Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.24; H, 6.87; N, 12.46. Found: C, 71.33; H, 6.86; N, 12.60.

Hydrogenation of **21** in 95% ethanol with 5% Pd/charcoal as catalyst yielded, after evaporation of solvent, a solid, mp 164–166°, whose mass spectrum has molecular ion peak *m/e* 339.1946 (calcd for **23**, 339.1946) with abundant fragments at 242.

Infrared shows no peak from 3600 to 3100 cm^{-1} (no N–H stretch), and NMR shows no peak from δ 4.5 to 7.5 (no vinylic protons).

4-Phenyl-1,2,4-triazoline-3,5-dione with Diene 1a. To 74 mg (0.50 mmol) of diene **1a** in 5 ml of acetone, at 0°, was added dropwise a solution of 88 mg (0.5 mmol) of the dienophile in 2 ml of acetone. The red color disappeared instantly. The diene peak at 262 nm disappeared on the uv, and TLC (85:15 ether–benzene, with a drop of triethylamine) showed only one spot, R_f 72. Evaporation of solvent and recrystallization from ether–pentane yielded one product in quantitative yield, mp 143–145°, identified as the Diels–Alder adduct, **20**: ir (KBr) ν 1750 (s), 1700 (s), 1440 (m), 1390 (s), 765 (s), 750 (m), 725 (m), and 690 cm^{-1} (m); NMR (acetone-d_6) δ 1.90 and 1.85 (2 s, 3 H, CH_3-1, two kinds), 4.55 and 4.62 (2 m, 1 H), 6.1–6.8 (six lines, 2 H), 7.40 (s, 5 H); mass spectrum M^+ 323.1633 (calcd, 323.1636) exhibiting retro-Diels–Alder reaction at *m/e* 241 (− cyclohexene).

Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.62; H, 6.55; N, 13.00. Found: C, 70.30; H, 6.51; N, 12.72.

Acknowledgment. We thank Professor Robert B. Fairweather for stimulating discussions concerning this project and help in spectra interpretations.

Registry No.—**1a**, 54306-51-3; **1b**, 54306-52-4; **3a**, 21102-88-5; **3b**, 22738-31-4; **4**, 56770-99-1; **5b**, 56763-83-8; **6a**, 56771-00-7; **6b**, 56763-86-1; **7a** isomer A, 56771-01-8; **7a** isomer B, 56771-02-9; **7b** isomer A, 56771-03-0; **7b** isomer B, 56771-04-1; **8**, 56771-05-2; **11**, 707-11-9; **12**, 56771-06-3; **13**, 2809-64-5; **14** isomer A, 56771-07-4; **14** isomer B, 56816-07-0; **15**, 56771-15-4; **16** isomer A, 56771-08-5; **16** isomer B, 56771-09-6; **17**, 56771-10-9; **18**, 4242-05-1; **19**, 4233-33-4; **20**, 56771-11-0; **21**, 56771-12-1; **22**, 56771-13-2; **23**, 56771-14-3.

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A Synthesis and X-Ray Structure Determination of the Photoproducts of *A*-Homocholestan-3-one

T. Akiyama,[1a] D. Pedder,[1b] and J. V. Silverton

Laboratory of Chemistry, NHLI, National Institutes of Health, Bethesda, Maryland 20014

Jeffrey I. Seeman[1c] and Herman Ziffer*

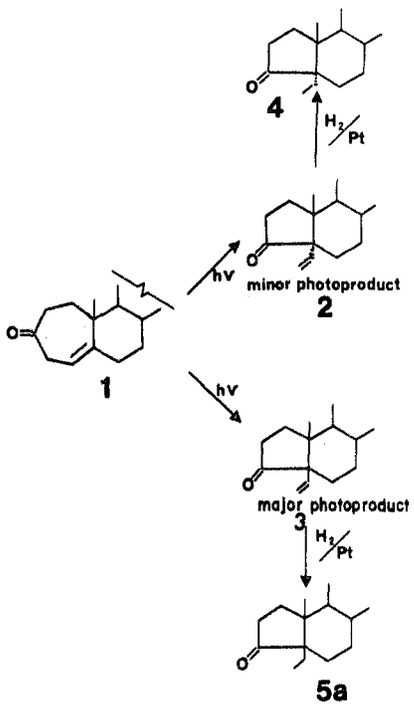
Laboratory of Chemical Physics, NIAMDD, National Institutes of Health, Bethesda, Maryland 20014

Received March 10, 1975

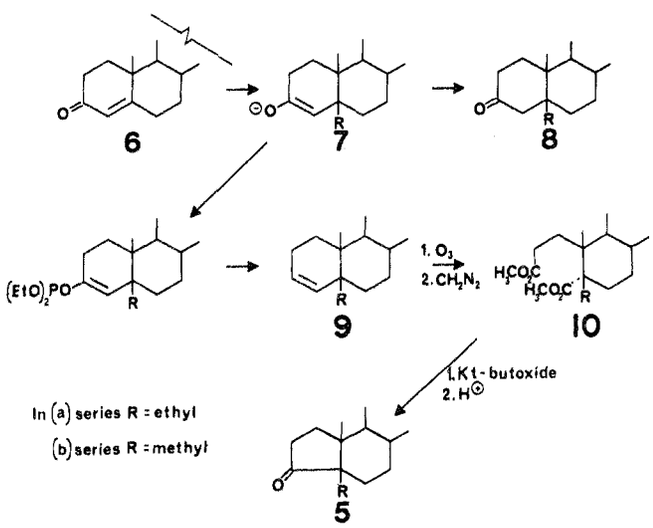
The stereochemistry assigned to the major (**3**) and minor (**2**) photoproducts of *A*-homocholest-4a(5)-en-3-one has been reinvestigated. The synthesis of 5β-ethyl-*A*-norcholestan-3-one is described; the compound is shown to be identical with the dihydro derivative of the major photoproduct. The synthesis of 5β-methyl-*A*-norcholestan-3-one is also described. The minor photoproduct, $C_{28}H_{46}O$, 5α-vinyl *A*-norcholestan-3-one, crystallizes in space group $P2_1$ with cell dimensions a = 10.429 (1), b = 7.369 (1), c = 15.605 (2) Å, β = 94.28 (2)°, and Z = 2. The structure was solved via the calculation of structure invariants and has been refined to a conventional R factor of 0.036. The relation of the absolute stereochemistry and the sign of the CD curves of the major and minor photoproducts and their dihydro derivatives are discussed.

The photochemistry of *A*-homocholest-4a(5)-en-3-one (**1**) and its photoproducts **2** and **3** have proven to be a rich source of mechanistic photochemical information.[2] The specificities of the observed oxadi-π-methane rearrangements and photoisomerizations of the β,γ-unsaturated ketones are summarized in Scheme I and are important in understanding the stereochemical consequences of these photoisomerizations. An essential aspect of these mechanistic evaluations centers on the stereochemical assignment of the major (**3**) and minor (**2**) photoproducts from the direct irradiation of **1**. A previous study of this system by Fisher and Zeeh[3] in 1969 led them to a set of structural assignments based on interpretations of the NMR and CD spectra of the photoproducts. In order to determine the stereochemistry of these compounds unequivocally, parallel studies of the synthesis of **5a** and an X-ray crystallographic structure determination of the minor photoproduct (**2**) were undertaken.

Scheme I



Scheme II



Synthesis. The syntheses of 5β-ethyl-*A*-norcholest-3-one (**5a**) and 5β-methyl-*A*-norcholestan-3-one (**5b**) followed the same general procedure and are shown in Scheme II. The key feature of these syntheses is the stereoselective introduction of the β-alkyl substituent at C-5 by the addition of a lithium dialkylcopper reagent to Δ^4-cholesten-3-one (**6**). While the factors which govern the stereochemistry of this addition are not completely understood, Ireland et al.[4] have shown that the addition of lithium dimethylcopper to **6** results in the formation of only the 5β-methyl derivative **8b**. That lithium diethylcopper introduces a 5β-ethyl group was proven by comparison of the CD curves of **8a** and **8b** (Table I) formed by quenching intermediates **7a** and **7b**, respectively, with water. Alternatively, treating **7a,b** with diethyl phosphochloridate followed by reduction of the intermediate phosphonate gave **9a,b** with the established 5β-alkyl configuration. Subsequent steps in the syntheses (ozonolysis, esterification, Dieckmann condensation, hydrolysis, and decarboxylation) do not affect the configuration at C-5. A comparison of

Table I
CD Data in Methanol

Compd	CD θ	CD (λ)	Comp	CD θ	CD (λ)
2	−13400	(300)	5b	+3960	(300)
3	+10000	(300)	8a	−950	(290)
4	−4200	(295)	8b	−1075	(240)
5a	+2620	(305)			

spectral characteristics and physical properties of **5a** and the dihydro derivative of **3** showed them to be identical and quite different from the dihydro derivative of **2**. These assignments *contradict* those made previously by Fisher and Zeeh.[3]

X-Ray Structure of the Minor Photoproduct. The bond lengths, valence angles, and torsion angles for the minor photoproduct are shown in Figures 1–3. Esd's for heavier atom bond lengths are <0.003 Å except for C(25)–C(26), 0.004 Å, and C(25)–C(27), 0.005 Å. The corresponding angular esd's are <0.2°. Despite the possible distortion introduced by the change of the A ring to a cyclopentanone ring with substituents on the bridgehead atoms, the compound is in many ways a very typical steroid. The C-17 side chain is extended and all substituents, including hydrogen atoms, are placed so as to achieve relatively good gauche conformations. A gauche conformation is also present on all methyl substituents and gives a satisfactory minimization of close hydrogen contacts. The moderately high thermal motion of the terminal atoms of the C-17 side chain has produced apparent bond lengths shorter than the standard 1.54 Å and the consistent decrease in apparent bond length with position along the chain is in accord with the thermal parameters which, in their turn, are what one might expect from packing considerations.

Including atoms C(1)–C(20), the average sp^3 C–C bond length is 1.542 Å and the observed significant deviations from the mean are not unusual in steroids. The average sp^3–sp^2 C–C bond length is 1.528 Å. The longest bonds, C(5)–C(10) and C(13)–C(17), are between those carbon atoms with the greatest number of carbon substituents. Aside from the modification of the A ring, the parameters of the remainder of the molecule are remarkably similar to the "standard values" obtained by averaging appropriate steroid molecules.[5] The B and C rings show the typical steroid expansion of bond angles from the tetrahedral value, the average angles being 111.0 and 111.2°, respectively, and the average torsion angles in these rings are therefore reduced to 56.0 and 55.4° from the 60° of an undistorted symmetrical cyclohexane "chair" molecule.

The A ring, with both bridgehead atoms quaternary, has corresponding internal angles of 100°, and the D ring, with only one quaternary bridgehead atom, has an internal angle at the quaternary atom of 100° and the other angle is about 104°. The external angles between the rings follow the usual pattern. Very little conformational strain appears to have been introduced by the modification of the A ring. Although the angle between the mean planes of the A ring and the B ring is 1.7° and the corresponding angle for the C ring and the D ring is 5.7°, there does not appear to be any trend to a division of the nucleus into two units with different mean planes.

The torsion angles of the two five-membered rings are somewhat different. In terms of Altona, Geise, and Romer's[5] cyclopentane parameters Δ and θm, the values for the A ring are 10.7 and 47.9°, while those for the D ring are 15.1 and 46.3°. Since the value of Δ for the conformation of cyclopentane described as "half-chair" [2 symmetry] is 0°

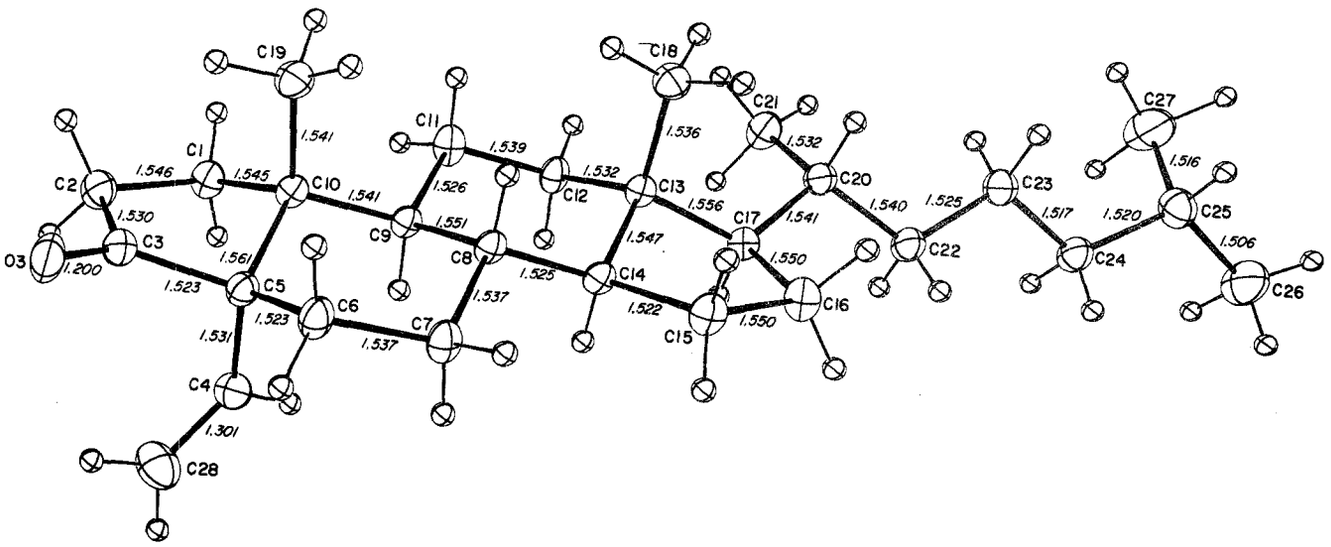


Figure 1. Bond lengths and thermal ellipsoids for the minor photoproduct **2**. The ellipsoids for the heavier atoms indicate 50% probability while those for hydrogen atoms are diagrammatic. Drawings were produced by ORTEP.[18]

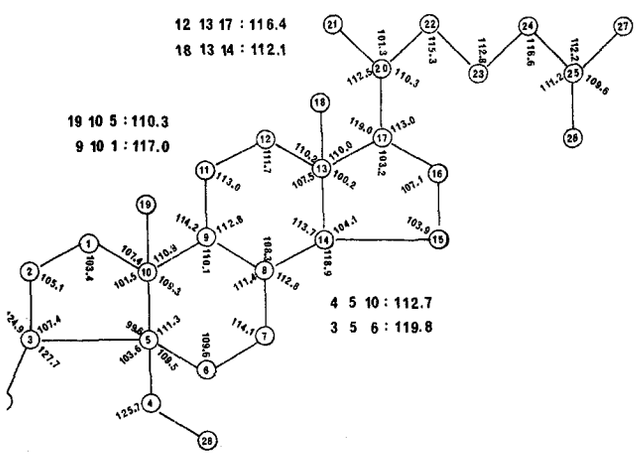


Figure 2. Bond angles.

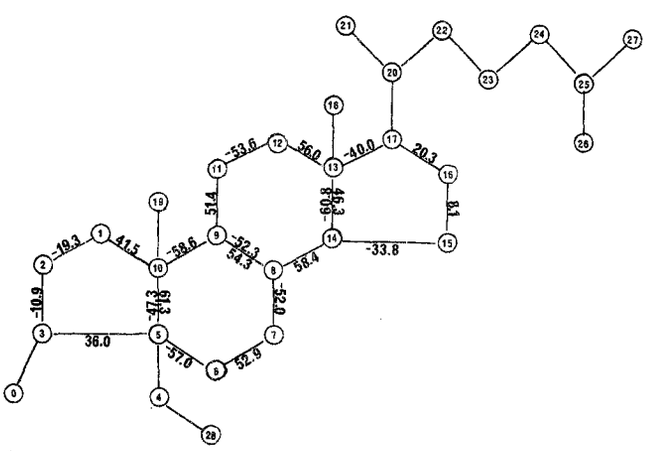


Figure 3. Torsion angles in the nucleus of **2**.

and that for the "envelope" [m symmetry] is 36°, the cyclopentane rings are intermediate between the two extreme forms; again not an unusual result in steroids without severe perturbing influences. The A ring, being a cyclopentanone ring, could be expected to adopt a conformation nearer to a "half-chair", as calculations on unsubstituted cyclopentanone[6] suggest, and the observed conformation is closer to this form than to the other; however, the Δ angle is quite large. It should be noted that ring D in 1-bromoestrone[7] is known to exist essentially in the "envelope" conformation with a Δ value of 32.2°, but that in 3α-ol-5α-androstan-17-one[8] is nearly "half-chair" with Δ = 7.9°.

The molecular packing is shown in Figure 4; it is that of a typical steroid crystallizing in $P2_1$. No intermolecular distances are significantly shorter than normal and the molecule appears to have been able to adopt a conformation of minimal energy without much crystal packing distortion.

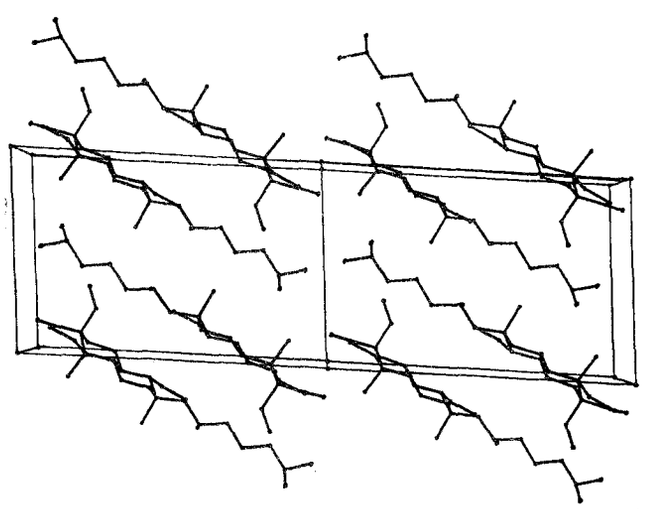


Figure 4. Packing diagram. The direction of projection is b and two unit cells are indicated.

Discussion

The synthesis of **5a** and the X-ray analysis of **2** unambiguously define the structures of both photoproducts formed in the direct irradiation of **1**. In view of the importance of the interpretation of the CD curves of **2** and **3** in the original[3] stereochemical assignment, the interpretation was reexamined.

Moscowitz, Djerassi, and Mislow have described a rule[9b] (MDM rule) relating the sign of the chiroptical effect to the molecular geometry of β,γ-unsaturated ketones. This rule was derived for and used to evaluate β,γ-unsaturated ketones possessing the specific spatial arrangement of unsaturated centers shown in Figure 5A,B. The application of the MDM rule to **2** and **3** is difficult, as these compounds are not constrained to a single fixed conformation. The orientation of the double bond of **2** is given in Figures 1–3.

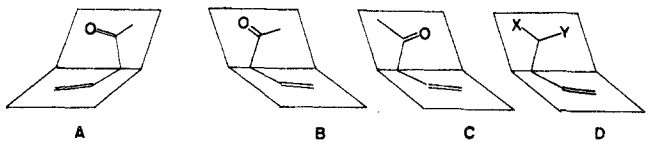


Figure 5. β,γ-Unsaturated ketones as disymmetric chromophores: A, MDM rule for positive Cotton effect; B, MDM rule for negative Cotton effect; C, relation of carboxyl and double bond in **2**; D, general description where X or Y can equal O.

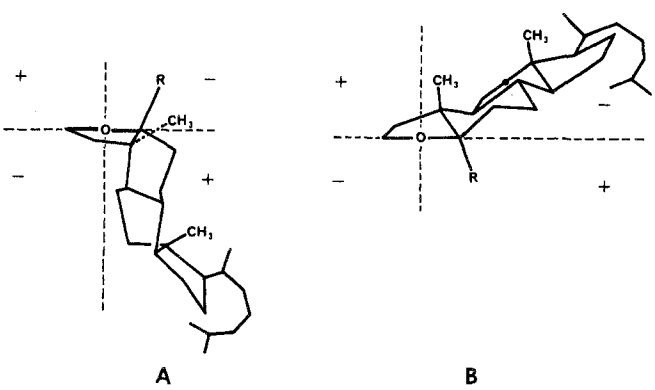


Figure 6. Octant diagrams for ketones **2–5**: A, **3** (R = vinyl) and **5** (R = ethyl); B, **2** (R = vinyl) and **4** (R = ethyl).

The conformation shown is likely to be that preferred in solution, since rotation of the double bond toward the steroid skeleton (i.e., so that its projection overlays the steroid skeleton) results in an increase in nonbonded interactions. For analogous reasons it is likely that a projection of **3** would show the double bond in a similar position. Thus, the vinyl and carbonyl groups in **2** and **3** do not have the spatial arrangements shown in either Figure 5A or 5B and the MDM rule is not applicable. The relation of the vinyl and carbonyl groups in **2** is given in Figure 5C. If the bond linking the α carbon and the carbonyl group in Figure 5C is rotated 180°, a figure is generated which is identical with Figure 5B. As **2** possesses a negative Cotton effect, and the MDM rule predicts a negative effect for Figure 5B, a relationship may exist between Figure 5B and 5C shown in Figure 5D, where either X or Y represents the carbonyl oxygen. The significance of this suggestion needs to be explored by theoretical calculations and examination of additional model compounds.

Alternatively, the CD of β,γ-unsaturated ketones may be considered as a special case of the ketone octant rule where the double bond has the effect of increasing the magnitude of the chiroptical effect;[9a] i.e., the olefin may be a "super-substituent". The octant rule for ketones **2–5** is shown in Figure 6 and the CD values for these compounds are listed in Table I. The structural assignments which follow the X-ray analysis and the syntheses are consistent with the octant rule, since the contribution of the steroid skeleton is greater than the contribution of R.

However, the amplitude of the chiroptical effect of **4** (−4000) is approximately one-fifth that of its unsaturated relative **2** (−13400) although the substituent group R is shown to be in a positive octant in Figure 6B. If the double bond is a "super-substituent", the CD of **2** should be more positive than that of **4**. This dilemma can be resolved by realizing that the vinyl group can make a significant contribution to the optical activity via a front octant where sign reversal for substituents has been demonstrated for saturated ketones.[10] An equivalent conclusion obtains from an analysis of the CD curves of **3** and **5**.

In conclusion, the above synthesis of **5a** and the X-ray determination of **2** unequivocally establish the structure of the photoproducts obtained from **1**. Although considerable evidence exists for interaction between the carbonyl and the double bond in **2** and **3**, the previous structural assignments were based on an inappropriate use of the MDM rule. The correct sign of the CD bands of **2–5** can be obtained using a modification of the octant rule in which the sign of the CD band is determined by the octant occupied by the double bond and the bulk of the steroid nucleus.

Table II
Crystal and Refinement Data

Molecular formula	$C_{28}H_{46}O$	Habit	Monoclinic plates elongation *b*
Formula weight	398.67	Crystal size	0.7 × 0.25 × 0.08 mm
		X-Radiation	Cu Kα (graphite monochromator)
a	10.429 (1) Å		
b	7.369 (1) Å	λ	1.5418 Å
c	15.605 (1) Å	*Diffractometer*	*Nonius CAD-4*
β	94.28 (2)°	Reflections	2270 (observed)
V	1195.2 Å^3		276 (unobserved 1σ)
Z	2	μ	4.9 cm^{-1}
*D*x	1.107 g/cm^3	Function minimized	$\Sigma w\Delta^2$
*D*m (flotn in aq KI)	1.09 (1) g/cm^3	Weighting	Peterson and Levy[19]
Space group	$P2_1$ (no. 4)	Refinement	Full-matrix least squares (partitioned)

Experimental Section

X-Ray Structure Determination. The minor photoproduct (**2**), obtained from the irradiation of **1**, crystallized from methanol–water as monoclinic prisms and was chosen for X-ray analysis since it gave considerably better crystals than the major product. Cell dimensions were determined by least-squares refinement using Bragg angles measured at ±θ. Lorentz and polarization corrections were applied by local programs but no absorption corrections were made or considered necessary (azimuthal scans of several reflections showed no significant variation). The basic experimental data are given in Table II. During data collection, three standard reflections were measured after every 50 reflections and no evidence of crystal deterioration was seen.

Many attempts were made to solve this structure by the symbolic addition procedure of Karle and Karle[11] but, in all cases, the *E* maps contained one single very large peak; while molecular fragments could apparently be seen, extension by the tangent formula[12] failed. In retrospect, it is considered that the source of the problem was the fact that definition of the enantiomorph in $P2_1$ is frequently difficult. The structure was finally solved by means of the MDKS and triple product formulae of Hauptman followed by his technique of "strong enantiomorph discrimination"[13] and application of the tangent formula. Two *E* maps were obtained; in one of them, the whole of the modified steroid skeleton was visible, although evidence for the substituents was somewhat nebulous. Refinement by least-squares techniques followed by difference maps resulted in the location of the missing heavier atoms and of all hydrogen atoms of the molecule. Final refinement utilized anisotropic temperature factors for the heavier atoms and isotropic factors for the hydrogen atoms, and was carried out by the full-matrix least-squares technique although, because of the size of the molecule, partitioning was necessary. The final conventional *R* factor was 0.036.[21] The direct methods calculations used programs developed by Weeks et al.;[14] all other calculations mentioned were carried out by the XRAY72 system of Stewart et al.[15] Scattering factors for carbon and oxygen were taken from the International Tables for X-Ray Crystallography,[16] and those for hydrogen from Stewart, Davidson, and Simpson.[17] In view of the absence of heavy atoms or a large fraction of oxygen atoms, we did not attempt to determine the absolute configuration by X-ray methods but, given the known stereochemistry of the parent steroid, the absolute

Table III
Atomic Parameters for Oxygen and Carbon Atoms ($\times 10^4$)[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O 3	1497 (2)	7333	155 (1)	916 (11)	731 (12)	496 (8)	124 (10)	274 (7)	163 (8)
C 1	632 (2)	3947 (3)	1604 (1)	670 (10)	374 (11)	459 (10)	70 (10)	126 (9)	−53 (9)
C 2	1242 (2)	4446 (3)	765 (1)	652 (13)	559 (13)	443 (10)	91 (11)	95 (9)	−78 (10)
C 3	1276 (2)	6448 (3)	762 (1)	526 (11)	601 (14)	413 (10)	99 (10)	84 (8)	34 (10)
C 4	2222 (2)	6860 (3)	2198 (1)	519 (11)	526 (13)	517 (10)	8 (10)	30 (8)	−15 (10)
C 5	951 (2)	7064 (3)	1648 (1)	494 (10)	380 (10)	395 (9)	44 (9)	71 (7)	44 (8)
C 6	425 (2)	8903 (3)	1761 (1)	649 (12)	360 (10)	494 (11)	30 (10)	162 (9)	89 (9)
C 7	5 (2)	9114 (3)	2679 (1)	639 (12)	279 (9)	509 (10)	−18 (9)	168 (9)	11 (8)
C 8	9075 (2)	7687 (2)	2946 (1)	472 (9)	259 (9)	368 (8)	23 (7)	67 (7)	8 (7)
C 9	9608 (2)	5829 (3)	2789 (1)	457 (9)	280 (9)	358 (8)	22 (7)	55 (7)	−2 (7)
C 10	9940 (2)	5644 (2)	1848 (1)	488 (10)	308 (10)	355 (8)	24 (8)	37 (7)	−16 (7)
C 11	8742 (2)	4380 (3)	3093 (1)	689 (13)	256 (10)	508 (10)	−46 (9)	189 (9)	−68 (8)
C 12	8389 (2)	4633 (3)	4025 (1)	623 (12)	283 (9)	475 (10)	1 (8)	162 (8)	22 (8)
C 13	7808 (2)	6446 (2)	4162 (1)	438 (9)	306 (9)	359 (8)	−5 (7)	56 (7)	−28 (7)
C 14	8784 (2)	7824 (2)	3888 (1)	458 (9)	280 (9)	375 (8)	8 (8)	38 (7)	−7 (7)
C 15	8279 (2)	9548 (3)	4217 (1)	645 (12)	296 (9)	501 (10)	2 (8)	132 (9)	−54 (8)
C 16	7677 (2)	9036 (3)	5060 (1)	664 (12)	384 (11)	489 (11)	−40 (10)	175 (9)	−90 (9)
C 17	7684 (2)	7010 (3)	5110 (1)	426 (9)	381 (10)	379 (8)	−27 (8)	45 (7)	−32 (7)
C 18	6501 (2)	6611 (3)	3646 (1)	468 (10)	592 (13)	439 (9)	−21 (9)	19 (7)	−43 (9)
C 19	8726 (2)	5829 (3)	1229 (1)	528 (10)	646 (15)	416 (9)	23 (10)	−5 (8)	−56 (9)
C 20	3430 (2)	1270 (3)	4404 (1)	454 (10)	513 (12)	408 (9)	52 (9)	67 (7)	23 (9)
C 21	3455 (2)	9264 (3)	4400 (1)	755 (14)	518 (13)	527 (11)	174 (11)	225 (10)	21 (10)
C 22	3342 (2)	1944 (3)	3472 (1)	539 (10)	568 (13)	433 (9)	73 (10)	117 (8)	57 (9)
C 23	4556 (2)	1711 (4)	2997 (1)	543 (11)	636 (14)	457 (10)	13 (10)	122 (8)	26 (10)
C 24	4375 (2)	2248 (3)	2060 (1)	603 (11)	596 (14)	484 (10)	78 (11)	148 (9)	72 (10)
C 25	5580 (2)	2350 (4)	1571 (1)	651 (13)	790 (18)	529 (11)	−37 (13)	180 (10)	35 (12)
C 26	5279 (3)	3027 (6)	673 (2)	1054 (21)	1334 (32)	707 (16)	236 (22)	390 (15)	402 (20)
C 27	6259 (3)	599 (6)	1537 (2)	1021 (21)	1299 (34)	858 (20)	526 (22)	446 (17)	284 (21)
C 28	3355 (2)	7262 (5)	1962 (2)	560 (13)	922 (22)	822 (16)	108 (14)	66 (11)	−98 (16)

[a] No esd is given for the oxygen *y* parameter since it was used to define the origin. The temperature factor used had the form $\exp 2\pi^2 (\sum_i \sum_j U_{ij} a_i^* a_j^* h_i h_j)$.

Table IV
Atomic Parameters for Hydrogen Atoms ($\times 10^3$)

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
1A	132 (2)	365 (4)	206 (2)	62 (8)	1B	999 (2)	296 (4)	152 (2)	73 (8)
2A	70 (3)	412 (5)	25 (2)	80 (8)	2B	212 (3)	407 (5)	72 (2)	91 (9)
4A	220 (3)	648 (5)	280 (2)	95 (10)	6A	967 (3)	910 (4)	132 (2)	69 (7)
6B	108 (3)	971 (5)	164 (2)	85 (9)	7A	956 (2)	25 (4)	274 (2)	65 (8)
7B	79 (2)	907 (4)	310 (2)	75 (8)	8A	823 (2)	783 (4)	260 (2)	64 (7)
9A	43 (2)	576 (4)	317 (1)	54 (7)	11A	796 (3)	436 (4)	274 (2)	71 (8)
11B	918 (3)	322 (5)	303 (2)	82 (9)	12A	781 (3)	365 (4)	417 (2)	72 (8)
12B	922 (3)	450 (4)	441 (2)	73 (8)	14A	959 (2)	763 (4)	424 (1)	60 (7)
15A	758 (2)	1003 (4)	380 (2)	71 (8)	15B	892 (2)	38 (5)	429 (2)	75 (8)
16A	677 (3)	943 (5)	503 (2)	76 (8)	16B	815 (3)	947 (5)	559 (2)	93 (10)
17A	154 (2)	167 (4)	457 (2)	56 (7)	18A	654 (2)	643 (5)	307 (2)	73 (8)
18B	603 (3)	782 (5)	373 (2)	93 (10)	18C	590 (3)	580 (5)	384 (2)	79 (9)
19A	896 (3)	585 (4)	61 (2)	81 (9)	19B	813 (3)	489 (5)	128 (2)	97 (10)
19C	816 (3)	679 (5)	129 (2)	90 (8)	20A	425 (2)	166 (4)	469 (2)	59 (7)
21A	372 (3)	884 (5)	500 (2)	84 (9)	21B	403 (3)	877 (4)	401 (2)	85 (9)
21C	251 (3)	880 (5)	426 (2)	94 (10)	22A	314 (3)	319 (5)	346 (2)	82 (9)
22B	264 (2)	146 (5)	315 (2)	78 (9)	23A	486 (2)	56 (4)	303 (2)	74 (8)
23B	535 (3)	223 (4)	334 (2)	79 (8)	24A	371 (3)	136 (5)	174 (2)	93 (10)
24B	393 (3)	330 (4)	202 (2)	89 (9)	25A	622 (3)	321 (6)	195 (2)	114 (12)
26A	459 (3)	215 (6)	38 (2)	121 (12)	26B	478 (3)	413 (6)	62 (2)	115 (11)
26C	599 (3)	312 (6)	29 (2)	113 (11)	27A	714 (3)	96 (5)	130 (2)	106 (10)
27B	661 (3)	37 (5)	220 (2)	109 (10)	27C	546 (3)	971 (5)	123 (2)	115 (10)
28A	418 (3)	718 (5)	234 (2)	107 (10)	28B	348 (3)	759 (5)	137 (2)	117 (10)

stereochemistry is that shown in Figure 1. The stereochemistry of the A/B ring junction is trans and therefore *opposite* to that assigned by Fisher and Zeeh.[3] The atomic parameters for heavier atoms are given in Table III and those for hydrogen atoms in Table IV.

5β-Methylcholestan-3-one (8b). The enolate **7b** was prepared by the addition of lithium dimethylcopper to **6** as described by Muchmore;[4b] quenching with water yielded **8b**, mp 82–83° (lit.[20] 88–89°).

5β-Methylcholest-3-ene (9b). The olefin **9b** was prepared as described by Muchmore;[4b] however, the final purification employed column chromatography on silica gel in lieu of vacuum distillation. Spectral properties were identical with those reported.

5β-Methyl-*A*-norcholestan-3-one (5b). A solution of 471 mg of **9b** in 50 ml of 1:1 ethyl acetate–acetic acid was treated with excess ozone at −10 to 0° until GC analysis indicated that no starting material remained. Hydrogen peroxide (0.5 ml, 30%) was added and the mixture was allowed to stand for 24 hr at room temperature. The solvent was removed under reduced pressure, and ether was added. The resulting mixture was washed with water, sodium bicarbonate, water, and brine, dried ($MgSO_4$), and evaporated in vacuo, giving 501 mg of crude diacid which was crystallized from ethyl acetate, mp 166–170° (lit.[4b] mp 168–172°).

The crude diacid was esterified with excess diazomethane and the crude ester purified via column chromatography: NMR ($CDCl_3$) δ 3.62 (s, 6 H, CO_2CH_3), 0.85 (s, 3 H, CH_3), 0.65 (s, 3 H, CH_3); ir (CCl_4) 1733, 1748 cm^{-1}. To the diester **10b** (50 mg) in 15 ml of benzene, 120 mg of freshly sublimed potassium *tert*-butoxide

was added and the mixture refluxed for 12 hr. The reaction mixture was cooled, acidified with dilute hydrochloric acid, and extracted with ether. The organic phase was washed with water, aqueous sodium bicarbonate, and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was dissolved in a 3:1 mixture of acetic acid and concentrated hydrochloric acid and refluxed for 5 hr. The cooled reaction mixture was made basic with aqueous sodium bicarbonate and extracted with ether. The ether layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo to yield a yellow solid which was purified by column chromatography over silica gel, mp 82–84° from methanol: NMR ($CDCl_3$, 220 MHz) 145 (s, 3 H), 175 (s, 3 H), 185 (s, 3 H), 495 Hz (m, 2 H); ir (CCl_4) 1748 cm^{-1}. Anal. Calcd for $C_{27}H_{40}O$: C, 83.87; H, 11.99. Found: C, 83.90; H, 12.40.

5β-Ethylcholestan-3-one (8a). To a solution of lithium diethylcopper in ether, prepared from 3.0 g (15. 7 mmol) of cuprous iodide and 42 ml (31.2 mmol) of 0.736 *M* ethyllithium, was added a solution of 2.0 g (5.2 mmol) of **6** in ether at 0°. The enolate **7a** was hydrolyzed as described for **8b** to yield **8a** from methanol, mp 85–87°, ir (CCl_4) 1723 cm^{-1}. Anal. Calcd for $C_{29}H_{50}O$: C, 83.99; H, 12.15. Found: C, 84.13; H, 12.17.

5β-Ethyl-*A*-norcholestan-3-one (5a). A sample of 5β-ethyl-*A*-norcholestan-3-one (**5a**) was prepared from **6** using lithium diethylcopper in the same sequence as described for **5b**. The intermediates **9a**, NMR ($CDCl_3$, 220 MHz) 1240 (t of d, J = 2.5, 10 Hz), 1165 (d, J = 10 Hz), 140 Hz (s, 3 H), and **10a**, ir (CCl_4) 1733, 1747 cm^{-1}, NMR ($CDCl_3$, 220 MHz) 802 (s, 6 H), 145 Hz (s, 3 H), were colorless oils and were obtained in yields of 80 and 87%, respectively. The sample of **5a** prepared in this manner was identical in all physical properties with the dihydro derivative of the major photoproduct **3** of **1**.

Acknowledgments. We wish to express our thanks to Dr. C. A. Weeks (Medical Foundation of Buffalo, Buffalo, N.Y.) for providing the programs of the Hauptman group and also to Dr. J. W. Edmonds (Medical Foundation of Buffalo) for discussions with T. A. while attending the Summer School in Direct Methods (Sept 1973).

Registry No.—**1**, 51355-04-5; **2**, 19682-31-6; **3**, 19594-90-2; **4**, 19682-32-7; **5a**, 19682-33-8; **5b**, 39932-87-1; **6**, 601-57-0; **7a**, 56829-83-5; **7b**, 56829-84-6; **8a**, 51355-05-6; **8b**, 13163-71-8; **9a**, 51355-07-8; **9b**, 23931-38-6; **10a**, 56829-85-7; **10b**, 56829-86-8.

Supplementary Material Available. A diagram showing deviations of atoms from mean planes and a listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-3675.

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(1) (a) Faculty of Pharmaceutical Sciences, University of Tokyo, Tokyo, Japan. (b) I. C. I. Pharmaceuticals Ltd., Mereside, Alderley Park, Cheshire SK10 4TG, England. (c) Philip Morris Research Center, Richmond, Va.
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Synthesis and C-25 Chirality of 26-Hydroxycholesterols

Ravi K. Varma,[1a,b] Masato Koreeda,[2a] Boris Yagen,[1a,c] Koji Nakanishi,[2a] and Eliahu Caspi*[1a]

Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts 01545,[1d] and Department of Chemistry, Columbia University, New York, New York 10027[2b]

Received June 2, 1975

Samples of cholest-5-ene-3β,26-diol 3-tetrahydropyranyl ether were prepared via hydroboration of cholest-5,25-dien-3β-ol tetrahydropyranyl ether with (a) disiamylborane, (b) (+)-diisopinocampheylboranes (DIPCB), and (c) (−)-(DIPCB). The 26-hydroxy compounds were converted first to cholest-4-en-3-on-26-ol *p*-bromobenzoates and then to cholest-4-ene-3β,26-diol 26-*p*-bromobenzoates. Authentic (25*R*)- and (25*S*)-cholest-4-ene-3β,26-diol *p*-bromobenzoates were prepared from kryptogenin and from (25*S*)-cholest-4-en-3-on-26-ol *p*-bromobenzoate, respectively. The magnitudes of the Cotton effects of the 25*R* and 25*S* samples were the same but of the opposite sign. The 25*R* compound had a negative Cotton effect while the 25*S* compound had a positive Cotton effect. Both compounds were assumed to be optically pure (100%). The CD spectra of the corresponding analogs derived from the hydroboration of the C-25 olefin were recorded. Based on the sign and amplitude of their Cotton effects, their stereochemistry and optical purity at C-25 was defined.

For studies of the stereochemistry of the reduction of the C-24 double bond of lanosterol in the course of the biosynthesis of cholesterol in the S-10 fraction of rat livers[3–5] we required samples of (25*R*)- and (25*S*)-26-hydroxycholestenone.[4–5] The attempted preparation of these compounds via the selective hydroboration of cholesta-5,25-dien-3β-ol