Reduction of Δ^{16}-22-Ketocholesterol. A. 3β-Hydroxy-5α-cholestan-22-one.—A solution of 200 mg of Δ^{16}-22-ketocholesterol in 10 ml of ethyl acetate was stirred in an atmosphere of hydrogen with 100 mg of 10% palladium on charcoal. Hydrogen (2 mol) was rapidly absorbed and the absorption was usually completed in 2 hr. After the usual work-up the product was crystallized from aqueous acetone, yield 175 mg, mp 125–127° (lit.[18] 125–127°); the 3-acetate had mp 112–114° (lit.[18] 114–115°).

B. 22-Ketocholesterol.—A solution of 200 mg of Δ^{16}-22-ketocholesterol in 10 ml of dioxane (or ethyl acetate) was stirred in a hydrogen atmosphere with 100 mg of 10% palladium on calcuim carbonate. The absorption of hydrogen stopped after 1.1 mol and the product was isolated in the usual way and crystallized from methanol, yield 160 mg, mp 140–142° (lit.[7] 140–142°); the 3-acetate had mp 155–158° (lit.[7] 154–155°).

Reduction of Δ^{17}-22-Ketocholesterol. A. 22-Ketocholesterol.—A solution of 500 mg of Δ^{17}-22-ketocholesterol in 2 ml of dry tetrahydrofuran was added to 50 ml of anhydrous liquid ammonia and this was followed by the addition of 100 mg of lithium. The mixture was stirred for 4 hr and then decomposed by the addition of solid ammonium chloride. After the evaporation of ammonia, water was added and the product was isolated by extraction with ethyl acetate. The solid, obtained after removal of ethyl acetate, was chromatographed on a column of alumina with 10% ethyl acetate in benzene. 22-Ketocholesterol was eluted first, followed by the 22-hydroxy compound. Further purification by crystallization from methanol yielded 300 mg of 22-ketocholesterol identical with an authentic sample (melting point, ir, and nmr).

B. (22*R*)-22-Hydroxycholesterol.—The reduction was carried out as described, except that 2 ml of ethanol was added after 3 hr and stirring continued for another 0.5 hr. The product was chromatographed on alumina and the first fraction, which was the major fraction (300 mg, 70%), was purified by crystallization: mp 186–188° (lit.[9] 814–185°); the ir spectrum had a band at 1021 cm^{-1}, characteristic of the 22*R*-hydroxy compound;[17] mass spectrum *m/e* 402 (M^+, base peak), 387 ($M - CH_3$, 10%), 384 ($M - H_2O$, 45%), 369 ($384 - CH_3$, 25%), 351 ($369 - H_2O$, 20%), 302 ($M - C_6H_{12}OH + 1$).

The second fraction (100 mg) was a mixture and the last fraction (50 mg) was crystallized from methanol, mp 180–182° (lit.[9] 181–182°). The ir spectrum had a band at 984 cm^{-1} characteristic of the 22*S*-hydroxy compound.[17]

Registry No.—Cholesterol, 57-88-5; **3**, 21903-10-6; 3-acetate of **3**, 21903-11-7; **6**, 21927-89-9; **9**, 21903-12-8; **10**, 21903-13-9; **12**, 21903-14-0; **13**, 21903-15-1; **14**, 21903-16-2; **15**, 21903-17-3; 3-acetate of **15**, 21897-75-6; 3-acetate of **16**, 21903-18-4; **17**, 21903-19-5; benzoate of **17**, 21903-20-8; **18**, 21903-21-9; dibenzoate of **21**, 21903-22-0; 22*R* epimer of **21**, 21903-23-1; 22*S* epimer of **21**, 21903-24-2; **23**, 21903-25-3; maleic anhydride adduct of **23**, 21897-66-5; **28**, 21897-67-6; **29**, 21897-68-7; 3-acetate of **29**, 21897-69-8; 22*R* epimer of **30**, 21897-70-1; 22*S* epimer of **30**, 21897-71-2; dibenzoate of **30**, 21897-72-3; **33**, 21897-73-4; 3-benzoate of **33**, 21897-74-5.

Acknowledgment.—We thank Dr. T. A. Wittstruck and Mr. J. Cronan for the nmr spectra and Mr. D. Quarton for the mass spectra reported in this paper.

Photosensitized Hydration of Cholesterol

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Irradiation of cholestrol (I) in the ternary solvent system composed of *t*-butyl alcohol, water, and *o*-xylene (photosensitizer) for 40 hr gave two main products, *i.e.*, 5β-cholestane-3β,5-diol (II, 54%), representing a stereospecific addition of water to the double bond of I, and 3ξ,5-oxidomethylene-5ξ-A-norcholestane (III, 21%). Irradiation of a solution of I in dioxane, deuterium oxide, and *o*-xylene for 74 hr gave 6ξ-d_1-5β-cholestane-3β,5-diol (IV, 58%) and 2′ξ,6ξ-d_2-3ξ,5-oxidomethylene-5ξ-A-norcholestane (V, 16%) as the principal deuterated species. Photohydration of 4-cholesten-3β-ol (VI) in a similar manner gave the same diol II and oxetane III obtained from the cholesterol irradiation. The mechanism of the formation of these compounds is discussed and correlated with the photohydrations of cyclohexenes reported previously.

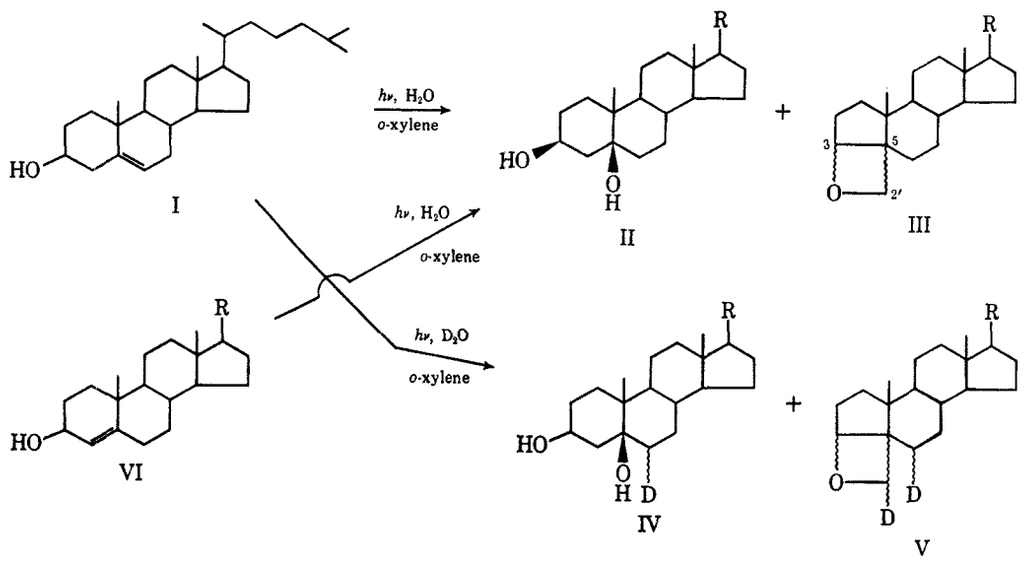
Cycloalkenes, such as (+)-3-carene and 1-methene, undergo the photosensitized addition of water and alcohols to the double bond to form alcohols and ethers.[1-3] Under the influence of light these cycloalkenes, which have a methyl group attached to the double bond, are also partially converted into their exocyclic methylene isomers. We have observed the formation of two cholestane-3,5-diols as by-products from the irradiation of 4-chloesten-3-one in the presence of sodium borohydride,[4] with the C-5 hydroxyl possibly due to traces of water or oxygen present in the alcoholic medium. In this paper we show that water can add to the double bond of cholesterol under photosensitizing conditions, a reaction which has synthetic and biosynthetic implications.

Methods and Results

The conditions for the photosensitized hydration of cholesterol were varied as described in the Experimental Section. Cholesterol (I) was completely converted into photoproducts when a solution in the ternary solvent system composed of *t*-butyl alcohol, water, and *o*-xylene (sensitizer) was irradiated with a 450-W Hanovia medium-pressure lamp (679A-36) equipped with a Vycor filter. The reactiom mixture obtained after 40 hr of irradiation contained mainly photoproducts II and III which were isolated by column and thin layer chromatography.[5] See Scheme I. The infrared spectrum of 5β-cholestane-3β,5-diol (II)[6,7] showed bands at 3608 and 3495 cm^{-1} (free and hydrogen-bonded hydroxyl absorptions, respectively) and the mass spectrum displayed a mass peak at M^+ 404 and *m/e* 386 ($M^+ - 18$, H_2O), 368 ($M^+ - 36$, $2H_2O$), 249 (fragmentation of ring D), and 110 (ring-B fission of the C-5,6 and C-9,10 bonds − 18, H_2O). The

(1) P. J. Kropp, *J. Amer. Chem. Soc.*, **88**, 4091 (1966).
(2) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).
(3) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4093 (1966).
(4) J. A. Waters and B. Witkop, *ibid.*, **90**, 758 (1968).
(5) The per cent yields of the photoproducts reported in this paper are *estimated* yields from the total reaction mixture as determined by tlc and glpc of the fractions obtained from column and preparative thin layer experiments.
(6) D. J. Collins, *J. Chem. Soc.*, 3919 (1959).
(7) E. M. Burgess, *J. Org. Chem.*, **27**, 1433 (1962).

SCHEME I



principal mass spectral peaks of all of the photoproducts described here are listed in Table I.

TABLE I

MASS SPECTRAL PEAKS OF THE PRINCIPAL PHOTOPRODUCTS

Photoproducts	M+	m/e			
5β-Cholestane-3β,5-diol (II)	404	386	368	249	110
6ξ-d_1-5β-Cholestane-3β,5-diol (IV)	405	387	369	250	110
3ξ,5-Oxidomethylene-5ξ-A-norcholestane (III)	386	371	356	276	231	111
2′ξ,6ξ-d_2-3ξ,5-Oxidomethylene-5ξ-A-norcholestane (V)	388	373	358	277	233	112

Acetylation of diol II with acetic anhydride–pyridine gave 5β-cholestane-3β,5-diol 3-acetate,[8] whose infrared spectrum displayed bands 3594 (OH) and 1735 cm^{-1} (O-acetyl).

The mass spectrum of photoproduct III displayed peaks at M+ 386 and *m/e* 371 (M+ − 15, CH_3), 356 (M+ − 30,2 CH_3), 231 (ring-D fission), 276 and 111 (ring-B fission of the C-5,6 and C-9,10 bonds with a gain of one hydrogen by the latter, oxygen-containing fragment). These principal mass peaks suggested an oxidocholestane derivative. Structure III[9] was further substantiated by nmr, which displayed a multiplet at 4.47 ppm (1 H) for the proton at C-3 and a quartet at 3.96 and 4.59 ppm (2 H, J = 6.5 cps) assignable to the coupling of nonequivalent protons[10] of the C-2′ methylene group.

Treatment of III with lithium aluminum hydride in refluxing ether, tetrahydrofuran, or dioxane, or with lithium aluminum hydride in tetrahydrofuran saturated with hydrogen chloride failed to open the oxetane ring. Starting material was recovered in each case. However, the oxetane when treated with lithium aluminum hydride in the presence of aluminum chloride[11] was converted into several products. Because of the paucity of III, the complex reaction mixture could not be examined further.

In the photodeuteration of cholesterol, irradiation of I (7.0 g, 0.018 mol) dissolved in 900 ml of dioxane, 140 ml of deuterium oxide, and 10.5 ml of *o*-xylene (sensitizer) for 72 hr afforded two principal products, IV and V, whose tlc R_f values were identical with those of diol II and oxetane III, respectively, obtained from the photosensitized hydration. Deuterated diol IV was obtained as colorless flakes (58%). The mass spectrum of IV displayed peaks analogous to diol II (one additional mass unit, 71% d_1 species) at M+ 405, *m/e* 387, 369, and 250, and a *m/e* 110 peak identical with that shown by II. The infrared spectrum of 6ξ-d_1-5β-cholestane-3β,5-diol (IV) displayed free and hydrogen-bonded hydroxyl absorptions (3608 and 3495 cm^{-1}, respectively) and a C–D band at 2160 cm^{-1}. Deuterated oxidocholestane V was isolated from the reaction mixture by column chromatography in 16% yield. The mass spectrum of the deuterated oxidocholestane (V) displayed principal peaks analogous to III (two additional mass units, 60% d_2 species) at M+ 388, *m/e* 373, 358, and 233, and, in addition, peaks at *m/e* 277 and 112 representing one additional mass unit analogous to oxido III. Careful analysis of the mass spectra of IV and V revealed additional deuterated species for both compounds (*cf.* Table II).

Irradiation of 4-cholesten-3β-ol (VI) in the presence of water, employing the same conditions used for cholesterol, gave diol II and oxido III. Also, irradiations of II and III in the presence of photosensitizer gave starting material in each case, thus excluding the possibility of one of the compounds being an intermediate.

Discussion

The photohydration of cholesterol represents an addition of the elements of water to an isolated double bond of a steroid molecule. The hydroxyl group attacks stereospecifically the 5β face of the molecule. The mechanism of the addition reactions has been considered as ionic, since the excessive strain of the triplet state of the olefin would convert into an intermediate possessing carbonium ion character.[1-3] Ir-

(8) S. M. Kupchan, S. P. Eriksen, and Y.-T. S. Liang, *J. Amer. Chem. Soc.*, **88**, 347 (1966).

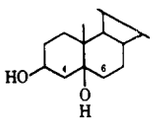
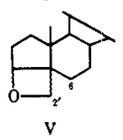
(9) Final confirmation of the structure and stereochemistry of this compound will be the subject of a forthcoming paper.

(10) L. F. Fieser, T. Goto, and B. K. Bhattacharyya, *ibid.*, **82**, 1700 (1960).

(11) G. R. Pettit and W. J. Bowyer, *J. Org. Chem.*, **25**, 84 (1960).

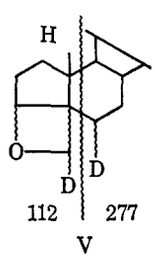
TABLE II

MASS SPECTRAL ANALYSES OF THE DEUTERATED PHOTOPRODUCTS

Photoproduct	Deuterium analyses, %	Positions substituted
 IV	d_1 species, 71	C-6
	d_2 species, 14	C-6, C-4
	d_3 species, 8	C-6, C-4
	d_4 species, 6	C-6, C-4
 V	d_1 species 14	C-6
	d_2 species, 60	C-6, C-2′ [a]
	d_3 species, 16	C-6, C-2′
	d_4 species, 10	C-6, C-2′

[a] The deuterium was distributed *ca.* 1:1 between the two positions.

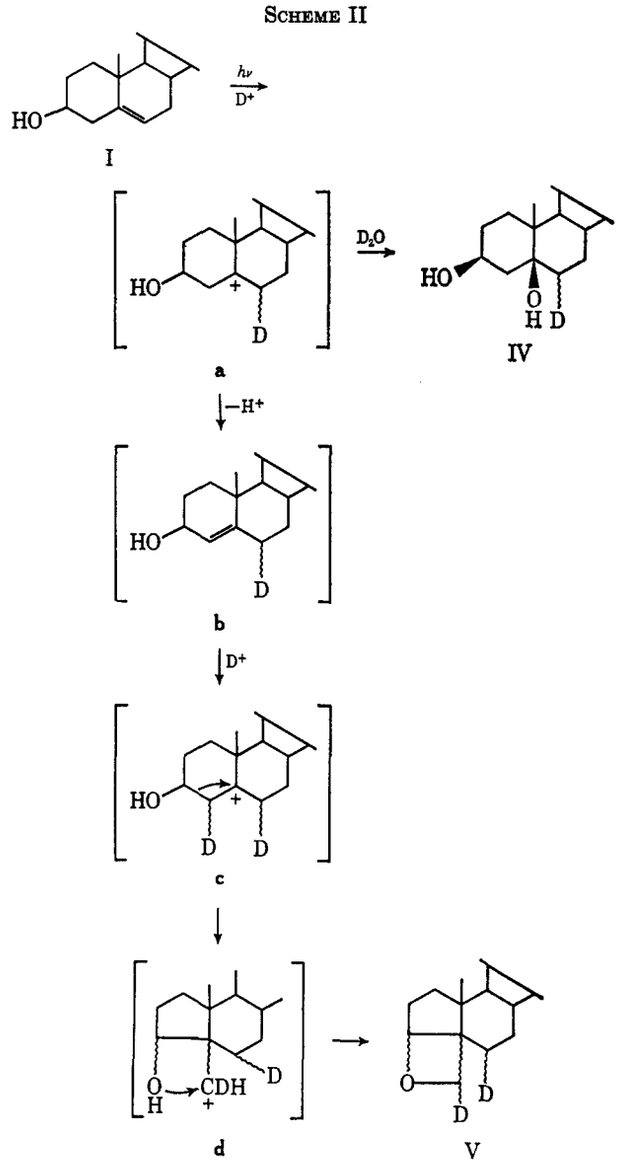
radiation of cholesterol in the presence of methanol and benzene gave several products, even a 5-methoxy derivative.[12] From an investigation of the stereochemistry of the photohydration process,[13] it was concluded that the first step, *i.e.*, protonation, occurs from the less hindered face of the olefin to form an incipient cation, which in turn loses a proton to give an exocyclic olefin or which reacts with water to produce epimeric alcohols. The cationic intermediate may revert to the original endocyclic olefin. An ionic mechanism for the formation of photoproducts II and III was supported by comparing the mass spectra of both diols with their corresponding deuterated analogs IV and V. The mass spectrum of diol IV showed one additional mass unit in the M^+ and *m/e* ions (main species) in comparison with that of the nondeuterated analog II, except for the *m/e* 110 peak which was predominant in both spectra of II and IV. This ion, $C_7H_{10}O$, arises from ring-B fragmentation of the C-5,6 and C-9,10 bonds[14] and loss of one H_2O. The deuterium atom in diol IV was, therefore, assigned to the C-6 position. Photoproduct III displayed prominent peaks at *m/e* 276 and 111, as a result of cleavage of the C-5,6 and C-9,10 bonds, while the spectrum of deuterated oxidocholestane V (principal species) showed two additional mass units at M^+ 388 and *m/e* 373, 358, and 233, but only one more unit at *m/e* 277 and 112 in comparison with III, as a result of the cleavage depicted below.



V

The formation of the principal deuterated compounds IV and V from cholesterol can best be depicted from the carbonium intermediate **a**, resulting from deuteration of the double bond at C-6.[15] This carbonium ion then adds deuterium oxide to give diol IV or loses a proton at C-4 to form a 4-cholesten-3-ol intermediate **b**. A deuterium atom can then add to C-4 with subsequent formation of a second tertiary carbonium ion **c**. Rearrangement of **c** then produces a primary carbonium ion **d**, in which the hydroxyl group is now suitably located to act as a nucleophile to produce V.

SCHEME II



Additional deuterated species as shown in Table II strongly suggest that the Δ^5 bond of cholesterol is readily photoisomerized into the Δ^4 position (and *vice versa*) *via* the C-5 carbonium ion. Supporting evidence comes from the photohydration of 4-cholesten-3β-ol (VI) which have the same two products, II and III, obtained from the cholesterol experiment. Recently, the photosensitized isomerizations of 10-methyl-1(9)-octalins were shown to proceed *via* an incipient cation, migration of a methyl or hydrogen to form another cation, and then elimination of a proton to give a new olefin.[16]

(12) H. Compaignon and R. Beugelmans, *Tetrahedron Lett.*, 6331 (1968).

(13) J. A. Marshall and M. J. Wurth, *J. Amer. Chem. Soc.*, **89**, 6788 (1967).

(14) H. Budzikiewicz and C. Djerassi, *ibid.*, **84**, 1430 (1962), and references cited therein.

(15) A photochemically induced protonation of a steroidal 5,6 double bond has been observed: S. Kuwata, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, to be published; private communication by K. Schaffner.

(16) J. A. Marshall and A. R. Hochstetler, *J. Amer. Chem. Soc.*, **91**, 648 (1969).

Photohydration studies of other steroidal olefins are currently under investigation in this laboratory.

Experimental Section

Materials and Apparatus.—Deuterium oxide (99.87 mol % D_2O, Bio-Rad Laboratories) was used in the appropriate experiments. Cholesterol (Eastman Kodak) was recrystallized two times from ethanol prior to irradiation. Silica gel G tlc plates (0.25 mm thick) were used routinely and were developed in hexane–acetone–ether, 8:1:1, unless designated otherwise. Melting points were taken on a Kofler hot stage and are corrected. Optical rotations were obtained on a Perkin-Elmer polarimeter (Model 141) in chloroform. The glpc data were obtained on a Barber–Coleman (series 5000) gas chromatograph using a 1% QF-1 column on Gas-Chrom P (80–100 mesh) at a temperature of 220°, 30 psi. The infrared spectra were measured on a Perkin-Elmer spectrometer (Model 21) in chloroform. The mass spectra were obtained on the Hitachi Perkin-Elmer RMU-6E mass spectrometer and the nmr spectra on a Varian A-60 in deuteriochloroform with tetramethylsilane as the internal standard. Samples were irradiated with a 450-W Hanovia mercury-vapor lamp, 679A-36, using a water-cooled quartz immersion well equipped with a Vycor filter. Nitrogen was passed through the solutions during the entire irradiation period.

Photosensitized Hydrations of Cholesterol. A.—A solution of 1.0 g of cholesterol in 150 ml of benzene saturated with water was irradiated for a period of 22 hr under conditions described in the above paragraph. On completion of the irradiation, most of the solvent was removed under reduced pressure. Methanol and benzene were successively added to the mixture and removed under reduced pressure. Tlc of the reaction mixture showed the presence of two reaction products at R_f 0.15 (trace) and 0.53 (major), and cholesterol (major, R_f 0.22). Glpc of the reaction mixture showed the major reaction product and cholesterol to exist in *ca.* 70:30 ratio, respectively.

B.—A solution of 1.0 g of cholesterol in the ternary solvent system composed of 105 ml of *t*-butyl alcohol, 30 ml of water, and 15 ml *o*-xylene (sensitizer) was irradiated as before for a period of 22 hr. The work-up of the reaction was carried out in the manner described above. Tlc of the mixture showed the presence of two reaction products at R_f 0.15 (major) and R_f 0.53 (minor), with no evidence of unreacted starting material. This result was confirmed by glpc on the reaction mixture.

C.—This experiment represents a reduced concentration of sensitizer in comparison with that used in part B. A solution of 1.0 g of cholesterol in the solvent system composed of 118.5 ml of *t*-butyl alcohol, 30 ml of water, and 1.5 ml *o*-xylene was irradiated for 22 hr. Tlc and glpc showed the presence of the two reaction products described in part B, but with an increased proportion of the R_f 0.15 compound (tlc). Again, evidence of any remaining cholesterol was not apparent.

D.—As a control, a solution of 1.0 g of cholesterol in 150 ml of *t*-butyl alcohol (no water or sensitizer present) was irradiated for 22 hr. Both tlc and glpc of the reaction mixture showed only the presence of cholesterol.

E.—In another control, a solution of 1.0 g of cholesterol in a binary solvent system containing 120 ml of *t*-butyl alcohol and 30 ml of water (no sensitizer present) was irradiated for 22 hr. Tlc and glpc of the reaction mixture showed only starting material plus a trace amount of the R_f 0.15 compound (tlc) and other trace impurities of lower R_f values.

Preparative-Scale Photosensitized Hydration of Cholesterol.—A solution of 7.0 g of cholesterol in the ternary solvent system composed of 829.5 ml of *t*-butyl alcohol, 210 ml of water, and 10.5 ml of *o*-xylene, was irradiated as described previously for a period of 40 hr. Work-up of the reaction mixture as before gave 8.05 g of yellow colored solid. Tlc showed the presence of the two major products at R_f 0.15 and 0.53. The crude mixture was subjected to column chromatography on alumina (Woelm, grade II, 225 g). The fractions were eluted as shown in Table III.

Table III

Fractionation of Products from the Photosensitized Hydration of Cholesterol

Fraction	Solvent, vol	Amount, g	Description
1	Hexane, 1.5 l.	0.156	Oil
2	Benzene–hexane (1:9), 1.5 l.	0.510	Colorless solid
3	Benzene–hexane (1:3), 1.5 l.	1.398	Colorless solid
4	Benzene–hexane (1:1), 1.5 l.	0.472	Oil
5	Benzene, 1.5 l.	0.386	Oil
6	Ether–benzene (1:9), 1.5 l.	0.426	Oil
7	Ether–benzene (1:3), 1.5 l.	0.211	Oil
8	Ether–benzene (1:1) to chloroform–ethyl acetate–methanol (1:1:1) 12 l.	4.248	Yellow semisolid

Fraction 3 (1.398 g of colorless solid) contained R_f 0.53 compound with little contamination as shown by tlc. Crystallization of the solid from acetone gave 864 mg of colorless flakes, mp 112–116°. The product was recrystallized from acetone–dichloromethane to give 700 mg of III, mp 114.5–116°. Recrystallization from the same solvent system gave the analytical sample of 3ξ,5-oxidomethylene-5ξ-A-norcholestane as colorless, glossy flakes: mp 115.5–117°, $[\alpha]^{21}D$ +60.0°; infrared spectrum 1490, 1468, 1445, 1385, 1370, 988, 968, 910, 878, and 854 cm^{-1}; mass spectrum M^+ 386, *m/e* 371, 356, 276, 231, 111, no predominant *m/e* 70 peak; nmr spectrum multiplet at 4.47 ppm (1 H, C-3 proton) and a quartet at 3.96 and 4.59 ppm (2 H, J = 6.5 cps, C-2′ methylene).

Anal. Calcd for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.97; H, 11.98.

Fraction 8 (4.248 g) was highly enriched in compound R_f 0.15. Crystallization of the product from methanol, followed by recrystallizations from methanol–ether and absolute ethanol gave 1.74 g of 5β-cholestane-3β,5-diol (II) as fine, pale yellow needles, mp 149–150°. The analytical sample melted at 150.5–151.5°, $[\alpha]^{21}D$ +35.6°. On occasion, a double melting point of 127.5–128.5 and 149–150° was also observed for this compound (lit. mp 147–149°, $[\alpha]D$ + 40°[6] and double mp 129–130 and 149°, $[\alpha]D$ +35.2°[7]). Spectroscopic data follow: infrared spectrum 3608 and 3495 cm^{-1} (free and hydrogen bonded hydroxyl absorptions, respectively); mass spectrum M^+ 404, *m/e* 386, 368, 249, and 110.

Anal. Calcd for $C_{27}H_{48}O_2$: C, 80.14; H, 11.96. Found: C, 80.45; H, 12.23.

5β-Cholestane-3β,5-diol (200 mg) was acetylated with 1.6 ml of acetic anhydride and 8.0 ml of pyridine. After storage at room temperature overnight, followed by 1 hr at 100°, the cooled mixture was poured into 60 ml of cold 5% sodium carbonate solution. The mixture was stirred for 10 min and the solid removed by suction filtration. The product was chromatographed on alumina (6.0 g, grade 2). Elution with benzene–hexane (1:3) to benzene gave 168 mg white solid, which on crystallization from methanol gave 131 mg of crystalline 5β-cholestane-3β,5-diol 3-acetate: mp 80–81°; $[\alpha]^{21}D$ +45.1° (lit. mp 79–81°[8]); infrared spectrum 3594 cm^{-1} (hydroxyl) and 1735 cm^{-1} (acetoxy); mass spectrum M^+ 446.

Anal. Calcd for $C_{29}H_{50}O_3$: C, 77.97; H, 11.28. Found: C, 78.25; H, 11.47.

Photosensitized Deuteration of Cholesterol.—A preliminary rate study consisted of the irradiation of a solution of 1.0 g of cholesterol in the ternary solvent system composed of 128.5 ml of dioxane, 1.5 ml of *o*-xylene, and 20 ml of deuterium oxide. Aliquots were removed periodically at 0, 4, 8, and 32 hr from the photolysis chamber. The aliquots were evaporated under reduced pressure and the residues subjected to tlc. The chromatogram indicated a *ca.* 90% disappearance of cholesterol and the presence of two products (R_f values the same as those of II and III from the photosensitized hydration experiment) after a 32-hr irradiation period.

In the preparative-scale experiment, 7.0 g of cholesterol dissolved in 900 ml of dioxane containing 10.5 ml of *o*-xylene and 140 ml of deuterium oxide was irradiated in the usual manner for a period of 72 hr. After evaporation of the solvent and addition of benzene to the residue, followed by evaporation, the mixture was subjected to column chromatography (230 g, grade II). The fractions obtained are summarized in Table IV.

Fraction D-2 (1.149 g, colorless solid) was highly enriched in the compound whose R_f value was identical with that of oxidocholestane III obtained from the photohydration experiment. The solid was crystallized from acetone–dichloromethane to give 590 mg of colorless flakes, mp 117–118°. Recrystallization of the product from the same solvent gave 515 mg of 2′ξ,6ξ-d_2-3ξ,5-oxidomethylene-5ξ-A-norcholestane (V, main species): mp 117.5–118.5°; $[\alpha]^{21}D$ + 61.2°; infrared spectrum 2140 (C–D)

TABLE IV

FRACTIONATION OF THE MIXTURE FROM THE PHOTOSENSITIZED DEUTERATION OF CHOLESTEROL

Fracture	Solvent, vol	Amount, g	Description
D-1	Hexane, 1.4 l.	0.198	Yellow oil
D-2	Benzene–hexane (1:19 to 1:7), 2.8 l.	1.149	Colorless solid
D-3	Benzene–hexane (1:3), 1.4 l.	0.348	Colorless solid
D-4	Benzene–hexane (1:1), 1.4 l.	0.611	Colorless solid
D-5	Benzene, 1.4 l.	1.131	Yellow semisolid
D-6	Ether–benzene (1:9), 1.4 l.	0.766	Yellow oil
D-7	Ether–Benzene (1:3), 1.4 l.	1.215	Yellow semisolid
D-8	Ether–benzene (1:1) to ether, 2.8 l.	1.263	Colorless solid
D-9	Methanol–ether (1:39), 1.4 l.	2.672	Colorless solid
D-10	Methanol–ether (1:19) to chloroform–ethyl acetate–methanol (1:1:1), 5.6 l.	1.763	Yellow oil

1468, 1384, 1369, 982, 952, 915, and 853 cm^{-1}; mass spectrum M^+ 388, *m/e* 373, 358, 277, 233, and 112.

Fraction D-8 (1.263 g) was recrystallized two times from methanol to give 880 mg of 6ξ-d_1-5β-cholestane-3β,5-diol (IV, main species) as white flakes, mp 151–152° with transcrystallization at 131–132°, $[\alpha]^{21}D$ + 36.0°. This compound had a tlc R_f value of 0.15, the same as 5β-cholestane-3β,5-diol obtained from the photosensitized hydration of cholesterol; infrared spectrum 3608 and 3495 cm^{-1} (free and hydrogen-bonded hydroxyl absorptions), 2160 cm^{-1} (C–D); mass spectrum M^+ 405, *m/e* 387, 369, 250, and 110.

Photosensitized Hydration of 4-Cholesten-3β-ol (VI).—A solution of 250 mg of pure 4-cholesten-3β-ol in the ternary solvent system composed of 118.5 ml of *t*-butyl alcohol, 30 ml of water, and 1.5 ml of *o*-xylene was irradiated as described previously for a period of 24 hr. Tlc showed the presence of two major products at R_f 0.15 and 0.53, identical with compounds II and III obtained from the photohydration of cholesterol. Column chromatography of the mixture (7.5 g of grade II alumina) on elution with hexane–benzene (19:1 and 7:1) gave 68 mg of oxido III, which gave mp 114–115° after two recrystallizations from acetone. Elution of the column with benzene–ether (1:1) and ether gave 26 mg of diol II, mp 149–150° after three recrystallizations from methanol. Both compounds displayed similar infrared spectra to those obtained from the cholesterol experiment.

Treatment of 3ξ,5-Oxidomethylene-5ξ-A-norcholestane (III) with Lithium Aluminum Hydride–Aluminum Chloride.—To a mixture of 66 mg of lithium aluminum hydride in 7.5 ml of anhydrous ether (cooled) was cautiously added 960 mg of anhydrous aluminum chloride in 7.5 ml ether. To the resulting solution was added 25 mg of oxido III in 4 ml of ether. The mixture was placed in an ice bath for 45 min and then refluxed for 24 hr. After work-up of the reaction, the mixture was subjected to tlc. The chromatogram indicated nearly complete conversion of starting material into at least six products.

Irradiation of 5β-Cholestane-3β,5-diol (II).—A solution of 200 mg of 3,5-diol II in the ternary solvent system containing 82.9 ml of *t*-butyl alcohol, 21 ml of water, and 1.05 ml of *o*-xylene was irradiated under the usual conditions for 24 hr. Work-up of the yellow solution and tlc of the reaction mixture showed the presence of starting material only, accompanied by streaking (most likely polymerization of *o*-xylene) and no spot corresponding to the R_f value of oxido III.

Irradiation of 3ξ,5-Oxidomethylene-5ξ-A-norcholestane (III).—Irradiation of 51 mg of oxidocholestane III in 82.9 ml of *t*-butyl alcohol, 21 ml of distilled water, and 1.05 ml of *o*-xylene for 24 hr gave only starting material and trace impurities and no evidence of conversion of III into diol II as shown by tlc.

Registry No.—I, 57-88-5; II, 570-97-8; II (3-Acetate), 4947-62-0; III, 21876-39-1; IV, 21876-40-4; V, 21876-41-5.

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