ALBERT, A. (1952). *Biochem. J.* **50**, 690.

DATTA, S. P., LEBERMAN, R. & RABIN, B. R. (1958). *Biochem. J.* **68**, 22P.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

DONOHUE, J. & CARON, A. (1964). *Acta Cryst.* **17**, 1178.

DORAN, M. A., CHABEREK, S. & MARTELL, A. E. (1963). *J. Amer. Chem. Soc.* **86**, 2129.

EDSALL, J. T., FELSENFELD, G., GOODMAN, D. S. & GURD, F. R. N. (1953). *J. Amer. Chem. Soc.* **76**, 3054.

FREEMAN, H. C. (1966). In '*The Biochemistry of Copper*', Eds. AISEN, P., BLUMBERG, W. & PEISACH, J. New York: Academic Press.

GIEBE, E. & SCHEIBE, A. (1925). *Z. Phys.* **33**, 760.

HAMBLING, P. (1953). *Acta Cryst.* **6**, 98.

HARDING, M. M. & COLE, S. J. (1963). *Acta Cryst.* **16**, 643.

HARE, C. R. (1966). Private communication.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 201.

International Tables for X-Ray Crystallography, (1962). Vol. III, 2nd Ed. p. 202, 270, 272. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations.* Document ORNC-3794, Oak Ridge National Laboratory, Tenn., U.S.A.

KRETZINGER, R. H., COTTON, F. A. & BRYAN, R. F. (1963). *Acta Cryst.* **16**, 651.

LANDOLT-BÖRNSTEIN, *Handbuch phys. Chem.* VI. Aufl. II. Band, 8. Teil, 5–703.

LANGENBECH, N. (1925). *Ber. dtsch Chem. Ges.* **58**, 227.

LEBERMAN, R. & RABIN, B. R. (1959). *Trans. Faraday Soc.* **55**, 1660.

LINDQVIST, O. & WENGELIN, F. (1967). *Ark. Kemi.* In the press.

LUNDGREN, I-O. & LIMINGA, I. (1966). Mimeographed copy.

MALEY, L. E. & MELLOR, D. P. (1949). *Aust. J. Sci. Research*, **2**A, 579.

MALEY, L. E. & MELLOR, D. P. (1950). *Nature, Lond.* **165**, 453.

SARKER, B. & WIGFIELD, Y. (1967). Private communication.

VALLADAS-DUBOIS, S. (1961). *Bull. Soc. chim. France*, 967·

Acta Cryst. (1969). B**25**, 41

The Crystal and Molecular Structure of 3β,17α-Dihydroxy-16β-bromo-5α-pregnan-11,20-dione and its Comparison with the Related -16β-Bromo-3β-acetate and -21-Bromo-3β-ol Steroids

BY JEAN M. OHRT, A. COOPER† AND DORITA A. NORTON†

Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14203, *U.S.A.*

(*Received* 6 *December* 1967)

The crystal structure of 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione ($C_{21}H_{31}O_4Br$, $M=427{\cdot}37$) has been determined by three-dimensional X-ray analysis and refined to a final R value of 0·045. Unit-cell constants are $a=11{\cdot}946$ Å, $b=11{\cdot}011$ Å, $c=7{\cdot}837$ Å, $\beta=107{\cdot}39°$, space group $P2_1$. Standard deviations for bond lengths and angles are in the ranges of 0·007–0·012 Å and 0·5–0·8°, respectively. There are two hydrogen bonds, 3β-hydroxyl to 11-keto oxygen (2·77 Å) and 17α-hydroxyl to 3β-hydroxyl oxygen (2·84 Å). The molecules are $\alpha-\beta$ (bottom to top) oriented, and arranged in sheets perpendicular to the b axis of the unit cell. Packing of the molecule as influenced by the position of heavy atoms and side chain substituents is discussed.

Introduction

The structural details of a series of 5α-pregnane adrenocortical metabolites are being investigated to ascertain features which are significant in the determination of biological function at the molecular level. The crystal and molecular structures of 3β-acetoxy-17α-hydroxy-16β-bromo-5α-pregnan-11,20-dione (Fig. 1, II) and 3β, 17α-dihydroxy-21-bromo-5α-pregnan-11,20-dione (Fig.1, III) have already been reported (Ohrt, Cooper, Kartha & Norton, 1968; Ohrt, Haner, Cooper & Norton, 1968). This paper reports the crystal and molecular structure determination of 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione (Fig. 1, I) and compares the architecture of the molecules and their packing as influenced by the position of attachment of the heavy atom and of side chain substituents.

Experimental

Crystals of 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione ($C_{21}H_{31}O_4Br$, $M=427{\cdot}37$) were grown from methanol solution by slow evaporation at room temperature. The crystal data are:

$a=11{\cdot}946\pm0{\cdot}002$, $b=11{\cdot}011\pm0{\cdot}002$, $c=7{\cdot}837\pm0{\cdot}001$ Å, $\beta=107{\cdot}39°\pm0{\cdot}01$ (at 20°C, $CuK\alpha_1=1{\cdot}54051$

---

† Present address: The Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203

Å), $V_0 = 983{\cdot}73\text{Å}^3$, $D_m = 1{\cdot}450 \pm 0{\cdot}002\,\text{g.cm}^{-3}$, $D_c = 1{\cdot}444\,\text{g.cm}^{-3}$ $Z = 2$, $F(000) = 448$. Space group $P2_1$ (C_2^2 No. 4) ($0k0$ absent for k odd).

The intensities of 2142 independent X-ray spectra were measured on a General Electric single crystal orienter by the stationary crystal/stationary counter method, using Cu $K\alpha$ radiation monochromatized by balanced nickel and cobalt filters (ten second count with each filter). Thirty-one reflections regarded as 'weak', for which the measured intensity was less than two standard deviations, were rejected. The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied ($\mu_{\text{Cu }K\alpha} = 33\ \text{cm}^{-1}$). The crystal used was cubic shaped, of side 0·1 mm, and the corners were rounded off so that absorption was approximately isotropic.

A three-dimensional Patterson synthesis was computed using $|F_o|^2$ values modified to represent point atoms with thermal motion, and the bromine atom was located from the Harker section. The positions of the carbon and oxygen atoms in the steroid molecule were determined by routine application of the heavy atom method.

Three cycles of block-diagonal least-squares refinement (4×4 matrices for x, y, z, and B) using these twenty-six atoms and isotropic temperature factors, reduced the R value (defined as $\Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$) to 0·19. All 2111 reflections, all with equal weights, were included in this refinement. At this point the

Table 1. *Final refined positional and thermal parameters*

Standard deviations are given in parentheses for the last two digits of each number. The thermal parameters are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

ATOM	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
C 1	0.53915(51)	0.26545(66)	0.43315(75)	0.0268(28)	0.0478(38)	0.0223(28)	0.0045(28)	0.0063(23)	0.0014(27)
C 2	0.40880(52)	0.28736(64)	0.40435(82)	0.0284(29)	0.0441(39)	0.0318(31)	0.0066(29)	0.0112(25)	-0.0029(29)
C 3	0.35622(49)	0.36158(57)	0.24099(80)	0.0222(27)	0.0291(31)	0.0335(31)	-0.0022(23)	0.0068(23)	-0.0007(25)
C 4	0.37460(51)	0.30284(60)	0.07826(80)	0.0253(28)	0.0368(35)	0.0289(29)	0.0060(26)	0.0046(23)	0.0019(26)
C 5	0.50575(49)	0.28199(59)	0.10466(76)	0.0231(26)	0.0359(34)	0.0246(27)	0.0028(25)	0.0056(22)	0.0009(25)
C 6	0.53117(53)	0.23725(72)	-0.06336(76)	0.0277(29)	0.0588(44)	0.0190(27)	0.0125(30)	-0.0002(22)	0.0041(29)
C 7	0.66291(53)	0.23638(76)	-0.03817(77)	0.0275(30)	0.0664(47)	0.0206(27)	0.0089(32)	0.0054(23)	0.0084(31)
C 8	0.73032(49)	0.16095(54)	0.12687(73)	0.0272(27)	0.0283(31)	0.0217(25)	-0.0019(24)	0.0083(21)	0.0018(24)
C 9	0.69715(48)	0.20446(52)	0.29587(72)	0.0264(27)	0.0240(28)	0.0210(25)	-0.0037(23)	0.0080(21)	-0.0001(22)
C 10	0.56314(48)	0.20293(52)	0.26977(75)	0.0247(26)	0.0240(29)	0.0263(27)	-0.0010(23)	0.0103(22)	0.0018(23)
C 11	0.77378(50)	0.13940(63)	0.46086(75)	0.0256(27)	0.0400(34)	0.0245(27)	0.0031(26)	0.0083(23)	-0.0035(26)
C 12	0.90590(48)	0.14828(70)	0.49317(76)	0.0203(27)	0.0541(41)	0.0232(27)	-0.0002(27)	0.0021(22)	0.0080(29)
C 13	0.93453(47)	0.10373(51)	0.32615(76)	0.0221(26)	0.0201(27)	0.0323(29)	0.0012(21)	0.0075(22)	-0.0000(24)
C 14	0.86310(48)	0.17703(56)	0.16457(73)	0.0234(26)	0.0314(30)	0.0214(25)	0.0032(23)	0.0071(21)	0.0019(23)
C 15	0.91762(53)	0.14534(70)	0.01684(80)	0.0306(30)	0.0517(42)	0.0268(29)	0.0021(30)	0.0118(25)	-0.0071(30)
C 16	1.04847(53)	0.13342(62)	0.11536(87)	0.0310(30)	0.0326(33)	0.0411(34)	0.0000(27)	0.0170(27)	-0.0045(28)
C 17	1.06224(49)	0.13149(60)	0.32266(81)	0.0228(27)	0.0317(31)	0.0350(30)	-0.0028(24)	0.0130(24)	-0.0020(26)
C 18	0.91024(60)	-0.03496(55)	0.30196(98)	0.0390(34)	0.0220(32)	0.0556(40)	-0.0040(25)	0.0139(30)	0.0091(27)
C 19	0.51401(54)	0.07154(60)	0.24469(97)	0.0302(30)	0.0252(32)	0.0532(38)	-0.0019(26)	0.0096(28)	0.0110(29)
C 20	1.15387(55)	0.04911(75)	0.44764(99)	0.0246(29)	0.0632(48)	0.0548(41)	0.0048(31)	0.0131(28)	0.0211(37)
C 21	1.22261(71)	0.10122(99)	0.62499(99)	0.0407(39)	0.0955(71)	0.0445(41)	-0.0063(43)	0.0019(33)	0.0136(45)
O 3	0.23218(34)	0.38120(42)	0.21381(59)	0.0220(20)	0.0363(24)	0.0425(24)	0.0013(18)	0.0071(18)	-0.0043(20)
O 11	0.73480(37)	0.08074(47)	0.56153(58)	0.0315(22)	0.0527(30)	0.0369(23)	0.0047(21)	0.0141(18)	0.0223(23)
O 17	1.08419(38)	0.25562(43)	0.37896(64)	0.0321(22)	0.0366(25)	0.0472(25)	-0.0104(20)	0.0178(19)	-0.0082(22)
O 20	1.16709(57)	-0.05466(59)	0.41350(97)	0.0606(36)	0.0600(38)	0.0881(44)	0.0328(30)	0.0109(33)	0.0093(33)
BR	1.11724(8)	0.00000(14)	0.01876(12)	0.0704(4)	0.0640(4)	0.0714(4)	0.0239(5)	0.0403(4)	-0.0116(5)

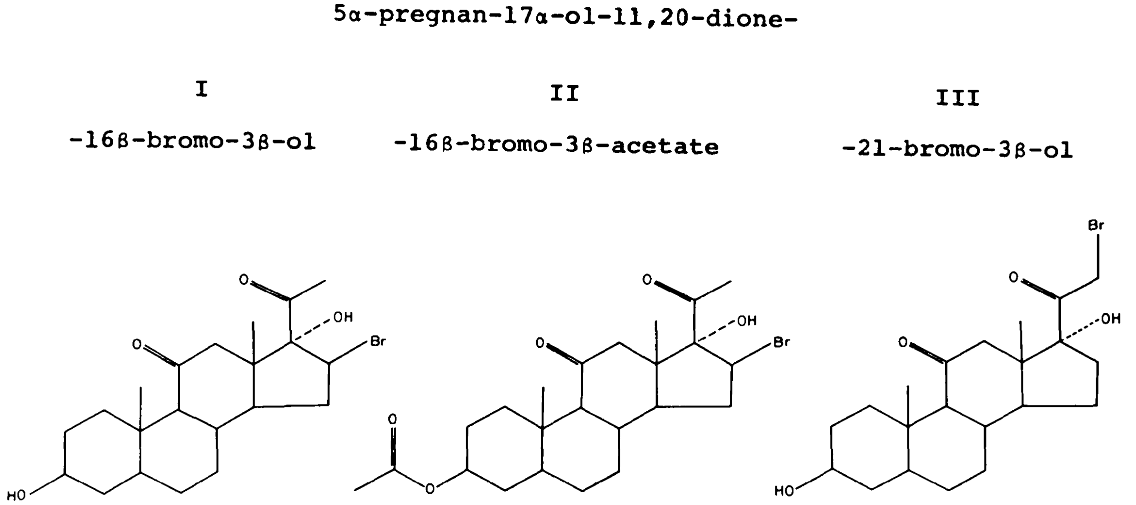


Fig. 1. Schematic drawings of the three 5α-pregnane steroids. I 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione. II 3β-acetoxy-17α-hydroxy-16β-bromo-5α-pregnan-11,20-dione. III 3β,17α-dihydroxy-21-bromo-5α-pregnan-11,20-dione.

Table 2. *Comparison between the values of* $|F_o|$ *and* $|F_c|$ *calculated for the refined atomic parameters*

$|F_o|$ and $|F_c|$ are given on ten times absolute scale.

H	K	L	FOBS	FCAL
0	0	1	276	262
0	0	2	656	652
0	0	3	475	469
0	0	4	255	244
0	0	5	155	160
0	0	6	34	28
0	0	7	134	119
0	0	8	27	17
0	0	9	41	35
0	1	1	849	954
0	1	2	48	42
0	1	3	170	160
0	1	4	243	244
0	1	5	86	87
0	1	6	129	131
0	1	7	146	149
0	1	8	67	72
0	1	9	52	52
0	2	0	740	743
0	2	1	281	259
0	2	2	371	356
0	2	3	317	312
0	2	4	368	364
0	2	5	264	261
0	2	6	211	211
0	2	7	124	110
0	2	8	49	41
0	2	9	75	69
0	3	1	157	159
0	3	2	433	440
0	3	3	365	357
0	3	4	114	111
0	3	5	207	212
0	3	6	215	223
0	3	7	104	92
0	3	8	64	62
0	3	9	60	56
0	4	0	328	305
0	4	1	460	474
0	4	2	537	535
0	4	3	456	463
0	4	4	142	142
0	4	5	197	186
0	4	6	91	89
0	4	7	95	54
0	4	8	21	29
0	5	1	242	231
0	5	2	181	182
0	5	3	118	113
0	5	4	62	56
0	5	5	120	109
0	5	6	63	55
0	5	7	104	104
0	5	8	99	98
0	6	0	247	227
0	6	1	494	493
0	6	2	298	289
0	6	3	138	130
0	6	4	291	290
0	6	5	83	76
0	6	6	175	165
0	6	7	74	65
0	6	8	77	75
0	7	1	86	88
0	7	2	162	157
0	7	3	362	367
0	7	4	93	80
0	7	5	63	51
0	7	6	29	23
0	7	7	77	79
0	7	8	46	41
0	8	0	272	268
0	8	1	224	230
0	8	2	240	241
0	8	3	239	231
0	8	4	140	119
0	8	5	128	111
0	8	6	97	91
0	8	7	24	22
0	9	1	96	90
0	9	2	86	72
0	9	3	83	81
0	9	4	187	185
0	9	5	24	22
0	9	7	59	63
0	10	0	117	113
0	10	1	154	156
0	10	2	68	71
0	10	3	147	150
0	10	4	48	47
0	10	5	39	45
0	10	6	37	43
0	11	1	57	54
0	11	2	65	63
0	11	3	27	19
0	11	4	42	38
0	11	5	25	23
0	12	0	31	12
0	12	1	86	83
0	12	2	123	123
0	12	3	40	38
0	12	4	41	34
0	13	1	57	58
0	13	2	53	66
0	13	3	8	7
1	0	0	496	457
1	0	1	23	17
1	0	-1	218	183
1	0	2	329	335
1	0	-2	487	473
1	0	3	125	108
1	0	-3	711	740
1	0	-4	75	71
1	0	4	154	160
1	0	5	110	106
1	0	-5	430	457
1	0	-6	535	558
1	0	6	124	115
1	0	7	48	32
1	0	-7	71	72
1	0	8	52	43
1	0	-8	75	74
1	0	-9	36	33
1	0	9	45	37
1	1	0	212	223
1	1	-1	50	41
1	1	1	532	551
1	1	-2	535	568
1	1	2	414	438
1	1	-3	121	119
1	1	3	619	616
1	1	4	160	158
1	1	-4	192	195
1	1	5	226	223
1	1	-5	226	231
1	1	6	91	85
1	1	-6	161	155
1	1	7	127	119
1	1	-7	228	228
1	1	8	62	58
1	1	-8	35	36
1	1	9	46	43
1	1	-9	33	29
1	2	0	506	1030
1	2	-1	714	701
1	2	1	557	560
1	2	-2	566	557
1	2	2	510	517
1	2	3	287	272
1	2	-3	413	424
1	2	-4	139	153
1	2	4	254	247
1	2	-5	184	197
1	2	5	74	73
1	2	-6	92	87
1	2	6	120	115
1	2	-7	177	178
1	2	7	31	26
1	2	8	66	70
1	2	-8	29	24
1	2	9	56	59
1	2	-9	43	36
1	3	0	868	908
1	3	-1	571	525
1	3	1	303	291
1	3	-2	528	510
1	3	2	352	355
1	3	3	118	116
1	3	-3	167	161
1	3	4	288	285
1	3	-4	212	205
1	3	-5	37	28
1	3	5	184	185
1	3	-6	177	180
1	3	6	126	132
1	3	-7	37	32
1	3	7	95	92
1	3	8	82	80
1	3	-8	44	46
1	3	-9	31	30
	4	0	342	324
1	4	1	308	286
1	4	-1	241	245
1	4	2	131	134
1	4	-2	156	155
1	4	-3	548	571
1	4	3	176	155
1	4	-4	300	304
1	4	4	98	82
1	4	5	141	144
1	4	-5	267	261
1	4	-6	6	163
1	4	6	133	128
1	4	7	33	38
1	4	-7	123	122
1	4	8	37	25
1	4	-8	120	115
1	4	-9	60	71
1	5	0	195	183
1	5	1	268	265
1	5	-1	247	245
1	5	2	404	402
1	5	-2	121	132
1	5	3	269	251
1	5	-3	111	101
1	5	-4	192	202
1	5	4	207	212
1	5	-5	70	61
1	5	5	254	250
1	5	-6	46	51
1	5	6	176	172
1	5	-7	62	63
1	5	7	40	29
1	5	8	44	41
1	5	-8	51	53
1	6	0	410	389
1	6	-1	269	277
1	6	1	409	407
1	6	-2	350	363
1	6	2	224	234
1	6	3	182	176
1	6	-3	177	172
1	6	4	66	52
1	6	-4	363	385
1	6	-5	166	169
1	6	5	54	45
1	6	6	64	61
1	6	-6	132	146
1	6	-7	75	70
1	6	7	58	58
1	6	8	41	43
1	6	-8	64	62
1	7	0	181	191
1	7	-1	169	168
1	7	1	322	305
1	7	-2	116	111
1	7	2	197	198
1	7	-3	320	340
1	7	3	117	108
1	7	4	154	164
1	7	-4	183	194
1	7	-5	25	18
1	7	5	63	76
1	7	6	49	59
1	7	-6	21	15
1	7	-7	36	33
1	7	7	80	72
1	7	-8	63	72
1	8	0	274	257
1	8	-1	254	246
1	8	1	20	23
1	8	2	63	64
1	8	-2	197	197
1	8	-3	133	136
1	8	3	236	242
1	8	-4	197	215
1	8	4	41	28
1	8	-5	31	38
1	8	5	51	51
1	8	-6	122	125
1	8	6	32	23
1	8	7	16	10
1	8	-7	20	25
1	9	0	101	106
1	9	1	184	184
1	9	-1	155	146
1	9	2	190	186
1	9	-2	127	117
1	9	-3	38	37
1	9	3	141	133
1	9	-4	41	32
1	9	4	102	100
1	9	-5	36	19
1	9	5	54	53
1	9	6	75	76
1	9	-6	40	33
1	9	-7	60	73
1	10	0	53	56
1	10	-1	110	100
1	10	1	130	133
1	10	-2	134	142
1	10	2	50	43
1	10	3	46	27
1	10	-3	115	118
1	10	4	67	66
1	10	-4	56	64
1	10	-5	100	108
1	10	5	69	63
1	10	6	20	28
1	10	-6	73	75
1	11	0	90	95
1	11	1	15	22
1	11	-1	119	123
1	11	-2	58	63
1	11	2	61	66
1	11	-3	68	67
1	11	3	94	89
1	11	4	100	97
1	11	-4	80	88
1	11	5	6	6
1	11	-5	61	73
1	12	0	60	61
1	12	-1	46	39
1	12	1	41	62
1	12	-2	54	46
1	12	2	89	83
1	12	-3	41	38
1	12	3	30	35
1	12	-4	58	73
1	12	4	20	24
1	13	0	45	38
1	13	1	29	27
1	13	-1	94	91
1	13	2	6	6
1	13	-2	31	48
1	13	-3	23	41
2	0	0	150	186
2	0	-1	338	317
2	0	1	234	247
2	0	-2	132	136
2	0	2	153	143
2	0	-3	411	402
2	0	3	40	13
2	0	4	74	67
2	0	-4	49	56
2	0	-5	31	16
2	0	5	134	133
2	0	6	16	6
2	0	-6	27	29
2	0	-7	21	10
2	0	7	12	17
2	0	-8	73	76
2	0	-9	18	23
2	1	0	684	739
2	1	1	684	768
2	1	-1	216	222
2	1	2	469	510
2	1	-2	678	652
2	1	3	46	351
2	1	-3	521	518
2	1	-4	224	215
2	1	4	156	196
2	1	-5	208	211
2	1	5	156	152
2	1	-6	38	38
2	1	6	45	42
2	1	-7	141	123
2	1	7	70	66
2	1	-8	75	69
2	1	8	19	18
2	1	-9	51	40
2	2	0	283	260
2	2	-1	430	417
2	2	1	245	243
2	2	-2	303	286
2	2	2	537	540
2	2	3	270	264
2	2	-3	477	471
2	2	-4	317	313
2	2	4	73	65
2	2	-5	207	206
2	2	5	185	182
2	2	-6	302	313
2	2	6	70	77
2	2	-7	202	208
2	2	7	67	68
2	2	8	31	37
2	2	-8	56	59
2	2	-9	50	50
2	3	0	467	473
2	3	1	322	320
2	3	-1	408	408
2	3	2	619	650
2	3	-2	632	619
2	3	-3	168	175
2	3	3	270	265
2	3	-4	328	337
2	3	4	225	226
2	3	5	222	217
2	3	-5	280	284
2	3	5	107	102
2	3	-6	259	315
2	3	7	66	64
2	3	-7	78	77
2	3	-8	58	51
2	3	8	34	30
2	3	-9	43	38
2	4	0	330	338
2	4	-1	80	75
2	4	1	190	200
2	4	-2	103	92
2	4	2	232	213
2	4	3	158	157
2	4	-3	111	105
2	4	4	35	44
2	4	-4	174	153
2	4	-5	243	240
2	4	5	25	15
2	4	6	125	138
2	4	-6	16	21
2	4	-7	55	90
2	4	7	69	65
2	4	-8	40	48
2	4	8	25	27
2	4	-9	77	86
2	5	0	539	530
2	5	-1	656	690
2	5	1	143	140
2	5	-2	45	256
2	5	2	331	336
2	5	-3	414	410
2	5	3	203	208
2	5	4	214	207
2	5	-4	378	373
2	5	5	100	94
2	5	-5	120	125
2	5	6	34	32
2	5	-6	89	88
2	5	7	33	51
2	5	-7	70	65
2	5	-8	43	38
2	5	8	18	21
2	5	-9	31	50
2	6	0	232	198
2	6	-1	68	52
2	6	1	129	134
2	6	-2	204	194
2	6	2	101	102
2	6	3	23	20
2	6	-3	59	118
2	6	4	87	83
2	6	-4	226	231
2	6	-5	165	157
2	6	5	35	27
2	6	6	16	16
2	6	-6	124	133
2	6	-7	80	83
2	6	-8	46	50
2	7	0	151	162
2	7	-1	264	253
2	7	1	322	320
2	7	-2	185	185
2	7	2	118	113
2	7	-3	204	204
2	7	3	153	202
2	7	4	141	137
2	7	-4	123	126
2	7	-5	171	178
2	7	5	50	44
2	7	6	52	92
2	7	-6	68	61
2	7	-7	67	67
2	7	7	29	27
2	7	-8	50	53
2	8	0	97	71
2	8	-1	44	37
2	8	1	86	102
2	8	2	96	91
2	8	-2	179	178
2	8	-3	160	162
2	8	3	52	48
2	8	-4	46	44
2	8	4	118	111
2	8	-5	54	49
2	8	5	44	44
2	8	-6	98	106
2	8	6	27	23
2	8	7	13	19
2	8	-7	63	68
2	9	0	195	198
2	9	1	235	232
2	9	-1	189	185
2	9	2	124	117
2	9	-2	128	135
2	9	-3	150	155
2	9	3	102	106
2	9	-4	186	187
2	9	4	104	105
2	9	-5	136	139
2	9	5	39	46
2	9	6	50	54
2	9	-6	56	52
2	9	-7	28	36
2	10	0	23	9
2	10	-1	59	55
2	10	1	46	39
2	10	-2	103	96
2	10	2	40	47
2	10	3	49	46
2	10	-3	105	107
2	10	4	53	53
2	10	-4	95	87
2	10	-5	73	80
2	10	5	80	87
2	10	-6	33	36
2	11	0	63	55
2	11	-1	87	85
2	11	1	90	91
2	11	2	64	64
2	11	-2	180	170
2	11	3	131	127
2	11	-3	51	47
2	11	-4	107	111
2	11	4	81	73
2	11	-5	20	31
2	11	5	64	69
2	12	0	12	7
2	12	1	26	21
2	12	-1	60	56
2	12	2	25	22
2	12	-2	21	15
2	12	-3	40	51
2	12	3	54	49
2	12	-4	55	71
2	12	4	39	37
2	13	0	48	44
2	13	1	50	35
2	13	-1	91	86
2	13	-2	82	93
2	13	2	14	5
2	13	-3	43	61
3	0	0	543	604
3	0	1	136	140
3	0	-1	46	39
3	0	2	15	302
3	0	-2	306	310
3	0	3	349	353
3	0	-3	513	486
3	0	-4	142	117
3	0	4	246	250
3	0	5	107	105
3	0	-5	218	208
3	0	-6	92	93
3	0	6	75	77
3	0	7	24	10
3	0	-7	87	72
3	0	-8	8	13
3	0	8	15	9
3	0	-9	28	36
3	1	0	357	354
3	1	1	236	237
3	1	-1	699	648
3	1	2	403	388
3	1	-2	417	406
3	1	3	60	49
3	1	-3	233	204
3	1	-4	449	454
3	1	4	177	180
3	1	-5	405	421
3	1	5	66	64
3	1	-6	150	153
3	1	6	39	37
3	1	-7	189	189
3	1	7	34	30
3	1	-8	68	64
3	1	8	31	35
3	1	-9	155	140
3	2	0	461	469
3	2	-1	483	485
3	2	1	166	174
3	2	-2	86	77
3	2	2	414	405
3	2	3	193	186
3	2	-3	464	420
3	2	-4	297	264
3	2	4	193	187
3	2	-5	146	145
3	2	5	160	164
3	2	-6	48	41
3	2	6	78	86
3	2	-7	28	22
3	2	7	80	79
3	2	8	48	53
3	2	-8	82	92
3	2	-9	66	63
3	3	0	383	369
3	3	1	184	183
3	3	-1	525	490
3	3	2	428	425
3	3	-2	524	497
3	3	-3	608	594
3	3	3	120	128
3	3	-4	463	445
3	3	4	140	138
3	3	5	154	156
3	3	-5	283	294
3	3	6	75	79
3	3	-6	155	152
3	3	7	52	46
3	3	-7	138	133
3	3	-8	112	119
3	3	8	50	45
3	3	-9	50	42
3	4	0	369	363
3	4	-1	168	170
3	4	1	279	300
3	4	-2	190	193
3	4	2	184	191
3	4	3	205	205
3	4	-3	150	148
3	4	4	96	95
3	4	-4	48	32
3	4	-5	68	68
3	4	5	112	108
3	4	6	128	130
3	4	-6	222	220
3	4	-7	81	82
3	4	7	69	74
3	4	-8	48	53
3	4	8	59	60
3	4	-9	67	61
3	5	0	92	95
3	5	-1	358	337
3	5	1	302	301
3	5	-2	368	364
3	5	2	134	125
3	5	-3	380	381
3	5	3	158	156
3	5	4	64	54
3	5	-4	250	246
3	5	5	78	64
3	5	-5	183	175
3	5	6	77	78
3	5	-6	260	262
3	5	7	27	20
3	5	-7	137	132
3	5	-8	112	101
3	5	-9	50	63
3	6	0	80	84
3	6	1	205	214
3	6	-1	253	245
3	6	2	222	221
3	6	-2	116	121
3	6	-3	96	98
3	6	3	134	146
3	6	-4	88	81
3	6	4	95	91
3	6	5	118	133
3	6	-5	51	47
3	6	-6	171	176
3	6	6	50	52
3	6	-7	29	31
3	6	7	63	58
3	6	-8	18	15
3	7	0	290	280
3	7	-1	215	216
3	7	1	200	212
3	7	-2	158	154
3	7	2	74	74
3	7	-3	217	207
3	7	3	114	116
3	7	4	37	33
3	7	-4	125	122
3	7	-5	148	148
3	7	-6	57	58
3	7	6	8	7
3	7	7	20	17
3	7	-7	73	66
3	7	-8	46	65
3	8	0	108	106
3	8	1	170	187
3	8	-1	90	74
3	8	-2	227	215
3	8	2	119	126
3	8	3	119	122
3	8	-3	48	48
3	8	4	71	72
3	8	-4	37	38
3	8	5	27	32
3	8	-5	58	58
3	8	-6	109	112
3	8	6	38	42
3	8	-7	52	64
3	9	0	119	130
3	9	1	200	212
3	9	-1	136	129
3	9	2	82	75
3	9	-2	205	194
3	9	-3	95	96
3	9	3	40	45
3	9	-4	196	203
3	9	4	57	64
3	9	-5	121	121
3	9	5	51	54
3	9	6	14	15
3	9	-6	113	115
3	9	-7	59	67
3	10	0	63	48
3	10	-1	193	184
3	10	1	81	76
3	10	-2	59	62
3	10	2	54	55
3	10	3	57	52
3	10	-3	60	56
3	10	4	51	55
3	10	-4	55	62
3	10	-5	31	33
3	10	5	70	67
3	10	-6	42	51
3	11	0	68	68
3	11	-1	106	95
3	11	1	52	48
3	11	2	15	14
3	11	-2	160	155
3	11	3	29	28
3	11	-3	126	123
3	11	-4	103	117
3	11	4	28	30
3	11	-5	59	67
3	12	0	67	61
3	12	-1	69	62
3	12	1	67	65
3	12	-2	63	68
3	12	2	29	32
3	12	-3	71	77
3	12	3	32	33
3	12	-4	12	5
3	13	0	63	71
3	13	-1	46	52
3	13	1	25	21
3	13	-2	25	29
3	13	-3	18	18
4	0	0	435	435
4	0	-1	393	392
4	0	1	430	445
4	0	-2	537	519
4	0	2	396	404
4	0	-3	480	463
4	0	3	372	382
4	0	4	190	183
4	0	-4	415	404
4	0	-5	256	267
4	0	5	150	151
4	0	6	139	124
4	0	-6	222	224
4	0	-7	109	104
4	0	7	12	6
4	0	8	23	22
4	0	-8	75	66
4	0	-9	110	121
4	1	0	173	161
4	1	-1	464	443
4	1	1	152	147
4	1	-2	267	267
4	1	2	37	32
4	1	-3	286	258
4	1	3	192	195
4	1	4	70	69
4	1	-4	179	172
4	1	5	58	59
4	1	-5	192	184
4	1	6	162	153
4	1	-6	151	157
4	1	7	72	76
4	1	-7	152	160
4	1	8	35	42
4	1	-8	121	117
4	1	-9	33	35
4	2	0	381	398
4	2	1	370	360
4	2	-1	654	624
4	2	2	391	419
4	2	-2	299	283
4	2	-3	441	423
4	2	3	152	156
4	2	4	172	179
4	2	-4	282	262
4	2	5	50	31
4	2	-5	129	130
4	2	6	110	106
4	2	-6	189	187
4	2	7	63	64
4	2	-7	126	119
4	2	-8	44	31
4	2	8	11	9
4	2	-9	92	85
4	3	0	158	134
4	3	-1	289	261
4	3	1	186	182
4	3	-2	253	235
4	3	2	78	78
4	3	3	93	88
4	3	-3	331	311
4	3	4	52	48
4	3	-4	293	285
4	3	-5	240	239
4	3	5	95	98
4	3	-6	145	151
4	3	6	80	82
4	3	-7	96	93
4	3	7	24	22
4	3	-8	102	98
4	3	-9	62	63
4	4	0	510	535
4	4	-1	299	286
4	4	1	224	241
4	4	-2	322	310
4	4	2	224	232
4	4	3	194	208
4	4	-3	301	294
4	4	4	77	74
4	4	-4	176	176
4	4	-5	227	222
4	4	5	141	148
4	4	-6	37	23
4	4	6	100	90
4	4	-7	66	64
4	4	7	56	59
4	4	-8	22	20
4	4	-9	26	32
4	5	0	112	110
4	5	1	49	60
4	5	-1	136	134
4	5	2	62	66
4	5	-2	249	229
4	5	3	76	78
4	5	-3	162	154
4	5	-4	232	217
4	5	4	63	68
4	5	-5	170	165
4	5	5	48	36
4	5	-6	80	86
4	5	6	8	14
4	5	-7	92	95
4	5	7	31	30
4	5	-8	84	90
4	5	-9	42	52
4	6	0	374	377
4	6	-1	257	257
4	6	1	228	232
4	6	-2	218	215
4	6	2	210	209
4	6	3	75	83
4	6	-3	238	240
4	6	4	180	178
4	6	-4	215	207
4	6	-5	150	150
4	6	5	57	65
4	6	6	31	24
4	6	-6	88	84
4	6	7	31	32
4	6	-7	101	93
4	6	-8	31	35
4	7	0	122	122
4	7	1	45	48
4	7	-1	57	56
4	7	2	147	154
4	7	-2	125	123
4	7	3	64	61
4	7	-3	58	58
4	7	-4	127	124
4	7	4	135	133
4	7	-5	70	58
4	7	5	46	37
4	7	-6	190	191
4	7	6	67	74
4	7	-7	100	95
4	7	-8	31	47
4	8	0	127	122
4	8	-1	124	128
4	8	1	190	183
4	8	2	45	34
4	8	-2	248	253
4	8	-3	133	137
4	8	3	189	203
4	8	-4	176	167
4	8	4	100	112
4	8	-5	169	178
4	8	5	32	30
4	8	-6	117	118
4	8	6	25	33
4	8	-7	56	58
4	9	0	96	82
4	9	-1	146	145
4	9	1	84	82
4	9	-2	164	159
4	9	2	42	34
4	9	3	83	91
4	9	-3	82	78
4	9	4	80	81
4	9	-4	138	137
4	9	5	31	30
4	9	-5	109	101
4	9	-6	43	57
4	10	0	86	87
4	10	1	100	104
4	10	-1	182	184
4	10	2	133	135
4	10	-2	89	88
4	10	-3	82	79
4	10	3	45	48
4	10	4	23	23
4	10	-5	103	64
4	10	5	26	34
4	10	-6	34	38
4	11	0	57	56
4	11	-1	30	30
4	11	1	20	18
4	11	2	31	21
4	11	-2	46	41
4	11	3	45	45
4	11	-3	58	54
4	11	-4	42	42
4	11	4	54	54
4	11	-5	71	80
4	12	0	52	52
4	12	1	80	75
4	12	-1	76	66
4	12	-2	123	111
4	12	2	26	23
4	12	-3	39	33
4	12	3	34	40
4	12	-4	56	78
4	13	0	39	42
4	13	-1	31	29
4	13	1	34	44
5	0	0	738	720
5	0	-1	679	651
5	0	1	302	275
5	0	-2	312	282
5	0	2	315	309
5	0	-3	586	572
5	0	3	142	144
5	0	4	50	52
5	0	-4	398	397
5	0	-5	290	284
5	0	5	142	146
5	0	6	114	116
5	0	-6	256	257
5	0	-7	179	185
5	0	7	43	43
5	0	-8	125	119
5	0	-9	140	129
5	1	0	479	474
5	1	1	150	184
5	1	-1	344	312
5	1	2	278	272
5	1	-2	326	310
5	1	3	34	35
5	1	-3	162	160
5	1	-4	84	78
5	1	4	250	243
5	1	-5	93	90
5	1	5	175	182
5	1	-6	114	102
5	1	6	123	130
5	1	-7	58	60
5	1	7	54	57
5	1	-8	80	82
5	1	-9	22	26
5	2	0	77	328
5	2	1	178	176
5	2	-1	339	351
5	2	2	189	179
5	2	-2	234	224
5	2	-3	359	393
5	2	3	109	101
5	2	4	142	140
5	2	-4	395	394
5	2	5	107	105
5	2	-5	185	174
5	2	6	24	24
5	2	-6	225	224
5	2	7	24	18
5	2	-7	154	153
5	2	-8	75	70
5	2	-9	69	68
5	3	0	277	265
5	3	1	134	128
5	3	-1	257	247
5	3	2	189	180
5	3	-2	141	126
5	3	-3	109	107
5	3	3	96	102
5	3	-4	88	86
5	3	4	120	110
5	3	5	88	91
5	3	-5	81	74
5	3	6	103	95
5	3	-6	28	33
5	3	7	28	27
5	3	-7	69	65
5	3	-8	43	49
5	3	-9	32	37
5	4	0	377	374
5	4	1	174	178
5	4	-1	365	364
5	4	2	142	134
5	4	-2	303	310
5	4	-3	356	356
5	4	3	107	107
5	4	-4	159	201
5	4	4	63	63
5	4	5	52	47
5	4	-5	265	263
5	4	-6	113	115
5	4	6	44	43
5	4	7	31	32
5	4	-7	125	114
5	4	-8	86	87
5	4	-9	39	37
5	5	0	78	88
5	5	-1	168	165
5	5	1	132	136
5	5	-2	125	123
5	5	2	78	86
5	5	-3	50	73
5	5	3	176	183
5	5	4	86	95
5	5	-4	130	125
5	5	5	31	40
5	5	-5	73	48
5	5	6	8	6
5	5	-6	29	26
5	5	7	50	61
5	5	-7	108	117
5	5	-9	35	45
5	6	0	134	125
5	6	-1	269	269
5	6	1	199	204
5	6	-2	260	269
5	6	2	90	94
5	6	3	62	53
5	6	-3	237	226
5	6	4	76	81
5	6	-4	219	215
5	6	-5	212	219
5	6	5	20	21
5	6	-6	209	215
5	6	6	72	75
5	6	-7	90	92
5	6	-8	81	78
5	7	0	72	65
5	7	-1	206	200
5	7	1	176	185
5	7	-2	90	96
5	7	2	207	212
5	7	-3	91	87
5	7	3	87	93
5	7	4	71	71
5	7	-4	134	139
5	7	5	46	46
5	7	-5	51	45
5	7	6	46	55
5	7	-6	50	44
5	7	-7	46	50
5	7	-8	59	68
5	8	0	160	152
5	8	1	167	168
5	8	-1	93	96
5	8	-2	228	234
5	8	2	153	158
5	8	3	164	176
5	8	-3	221	227
5	8	4	44	38
5	8	-4	101	95
5	8	5	40	31
5	8	-5	15	154
5	8	-6	100	92
5	8	-7	91	107
5	9	0	48	37
5	9	1	68	75
5	9	-1	108	105
5	9	2	66	69
5	9	-2	121	121
5	9	3	59	64
5	9	-3	78	75
5	9	-4	110	112
5	9	4	25	34
5	9	-5	112	112
5	9	5	51	48
5	9	-6	22	25
5	9	-7	63	88
5	10	0	72	63
5	10	1	59	56
5	10	-1	56	97
5	10	2	20	21
5	10	-2	83	87
5	10	3	42	41
5	10	-3	89	87
5	10	-4	187	191
5	10	4	65	67
5	10	-5	48	48
5	10	-6	73	89
5	11	0	59	57
5	11	1	62	55
5	11	-1	75	69
5	11	-2	43	42
5	11	2	31	29
5	11	3	90	99
5	11	-3	91	89
5	11	-5	44	43
5	12	0	95	91
5	12	-1	46	40
5	12	1	45	48
5	12	-2	109	107
5	12	2	31	36
5	12	-3	51	46
5	12	-4	54	64
6	0	0	350	375
6	0	-1	470	454
6	0	1	110	97
6	0	-2	19	14
6	0	2	120	130
6	0	3	63	52
6	0	-3	421	410
6	0	-4	181	164
6	0	4	27	22
6	0	-5	233	233
6	0	5	25	19
6	0	-6	311	325
6	0	6	12	3
6	0	7	41	47
6	0	-7	210	214
6	0	-8	58	102
6	0	-9	111	112
6	1	0	39	517
6	1	1	246	236
6	1	-1	405	415
6	1	2	284	279
6	1	-2	301	276
6	1	3	134	128
6	1	-3	357	358
6	1	4	275	280
6	1	-4	88	96
6	1	-5	301	303
6	1	5	75	69
6	1	-6	142	133
6	1	6	95	102
6	1	-7	29	39
6	1	7	28	32
6	1	-8	27	29
6	1	-9	27	19
6	2	0	158	182
6	2	1	158	161
6	2	-1	512	488
6	2	-2	114	108
6	2	2	180	180
6	2	3	46	39
6	2	-3	302	295
6	2	4	43	43
6	2	-4	242	242
6	2	-5	132	134
6	2	5	148	143
6	2	6	58	50
6	2	-6	175	163
6	2	7	19	22
6	2	-7	149	137
6	2	-8	63	69
6	2	-9	78	76
6	3	0	312	305
6	3	1	206	211
6	3	-1	373	385
6	3	2	185	188
6	3	-2	265	273
6	3	-3	363	358
6	3	3	86	83
6	3	-4	164	166
6	3	4	42	34
6	3	5	56	102
6	3	-5	160	156
6	3	6	126	135
6	3	-6	129	122
6	3	-7	122	126
6	3	7	66	64
6	3	-8	33	30
6	3	-9	42	39
6	4	0	144	143
6	4	-1	119	121
6	4	1	208	197
6	4	-2	222	215
6	4	2	238	232
6	4	-3	175	168
6	4	3	89	86
6	4	-4	229	234
6	4	4	85	92
6	4	-5	184	185
6	4	5	54	99
6	4	-6	155	162
6	4	6	83	83
6	4	-7	80	94
6	4	-8	107	103
6	4	-9	26	37
6	5	0	185	187
6	5	1	235	227
6	5	-1	231	230
6	5	-2	290	285
6	5	2	327	331
6	5	3	118	114
6	5	-3	212	213
6	5	4	31	31
6	5	-4	128	119
6	5	5	102	113
6	5	-5	103	103
6	5	-6	46	39
6	5	6	112	109
6	5	-7	114	108
6	5	-8	59	53
6	5	-9	32	49
6	6	0	203	197
6	6	1	190	192
6	6	-1	97	105
6	6	-2	158	152
6	6	2	118	126
6	6	-3	80	64
6	6	3	187	198
6	6	4	88	84
6	6	-4	192	194
6	6	-5	118	114
6	6	5	81	80
6	6	6	33	25
6	6	-6	135	171
6	6	-7	110	115
6	6	-8	97	101
6	7	0	163	165
6	7	1	205	208
6	7	-1	92	96
6	7	-2	222	218
6	7	2	68	68
6	7	3	115	123
6	7	-3	115	108
6	7	-4	301	314
6	7	4	78	92
6	7	5	80	84
6	7	-5	120	122
6	7	-6	75	78
6	7	-7	98	103
6	7	-8	25	23
6	8	0	143	142
6	8	1	48	45
6	8	-1	66	63
6	8	-2	107	101
6	8	2	48	52
6	8	-3	185	184
6	8	3	34	41
6	8	4	64	71
6	8	-4	133	129
6	8	5	15	15
6	8	-5	127	122
6	8	-6	133	132
6	8	-7	63	71
6	9	0	160	160
6	9	1	112	114
6	9	-1	99	107
6	9	2	68	73
6	9	-2	110	111
6	9	3	80	65
6	9	-3	45	38
6	9	-4	89	96
6	9	4	40	48
6	9	-5	73	78
6	9	-6	81	84
6	9	-7	31	46
6	10	0	49	54
6	10	-1	29	30
6	10	1	60	54
6	10	-2	56	58
6	10	2	48	41
6	10	-3	104	93
6	10	3	35	26
6	10	-4	96	92
6	10	4	42	43
6	10	-5	82	87
6	10	-6	25	31
6	11	0	45	45
6	11	1	50	55
6	11	-1	132	129
6	11	-2	124	114
6	11	2	29	24
6	11	3	70	82
6	11	-3	134	125
6	11	-4	75	77
6	11	-5	20	27
6	12	0	55	46
6	12	-1	74	72
6	12	1	43	47
6	12	-2	73	72
6	12	-3	11	14
7	0	0	148	146
7	0	1	111	99
7	0	-1	94	86
7	0	2	58	40
7	0	-2	213	209
7	0	-3	50	40
7	0	3	58	60
7	0	-4	46	46
7	0	4	21	16
7	0	5	93	87
7	0	-5	70	54
7	0	-6	92	96
7	0	6	15	20
7	0	-7	158	154
7	0	-8	94	103
7	0	-9	32	37
7	1	0	177	164
7	1	1	229	234
7	1	-1	393	390
7	1	-2	301	290
7	1	2	48	45
7	1	3	187	179
7	1	-3	400	392
7	1	4	93	91
7	1	-4	224	217
7	1	-5	249	243
7	1	5	63	63
7	1	-6	266	276
7	1	6	59	65
7	1	-7	50	47
7	1	-8	140	138
7	1	-9	55	50
7	2	0	171	165
7	2	1	101	90
7	2	-1	278	264
7	2	-2	108	102
7	2	2	424	424
7	2	-3	73	74
7	2	3	142	151
7	2	4	75	75
7	2	-4	128	112
7	2	-5	49	43
7	2	5	60	61
7	2	-6	130	128
7	2	6	65	71
7	2	-7	173	169
7	2	-8	31	35
7	2	-9	54	59
7	3	0	366	371
7	3	1	340	345
7	3	-1	204	205
7	3	2	326	331
7	3	-2	260	260
7	3	3	104	113
7	3	-3	291	295
7	3	4	48	56
7	3	-4	207	202
7	3	5	78	75
7	3	-5	222	231
7	3	6	31	32
7	3	-6	207	210
7	3	-7	189	195
7	3	-8	120	116
7	3	-9	72	82
7	4	0	234	225
7	4	1	56	50
7	4	-1	113	114
7	4	-2	222	216
7	4	2	156	147
7	4	-3	96	75
7	4	3	162	170
7	4	4	103	110
7	4	-4	209	211
7	4	5	70	61
7	4	-5	83	80
7	4	6	22	12
7	4	-6	91	105
7	4	-7	46	49
7	4	-8	43	46
7	4	-9	35	54
7	5	0	290	282
7	5	1	72	71
7	5	-1	308	304
7	5	2	88	83
7	5	-2	248	235
7	5	3	56	50
7	5	-3	236	221
7	5	4	34	41
7	5	-4	359	368
7	5	5	75	86
7	5	-5	201	195
7	5	6	69	70
7	5	-6	66	73
7	5	-7	190	187
7	5	-8	80	73
7	6	0	238	227
7	6	1	77	88
7	6	-1	180	182
7	6	-2	151	138
7	6	2	54	49
7	6	-3	203	220
7	6	3	56	60
7	6	4	50	50
7	6	-4	170	167
7	6	-5	61	65
7	6	5	100	102
7	6	-6	180	182
7	6	-7	86	95
7	6	-8	34	35
7	7	0	85	89
7	7	-1	130	130
7	7	1	172	175
7	7	2	97	104
7	7	-2	229	242
7	7	-3	93	98
7	7	3	103	106
7	7	-4	38	31
7	7	4	54	53
7	7	-5	211	216
7	7	5	60	63
7	7	-6	119	122
7	7	-7	80	85
7	7	-8	31	44
7	8	0	148	140
7	8	1	86	93
7	8	-1	127	121
7	8	2	32	36
7	8	-2	93	98
7	8	3	55	51
7	8	-3	70	62
7	8	4	34	35
7	8	-4	80	78
7	8	-5	87	93
7	8	-6	82	84
7	8	-7	50	66
7	9	0	121	117
7	9	1	59	62
7	9	-1	144	152
7	9	-2	160	159
7	9	2	46	48
7	9	-3	102	108
7	9	3	71	71
7	9	-4	158	153
7	9	4	27	25
7	9	-5	127	128
7	9	-6	126	137
7	10	0	84	84
7	10	1	63	62
7	10	-1	91	87
7	10	2	31	30
7	10	-2	15	15
7	10	-3	110	109
7	10	3	58	66
7	10	-4	75	65
7	10	-5	107	114
7	10	-6	14	12
7	11	0	98	106
7	11	-1	24	26
7	11	1	29	34
7	11	2	41	42
7	11	-2	130	124
7	11	-3	100	93
7	11	-4	65	73
7	12	0	70	72
7	12	-1	53	61
7	12	-2	63	78
8	0	0	194	193
8	0	1	277	261
8	0	-1	313	315
8	0	-2	41	36
8	0	2	326	315
8	0	3	158	156
8	0	-3	114	110
8	0	-4	27	31
8	0	4	138	140
8	0	5	30	32
8	0	-5	249	252
8	0	6	37	39
8	0	-6	125	124
8	0	-7	9	17
8	0	-8	29	17
8	0	-9	16	10
8	1	0	92	89
8	1	-1	59	59
8	1	1	181	173
8	1	-2	225	234
8	1	2	319	320
8	1	3	44	44
8	1	-3	181	176
8	1	4	62	51
8	1	-4	171	159
8	1	-5	178	180
8	1	5	16	14
8	1	-6	187	179
8	1	6	26	17
8	1	-7	135	143
8	1	-8	116	119
8	1	-9	74	81
8	2	0	233	235
8	2	-1	255	253
8	2	1	112	111
8	2	-2	186	182
8	2	2	168	156
8	2	-3	304	314
8	2	3	116	113
8	2	-4	315	315
8	2	4	84	75
8	2	-5	272	274
8	2	5	31	40
8	2	-6	94	93
8	2	6	16	16
8	2	-7	149	150
8	2	-8	64	59
8	2	-9	31	30
8	3	0	105	101
8	3	-1	240	233
8	3	1	43	35
8	3	-2	222	220
8	3	2	73	66
8	3	3	93	94
8	3	-3	165	170
8	3	-4	478	434

Table 2 (*cont.*)

H	K	L	FOBS	FCAL
8	3	4	27	25
8	3	5	43	44
8	3	-5	233	231
8	3	6	52	57
8	3	-6	175	178
8	3	-7	52	57
8	3	-8	105	103
8	3	-9	42	59
8	4	0	183	178
8	4	-1	271	275
8	4	1	182	179
8	4	2	109	111
8	4	-2	225	224
8	4	-3	187	181
8	4	3	185	200
8	4	-4	77	58
8	4	4	106	97
8	4	5	51	48
8	4	-5	33	22
8	4	-6	102	108
8	4	-7	57	58
8	4	-8	63	58
8	5	0	151	145
8	5	-1	182	163
8	5	1	120	127
8	5	2	31	31
8	5	-2	39	24
8	5	-3	106	113
8	5	3	55	51
8	5	-4	85	85
8	5	4	88	83
8	5	5	50	50
8	5	-5	120	122
8	5	-6	154	153
8	5	-7	181	182
8	5	-8	80	53
8	6	0	154	157
8	6	1	176	175
8	6	-1	174	176
8	6	2	76	72
8	6	-2	160	151
8	6	-3	138	140
8	6	3	57	57
8	6	4	55	47
8	6	-4	155	158
8	6	-5	117	120
8	6	5	76	78
8	6	-6	187	184
8	6	-7	68	60
8	6	-8	22	23
8	7	0	46	40
8	7	1	73	76
8	7	-1	132	136
8	7	2	26	29
8	7	-2	96	101
8	7	3	69	65
8	7	-3	175	167
8	7	4	59	55
8	7	-4	114	116
8	7	-5	202	202
8	7	-6	63	63
8	7	-7	63	75
8	8	0	78	85
8	8	1	95	98
8	8	-1	54	47
8	8	-2	94	101
8	8	2	16	21
8	8	-3	126	130
8	8	3	39	46
8	8	-4	158	159
8	8	4	59	64
8	8	-5	66	71
8	8	-6	94	88
8	8	-7	60	92
8	9	0	82	81
8	9	1	48	44
8	9	-1	115	112
8	9	2	87	85
8	9	-2	197	196
8	9	-3	130	125
8	9	3	31	33
8	9	-4	112	101
8	9	-5	113	120
8	9	-6	84	100
8	10	0	51	88
8	10	1	90	78
8	10	-1	95	97
8	10	2	73	80
8	10	-2	180	176
8	10	-3	88	83
8	10	-4	44	44
8	10	-5	50	59
8	11	0	101	99
8	11	1	25	30
8	11	-1	81	96
8	11	-2	93	85
8	11	-3	22	32
8	11	-4	63	83
9	0	0	95	92
9	0	1	78	67
9	0	-1	264	253
9	0	-2	221	229
9	0	2	50	55
9	0	3	80	88
9	0	-3	154	150
9	0	4	41	48
9	0	-4	505	508
9	0	5	16	8
9	0	-5	404	423
9	0	-6	155	155
9	0	-7	131	134
9	0	-8	70	66
9	0	-9	15	30
9	1	0	66	53
9	1	1	49	63
9	1	-1	158	155
9	1	2	142	145
9	1	-2	86	87
9	1	-3	140	142
9	1	3	113	108
9	1	-4	319	324
9	1	4	27	30
9	1	5	23	23
9	1	-5	201	193
9	1	-6	57	56
9	1	-7	60	61
9	1	-8	70	70
9	1	-9	34	57
9	2	0	110	115
9	2	-1	311	315
9	2	1	137	147
9	2	-2	80	73
9	2	2	186	185
9	2	3	63	69
9	2	-3	320	314
9	2	4	50	56
9	2	-4	63	53
9	2	5	15	26
9	2	-5	55	88
9	2	-6	147	155
9	2	-7	84	79
9	2	-8	139	132
9	2	-9	66	94
9	3	0	144	128
9	3	1	142	137
9	3	-1	77	65
9	3	2	116	112
9	3	-2	105	94
9	3	-3	39	24
9	3	3	62	58
9	3	-4	98	102
9	3	4	46	51
9	3	-5	71	69
9	3	5	81	79
9	3	-6	78	70
9	3	-7	85	89
9	3	-8	51	93
9	4	0	188	192
9	4	1	180	185
9	4	-1	146	152
9	4	2	49	58
9	4	-2	227	236
9	4	3	123	128
9	4	-3	247	250
9	4	4	56	53
9	4	-4	237	249
9	4	-5	110	105
9	4	5	48	42
9	4	-6	113	119
9	4	-7	208	208
9	4	-8	61	62
9	5	0	142	140
9	5	-1	175	178
9	5	1	89	89
9	5	-2	83	78
9	5	2	17	20
9	5	3	38	30
9	5	-3	58	60
9	5	-4	48	43
9	5	4	97	99
9	5	-5	109	111
9	5	-6	174	179
9	5	-7	55	96
9	5	-8	13	23
9	6	0	157	156
9	6	-1	130	125
9	6	1	17	6
9	6	-2	140	154
9	6	2	87	91
9	6	3	50	46
9	6	-3	126	123
9	6	4	45	48
9	6	-4	204	220
9	6	-5	152	153
9	6	-6	132	139
9	6	-7	34	46
9	6	-8	46	66
9	7	0	65	68
9	7	1	31	34
9	7	-1	129	132
9	7	2	78	73
9	7	-2	204	220
9	7	-3	116	104
9	7	3	36	37
9	7	-4	45	50
9	7	-5	125	129
9	7	-6	44	40
9	7	-7	96	121
9	8	0	157	150
9	8	-1	160	168
9	8	1	18	24
9	8	2	29	30
9	8	-2	226	231
9	8	-3	46	41
9	8	3	21	26
9	8	-4	141	142
9	8	-5	150	152
9	8	-6	111	125
9	9	0	56	59
9	9	1	32	25
9	9	-1	59	64
9	9	-2	80	80
9	9	2	31	22
9	9	-3	41	36
9	9	-4	132	131
9	9	-5	86	101
9	9	-6	29	30
9	10	0	38	50
9	10	-1	92	95
9	10	1	26	35
9	10	-2	53	45
9	10	-3	75	76
9	10	-4	67	88
10	0	0	42	24
10	0	1	31	35
10	0	-1	77	68
10	0	2	33	26
10	0	-2	211	213
10	0	-3	93	90
10	0	3	85	88
10	0	-4	175	174
10	0	-5	82	90
10	0	-6	176	179
10	0	-7	78	79
10	0	-8	156	158
10	1	0	162	152
10	1	1	115	114
10	1	-1	149	146
10	1	2	73	79
10	1	-2	160	151
10	1	3	52	49
10	1	-3	251	254
10	1	4	24	27
10	1	-4	104	113
10	1	-5	17	19
10	1	-6	51	48
10	1	-7	51	54
10	1	-8	31	29
10	2	0	54	53
10	2	1	36	46
10	2	-1	202	216
10	2	2	65	70
10	2	-2	90	96
10	2	3	48	53
10	2	-3	80	74
10	2	-4	314	322
10	2	4	31	22
10	2	-5	132	128
10	2	-6	166	160
10	2	-7	134	137
10	2	-8	75	77
10	3	0	175	170
10	3	1	95	98
10	3	-1	89	88
10	3	-2	29	16
10	3	2	43	48
10	3	3	48	48
10	3	-3	105	96
10	3	4	78	81
10	3	-4	144	140
10	3	-5	176	163
10	3	-6	105	96
10	3	-7	69	69
10	3	-8	40	49
10	4	0	133	135
10	4	1	54	61
10	4	-1	75	71
10	4	2	32	32
10	4	-2	96	97
10	4	3	14	9
10	4	-3	184	186
10	4	4	43	36
10	4	-4	85	97
10	4	-5	137	128
10	4	-6	70	78
10	4	-7	139	144
10	4	-8	86	108
10	5	0	63	58
10	5	1	111	109
10	5	-1	187	199
10	5	-2	158	159
10	5	2	62	57
10	5	-3	78	74
10	5	3	18	27
10	5	-4	54	51
10	5	4	69	72
10	5	-5	97	107
10	5	-6	69	81
10	5	-7	116	123
10	5	-8	8	14
10	6	0	102	104
10	6	-1	38	40
10	6	1	16	26
10	6	-2	139	143
10	6	2	75	87
10	6	-3	167	175
10	6	3	27	27
10	6	-4	178	182
10	6	-5	111	105
10	6	-6	132	137
10	6	-7	44	61
10	7	0	57	64
10	7	-1	100	108
10	7	1	72	73
10	7	2	53	52
10	7	-2	121	121
10	7	-3	125	121
10	7	3	34	38
10	7	-4	96	94
10	7	-5	96	69
10	7	-6	66	77
10	7	-7	65	107
10	8	0	27	27
10	8	-1	31	32
10	8	1	39	41
10	8	-2	137	136
10	8	2	22	21
10	8	-3	60	63
10	8	-4	81	74
10	8	-5	143	135
10	8	-6	74	100
10	9	0	23	24
10	9	-1	142	144
10	9	1	25	26
10	9	-2	77	75
10	9	-3	71	74
10	9	-4	77	78
10	9	-5	50	67
10	10	-1	66	77
10	10	-2	34	36
10	10	-3	55	75
11	0	0	23	15
11	0	-1	126	115
11	0	1	12	2
11	0	2	24	17
11	0	-2	128	138
11	0	-3	31	34
11	0	3	15	13
11	0	4	31	28
11	0	-4	141	146
11	0	-6	52	48
11	0	-7	42	54
11	0	-8	61	76
11	1	0	78	68
11	1	-1	141	148
11	1	1	85	85
11	1	2	25	32
11	1	-2	137	130
11	1	3	34	40
11	1	-3	184	187
11	1	-4	105	112
11	1	4	28	34
11	1	-5	178	184
11	1	-6	87	85
11	1	-7	114	118
11	1	-8	43	53
11	2	0	48	43
11	2	1	32	17
11	2	-1	31	22
11	2	2	33	37
11	2	-2	59	58
11	2	3	30	19
11	2	-3	75	75
11	2	-4	45	50
11	2	4	35	39
11	2	-5	19	20
11	2	-6	90	89
11	2	-7	122	122
11	2	-8	36	43
11	3	0	57	50
11	3	1	115	121
11	3	-1	84	82
11	3	-2	134	147
11	3	2	63	64
11	3	3	22	27
11	3	-3	164	160
11	3	-4	131	147
11	3	-5	96	95
11	3	-6	161	162
11	3	-7	59	55
11	3	-8	26	41
11	4	0	63	62
11	4	-1	58	57
11	4	1	78	67
11	4	-2	58	54
11	4	2	58	53
11	4	-3	68	66
11	4	3	33	31
11	4	-4	16	17
11	4	-5	91	101
11	4	-6	41	45
11	4	-7	13	10
11	5	0	58	59
11	5	-1	78	80
11	5	1	66	66
11	5	-2	127	133
11	5	2	34	39
11	5	-3	68	73
11	5	3	22	26
11	5	-4	141	138
11	5	-5	116	117
11	5	-6	137	134
11	5	-7	97	121
11	6	0	48	43
11	6	1	15	12
11	6	-1	72	69
11	6	2	32	33
11	6	-2	55	59
11	6	-3	68	65
11	6	-4	108	100
11	6	-5	114	116
11	6	-6	103	105
11	6	-7	39	68
11	7	0	66	68
11	7	-1	97	105
11	7	1	44	51
11	7	2	41	46
11	7	-2	103	109
11	7	-3	56	52
11	7	-4	114	122
11	7	-5	91	93
11	7	-6	28	57
11	8	0	61	60
11	8	1	15	14
11	8	-1	53	51
11	8	-2	21	18
11	8	-3	63	60
11	8	-4	46	54
11	8	-5	62	92
11	9	-1	20	19
11	9	-2	43	51
11	9	-3	66	78
12	0	0	12	8
12	0	-1	125	113
12	0	1	84	87
12	0	-2	66	65
12	0	2	28	21
12	0	3	6	6
12	0	-3	32	24
12	0	-4	63	58
12	0	-5	32	32
12	0	-6	23	13
12	0	-7	18	14
12	1	0	15	23
12	1	1	46	64
12	1	-1	63	71
12	1	2	49	48
12	1	-2	63	68
12	1	3	15	13
12	1	-3	52	100
12	1	-4	100	102
12	1	-5	111	111
12	1	-6	120	117
12	1	-7	61	58
12	2	0	31	33
12	2	1	65	75
12	2	-1	78	75
12	2	2	77	80
12	2	-2	110	99
12	2	-3	86	89
12	2	3	34	37
12	2	-4	24	24
12	2	-5	66	68
12	2	-6	39	39
12	2	-7	22	24
12	3	0	66	68
12	3	1	32	77
12	3	-1	34	35
12	3	2	42	38
12	3	-2	94	98
12	3	-3	107	102
12	3	-4	112	114
12	3	-5	94	96
12	3	-6	114	109
12	3	-7	61	108
12	4	0	42	38
12	4	-1	62	58
12	4	1	75	71
12	4	-2	61	52
12	4	2	81	87
12	4	-3	100	93
12	4	-4	118	114
12	4	-5	89	85
12	4	-6	78	76
12	4	-7	38	60
12	5	0	26	28
12	5	-1	39	44
12	5	1	44	38
12	5	-2	112	114
12	5	2	42	51
12	5	-3	74	78
12	5	-4	65	67
12	5	-5	101	99
12	5	-6	84	97
12	6	0	86	92
12	6	1	14	16
12	6	-1	75	74
12	6	-2	31	22
12	6	-3	114	105
12	6	-4	44	45
12	6	-5	88	86
12	6	-6	55	79
12	7	-1	35	40
12	7	-2	116	120
12	7	-3	50	54
12	7	-4	63	73
12	7	-5	76	108
12	8	-2	56	70
12	8	-3	42	53
13	0	0	31	25
13	0	1	110	107
13	0	-1	113	114
13	0	2	33	24
13	0	-2	111	113
13	0	-3	16	2
13	0	-4	103	101
13	0	-5	63	65
13	0	-6	19	3
13	0	-7	43	61
13	1	0	46	41
13	1	-1	80	71
13	1	1	32	27
13	1	2	111	112
13	1	-2	55	62
13	1	-3	37	33
13	1	-4	25	28
13	1	-5	15	15
13	1	-6	74	79
13	1	-7	25	42
13	2	0	53	56
13	2	1	70	59
13	2	-1	85	86
13	2	-2	66	76
13	2	-3	90	88
13	2	-4	96	96
13	2	-5	108	112
13	2	-6	78	82
13	3	0	65	56
13	3	-1	48	47
13	3	1	49	49
13	3	-2	32	38
13	3	-3	27	27
13	3	-4	30	29
13	3	-5	103	103
13	3	-6	61	71
13	4	0	42	48
13	4	1	65	78
13	4	-1	50	52
13	4	-2	77	81
13	4	-3	80	76
13	4	-4	115	115
13	4	-5	81	79
13	4	-6	68	103
13	5	0	27	32
13	5	-1	66	63
13	5	-2	50	48
13	5	-3	53	53
13	5	-4	31	27
13	5	-5	55	66
13	6	-1	56	64
13	6	-2	17	23
13	6	-3	101	111
13	6	-4	46	56
14	0	0	55	50
14	0	-1	26	31
14	0	-2	44	48
14	0	-3	44	49
14	0	-4	94	100
14	0	-5	125	129
14	0	-6	13	1
14	1	0	38	40
14	1	-1	77	73
14	1	-2	43	30
14	1	-3	58	49
14	1	-4	114	107
14	1	-5	17	17
14	2	0	42	51
14	2	-1	46	56
14	2	-2	33	35
14	2	-3	66	71
14	2	-4	46	52
14	2	-5	15	35
14	3	-1	74	72
14	3	-2	45	36
14	3	-3	42	40
14	3	-4	48	52
14	3	-5	50	70
14	4	-1	37	48
14	4	-2	45	56
14	4	-3	28	34
14	4	-4	89	114

Table 3. *Positional parameters for the atoms, connected for libration of the molecule*

ATOM	X/A	Y/B	Z/C
C 1	0.53908	0.20566	0.43379
C 2	0.40863	0.28758	0.40491
C 3	0.35598	0.36205	0.24095
C 4	0.37424	0.30312	0.07763
C 5	0.50549	0.28227	0.10409
C 6	0.53086	0.23738	-0.06436
C 7	0.66272	0.23657	-0.03912
C 8	0.73020	0.16092	0.12634
C 9	0.69712	0.20456	0.29600
C 10	0.56297	0.20294	0.26981
C 11	0.77387	0.13930	0.46157
C 12	0.90613	0.14827	0.49397
C 13	0.93469	0.10358	0.32637
C 14	0.86314	0.17713	0.16416
C 15	0.91764	0.14536	0.01598
C 16	1.04862	0.13346	0.11476
C 17	1.06251	0.13152	0.32285
C 18	0.91030	-0.03555	0.30206
C 19	0.51374	0.07109	0.24463
C 20	1.15423	0.04889	0.44825
C 21	1.22309	0.10120	0.62602
O 3	0.23187	0.38166	0.21369
O 11	0.73485	0.08045	0.56244
O 17	1.08456	0.25606	0.37932
O 20	1.16739	-0.05519	0.41395
BR	1.11735	-0.00033	0.01793
H 1A	0.5687	0.2003	0.5517
H 1B	0.5844	0.3260	0.4661
H 2A	0.4090	0.3647	0.5087
H 2B	0.3638	0.2105	0.4041
H 3	0.3822	0.4736	0.2464
H'3	0.2338	0.4339	0.2832
H 4A	0.3455	0.3903	-0.0234
H 4B	0.3473	0.2187	0.0423
H 5	0.5492	0.3879	0.1563
H 6A	0.4898	0.3036	-0.1557
H 6B	0.4991	0.1249	-0.1132
H 7A	0.6812	0.3145	0.0118
H 7B	0.6727	0.2136	-0.1505
H 8	0.7106	0.0936	0.0981
H 9	0.7262	0.2565	0.3281
H12A	0.9360	0.0681	0.6062
H12B	0.9397	0.2191	0.5310
H14	0.8784	0.2835	0.2091
H15A	0.8970	0.2127	-0.0585
H15B	0.8810	0.0391	-0.0298
H16	1.0845	0.2105	0.1161
H'17	1.1274	0.2728	0.3307
H18A	0.8320	-0.0474	0.2774
H18B	0.9518	-0.0764	0.3850
H18C	0.9181	-0.0693	0.2160
H19A	0.5257	0.0220	0.1303
H19B	0.4155	0.0885	0.1953
H19C	0.5478	0.0302	0.3302
H21A	1.1995	0.1388	0.6639
H21B	1.2747	0.1477	0.6203
H21C	1.2869	0.0823	0.6821

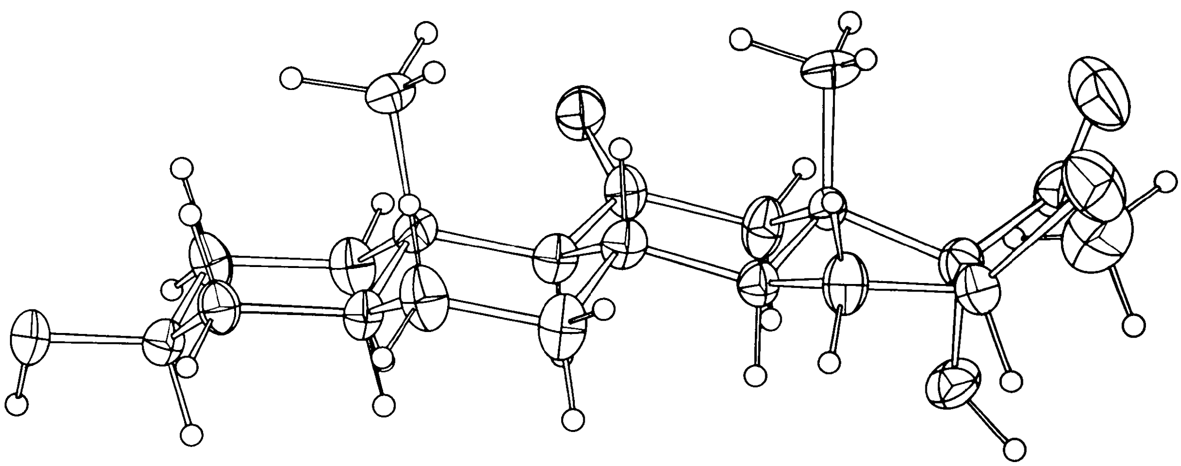


Fig. 2. Perspective view of 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione (I), showing the thermal vibrational ellipsoids.

weighting scheme was changed to $\omega^{-1}=1{\cdot}56-0{\cdot}075|F_o|+0{\cdot}0025|F_o|^2$, such that $<\omega\Delta^2>$ remained invariant with increasing $|F_o|$. Further refinement using anisotropic thermal parameters for all atoms (9×9 matrix blocks) converged with $R=0{\cdot}069$.

A three-dimensional Fourier difference synthesis was now computed and the positions of the thirty-one hydrogen atoms were located. These atoms were included in the least-squares calculations, and after four cycles of refinement (keeping the isotropic thermal parameters of the hydrogen atoms fixed at 1·5 Å^2), the R value had decreased to 0·045 (omitting 238 reflections with sin θ/λgreater than 0·6). Refinement was terminated at this point with the minimization function, $\Sigma\,\omega(|F_o|-|F_c|)^2/m-n$, at 0·80 and with the calculated shifts about one tenth of a standard deviation.

The scattering factors used in the refinement were obtained from *International Tables* (1962). The bromine factors were corrected for the real part of the anomalous dispersion correction ($\Delta f'_{\rm Br}=-0{\cdot}96$), but not for the imaginary part of the correction. When the refinement had been terminated, two separate structure factor calculations were performed using $\Delta f''_{\rm Br}=1{\cdot}46$ and $\Delta f''_{\rm Br}=-1{\cdot}46$ In neither case was the R factor significantly better than that obtained using $\Delta f''_{\rm Br}=0$, and hence, the absolute configuration of the steroid was not experimentally determined. However, the parameters listed in the tables have been given in the same absolute configuration as is normally observed in naturally occurring steroids.

The final positional and thermal parameters of the non-hydrogen atoms are listed in Table 1. Table 2 compares the observed structure amplitudes with those calculated from the final parameters for all atoms. The positional parameters for the atoms, corrected for libration of the molecule (Schomaker & Trueblood, 1968)* are given in Table 3. These corrected parameters were used in all calculations pertaining to the geometry of the molecule. Of course, these corrections are only applicable to intramolecular geometry, and the uncorrected coordinates were used for calculations of intermolecular geometry and packing. All the atoms in the molecule, with the exception of C(21), O(20), and bromine appear to behave as a rigid body; these three atoms appear to have some independent motion as well. The configuration of the molecule and the thermal vibration ellipsoids of the atoms are shown in Fig. 2.

Results and accuracy

Interatomic distances and angles are shown in Fig. 3. Standard deviations are 0·08 Å for hydrogen–non-hydrogen bonds, 0·12 Å for hydrogen–hydrogen bonds, and 0·009 Å when only heavier atoms are considered. Bond angle standard deviations are 0·5° for angles not involving hydrogen, 5° for H–C–C type angles, and 7° for H–C–H angles.

Average distances for hydrogen–carbon and hydrogen–oxygen are 1·00 Å and 0·77 Å, respectively.

The only significant deviation from currently reported bond lengths is that for C(21)–Br in 3β,17α-dihydroxy-21-bromo-5α-pregnan-11,20-dione (III). In this case, a correction of 0·04 Å, which may be applied to compensate for the thermal motion of the bromine atom (Busing & Levy, 1964), makes this seemingly short observed distance of 1·84 ± 0·02 Å just barely significant. (*cf.* Romers, Hesper, van Meijkoop & Geise (1966), in which a value of 1·89 Å was reported for C–Br in 4-bromo-9β,10α-pregna-4,6-diene-3,20-dione.)

Intra- and extranuclear sp^3–sp^2–sp^3 angles [those involving C(11) and C(20)] are decreased to 117 ± 1° while the sp^3–sp^2–0 angles have an average value of 122 ± 1°. The sp^3–sp^3–sp^2 type angles in the acetyl side chain have an average value of 115·4 ± 0·9° for the structures studied; however, in the 3β-ol,16β-bromo compound (I), angle C(16)–C(17)–C(20) equals 120·1 ± 0·5°.

---

* The significance of the rigid body vibrational analysis for this and other steroid molecules will be discussed in another communication.

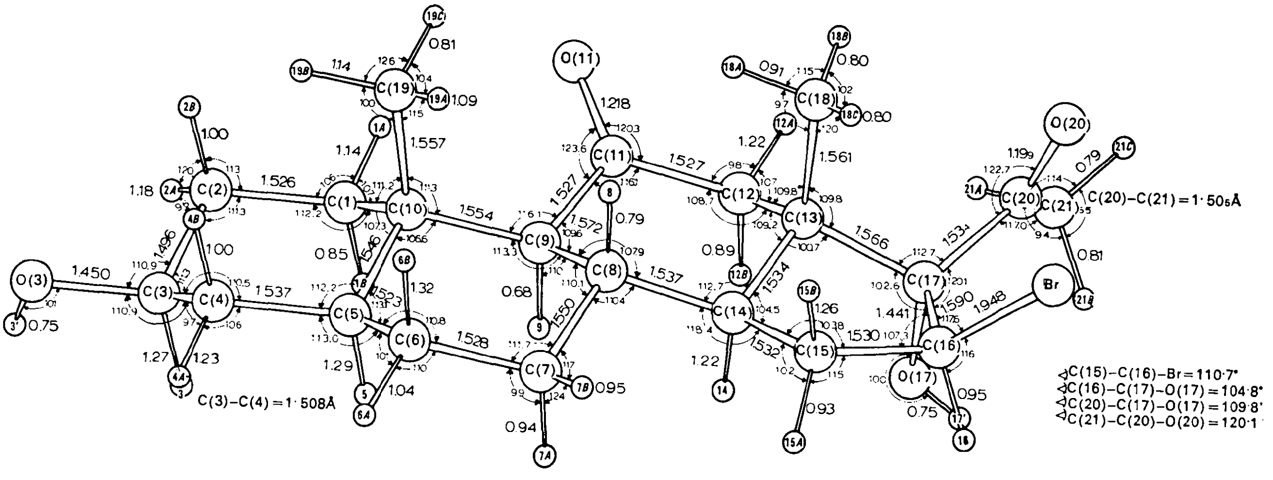


Fig. 3. Interatomic distances and angles in 3β, 17α-dihydroxy-16β-bromo-5α-pregnan-11, 20-dione.

The extranuclear angles at C(3) and C(17), involving the 2β and 17α hydroxyl oxygen atoms, have an average value of 108·2 ± 0·8 °. If the α and β groups are considered separately, the 17α value tends to be lower (107·2 ± 0·9 °) and the 3β value higher (110·2 ± 0·6 °). Substitution of an acetoxy group at the 3β position decreases angles O(3)–C(3)–O(2) and O(3)–C(3)–C(4) to 106 ± 1 °; this effect has also been observed in 3β-acetoxy-7α, 11α-dibromolanostane-8α,9α-epoxide (Fawcett & Trotter, 1966) and in euphenyl iodoacetate (Carlisle & Ladd, 1966) where the corresponding values are 106 and 107 °. The average values for the intranuclear sp^3 angles in the *A*, *B* and *C* rings is 110·2 ± 0·9 °. In all three steroids, angle C(5)–C(10)–C(9) tends to be significantly smaller and angle C(8)–C(9)–C(10) tends to be larger, having average values of 105·2 ± 0·8 ° and 114·2 ± 0·8 °, respectively. Although the three *D* rings have different stereochemistries (I and II being distorted half-chairs and III a β-envelope) these differences are not obvious from consideration of the intranuclear angles but are clearly shown by differences in torsional angles (Table 5 and Fig. 5). Angle C(14)–C(13)–C(17) has an average value of 99·7 ± 0·8 ° and the remaining angles in this ring have an average value of 104·8 ± 0·9 °, with no significant variations observed. Values similar to these have been observed in other steroids, such as androsterone (High & Kraut, 1966) and 17β-bromoacetoxy-9β,10α-androst-4-en-3-one (Oberhansli & Robertson, 1967).

The six extranuclear sp^3 angles at the ring junctions have an average value of 113·6 ± 0·9 °, the tendency being for enlargement to 115·2 ± 0·8 ° at angle C(10)–C(9)–C(11) (*B*/*C* ring junction) and at angle C(12)–C(13)–C(17) (*C*/*D* junction) and to 120·1 ± 0·9 ° at angle C(8)–C(14)–C(15) (*C*/*D* junction). The average value for the six angles involving each of the methyl groups attached to C(10) and C(13) 111·2 ± 0·9 ° with no significant variations from values found in other steroids.

The least-squares planes through important regions of the steroid nucleus, distances of atoms from these planes, and interplanar angles are given in Table 4. The least-squares planes through rings *A*, *B*, *C* and *D* (as defined in Table 4) are almost parallel and the root

Table 4(*a*). *Least-squares planes through the atoms*

The planes are in the form $lX+mY+nZ=p$, where *X*, *Y*, *Z* and *p* are in Å units referred to an orthogonal coordinate system with $X\|\mathbf{a}$, $Y\|\mathbf{b}$ and $Z\|(\mathbf{a}\times\mathbf{c})$.

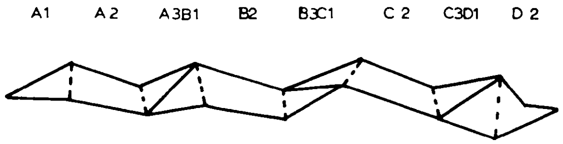
Plane	Atom	*l*	*m*	*n*	*p*
*A*1	C(2), C(3), C(4)	0·8554	0·4931	0·1587	5·406
*A*2	C(1), C(2), C(4), C(5)	0·1421	0·9856	0·0920	3·956
*A*3*B*1	C(1), C(5), C(6), C(10)	0·8202	0·5398	0·1896	6·613
*B*2	C(6), C(7), C(9), C(10)	−0·0208	0·9897	0·1414	2·377
*B*3*C*1	C(7), C(8), C(9), C(11)	0·6960	0·6974	0·1708	7·302
*C*2	C(8), C(11), C(12), C(14)	−0·1087	0·9891	0·0990	0·951
*C*3*D*1	C(12), C(13), C(14), C(15)	0·6466	0·7300	0·2214	8·183
*D*2	C(13), C(15), C(16), C(17)	−0·0929	0·9884	0·1201	0·517
*D*3	C(14), C(15), C(16), C(17)	0·2095	0·9777	−0·0161	3·922
*D*4	C(15), C(16), C(17)	0·0810	0·9962	0·0304	2·483
A	C(1), C(2), C(3), C(4), C(5), C(10)	0·4401	0·8887	0·1284	5·167
B	C(5), C(6), C(7), C(8), C(9), C(10)	0·2846	0·9409	0·1832	4·459
C	C(8), C(9), C(11), C(12), C(13), C(14)	0·2086	0·9699	0·1254	3·840
D	C(13), C(14), C(15), C(16), C(17)	0·1014	0·9821	0·1589	2·843
C(1)–C(17)		0·2618	0·9568	0·1264	4·440

Table 4(*b*). *Deviations* (Å) *from the least- squares planes*

Atom	*A*	*B*	*C*	*D*	*A*2	*A*3*B*1	*B*2	*B*3*C*1	*C*2	*C*3*D*1	*D*2	*D*3	*D*4	*C*1–*C*17
C(1)	0·24				−0·00	0·03								0·19
C(2)	−0·23				0·00									0·00
C(3)	0·23				0·66									0·57
C(4)	−0·24				−0·00									−0·05
C(5)	0·25	0·26			0·00	−0·03	0·69							0·15
C(6)		−0·24				0·03	0·01							−0·30
C(7)		0·22					−0·01	0·04						0·11
C(8)		−0·22	−0·24				−0·66	−0·04	−0·02					−0·42
C(9)		0·24	0·22				0·01	−0·04	0·67					−0·01
C(10)	−0·24	−0·25			−0·70	−0·03	−0·01							−0·45
C(11)			−0·22					0·04	0·02					−0·40
C(12)			0·22						−0·02	0·08				0·12
C(13)			−0·26	−0·28					−0·71	−0·08	−0·06	−0·67	−0·43	−0·32
C(14)			0·28	0·27					0·02	−0·07	0·64	0·05	+0·30	0·18
C(15)				−0·14						0·08	0·07	−0·07	+0·00	−0·03
C(16)				−0·02							−0·10	0·07	−0·00	0·28
C(17)				0·17							0·10	−0·04	+0·00	0·38

Table 4(*c*). *Interplanar angles*

Plane 1	Plane 2	Angle I	Angle II	Angle III
A1	A2	128.5°	123.4°	124.4°
A3B1	A2	131.8	131.3	131.4
A3B1	B2	123.0	122.3	121.1
B3C1	B2	134.4	131.2	136.6
B3C1	C2	129.1	126.9	130.5
C3D1	C2	132.4	130.5	135.5
C3D1	D2	133.5	131.4	138.4
C3D1	D3	147.7	146.7	150.5
A	B	170.1	170.7	167.7
B	C	174.3	171.5	173.4
C	D	173.5	174.9	175.2
C1-C17	(100)	105.2	145.8	104.8
C1-C17	(010)	163.1	93.2	163.9
C1-C17	(001)	97.3	124.0	96.2



mean square deviation of atoms (1) to C(17) from the least-squares plane through the steroid nucleus is 0·29 Å. For the 3β-acetoxy and the 21-bromo compounds these values are 0·28 and 0·30 Å respectively. Projections parallel to the plane of the molecule for the three steroids are given in Fig. 4. In I, the length of the steroid nucleus, C(3)–C(16), is 8·98 Å, and II and III have similar values of 8·98 and 9·04 Å.

In all three structures, rings *A*, *B*, *C* and *D* are *trans*-fused, rings *A*, *B* and *C* are chair-shaped, and the ring junctions are somewhat flattened, as is the entire molecule. Ring *D* of the 16β-bromo-3β-ol steroid (I) is a distorted half-chair, as shown by the torsional angles C(14)–C(15)–C(16)–C(17) and C(15)–C(16)–C(17)–C(13) of +11·7° and +16·3° (Table 5). This is further illustrated by the fact that C(13) and C(14) lie at 0·43 Å and 0·30 Å below and above the plane of *D*4. In the 3β-acetoxy derivative (II), ring *D* is also a half-chair, C(13) and C(14) being −0·44 and +0·34 Å from the plane of *D*4, whereas in the 21-bromo compound (III) ring *D* is a β-envelope with C(13) and C(14) lying +0·68 and −0·04 Å from the *D*4 plane. The conformations of the *D* rings for the three steroids are shown in Fig. 5.

The angle which the acetyl side chain C(17), C(20), O(20), C(21) makes with the *D*3 plane decreases from 61·4° in I to 52·7° in II and to 39·4° in III. Torsional angle C(13)–C(17)–C(20)–C(20) is 80·0° in both the 16 β and 21-bromo steroids (I and III), but the acetyl group is rotated in the 3β-acetoxy compound (II) so that this angle is increased to 178·0°. This rotation is also shown by the increase of φ[C(18)–C(13)–C(17)–O(20)] to 51·8° in III, from values of 24·8° and 21·6° in the

Table 5. *Torsional angles in the rings*

$\varphi A-B$ is the torsional angle about the $A-B$ bond in which the other two atoms required to define the angle are those attached to either end of the bond and are in the ring in question.

Ring *A*	I $\varphi A-B$	II $\varphi A-B$	III $\varphi A-B$	Ring *B*	I $\varphi A-B$	II $\varphi A-B$	III $\varphi A-B$
C(1)–C(2)	−57·0	−55·0	−57·6	C(5)–C(6)	−59·8	−61·3	−61·4
C(2)–C(3)	+56·9	+58·5	+60·6	C(6)–C(7)	+55·4	+58·5	+56·0
C(3)–C(4)	−57·0	−63·1	−61·5	C(7)–C(8)	−52·6	−56·7	−51·2
C(4)–C(5)	+57·8	+62·6	+60·8	C(8)–C(9)	+54·7	+60·6	+53·6
C(5)–C(10)	−55·7	−59·5	−56·9	C(9)–C(10)	−56·1	−60·7	−55·6
C(1)–C(10)	+55·2	+54·5	+54·8	C(5)–C(10)	+58·7	+59·0	+58·9

Ring *C*	I $\varphi A-B$	II $\varphi A-B$	III $\varphi A-B$	Ring *D*	I $\varphi A-B$	II $\varphi A-B$	III $\varphi A-B$
C(8)–C(9)	−53·2	−52·0	−51·0	C(13)–C(14)	+46·7	+47·9	+45·2
C(9)–C(11)	+54·0	+53·3	+53·8	C(14)–C(15)	−36·5	−39·1	−29·2
C(11)–C(12)	−55·0	−54·3	−56·2	C(15)–C(16)	+11·7	+13·2	+1·4
C(12)–C(13)	+55·9	+58·6	+54·4	C(16)–C(17)	+16·3	+17·2	+26·5
C(13)–C(14)	−62·2	−63·8	−57·7	C(13)–C(17)	−37·6	−39·9	−44·1
C(14)–C(8)	+59·9	+58·3	+56·1				

16β- and 21-bromo derivatives; φ[O(20)–C(13)–C(18)–C(20)], likewise, increases from 5·2° in I to 10·1° in III and to 19·6° in II, as does φ[O(17)–C(17)–C(20)–C(21)], values being 17·1° (I), 39·1° (III) and 58·6°(II). Angle φ[O(20)–C(16)–C(17)–O(17)] is almost equal in the 16β-bromo steroids, 38·2° (I) and 39·4° (II), whereas in the 21-bromo compound it has increased to 51·6°.

In the three cases, the C(10)–C(19) and C(13)–C(18) nuclear to methyl group bonds are parallel to within 1–2°.

Table 6(*a*). *Intermolecular distances less than* 4·0 Å

	I		II		III	
	Position	Distance	Position	Distance	Position	Distance
O(3)—O(11)	2/101	2·77*			$2/1\bar{1}0$	2·75*
O(3)—C(11)	2/101	3·83			$2/1\bar{1}0$	3·79
C(2)—O(11)	2/101	3·70			$2/1\bar{1}0$	3·45
C(3)—O(11)	2/101	3·23			$2/1\bar{1}0$	3·06
C(15)–O(3)	$2/1\bar{1}0$	3·60			2/101	3·70
C(18)–O(3)	$2/1\bar{1}0$	4·00	$4/1\bar{1}1$	3·86		
C(19)–C(4)					2/101	3·94
C(19)–C(5)					2/101	3·91
C(19)–C(6)	$2/1\bar{1}0$	3·92			2/101	3·81
O(3)—C(8)					2/101	3·79
O(17)–O(3)	1/100	2·84*			$1/\bar{1}00$	2·73*
O(17)–C(2)	1/100	3·84			$1/\bar{1}00$	4·00
O(17)–C(3)	1/100	3·90			$1/\bar{1}00$	3·86
C(16)–O(3)	1/100	3·44			$1/\bar{1}00$	3·74
C(17)–O(3)	1/100	3·67			$1/\bar{1}00$	3·62
C(21)–C(2)	1/100	3·80			$1/\bar{1}00$	3·92
C(20)–C(2)					$1/\bar{1}00$	3·96
Br —C(2)					$1/\bar{1}00$	3·88
O(11)–C(7)	1/001	3·89			$1/00\bar{1}$	3·63
O(11)–C(15)	1/001	3·65				
C(1)—C(6)	1/001	3·99			$1/00\bar{1}$	3·77
C(1)—C(7)	1/001	3·98				
C(12)–C(15)			$3/01\bar{1}$	3·94	$1/00\bar{1}$	3·96
C(21)–Br	1/001	3·83				
C(4)–Br					1/101	3·93
O(17)–C(18)					$2/0\bar{1}0$	3·83
C(9)—Br					$2/0\bar{1}0$	3·85
C(7)—O(20)			$3/01\bar{1}$	3·70	$2/0\bar{1}1$	3·85
C(12)—C(16)			$3/01\bar{1}$	3·92		
O(11)–O(17)			$3/01\bar{1}$	2·70*		
O(11)–C(16)			$3/01\bar{1}$	3·48		
O(11)–C(17)			$3/01\bar{1}$	3·63		
O(11)–C(21)			$3/01\bar{1}$	3·76		
C(11)–O(17)			$3/01\bar{1}$	3·50		
C(12)–O(17)			$3/01\bar{1}$	3·49		
O(20)–C(9)			$3/01\bar{1}$	3·81		
O(20)–C(14)			$3/01\bar{1}$	3·94		
C(18)–C(2)			$4/1\bar{1}1$	3·80		
C(18)–C(22)			$4/1\bar{1}1$	3·99		
C(18)–C(23)			$4/1\bar{1}1$	3·96		
O(20)–C(2)			$4/1\bar{1}1$	3·82		
O(20)–C(19)			$4/1\bar{1}1$	3·63		
C(21)–C(19)			$4/1\bar{1}1$	3·92		

The equivalent positions are:

$$1=x,\ y,\ z;\ 2=\bar{x},\ \tfrac{1}{2}+y,\ \bar{z};\ 3=\tfrac{1}{2}-x,\ \bar{y},\ \tfrac{1}{2}+z;\ 4=\bar{x},\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z.$$

* The hydrogen bonded oxygen atoms are marked by an asterisk.

Table 6(*b*). *Intermolecular distances less than* 3·0 Å *between hydrogen and non-hydrogen atoms.*

	Position	Distance		Position	Distance
H(2*A*)—C(19)	2/101	2·96 Å	O(17) –H′(3)	1/100 Å	2·90 Å
H(2*A*)—O(11)	2/101	2·89	H(16) –O(3)	1/100	2·54
H(3)—O(11)	2/101	2·63	H′(17)–O(3)	1/100	2·13
*H′(3)—O(11)	2/101	2·00	O(11) –H(7*B*)	1/001	2·97
H(15*B*)–O(3)	$2/1\bar{1}0$	2·41			

* H′ refers to a hydroxyl hydrogen atom.

Table 6(*c*). *Intermolecular distances less than* 0·3 Å *Between hydrogen atoms*

	Position	Distance		Position	Distance
H(2*A*)—H(19*C*)	2/101	2·20 Å	H(19*A*)-H(6*A*)	2/1$\bar{1}$0	2·43 Å
H(3)—-H(1*A*)	2/101	2·93	H(19*C*)-H(6*A*)	2/1$\bar{1}$0	2·83
H′(3)—-H(12*A*)	2/101	2·86	H′(17)—H′(3)	1/100	2·28
H(15*B*)-H′(3)	2/1$\bar{1}$0	2·36	H′(17)—H(2*B*)	1/100	2·80
H(6*B*)—H(3)	2/1$\bar{1}$0	2·61	H(21*B*)-H(2*B*)	1/100	2·36
H(7*B*)—H(3)	2/1$\bar{1}$0	2·78	H(21*C*)-H(2*B*)	1/100	2·96
H(8)—-H(3)	2/1$\bar{1}$0	2·92	H(1*A*)—H(6*A*)	1/001	2·97
H(8)—-H(4*A*)	2/1$\bar{1}$0	2·37	H(1*A*)—H(7*B*)	1/001	2·31
H(18*A*)-H(4*A*)	2/1$\bar{1}$0	2·54	H(2*A*)—H(6*A*)	1/001	2·62
H(19*A*)-H(4*A*)	2/1$\bar{1}$0	2·44	H(21*B*)-H(6*B*)	1/101	2·89
H(6*B*)—H(5)	2/1$\bar{1}$0	2·68	H(21*C*)-H(6*B*)	1/101	2·62
H(19*A*)-H(5)	2/1$\bar{1}$0	2·62			

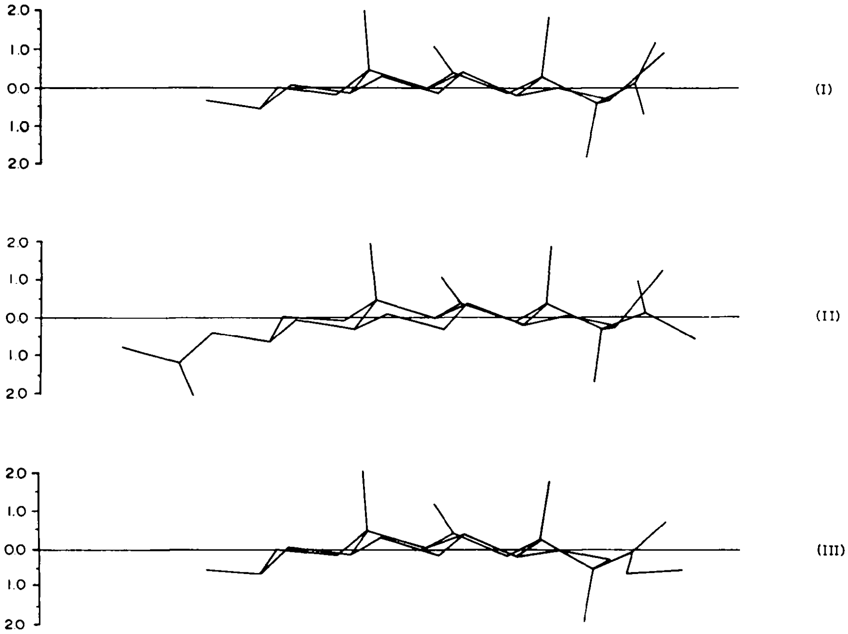

2.0
1.0
0.0
1.0
2.0
(I)
2.0
1.0
0.0
1.0
2.0
(II)
2.0
1.0
0.0
1.0
2.0
(III)

Fig. 4. Projections perpendicular to best planes C(1)–C(17) of steroids 3*β*, 17*α*-dihydroxy-16*β*-bromo-5*α*-pregnan-11,20-dione, (I). 3*β*-acetoxy-17*α*-hydroxy-16*β*-bromo-5*α*-pregnan-11,20-dione, (II). 3*β*, 17*α*-dihydroxy-21-bromo-5*α*-pregnan-11,20-dione, (III).

Packing of the molecule

The position of attachment of the bromine atom is the same (16*β*) in both I and II. In II, the presence of acetate side chain attached to C(3) removes the oxygen available for hydrogen bonding at this site, and results

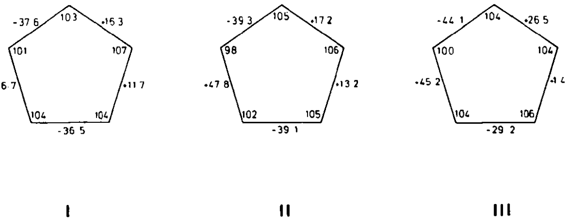

-37 6
103
+15 3
101
107
+46 7
+11 7
104
104
-36 5
I
-39 3
105
+17 2
98
106
+47 8
+13 2
102
105
-39 1
II
-44 1
104
+26 5
100
104
+45 2
+1 4
104
106
-29 2
III

Fig. 5. Torsional angles in ring *D* for steroids 3*β*, 17*α*-dihydroxy-16*β*-bromo-5*α*-pregnan-11,20-dione (I), 3*β*-acetoxy-17*α*-hydroxy-16*β*-bromo-5*α*-pregnan-11,20-dione (II), 3*β*, 17*α*-dihydroxy-21-bromo-5*α*-pregnan-11,20-dione (III).

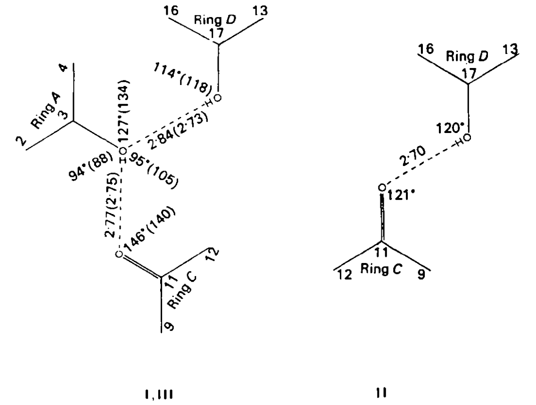

16
Ring D
13
17
4
Ring A
3
2
114°(118)
127°(134)
2·84(2·73)
HO
94°(88)
95°(105)
2·77(2·75)
146°(140)
12
11
Ring C
9
I, III
16
Ring D
13
17
120°
HO
2·70
121°
11
12
Ring C
9
II

Fig. 6. Hydrogen bonding for steroids 3*β*, 17*α*-dihydroxy-16*β*-bromo-5*α*-pregnan-11,20-dione (I), 3*β*-acetoxy-17*α*-hydroxy-16*β*-bromo-5*α*-pregnan-11,20-dione (II), 3*β*, 17*α*-dihydroxy-21-bromo-5*α*-pregnan-11,20-dione (III); the respective dimensions for 3*β*, 17*α*-dihydroxy-21-bromo-5*α*-pregnan-11,20-dione (III) are given in parentheses.

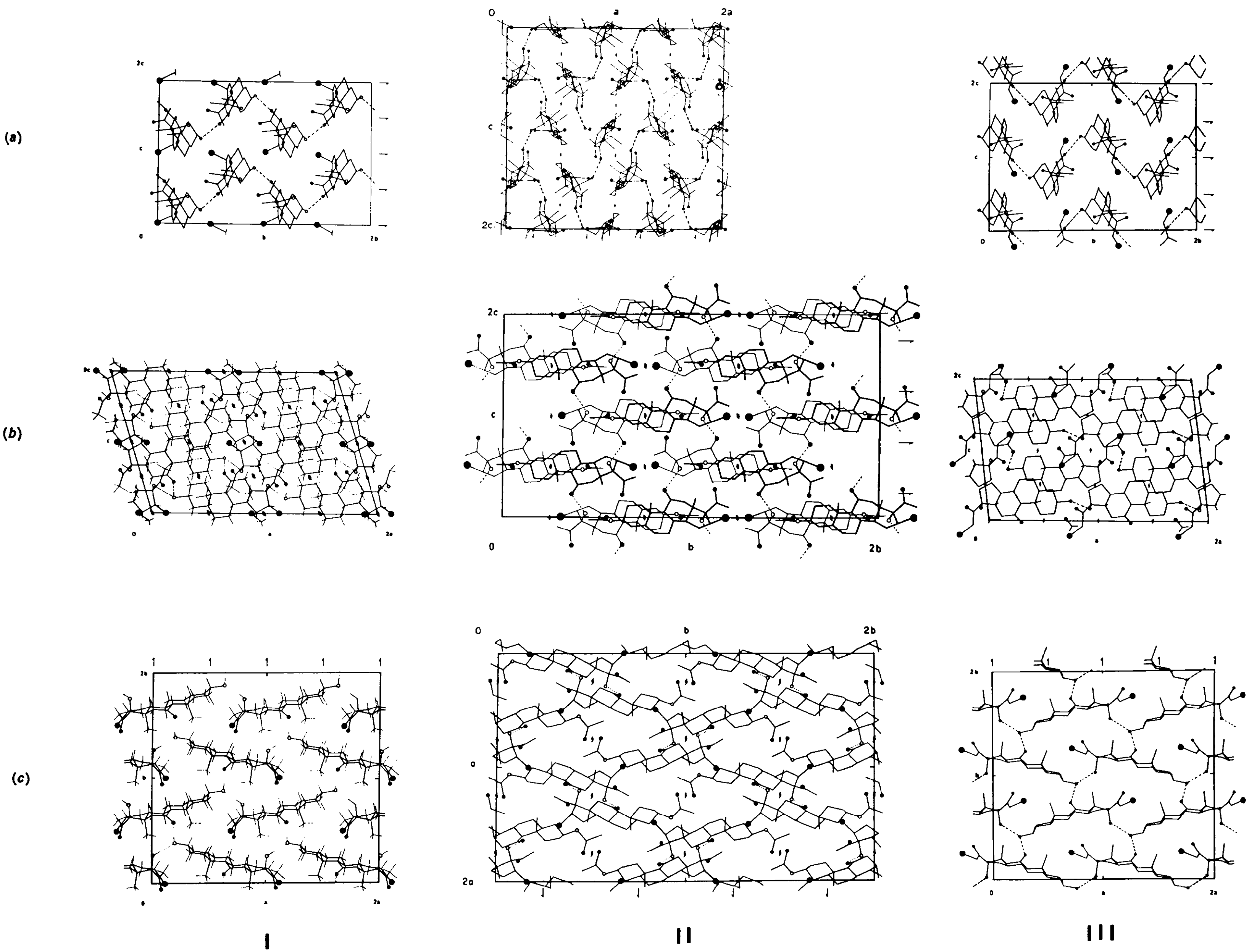


Fig. 7. Comparative projections of the steroids I, II and III (as defined in Fig. 1), showing packing modifications due to the variation in ring substituents and side chains. The hydrogen bonding is shown by broken lines. Large black dot = bromine; small black dot = keto oxygen; open circle = hydroxyl oxygen.

in a change in stacking arrangement, with a single 11-keto 17α-hydroxyl hydrogen bond of 2·70 Å. Although I and III differ in the position of attachment of the heavy atom, the functional group at C(3) is the same; namely, 3β-hydroxyl. In both compounds there are two hydrogen bonds: 3β-hydroxyl to 11-keto oxygen and 3β-hydroxyl to 17α-hydroxyl oxygen. In I, these distances are 2·77 Å and 2·84 Å and in III, they are epual to 2·75 Å and 2·73 Å, respectively, as shown in Fig. 6.

In both steroids I and II, there are sixteen additional contacts less than 4·0 Å, but these are to different portions of the molecules in the two cases. In III, there are twenty-two additional contacts less than 4·0 Å, twelve of which are to the same portions of the molecule as in I, the differences being mainly those involving the tail to which the bromine is attached in III, and the methyl groups at C(18) and C(19). Steroids II and III also have similar contacts involving C(7)–O(20) and C(12)–C(15). In I, aside from the contacts mentioned above (Table 6), there are nine contacts less than 3·0 Å between hydrogen non-hydrogen atoms, eight with the oxygens attached to C(3), C(11), C(17), and the other one with the C(19) methyl group. There are twenty-three hydrogen–hydrogen contacts less than 3·0 Å, ten of which involve the methyl groups at C(18), C(19) and C(21).

The molecules in I and III are α–β(bottom-to-top) oriented and arranged in sheets perpendicular to the *b* axis of the unit cell [Fig. 7(*b*)]. The hydrogen bonding *via* the axial 3β-hydroxyl oxygen atom to the 17α-hydroxyl oxygen atom is of the head-to-tail type wherein the bonded molecules are related by one unit-cell translation in the *a* direction. The 3β-hydroxyl hydrogen atom bonds to the 11-keto oxygen of the molecule generated by the 2_1 screw axis [Fig. 7(*a*) and (*c*)].

In II the hydrogen bonding *via* the 17α-hydroxyl oxygen and the 11-keto oxygen is of a modified paired tail-to-tail type resulting in an α – α(bottom-to-bottom) orientation [Fig. 7(*b*)]. These paired molecules extend in sheets in the **c** direction and these sheets in turn are arranged in pairs which are packed β–β(top-to-top) [Fig. 7(*a*) and (*c*)]. This represents the closest packing in that each sheet has six similar sheets in contact with it.

The assistance of Mr C. T. Lu, who measured the intensity data, and Mrs C. DeVine and Mr A. Greaver is gratefully acknowledged. We also wish to thank Dr C. Johnson who supplied his program *ORTEP* with which Fig. 2 was prepared.

This investigation was supported by Public Health Service research grant CA–6183 from the National Cancer Institute.

References

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.
Carlisle, C. H. & Ladd, M. C. F. (1966). *Acta Cryst.* **21**, 689.
Fawcett, J. K. & Trotter, J. (1966). *J. Chem. Soc.* B, 174.
High, D. F. & Kraut, J. (1966). *Acta Cryst.* **21**, 88.
International Tables for X-*ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
Oberhansli, W. E. & Robertson, J. M. (1967). *Helv. Chim. Acta*, **50**, 53.
Ohrt, J. M., Cooper, A., Kartha, G. & Norton, D. A. (1968). *Acta Cryst.* **B24**, 824.
Ohrt, J. M., Haner, B. A., Cooper, A. & Norton, D. A. (1968). *Acta Cryst.* **B24**, 312.
Romers, C., Hesper, B., van Heijkoop, E. & Geise, H. J. (1966). *Acta Cryst.* **20**, 363.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63.

Acta Cryst. (1969). **B25**, 51

Structure Cristalline et Moléculaire de la Méthyl-2-naphtohydroquinone-1,4

Par Jacques Gaultier et Christian Hauw

Laboratoire de Cristallographie et Minéralogie, associé au C.N.R.S., Faculté des Sciences de Bordeaux, Bordeaux, France

(*Reçu le* 3 *janvier* 1968)

Crystals of 2-methylnaphthalene-1,4-diol are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a=13{\cdot}50$ $b=4{\cdot}49$ $c=14{\cdot}83$ Å $\beta=104°$. The structure was solved with data from three projections and refined by least-squares techniques. The final R index is 0·086. The naphthyl group is exactly planar, the oxygen atoms are displaced orthogonally from the plane. The methyl group does not disturb the symmetry of naphthalene-1,4-diol. Molecules are connected by four hydrogen bonds OH · · · O. The geometry of these bonds is discussed. Molecules overlap each other with an average interplanar spacing of 3·55 Å. A comparison is made with the structure of 1,4-naphthalene diol.

Données expérimentales

Nous avons préparé la méthyl-2 naphtohydroquinone-1,4 suivant la méthode préconisée par Fieser (1940). En solution, le composé très instable se transforme rapidement en composé quinonique, le déplacement de l'équilibre pouvant être suivi facilement par l'évolution de la couleur. Aussi, nous l'avons cristallisé par refroi-