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Sterol Biosynthesis: Establishment of the Structure of 3β-*p*-Bromobenzoyloxy-5α-Cholest-8(14)-en-15β-ol

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Previous studies have established that hydride reduction of 3β-benzoyloxy-5α-cholest-8(14)-en-15-one yields two epimers (at C-15) of 5α-cholest-8(14)-en-3β,15-diol which were designated as diol A and B. Efficient enzymatic conversion of both compounds to cholesterol was observed. To determine the absolute configuration of the 15-OH function in the two compounds, the 3β-*p*-bromobenzoyl ester of diol B was prepared from 3β-*p*-bromobenzoyloxy-5α-cholest-8(14)-en-15-one by reduction with sodium borohydride. Crystals of the derivative were found to belong to the space group P1, with unit cell parameters; $a = 9.24$ Å, $b = 12.61$ Å, $c = 7.03$ Å, $\alpha = 93.05°$, $\beta = 100.27°$, $\gamma = 90.82°$, and one molecule per unit cell. Least-squares refinement of the structure was carried out to final R value of 0.14. The configuration of the hydroxyl group at the 15 position of diol B has been determined to be β.

INTRODUCTION

5α-Cholest-8(14)-en-3β-ol has been isolated from animal tissues (*1–3*) and has been shown to serve as an efficient precursor of cholesterol upon feeding to intact rats (*3, 4*). Incubation of isotopically labeled 5α-cholest-8(14)-en-3β-ol with rat liver homogenate preparations under aerobic conditions led to the formation of labeled 5α-cholesta-8,14-dien-3β-ol, cholest-7-en-3β-ol, and cholesterol (*3–6*). While the efficient conversion of 5α-cholest-8,14-dien-3β-ol and 5α-cholest-8-en-3β-ol to cholest-7-en-3β-ol can readily be demonstrated under anaerobic conditions (*7–10*), only unreacted substrate was detected after incubation of 5α-cholest-8(14)-en-3β-ol with rat liver homogenate preparations under anaerobic conditions. This finding suggested the possibility of an oxygen-dependent step in the enzymatic conversion of 5α-cholest-8(14)-en-3β-ol to 5α-cholesta-8,14-dien-3β-ol and led us to investigate the possible role of 5α-cholest-8(14)-en-3β,15-diol in the conversion of the $\Delta^{8(14)}$-sterol to the $\Delta^{8,14}$-sterol. Reduction of 3β-benzoyloxy-cholest-8(14)-en-15-one with lithium aluminum hydride yielded two epimers (at C-15) of cholest-8(14)-en-3β,15-diol which were readily separable by silica gel thin-layer and silicic acid column chromatography (*3, 11*). The less polar diol was designated as diol A and the more polar compound as diol B (*3, 11*). Reduction of the 15-keto compound with lithium aluminum tritide yielded [15-^{3}H]diol A and [15-^{3}H]diol B. Upon incubation with rat liver homogenates under aerobic conditions, efficient conversion of both epimers to cholesterol was observed (*11*). Under anaerobic conditions

labeled 5α-cholesta-8,14-dien-3β-ol, 5α-cholest-8-en-3β-ol, 5α-cholest-8(14)en-3β-ol, and 5α-cholest-7-en-3β-ol were formed from both substrates.

The purpose of the present study was to unequivocally establish the structures of diols A and B.

GENERAL METHODS

Melting points were recorded on a Thomas–Hoover melting point apparatus and are uncorrected. Mass spectra were recorded using a CEC Model 21-110B spectrometer. Nuclear magnetic resonance (nmr) spectra were recorded on a Perkin–Elmer HR-12 spectrometer. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) was employed as the internal standard. The nmr absorptions are reported as ppm (δ) downfield from the TMS internal standard. Ultraviolet spectra were recorded in ethanol.

Precession photographs were taken with a Buerger type camera using Ni-filtered CuK_α radiation from an Elliot GX-6 generator. Diffraction data were collected on a Phillips PAILRED diffractometer using Nb-filtered MoK_α radiation. Several reflections were checked regularly to insure that no substantial deterioration occurred.

3β-Hydroxy-5α-cholest-8(14)-en-15-one

3β-Hydroxy-5α-cholest-8(14)en-15-one was prepared in this laboratory by Dr. Roger Shaw by acid hydrolysis of the 3β-benzoate (experimental details to be presented elsewhere (*12*)). The compound was homogeneous on thin-layer chromatographic analysis on silica gel H in two solvent systems (chloroform and 30% ethyl acetate in chloroform). The mass spectrum showed major peaks in the high mass region at *m/e* 400 (M; 100%), 385 (M-15, corresponding to M-CH_3; 15%), 382 (M-18, corresponding to M-H_2O; 18%), 367 (M-33, corresponding to M-CH_3–H_2O; 18%), 287 (M-113, corresponding to M-C_8H_{17}, the alkyl sidechain; 6%), 269 (M-H_2O-sidechain; 14%), 261 (5%), 259 (4%), 251 (5%), 241 (3%), 233 (2%), 217 (3%), 215 (3%), 213 (5%), and 209 (4%). The nmr spectrum showed absorptions at 2.70 (m, 1H, C-3-H) and 4.20 (m, 1H, 7α-H, deshielded). The ultraviolet spectrum showed an absorption maximum at 263 nm ($\log \varepsilon = 4.06$).

3β-p-Bromobenzoyloxy-5α-cholest-8(14)-en-15-one

After gentle warming to dissolve the reactants, 3β-hydroxy-5α-cholest-8(14)-en-15-one (0.145 g) and *p*-bromobenzoyl chloride (0.3 g) in pyridine (20 ml) were stirred overnight at room temperature. The resulting mixture was three times extracted with ether, and the combined ether extracts were washed three times with 2 *N* HCl, three times with a saturated solution of sodium bicarbonate, and three times with water. The residue obtained upon evaporation of the solvent was applied to an alumina column (grade III; 100 g), and the ester was eluted with a mixture of 5% ether in benzene. After evaporation of the solvent the residue was crystallized from methanol-ether, yielding 3β-*p*-bromobenzoyloxy-5α-cholest-8(14)-en-15-one (141 mg) melting at 195–197°C. The mass spectrum showed significant peaks in the high mass region at *m/e* 582 and 584 (M;

90 and 100%, respectively), 567 and 569 (M-15; corresponding to M-CH_3, 5 and 6%, respectively), 504 (4%), 469 and 471 (M-C_8H_{17}, the alkyl sidechain; 3 and 4%, respectively), 453 and 451 (3 and 3%), 443 and 441 (3 and 2%, respectively), 381 (M-bromobenzoic acid; 3%), 367 (21%), 269 (M-side-chain-bromobenzoic acid; 11%), 261 (5%), 251 (8%), 227 (3%) and 213 (4%). The nmr spectrum showed absorptions at 5.00 (m, 1H, C-3-H, deshielded) and 4.20 (m, 1H, C-7α-H, deshielded).

Borohydride Reduction of 3β-p-Bromobenzoyloxy-5α-cholest-8(14)-en-15-one

Sodium borohydride (300 mg) was added to 3β-*p*-bromobenzoyloxy-5α-cholest-8(14)-en-15-one (121 mg) in a 1:1 mixture of ether and methanol (40 ml). After stirring at room temperature for 30 min, the mixture was diluted with ether, washed thoroughly with water, dried over anhydrous Na_2SO_4, and the solvent removed *in vacuo* to give a brown gummy solid (115 mg). The product was purified by preparative tlc on silica gel H plates developed in $CHCl_3$ and crystallized from ethanol–water to give 3β-*p*-bromobenzoyloxy-5α-cholest-8(14)-en-15ξ-ol (38.8 mg) in the form of needles which melted at 157–159°C. The mass spectrum showed significant peaks in the high mass region at *m/e* 584 and 586 (M; 6 and 4%), 569 and 571 (M-15; corresponding to M-CH_3, 39 and 11%, respectively), 566 and 568 (M-18; corresponding to M-H_2O, 86 and 93%), 551 and 553 (M-33; corresponding to M-CH_3–H_2O, 6% and 5%), 504 and 506 (4 and 5%), 488 (M-H_2O-HBr; 100%), 473 (7%), 453 and 455 (M-H_2O-sidechain; 29% and 31%), 439 and 441 (M-H_2O–CH_3-sidechain; 8 and 9%), 375 (35%), 366 (10%), 361 (11%), 351 (M-CH_3–H_2O-bromobenzoic acid; 44%), 253 (34%), 239 (11%), 238 (9%), 227 (5%), 225 (5%), 213 (5%), and 211 (7%). The nmr spectrum showed a broad absorption at 5.00 (m, 2H, C-15-H and C-3-H).

Interrelation with the Epimeric 3β,15-Diols

The 3β-*p*-bromobenzoyloxy-5α-cholest-8(14)-en-15ξ-ol (10 mg) was dissolved in 50 ml of dry ether, 60 mg of $LiAlH_4$ added, and the mixture stirred at room temperature for 30 min. Excess hydride was destroyed by the addition of ethyl acetate. The solution was washed once with dilute HCl, dilute $NaHCO_3$ and thoroughly with water, dried, and the solvent removed *in vacuo*. The product gave one spot on tlc (35% EtOAc–$CHCl_3$, silica gel H) with an R_f value of 0.26. The R_f values of diol A and diol B, prepared previously by lithium aluminum hydride reduction of 3β-benzoyloxy-5α-cholest-8(14)-en-15-one(4), were 0.40 and 0.26, respectively, in this chromatographic system. These results establish that the product isolated from the sodium borohydride reduction of *p*-bromo-benzoyloxy-5α-cholest-8(14)-15-one has the same configuration at C-15 as does diol B derived from the lithium aluminum hydride reduction of 3β-benzoyloxy-5α-cholest-8(14)-en-5-one. These reactions are illustrated in Fig. 1.

Crystallographic Data

The 3β-*p*-bromobenzoyloxy-5α-cholest-8(14)-15ξ-ol from the borohydride reduction was recrystallized from ethanol–water to yield colorless needle-shaped crystals with cross sectional areas varying from 0.01 to 0.25 mm^2 and lengths varying from 0.5 to

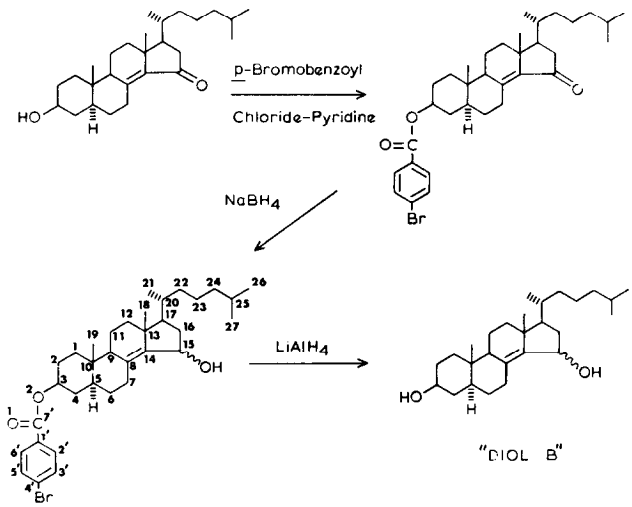

FIG. 1. Synthesis of 3β-*p*-bromobenzoloxy-5α-cholest-8(14)-en-15ξ-ol.

2.0 mm. Precession photographs indicated that the unit cell was triclinic by displaying two nets 86.95° apart, neither showing mirror symmetry. From these photographs the space group was determined to be P1, with unit cell dimensions: $a = 9.24 \pm 0.03$ Å, $b = 12.61 \pm 0.04$ Å, $c = 7.03 \pm 0.03$, $\alpha = 93.05 \pm 0.08$, $\beta = 100.27 \pm 0.08°$, $\gamma = 90.82 \pm 0.08°$. From the molecular weight and unit cell volume, the density of the crystal was calculated to be 1.17 g/cm^3 assuming one molecule per unit cell. This density is consistent with densities found for other similar compounds.

A Wilson plot (*13*) of the 2600 unique reflections collected revealed that data corresponding to $\sin\theta^2/\lambda^2$ greater than 0.27/Å^2 forced the straight line fit to result in a negative temperature factor. Similar problems were encountered in the refinement, hence these data were excluded from the structure analysis. Remaining were 1836 reflections whose relative statistical error was calculated by

$$\frac{\Delta I}{I} = \frac{(T + t^2B)^{1/2}}{T - tB},$$

where T = total counts in ω –scan time, t_T; B = total background counts; and $t = t_T/t$ background. Reflections with $\Delta I/I$ greater than 0.4 were considered to be unobserved. The number of observed reflections was found to be 869. The ratio of observations to variables was calculated to be 5.6.

Structure Analysis

Initial phases were calculated based on the assignment of the bromine atom to an arbitrary position in the unit cell. Applying these phases to the observed data provided an electron density map from which the atoms of the aromatic ring and the D-ring of the sterol were recognizable. Two more electron density maps based on the calculated phases of models of increasing numbers of atoms were necessary to locate all atoms heavier than hydrogen. Two cycles of diagonal matrix least squares refinement of X, Y,

Z, and B parameters of all nonhydrogen atoms yielded a weighted R value of 0.08, where R is defined as:

$$R = \frac{\sum \sqrt{w}(|kF_{obs}| - |F_{calc}|)}{\sum kF_{obs}}$$

TABLE 1

FRACTIONAL COORDINATES OF THE BONDED ATOMS

		X	Y	Z	B
1	Br	0.5938 (0)	0.6193 (0)	0.825 (0)	[a]
2	O1	0.6783 (29)	0.9038 (22)	0.2526 (41)	8.79 (0.78)
3	O2	0.9123 (29)	0.8783 (20)	0.3959 (36)	7.69 (0.74)
4	O3	0.7142 (27)	0.0097 (19)	0.8661 (36)	7.02 (0.68)
5	C1′	0.7394 (44)	0.8069 (27)	0.5624 (58)	5.49 (0.91)
6	C2′	0.5924 (44)	0.7732 (30)	0.5637 (56)	6.41 (1.01)
7	C3′	0.5471 (31)	0.7204 (23)	0.7069 (52)	3.11 (0.70)
8	C4′	0.6297 (36)	0.6868 (28)	0.8590 (55)	5.80 (0.96)
9	C5′	0.7907 (48)	0.7300 (33)	0.8785 (67)	8.78 (1.22)
10	C6′	0.8386 (36)	0.7784 (28)	0.7092 (48)	4.64 (0.85)
11	C7′	0.7620 (38)	0.8602 (26)	0.3861 (59)	5.62 (0.93)
12	C1	0.0696 (56)	0.1270 (38)	0.1289 (74)	9.59 (1.30)
13	C2	0.0094 (48)	0.0459 (32)	0.3066 (63)	7.87 (1.20)
14	C3	0.9637 (38)	0.9445 (27)	0.2390 (59)	5.80 (0.95)
15	C4	0.1022 (49)	0.8837 (31)	0.1995 (52)	8.08 (1.18)
16	C5	0.1568 (43)	0.9500 (34)	0.0237 (65)	8.53 (1.21)
17	C6	0.2873 (44)	0.8870 (31)	0.9721 (64)	7.30 (1.09)
18	C7	0.3352 (43)	0.9523 (29)	0.7940 (60)	5.66 (0.96)
19	C8	0.3831 (42)	0.0682 (28)	0.8427 (53)	5.71 (0.94)
20	C9	0.2472 (36)	0.1300 (28)	0.8945 (46)	4.00 (0.78)
21	C10	0.2177 (45)	0.0669 (32)	0.0865 (61)	7.13 (1.14)
22	C11	0.2816 (52)	0.2454 (31)	0.9034 (62)	6.82 (1.07)
23	C12	0.3702 (39)	0.2928 (28)	0.7559 (59)	5.62 (0.91)
24	C13	0.5361 (50)	0.2406 (33)	0.8039 (65)	7.53 (1.14)
25	C14	0.4963 (36)	0.1173 (28)	0.7842 (52)	4.21 (0.82)
26	C15	0.6168 (37)	0.0559 (31)	0.7058 (56)	4.44 (0.84)
27	C16	0.6998 (37)	0.1550 (27)	0.6185 (50)	4.64 (0.83)
28	C17	0.6069 (49)	0.2530 (35)	0.6347 (68)	7.34 (1.06)
29	C18	0.6193 (47)	0.2542 (38)	0.9849 (64)	8.03 (1.18)
30	C19	0.3394 (50)	0.0694 (37)	0.2466 (73)	9.65 (1.39)
31	C20	0.7249 (42)	0.3610 (43)	0.6329 (55)	5.44 (0.90)
32	C21	0.6276 (50)	0.4521 (34)	0.6170 (68)	8.27 (1.18)
33	C22	0.7953 (39)	0.3542 (26)	0.4492 (48)	4.24 (0.80)
34	C23	0.9319 (49)	0.4562 (34)	0.4786 (62)	7.92 (1.13)
35	C24	0.9977 (60)	0.4397 (40)	0.2931 (75)	11.12 (1.59)
36	C25	0.0982 (63)	0.5388 (42)	0.2461 (89)	13.35 (1.80)
37	C26	0.2082 (63)	0.5451 (49)	0.4181 (89)	14.21 (1.89)
38	C27	0.1674 (57)	0.5271 (41)	0.705 (81)	13.11 (1.69)

[a] Anisotropic temperature factors for bromine: *B11*, 0.0430 (14); *B22*, 0.0142 (05); *B33*, 0.0650 (21); *B12*, 0.0052 (10); *B13*, 0.0495 (22); *B23*, 0.0008 (14).

TABLE 2

FINAL STRUCTURE FACTORS

H=8 L=2

0	7.1	2.0	2.0	0.1

H=7 L=2

1	6.9	8.5	7.7	-3.0
0	8.9	6.0	-0.8	0.0

H=7 L=1

7	7.4	1.7	-1.7	0.3
-2	11.3	12.2	9.3	7.9
-3	13.5	9.3	-0.2	9.3

H=6 L=3

5	9.1	9.0	9.0	-0.7

H=6 L=2

3	6.9	7.0	1.1	-7.0
2	6.9	6.0	4.9	4.4
0	7.5	9.0	-7.8	-5.7

H=6 L=1

3	8.0	7.4	-7.3	1.3
2	6.6	3.9	0.4	-3.9
0	7.1	5.3	4.4	-2.9
-1	12.5	9.0	6.3	3.7
-2	14.3	14.6	-3.3	14.4
-4	10.1	6.0	5.0	3.8

H=5 L=3

5	7.9	8.5	-4.0	7.1
4	7.7	3.3	-2.3	-2.4
0	8.7	7.3	4.9	5.5
-3	7.4	7.0	-3.9	5.9

H=5 L=2

2	9.5	8.2	-0.7	4.7
1	6.0	6.0	-6.0	0.1
0	7.1	6.1	3.6	5.0
-3	9.8	8.9	-5.6	6.7
-5	7.9	7.0	4.2	6.3

H=5 L=1

5	8.8	7.9	2.8	7.3
4	8.9	10.5	-7.9	-7.3
2	6.7	7.3	-1.3	7.2
1	7.8	10.8	-8.0	-7.0
0	8.0	7.1	3.0	6.4
-1	6.1	5.8	0.4	5.6
-2	9.3	11.8	4.8	-10.6
-4	10.1	9.8	-8.2	-5.0
-6	8.4	8.3	-2.1	8.0

H=4 L=4

-1	6.6	6.1	1.0	6.0
-3	6.1	6.3	4.3	-4.6

H=4 L=3

6	8.0	6.2	-4.5	4.1
5	9.0	7.4	-7.4	-0.1
0	9.5	8.3	-8.2	-3.6
-3	7.3	4.8	2.4	-4.3

H=4 L=2

6	11.5	8.2	-1.1	8.2
3	11.1	7.1	-0.8	7.0
2	10.1	10.8	3.3	-10.3
1	11.2	9.8	5.8	8.0
0	11.6	13.7	-2.7	-13.4
-1	7.9	7.2	2.5	-0.8
-2	9.6	10.3	-8.7	5.5
-3	7.6	4.8	-4.2	2.4
-4	7.0	11.3	-0.6	-11.3
-5	6.4	7.4	-7.3	1.2
-10	7.4	6.3	-4.0	4.9

H=4 L=1

8	7.2	4.2	-2.9	-3.0
5	17.4	18.9	-18.4	-3.9
4	19.6	19.4	17.4	-7.7
3	5.4	5.5	-4.8	2.6
2	13.3	12.9	-4.0	-12.2
1	16.2	13.4	12.7	-4.3
0	7.1	8.7	-1.7	8.0
-1	14.0	11.8	11.3	-3.5
-2	12.6	14.3	-6.1	12.9
-3	10.2	10.2	-10.1	-1.5
-4	14.7	15.0	12.7	6.1
-6	14.7	13.9	-13.0	-5.1
-8	6.6	6.4	0.9	-6.3
-9	7.4	3.4	1.3	-3.2

H=3 L=6

-5	5.8	2.0	-0.2	2.0

H=3 L=5

2	5.8	6.4	-6.4	0.4
0	5.2	5.8	0.5	5.8

H=3 L=4

3	5.4	5.3	3.7	-3.7
1	8.4	6.6	0.9	-6.6
-1	5.7	6.6	-6.5	-1.4
-3	6.0	7.0	1.1	6.9
-6	6.4	3.7	-3.7	0.3

H=3 L=3

7	8.7	6.7	-1.4	6.5
5	11.7	9.8	4.4	8.7
3	6.1	3.4	3.4	-0.3
2	6.2	4.7	1.7	4.4
1	13.5	11.8	-4.3	-11.0
0	22.9	21.6	8.7	-19.8
-1	11.8	9.6	-4.5	-6.5
-2	8.4	9.4	4.9	-8.0
-3	5.3	3.2	-2.6	1.8
-4	8.8	10.9	-9.2	-5.9
-6	5.6	5.5	-5.5	-0.5

H=3 L=2

8	12.2	9.7	8.9	-3.7
7	8.7	6.4	2.5	5.8
5	18.3	20.0	17.3	10.0
3	7.0	1.4	-1.4	0.1
2	9.6	8.7	-6.1	6.3
1	20.3	21.6	-17.3	-12.9
0	13.0	12.1	-1.1	-12.1
-1	8.1	11.3	-5.9	9.7
-2	23.7	24.0	-10.8	-22.4
-3	11.8	12.4	10.8	-6.2
-5	6.5	6.1	1.4	-5.9
-6	6.5	7.5	-2.9	6.9
-7	7.6	6.3	-2.7	-5.7

H=3 L=1

9	9.2	3.6	-1.5	3.3
8	6.4	4.2	1.7	-3.8
7	10.8	9.1	-4.6	7.8
6	11.6	12.6	-0.7	-12.6
5	14.8	15.7	14.2	-6.7
4	20.0	20.7	-2.4	20.6
3	23.1	22.0	-1.7	-21.9
2	12.9	14.4	12.0	8.1
1	7.8	4.3	1.3	4.1
0	8.2	10.7	0.5	-10.7
-1	23.3	21.9	-10.4	15.3
-2	6.8	7.3	-6.5	3.4
-3	31.7	34.7	34.7	-1.6
-4	17.1	17.9	-15.9	8.2
-5	12.3	10.2	4.4	-5.2
-6	8.5	8.2	5.9	-5.7
-9	9.0	7.6	-2.5	7.1
-11	7.8	4.9	4.9	0.1

H=2 L=6

-2	7.2	5.6	-5.1	-2.3
-6	6.2	2.3	1.8	1.4

H=2 L=5

4	6.0	6.4	2.6	5.6
2	9.3	3.8	3.5	-1.4
0	5.5	5.0	-2.9	-4.0
-1	6.1	6.7	3.1	-5.9
-2	7.6	6.9	-4.5	-2.3
-3	10.4	10.3	-4.2	-9.3
-5	5.1	2.9	1.4	2.5
-9	6.6	2.3	2.1	1.0

H=2 L=4

4	6.3	3.9	1.5	-3.6
3	7.7	5.6	-4.9	-2.7
1	9.6	11.0	4.8	5.9
-1	10.4	10.7	8.0	-6.2
-3	10.1	7.7	-2.5	-8.3
-6	6.3	8.7	5.4	-6.4
7	9.4	4.2	4.2	0.6
6	8.4	6.6	6.6	0.4
5	8.6	6.1	-4.8	-3.8
4	12.2	12.9	12.6	-3.0
3	8.0	6.5	-1.8	6.2
2	22.5	22.3	-12.6	-18.4
1	5.1	5.0	-4.0	3.1
0	15.1	16.6	1.7	16.6
-1	12.2	14.7	14.6	2.2
-2	13.6	14.0	5.1	13.0
-4	8.7	7.3	7.3	0.3
-6	9.1	6.6	-1.0	-6.5
-9	8.2	9.2	7.1	-5.6

H=2 L=2

9	7.2	8.5	7.9	-3.1
8	11.4	10.2	-3.0	9.7
7	6.1	3.6	2.3	-2.7
6	20.3	21.0	21.0	-0.6
4	5.3	9.0	8.9	-1.0
3	20.5	20.8	13.9	15.5
2	20.9	20.2	-17.1	-10.7
1	6.7	6.7	5.8	-3.5
0	49.7	53.3	-49.8	19.0
-1	13.1	13.1	-13.1	0.9
-2	11.1	12.0	12.0	-0.0
-3	14.2	12.7	-7.5	10.2
-4	12.6	16.2	14.4	7.5
-5	12.7	11.0	0.2	11.0
-6	7.0	8.6	-7.9	-3.6
-7	5.6	3.4	-0.0	3.4
-8	6.4	6.0	-5.9	1.2

H=2 L=1

10	7.9	5.8	-5.8	-0.5
7	10.2	10.1	-7.7	-6.6
6	25.2	24.9	22.7	10.2
5	14.8	16.1	1.6	16.0
4	14.1	15.5	-0.9	-15.5
3	31.1	32.5	18.1	27.0
2	25.0	25.9	-22.6	12.5
1	3.9	4.5	4.5	0.3
0	44.1	42.8	-13.2	40.7
-1	27.0	29.5	-22.2	-19.4
-2	12.5	15.5	-3.5	15.1
-3	18.2	16.8	-16.1	4.7
-4	19.4	19.9	-11.2	-16.5
-5	16.7	16.0	12.1	13.2
-7	8.7	5.8	5.2	2.6
-8	9.0	10.6	-1.1	10.6
-9	8.2	6.8	-0.6	-6.7

H=1 L=7

-1	5.1	3.1	-0.0	-3.1

H=1 L=6

1	6.9	5.1	3.0	-4.1
0	4.6	1.8	1.6	0.8
-1	5.3	7.4	-0.9	7.4
-3	4.6	4.8	-3.5	-3.4
-4	5.0	4.4	0.4	-4.4
-6	5.5	2.8	-2.6	1.0

H=1 L=5

4	6.1	4.0	-3.9	0.6
3	5.5	7.4	7.2	-1.7
1	5.3	5.0	2.4	-4.4
-1	9.5	8.4	-7.8	3.2
-3	11.2	11.7	7.0	9.3
-4	10.5	9.2	-5.4	7.4
-7	7.6	5.6	2.7	-4.9

H=1 L=4

5	8.6	7.9	6.7	2.9
4	4.9	0.8	-0.2	0.7
2	8.1	8.7	4.8	7.3
1	10.9	10.4	-9.1	-5.0
0	3.6	3.3	3.1	-0.8
-1	12.8	11.1	-8.4	7.4
-2	4.1	4.7	-3.8	-2.9
-3	11.4	13.2	1.8	10.0
-4	7.8	8.8	-3.1	8.3
-5	9.5	9.6	8.4	-4.6
-6	13.6	13.6	8.6	10.6
-8	6.0	9.4	0.4	-3.4
-11	7.0	1.9	0.3	1.9
10	7.9	3.6	3.1	1.9
8	8.7	9.8	-8.5	4.4
5	9.4	8.2	6.8	4.6
4	14.3	16.1	-7.8	14.1
3	13.1	9.4	-4.7	-8.1
2	19.1	18.7	14.8	8.3
0	11.7	13.2	0.8	-13.1
-1	11.1	8.7	-2.3	8.3
-2	16.3	16.7	-16.6	-8.0
-3	7.4	9.4	8.9	-3.3
-4	13.7	13.7	-13.4	2.9
-5	8.7	8.9	1.2	-8.9
-6	9.3	7.8	5.3	5.3
-7	6.9	6.5	-6.5	0.1
-8	8.0	7.0	7.0	-0.1
-9	9.7	10.2	4.2	9.3

H=1 L=2

9	9.3	10.5	-8.2	9.1
8	8.7	8.2	-4.8	-6.7
7	6.6	8.6	8.5	-1.2
6	15.6	17.3	-15.2	-8.4
5	16.3	19.0	8.2	-17.2
4	13.0	13.4	4.4	12.7
3	10.4	10.9	-9.7	-5.0
2	15.9	14.7	0.1	14.7
1	45.4	48.2	-10.3	47.1
0	26.1	25.6	14.0	-21.4
-1	8.4	10.1	6.5	7.7
-2	14.3	14.7	-13.6	-5.6
-3	12.5	13.9	0.8	-13.9
-4	12.5	14.9	-10.2	10.9
-5	16.1	17.9	-14.7	-10.3
-6	7.9	9.7	5.4	8.1
-7	12.9	14.1	-13.4	4.3

H=1 L=1

7	17.0	12.6	12.5	-1.6
6	15.6	13.7	-12.1	-6.3
5	42.0	38.7	-6.7	-38.1
4	6.3	2.7	-0.2	-2.7
3	46.7	46.8	-29.7	-36.2
2	39.7	36.5	31.5	-18.4
1	53.3	53.2	-16.0	50.7
0	92.9	91.3	-39.2	82.4
-1	6.9	5.6	-5.0	2.4
10	12.0	8.8	4.2	-7.7
-10	8.6	9.3	-4.8	-8.0
-1	63.9	62.9	52.0	35.4
-2	49.8	48.9	-39.0	29.6
-3	22.8	19.3	10.1	-17.2
-4	12.9	15.0	-3.5	14.5
-5	22.1	19.5	-15.1	-12.3
-6	9.5	9.1	9.1	-0.4
-7	12.3	10.9	-7.1	8.2
-8	9.0	6.8	-3.6	-5.8
-9	8.6	7.4	5.2	5.2

H=0 L=7

-1	3.1	3.9	3.8	1.0

H=0 L=6

1	7.1	8.3	7.2	4.1
0	4.9	5.1	-4.9	1.4
-1	3.8	7.0	-6.9	1.1
-2	3.4	1.4	1.3	-0.6
-4	4.4	5.5	3.9	-3.8

H=0 L=5

7	5.	5.0	0.2	-5.0
4	5.2	1.4	0.9	-4.3
2	4.0	5.2	-3.0	-4.2
1	4.7	3.6	3.2	1.1
0	5.8	6.4	-2.3	6.1
-1	6.4	7.4	5.7	-4.7
-2	14.2	15.7	2.1	15.5
-3	11.0	13.6	-6.4	11.7
-5	5.8	3.7	-2.8	2.4

H=0 L=4

7	6.4	5.1	-2.6	-4.3
5	6.6	4.8	4.3	-1.9
3	9.0	8.5	-7.9	3.2
1	6.7	3.1	2.4	2.0
0	11.2	10.2	-8.7	-8.2
-2	16.7	20.9	14.8	14.8
-3	6.2	7.2	-2.1	6.9

TABLE 2—*continued*

H=0 L=3

9	7.3	6.0	3.2	-5.1
8	7.9	7.0	4.9	0.0
6	6.7	4.3	3.2	2.8
5	9.6	7.3	-4.1	0.0
4	15.2	15.4	-8.3	-12.9
3	9.3	9.5	7.0	5.8
2	16.3	17.0	-10.8	-5.3
-2	14.4	15.3	12.1	9.3
-3	17.3	19.0	-12.9	13.9
-4	15.7	16.9	8.8	-14.4
-5	8.1	5.5	5.4	0.6
-6	10.8	8.8	-7.9	-4.0
-7	8.4	8.1	5.2	-6.2
-8	5.9	5.5	-4.9	2.5
-9	10.2	9.9	-9.2	-3.7

H=0 L=2

7	10.4	12.3	-10.0	-7.2
6	22.7	24.8	22.8	-9.9
5	22.8	24.0	14.9	18.9
-7	11.7	14.6	9.7	-13.4
-8	8.7	9.2	8.3	4.1
-9	8.7	7.8	-0.7	-7.8

H=0 L=1

10	10.4	7.6	2.1	7.3
8	6.9	8.9	8.9	-9.0
7	18.1	14.8	-13.5	-5.0
6	19.6	18.1	-11.4	-14.1
5	13.7	10.9	-4.9	9.8
4	40.0	37.8	-12.1	-35.8
3	71.9	67.9	56.3	-37.9
2	99.1	93.4	12.8	92.8
-2	6.4	9.2	2.4	-8.9
-3	21.0	21.0	-2.1	20.9
-4	32.2	31.4	-9.2	-30.0
-5	13.5	14.0	10.7	-9.0
-6	9.1	11.4	-5.7	9.8
-7	10.9	9.8	7.0	-8.1
-8	11.9	10.3	9.8	3.0
-9	14.2	12.8	-12.6	1.9
-10	8.0	7.6	5.0	-5.8

H=-1 L=7

-2	2.8	1.2	-0.7	-1.0
-3	4.8	3.9	3.5	3.8

H=-1 L=6

-2	5.1	3.3	-0.5	-3.3
-4	4.6	4.5	-4.1	1.8

H=-1 L=5

9	6.4	4.1	-3.8	-1.4
7	5.6	3.9	4.3	3.2
5	5.1	3.9	3.0	-0.8
4	7.9	4.5	-1.2	4.4
-2	6.1	8.0	-4.0	-6.5
-3	4.7	5.6	0.3	-5.5
-4	6.4	2.2	-1.4	-1.7
-5	7.0	5.4	-2.1	-5.0
-7	6.8	4.9	-4.7	1.5

H=-1 L=4

10	7.9	5.0	-3.9	-3.0
9	7.2	3.5	-3.5	-0.5
8	9.4	8.3	-4.5	-8.9
7	5.6	0.6	-0.6	0.1
6	5.7	6.2	-5.9	-2.0
5	6.4	7.8	3.7	-8.9
4	9.4	8.9	3.4	8.2
3	6.3	4.1	-4.0	-0.9
-2	3.1	7.2	5.7	4.3
-3	18.1	18.0	10.3	-8.9
-4	12.8	13.7	9.7	12.4
-5	4.8	4.3	0.4	-4.3
-6	5.5	7.5	0.3	-3.7
-7	9.1	8.8	-8.8	-0.2
-8	7.2	4.7	-3.2	-3.4
-9	6.0	0.3	0.3	-6.0

H=-1 L=3

10	11.8	8.8	7.2	-5.1
9	8.0	4.6	-0.6	4.6
8	10.8	11.2	-13.9	2.5
7	8.4	5.9	2.7	-5.2
5	19.7	14.8	0.2	-14.8
4	10.8	11.6	11.2	2.9
3	11.5	14.3	-8.7	-11.4
2	22.7	24.0	20.3	-12.8
-2	10.4	8.2	-8.8	0.0
-3	26.7	28.4	11.3	-26.0
-4	16.8	17.4	16.8	4.7
-5	7.7	2.6	-2.6	0.6
-6	9.2	9.4	9.4	-1.0
-7	8.8	8.0	-4.2	6.8
-8	9.1	7.7	-5.0	-5.4
-10	7.2	5.2	-4.9	-1.7

H=-1 L=2

9	8.6	3.6	3.3	1.0
8	10.2	9.1	-3.6	-8.3
7	19.8	20.9	20.6	-3.9
6	25.2	26.8	6.5	26.0
5	16.8	18.7	-17.9	-5.4
4	6.6	7.9	7.5	2.2
3	14.8	14.9	-5.1	14.0
2	22.0	24.3	7.9	-22.9
-2	12.0	13.4	4.8	12.5
-3	20.9	19.5	10.2	-16.8
-4	21.3	22.1	19.5	10.4
-5	28.1	29.4	-29.2	-3.4
-6	17.3	16.3	4.5	-15.6
-7	9.4	8.4	-1.3	6.2
-8	8.3	6.9	-6.9	0.2

H=-1 L=1

10	7.7	6.4	-5.7	-3.0
9	6.6	5.4	5.0	1.4
5	29.0	27.9	-11.2	-25.6
4	49.7	48.3	42.0	23.9
3	73.5	69.5	-11.9	69.4
2	31.1	27.5	-27.3	3.3
-2	23.4	22.4	19.1	11.0
-3	36.3	36.1	-20.1	-29.9
-4	32.0	33.7	31.4	12.2
-5	16.8	17.1	1.7	17.3
-6	22.9	21.7	8.4	-20.1
-7	20.0	19.0	1.1	19.0
-8	16.7	12.8	-10.4	-6.7
-9	10.3	7.6	3.6	-6.0
-10	8.4	5.8	1.5	5.6

H=-1 L=0

8	11.3	13.9	-8.6	12.1
7	9.5	9.9	-8.5	-5.0
6	23.3	22.4	12.2	18.4
5	14.9	18.1	-17.3	5.5
4	16.9	20.1	12.3	-15.8
3	42.7	43.2	-33.7	27.1
2	84.2	85.3	44.3	-72.4
-2	24.3	23.2	19.2	13.0
-3	19.9	23.0	-23.0	1.5
-4	8.3	3.7	0.7	-3.7
-5	34.8	37.6	-1.2	37.5
-6	4.7	8.7	5.2	-7.0
-7	18.9	18.8	18.7	1.9
-8	12.9	11.5	-9.9	5.9
-9	11.0	12.4	12.4	-0.4

H=-2 L=6

3	4.9	4.5	1.7	4.2
-2	4.8	2.8	2.1	1.4
-4	5.3	4.4	0.1	-4.4
-7	5.9	4.2	3.5	-2.1

H=-2 L=5

5	7.1	6.5	-6.2	2.1
4	7.5	5.4	-0.5	-5.3
-2	5.2	3.1	1.0	0.9
-3	10.8	11.2	-6.2	9.1
-5	6.9	4.2	4.1	0.8
-6	5.3	3.5	-3.1	1.5
-7	7.1	3.2	3.1	1.1
-9	11.9	4.9	-0.4	-4.4

H=-2 L=4

10	10.4	1.7	-1.4	1.0
9	6.4	1.0	-0.6	3.0
8	7.8	11.1	10.2	-4.3
5	5.6	6.0	4.0	4.5
4	10.8	8.6	-4.6	-7.2
3	7.6	6.2	2.0	5.9
-2	14.2	12.2	8.4	-8.8
-3	10.2	4.6	0.2	4.6
-4	6.2	7.0	-1.5	-6.8
-5	13.5	11.4	9.3	0.7
-6	11.1	9.7	-7.1	6.6
-7	5.7	3.9	2.6	-2.9
-8	9.3	8.3	5.8	5.9
-10	8.4	2.8	-0.3	-2.8
-11	13.0	0.6	-0.2	-0.6

H=-2 L=3

10	15.5	12.0	-2.5	11.7
9	11.7	11.1	-10.8	2.4
7	10.2	10.2	-5.7	8.4
6	6.8	0.5	-0.1	0.5
5	11.8	12.8	9.3	8.7
4	5.7	6.9	-0.3	-6.9
3	20.9	21.6	20.9	-5.4
2	18.2	17.1	-1.1	17.0
1	8.3	6.6	2.2	-6.2
0	9.3	7.3	3.5	6.4
-1	23.5	24.4	-20.9	12.6
-2	48.7	48.3	19.0	-44.4
-3	16.6	18.0	17.3	-4.8
-4	20.0	19.2	-5.3	-18.5
-5	14.8	13.4	11.9	-6.1
-6	9.7	8.4	-5.7	6.2
-7	9.6	1.9	-1.2	1.4
-8	17.3	15.2	4.5	14.5
-9	7.1	9.5	-5.8	7.4
-10	14.7	4.4	4.3	-0.6

H=-2 L=2

10	7.4	3.8	-3.8	-0.3
9	9.2	7.5	-7.4	-0.7
8	10.7	10.8	9.4	5.4
7	22.7	24.6	-8.7	23.1
6	20.2	22.0	-19.9	-9.4
5	18.3	18.4	8.3	-16.3
3	14.3	15.1	7.9	12.9
1	9.9	12.1	-3.7	-11.5
0	27.3	28.9	28.9	-0.2
-1	24.0	26.4	-20.9	18.2
-2	11.8	12.0	-1.1	-11.9
-3	10.1	11.4	0.9	11.4
-4	29.0	29.1	-28.7	-4.8
-5	21.0	22.1	9.6	-19.9
-6	17.1	17.5	8.0	15.5
-7	6.1	6.2	-3.3	-5.2
-8	9.3	9.7	5.6	7.9
-9	9.4	9.6	-3.1	9.1
-10	10.7	2.3	2.3	0.2
-11	6.7	5.3	1.4	5.5

H=-2 L=1

11	7.9	2.5	0.2	-2.4
10	8.2	5.3	5.1	-1.3
9	9.9	8.9	-6.3	-2.6
7	8.3	9.0	-7.0	5.7
6	11.4	12.0	1.1	-11.9
5	21.6	22.2	21.6	-5.1
4	40.3	39.7	-24.2	31.4
3	40.3	39.9	-21.6	-32.3
2	12.6	15.7	12.6	9.3
1	36.4	37.0	-37.0	-2.0
0	15.5	16.7	13.2	-10.2
-1	35.6	34.2	-11.1	32.4
-2	22.3	21.2	-19.4	-7.6
-3	33.8	30.5	23.5	19.5
-4	15.6	12.0	-31.7	4.4
-5	12.7	12.3	0.6	12.2
-6	18.1	19.0	3.0	18.8
-7	11.3	11.5	-11.5	-0.9
-8	13.6	13.4	10.8	-7.2

H=-2 L=0

8	9.0	11.2	1.6	-11.1
7	8.2	6.4	4.1	4.9
6	19.2	18.5	-14.6	-7.6
5	10.2	8.0	8.0	1.1
4	4.0	3.5	-3.3	-1.2
3	21.6	18.7	-16.6	-8.6
2	42.0	41.1	38.2	15.2
1	40.2	39.7	-33.4	21.4
0	57.2	53.1	-15.2	-50.9
-1	27.4	25.5	-2.6	25.4
-2	41.8	40.3	-33.8	-21.9
-3	27.2	25.8	25.2	-5.7
-4	19.1	18.9	1.9	18.8
-5	28.9	24.3	-7.0	-23.3
-6	15.6	13.5	-1.8	13.3
-7	5.3	4.9	-4.8	-1.1
-8	5.8	6.0	-1.2	-5.9
-9	6.2	9.3	-5.1	7.8

H=-3 L=7

2	6.2	1.5	1.2	-0.9
-3	4.5	3.3	3.2	-0.8

H=-3 L=6

4	5.0	2.9	0.4	2.8
3	5.3	2.9	-2.8	-0.8
2	5.9	4.5	3.9	-2.2
-1	4.3	4.0	3.9	0.8
-2	3.6	0.7	-0.6	0.4
-4	4.9	3.3	3.2	0.8
-6	7.1	2.7	2.6	0.7
0	9.0	6.2	-2.2	-5.8

H=-3 L=5

5	7.9	6.0	-0.4	-7.9
4	10.5	7.8	6.8	3.8
2	8.2	4.9	2.7	-4.0
1	7.5	5.0	1.2	4.9
0	6.6	5.9	-2.2	-5.5
-1	6.9	6.1	4.3	4.4
-2	10.9	9.7	-6.5	7.1
-3	6.8	7.4	0.7	-7.4
-4	6.9	5.3	0.9	5.2
-5	5.8	5.7	-1.9	5.4
-6	8.1	5.4	2.6	-4.9
-7	5.7	2.6	-2.6	-0.0

H=-3 L=4

8	8.6	4.6	-4.5	-0.6
6	8.1	9.3	-5.7	7.4
5	8.3	4.6	-4.0	2.2
4	8.4	9.7	9.0	3.7
3	16.7	15.8	-15.1	4.8
1	17.9	17.2	15.2	8.0
0	9.2	6.8	-6.4	2.3
-1	12.2	8.5	8.5	0.1
-2	14.8	13.3	-3.6	12.8
-4	10.2	8.5	7.8	3.5
-5	15.0	14.6	-14.4	2.5
-6	8.2	3.0	0.8	-2.9
-7	5.7	6.2	5.3	3.3
-9	7.9	1.0	-0.3	-0.9

H=-3 L=3

9	18.9	8.2	8.2	0.6
8	14.2	2.0	0.4	2.0
5	14.0	13.6	-13.4	-2.3
3	14.1	14.4	-6.7	12.8
2	20.0	19.9	-12.3	-15.6
1	29.8	27.7	9.7	25.9
0	17.1	19.3	-16.1	-10.6
-1	27.6	27.4	2.0	-27.3
-2	13.9	14.6	-6.0	13.3
-3	16.8	16.5	-16.5	-1.1
-4	12.7	12.3	11.8	3.6
-5	7.6	7.1	-5.3	4.7
-6	5.6	4.6	-0.4	-4.5
-7	11.4	12.6	8.3	9.5
-8	9.8	1.2	-0.7	-1.0

H=-3 L=2

9	12.2	12.2	10.2	6.7
8	11.2	11.5	3.7	10.9
7	8.2	8.7	1.3	-8.7
6	13.7	13.0	13.0	0.5
5	14.7	12.4	-10.6	-6.4
4	21.4	23.0	-2.7	-22.8
3	14.7	15.5	-15.4	-2.0
2	31.9	34.0	-32.4	-10.4
1	4.7	5.7	-1.1	-5.5
0	31.8	31.0	-24.1	19.4
-1	26.3	28.1	1.2	-28.1
-2	19.4	16.8	-15.3	6.9
-3	42.1	44.1	-42.6	-11.6
-4	13.1	11.6	3.5	-11.1
-5	11.0	12.6	-3.8	12.0
-6	10.6	8.6	-4.4	-7.4
-7	19.2	20.2	17.0	11.0

TABLE 2—*continued*

H=-3 L=1

10	7.0	6.5	-0.4	1.1
8	11.3	9.0	5.3	7.2
7	13.2	12.4	0.9	-12.4
5	15.7	16.3	-11.9	11.1
4	25.3	24.9	2.5	-24.7
2	38.7	35.8	-31.7	-16.5
1	17.1	15.9	15.3	-4.3
0	20.5	21.3	-0.1	21.3
-1	9.6	11.0	-8.3	-8.1
-2	11.8	9.8	5.7	-8.0
-3	18.5	17.9	-15.7	8.8
-4	28.3	25.3	7.0	-24.3
-5	8.0	8.1	-3.0	7.5
-6	23.1	21.4	-13.3	-16.7
-7	10.0	8.0	7.3	-3.3
-8	10.9	9.1	-0.5	9.1
-9	9.5	9.5	0.2	-7.2
-10	9.6	6.6	9.1	2.0

H=-3 L=0

10	5.4	4.7	-3.9	-2.0
8	8.1	9.2	-2.3	8.9
7	7.9	5.3	-5.2	1.3
6	20.6	19.3	8.4	-17.4
5	25.8	23.0	-15.9	17.5
3	25.4	26.7	25.7	-9.3
2	7.9	12.2	-10.0	-7.0
1	27.4	25.9	24.7	-8.0
0	37.8	36.8	24.1	27.8
-1	30.4	27.0	9.5	-27.0
-2	33.7	34.5	34.4	-3.0
-3	12.8	13.4	-8.9	11.5
-4	10.4	10.0	-10.0	1.1
-5	20.0	19.8	17.7	-9.0
-6	18.7	17.2	-14.1	-9.9
-7	9.5	11.1	3.8	-9.4
-8	6.9	6.9	-0.1	3.3
-9	5.0	6.0	-0.2	-5.1

H=-4 L=7

0	4.1	1.4	-1.2	0.0
-2	5.2	4.0	3.0	3.0

H=-4 L=6

3	5.8	2.9	2.3	1.0
2	8.8	3.7	-3.0	1.0
1	8.8	7.5	-4.3	-8.7
-1	8.2	5.8	-5.8	-0.1
-4	6.4	1.0	-0.8	0.8
-6	7.1	3.8	-3.4	1.3

H=-4 L=5

5	8.9	8.9	0.4	3.5
4	8.4	7.0	-6.0	3.7
2	7.1	3.8	-2.8	2.3
1	11.8	8.8	-7.2	-5.1
-1	10.2	7.7	-7.5	1.8
-2	10.1	9.8	-1.3	-9.5
-3	7.3	6.0	3.9	5.0
-4	10.2	8.0	-8.4	-8.8

H=-4 L=4

9	14.8	1.3	-1.3	-0.3
8	9.1	3.0	-0.1	-3.0
6	7.2	8.8	-0.3	-8.8
5	7.4	3.9	0.0	3.9
4	5.7	6.0	-5.9	-1.2
3	11.8	11.3	1.7	-11.2
2	9.5	10.3	0.0	8.4
1	12.7	11.8	-11.0	-4.2
0	5.9	4.1	0.8	-4.1
-1	14.6	13.5	-7.1	11.5
-2	10.9	8.8	0.1	-8.8
-3	9.2	5.4	4.4	3.1
-4	11.7	10.4	-7.2	7.4
-8	15.6	11.2	8.8	-8.9
-6	9.4	5.8	-3.8	4.5
-7	8.0	5.4	-4.3	-2.9
-9	8.6	2.9	-0.2	2.9

H=-4 L=3

7	8.0	5.8	3.1	4.9
5	11.7	12.4	8.8	-9.0
4	9.9	10.4	-9.9	-3.1
3	9.2	11.0	5.9	-9.3
2	7.6	7.7	7.6	1.5
1	13.8	13.8	-12.0	-6.7
0	15.2	15.3	9.9	-11.7
-1	13.6	13.4	4.3	12.7
-2	10.0	8.7	-5.6	-6.7
-3	13.5	15.0	14.4	-4.1
-4	17.4	17.8	-10.7	6.2
-5	7.6	5.8	-1.5	-5.6
-6	11.6	11.5	11.0	3.5
-7	12.1	9.5	-7.9	-5.2
-9	7.7	5.6	-4.6	3.9

H=-4 L=2

10	9.0	7.0	6.9	-0.9
9	6.6	3.7	1.6	-3.4
8	9.7	7.0	0.7	-6.9
7	8.2	8.5	0.7	5.3
6	7.4	8.4	-7.9	2.9
5	5.3	5.5	4.8	-2.7
4	18.5	21.3	-3.2	21.1
3	14.9	14.4	-13.4	-5.1
2	6.4	9.7	9.6	1.2
0	14.6	19.6	7.5	-18.1
-1	16.9	19.4	6.9	18.1
-2	7.7	7.2	-6.4	-3.3
-3	15.2	16.5	10.1	-3.6
-4	7.7	6.7	-4.8	4.6
-5	13.4	10.1	-6.7	-14.6
-6	9.7	10.3	9.7	3.3
-7	7.7	8.7	-7.8	-3.8
-8	14.8	15.0	-0.3	-15.0

H=-4 L=1

10	10.6	6.2	5.5	-3.0
9	10.1	5.9	5.9	-0.3
8	11.2	9.9	1.0	-9.9
7	8.3	8.5	8.3	-1.8
6	28.9	28.8	-8.6	25.4
3	32.7	30.2	-22.0	20.8
2	23.7	23.9	20.6	12.1
1	27.2	26.3	-4.1	26.3
0	19.4	20.9	-14.7	-14.9
-1	14.5	14.3	13.5	-4.9
-2	13.5	9.7	-9.3	-2.9
-3	14.9	13.6	12.7	-4.6
-4	19.8	19.4	4.0	19.3
-5	8.4	6.3	-0.9	-8.3
-6	11.4	11.6	11.4	-6.2
-8	13.5	16.7	8.7	-16.1

H=-4 L=0

9	5.9	6.0	1.5	5.8
8	7.8	7.9	-1.0	-7.8
7	5.3	6.3	6.0	-1.9
6	12.3	11.7	1.0	11.3
5	11.9	13.1	3.4	-12.6
4	9.8	3.9	3.8	-0.9
3	13.7	10.4	-8.6	5.5
2	15.2	15.7	10.4	11.8
1	21.2	20.0	3.2	19.7
0	15.8	15.1	-10.0	-11.4
-1	15.3	17.9	17.8	-6.8
-2	28.4	27.4	-11.8	26.7
-3	23.8	21.9	-9.8	-21.1
-4	4.9	5.4	-4.5	3.1
-6	8.6	10.1	10.1	0.1
-7	8.5	9.6	3.0	9.2
-9	6.9	5.3	4.9	-1.9

H=-5 L=6

3	8.2	4.1	-4.1	-0.2
1	8.8	5.5	1.3	5.8

H=-5 L=5

4	9.1	8.8	4.5	-4.8
2	9.9	7.4	-5.3	-5.2
1	7.0	4.4	-0.4	4.3
0	12.5	10.6	-4.4	4.8
-2	8.0	6.2	-2.6	5.8
-3	5.9	4.0	-4.0	-0.3
-4	9.3	8.9	8.3	-3.3
-8	8.3	2.6	-0.5	-2.5

H=-5 L=4

8	8.9	8.3	8.1	1.9
4	5.6	6.3	5.1	-2.7
3	9.0	7.1	1.8	5.9
2	6.7	8.2	-7.5	-3.4
1	6.1	5.7	5.4	1.7
0	9.4	11.8	-7.4	9.1
-1	9.3	10.0	-2.1	-9.8
-2	8.7	9.4	6.8	6.6
-3	7.7	2.2	-2.0	-0.7
-6	8.8	8.3	-1.9	-8.1
-7	7.3	6.2	6.2	-0.1
-8	7.6	1.6	-1.6	-0.1
-9	12.2	3.6	-1.4	-3.3

H=-5 L=3

9	6.7	2.7	1.0	-2.5
8	11.1	4.7	-1.2	4.5
4	10.0	7.5	3.3	-6.7
3	14.8	13.6	7.0	11.6
1	12.3	11.4	10.6	-4.2
0	9.3	10.5	-2.1	10.3
-1	10.2	10.4	0.4	-10.4
-2	13.2	14.2	14.2	-0.5
-3	9.2	9.6	-9.3	2.3
-4	19.1	20.4	9.6	-18.0
-9	7.3	4.7	0.5	-4.7

H=-5 L=2

5	10.7	11.6	-7.0	9.3
4	7.7	6.9	-6.8	-1.2
3	7.4	8.8	7.0	-4.9
1	14.4	13.9	12.7	-5.6
0	12.0	11.9	7.7	9.0
-1	9.4	11.3	-10.8	-3.3
-2	8.2	8.9	8.2	3.5
-4	5.9	5.8	-0.5	-5.7
-5	10.3	14.6	11.1	9.4
-6	9.9	10.5	-10.5	-0.9

H=-5 L=1

9	6.5	5.9	-4.8	-3.5
5	12.6	11.4	3.8	10.7
3	13.7	12.3	11.6	4.1
2	22.8	22.5	-11.9	19.1
1	13.0	12.2	-8.2	-9.0
-2	11.5	7.7	7.7	0.3
-3	14.9	15.3	2.4	15.1
-4	7.5	7.5	-7.5	0.1
-5	9.7	9.4	-0.5	9.3
-6	10.2	8.8	-7.4	4.7
-7	7.9	6.1	0.7	-6.1
-9	9.7	7.8	-7.7	-1.2

H=-5 L=0

9	7.5	6.5	-2.3	-0.1
7	9.5	6.1	-5.8	1.9
5	7.4	5.3	-4.6	-2.7
5	11.7	9.9	6.3	7.6
4	11.5	10.1	3.4	9.6
3	14.1	10.2	15.9	8.8
2	10.5	13.9	9.1	12.9
1	9.0	9.1	-8.3	-3.8
0	10.2	12.9	9.1	9.2
-1	19.1	19.2	-18.6	4.7
-2	11.2	13.0	-9.2	-9.1
-3	9.7	8.2	7.7	2.7
-6	7.6	5.3	1.5	-5.1
-9	7.9	7.6	-7.5	-1.4

H=-6 L=6

0	7.5	4.0	2.5	-3.1
-1	5.8	1.8	-1.4	1.1

H=-6 L=5

2	11.7	10.0	8.0	6.0
1	8.7	7.0	4.1	5.7
-1	6.6	1.7	-0.4	1.7
-2	7.3	7.3	-1.6	-7.1

H=-6 L=4

6	9.3	4.9	-4.8	1.0
3	7.2	4.6	-2.2	-3.9
2	9.9	7.4	4.9	5.6
1	13.2	12.7	-1.1	12.6
0	13.8	10.7	10.7	-0.1
-1	14.0	16.0	15.1	5.3
-2	9.6	9.0	-2.5	8.6
-4	7.5	8.5	-5.7	-3.1

H=-6 L=3

7	7.5	6.4	6.3	-1.2
4	8.0	7.0	3.3	6.2
3	5.9	5.9	-8.2	-2.7
1	10.9	9.4	-7.0	6.3
0	6.0	3.5	2.1	-2.8
-1	7.9	11.7	8.3	8.2
-2	6.6	6.5	-6.4	1.4
-4	16.3	15.7	11.3	10.9

H=-6 L=2

5	9.8	11.0	-3.7	-10.4
1	9.0	8.1	-6.2	8.2
0	10.5	11.2	-11.1	0.9
-2	13.3	13.3	-13.2	-0.8
-6	11.8	11.0	8.1	-7.5
-7	7.7	8.3	2.9	7.7

H=-6 L=1

6	7.6	7.2	7.0	1.7
3	7.9	6.4	-4.5	4.5
2	9.6	11.5	0.2	-11.5
1	7.1	3.7	2.8	-2.4
0	6.3	6.3	-6.3	0.0
-1	6.3	3.0	2.8	1.1
-2	7.6	5.4	6.8	5.4
-3	7.2	8.3	-7.7	-3.3
-5	7.1	5.2	-4.4	-2.7

H=-6 L=0

5	7.5	7.0	-4.8	-5.2
4	11.5	9.9	8.8	-4.6
3	8.0	7.0	6.5	2.7
2	6.2	7.7	7.2	-2.7
1	8.8	7.2	7.2	-0.8
-1	8.6	8.5	0.6	-8.5
-3	5.1	4.4	-3.7	-2.4

H=-7 L=5

3	7.5	4.8	4.2	2.2
2	6.6	4.9	-3.8	3.1
0	7.5	3.0	-3.0	-0.2

H=-7 L=4

1	13.6	12.9	3.1	-12.8
0	8.5	5.8	3.2	4.9

H=-7 L=3

4	6.8	4.3	-4.1	-1.3
2	8.4	1.8	0.4	1.7
1	12.3	12.2	9.8	-7.2
0	12.6	11.0	9.1	-6.2
-2	9.5	9.9	8.1	-5.6
-4	11.3	12.3	-11.7	3.9
-5	6.5	5.6	-3.8	4.1

H=-7 L=2

2	6.2	5.4	-1.3	5.2
0	6.9	6.3	6.2	-1.0
-2	7.2	7.2	2.3	-6.9
-3	7.1	6.3	5.0	3.8
-4	7.6	8.5	-3.2	-7.9

H=-7 L=0

5	11.5	10.6	9.8	-4.1
4	6.3	4.5	4.5	-0.1

H=-8 L=3

2	6.8	6.7	-0.0	-6.7
-1	7.2	5.2	4.1	-3.2

H=-8 L=2

0	10.1	8.4	-7.7	-3.3
-1	8.1	2.1	-0.3	-2.1
-2	6.5	0.8	0.8	0.1

H=-8 L=0

4	5.2	4.0	-2.7	3.0

H=0 L=0

11	7.1	8.4	-0.2	-8.4
9	7.4	5.2	-4.1	3.2
8	10.8	12.8	12.8	-1.0
7	11.8	11.9	-0.8	10.3
6	16.2	20.0	-18.5	-9.6
5	15.0	17.0	-0.1	15.9
4	16.3	20.0	-18.2	8.4
3	11.2	10.6	6.3	-15.4
2	17.3	21.4	18.4	17.5

Indices h and l are listed at the top of each group. In each column k, F_{obs}, F_{calc}, A, and B are given.

The weighting function used was:

$$\sqrt{w} = 1/F_{obs}, \qquad \text{where } F_{obs} > 15.0,$$

$$\sqrt{w} = 1/F_{obs}\ 15.0, \qquad \text{where } F_{obs} < 15.0$$

The quantity minimized was:

$$\sum w(k^2|F_{obs}|^2 - |F_{calc}|^2)^2.$$

After two cycles of diagonal matrix refinement with anisotropic temperature factors for the bromine atom, the weighted R value was 0.06, the unweighted R was 0.16. Four cycles of full matrix least-squares treatment using a shift factor of 0.3 resulted in converged weighted and unweighted R values of 0.04 and 0.14, respectively.

The largest peak in the final difference Fourier synthesis was 0.8 $e/Å^3$, indicating that all of the significant density was accounted for by the molecular model. Final atomic

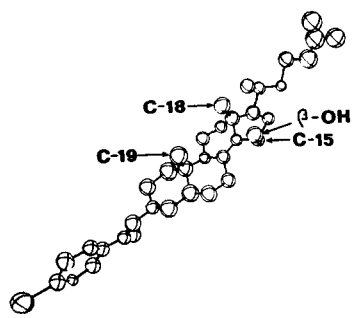

FIG. 2. Computer (ORTEP) drawing of final positional and thermal parameters of the crystal structure of 3β-*p*-bromobenzoyloxy-cholest-8(14)-en-15β-ol.

coordinates and temperature factors, along with estimated standard deviations as calculated by the variance method, are given in Table 1. Final observed and calculated structure factors are given in Table 2. The atomic numbering scheme and a projection of the molecule displaying relative positions and thermal ellipsoids are given in Figs. 1 and 2. The configuration of the hydroxyl group at the 15-position has been determined to be β.

These results establish that hydroxyl function of the epimer of cholest-8(14)-en-3β,-15ξ-diol which has arbitrarily been designated as diol B has the 15β-configuration. The 15-hydroxyl group of diol A therefore has the 15α-configuration.

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