	55	0.744
H(28)	0.5302	0 6837	8.7615	нс	1983	0,7023	0.77	94	0.803
41243	0, 2982	0 4030	0 5280	HI	(30)	0.6530	0.75	36	0.909
	0 4073	0,0735 D 7377	0,3703	н	20141	0.3276	1.00	42	0.909
11(4A)	2,4733	0,7535	0 1040		2081	0 2155	0.08	90	0.997
n(40)	0.0015	0,/164	0.4044		2001	0 1397	0.00	111	1 121
H(6)	0.4201	0,7884	0.3470		2063	0,2601	0.07	1.1.1	1
H(7A)	0,3161	0.8346	0,5347	11.1	210)	0,3247	2,70		1.217
H(7B)	0.4702	0.8477	0,4719	нц	210)	0.3155	0.94	43	1.271
H(86)	0,5703	0,8366	0,7242	HG	234)	0,4977	0.60	45	0.516
H(9A)	0.3004	0.7982	0,7923	н(;	238)	0,3679	0.58	40	0,327
H(11A)	0.4033	0.7844	1.0471	нG	24A)	0,1358	0,88	46	1,559
H(118)	0.5603	0.8047	1.0232	HG	248)	0.1376	0,93	33	1.555
H(124)	0.2792	0.8427	1.0446	нt	25A)	-0.1008	0.90	41	1.196
H(128)	0.4077	0.8422	1.1684	H C	258)	-0.0357	0.88	79	1,031
HILLAN	0.2956	0 8719	0.7832	нс	170)	0.5780	0.98	512	0.893
U/1511	0 /110	0 0020	0 5758	T f	2141	0.4004	0.89	53	1.268
	W . 4117 A 5514	0,7057 0,010#	0.42120 0.4253	τ.	2301	0.5009	0.57	53	0.485
n(198)	0,34	0,7104	** • 0002C		2741	-0.2169	0 Q	91	0.895
H(16A)	0.2000	0,93/3	0.1474	11	2783		4 5 1	101	1.048
H(168)	0.3765	0,9625	0.64/0	10	2701	-0,0300 -0,0300	4,000		3 9040 8 9040
H(18A)	0.6577	0,8574	0,9288	16	erc)	-2.0384	1.01	?	4.784

 $^{\rm *}\ensuremath{^{\prime\prime}}\ensuremath{T^{\prime\prime}}\xspace$ indicates a hydrogen atom placed at its geometrically expected position.