THE OCTANT RULE VIII.* VARIABLE TEMPERATURE CIRCULAR DICHROISM SPECTRA OF α-METHYL- AND METHOXYL-SUBSTITUTED 5α-CHOLESTAN-2- AND -3-ONES.

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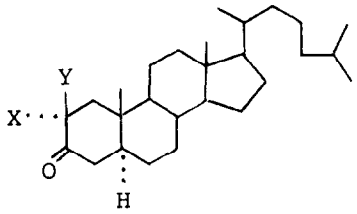
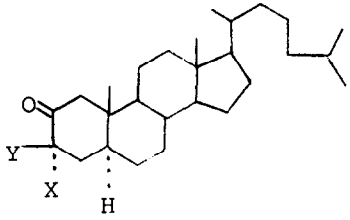
Abstract. 2α- and 2β-Methyl- and methoxy-5α-cholestan-3-ones and 3α- and 3β-methyl- and methoxy-5α-cholestan-2-ones have been synthesized and their variable temperature circular dichroism spectra obtained and analyzed. Rotatory strength (R) values for α-axial and equatorial CH_3 and OCH_3 groups are determined by difference measurements with the parent ketone. The (small) equatorial CH_3 R-values do not consistently follow the Octant Rule. Axial OCH_3 groups do not obey the Octant Rule ("anti-octant" behavior) and impose a bathochromic shift on the C=O n-π* transition. Equatorial OCH_3 groups do not consistently follow octant or "anti-octant" behavior.

Introduction

From an analysis of circular dichroism (CD) data of available polycyclic ketones, Kirk and Klyne [2] determined contributions ($\delta\Delta\varepsilon$) of methyl substituents to $\Delta\varepsilon$ values for the n-π* transition of cyclohexanone. In a variety of solvents the contributions of α-axial CH_3 and α-equatorial CH_3 groups were consignate with the former ($\delta\Delta\varepsilon$ = +1.2 to 1.5) being about one order of magnitude larger than the latter ($\delta\Delta\varepsilon$ = +0.15 to 0.20) [3]. These findings are in keeping with those of earlier workers [4,5,6], and the classical Octant Rule [7], but the value of an α-equatorial CH_3 group has also been calculated to be small and dissignate [8]. The contribution ($\delta\Delta\varepsilon$) of α-axial OCH_3 groups to $\Delta\varepsilon$ values has been assessed as dissignate (-0.05) [3-9]. No assessment has been made for the contribution ($\delta\Delta\varepsilon$) of an α-equatorial OCH_3 group, but an α-equatorial OH group has been assigned a dissignate contribution (-0.8) [3]. In view of the conflict between theory [8] and experiment for the α-equatorial CH_3 group and the lack of data on α-OCH_3 groups, we prepared and investigated (variable temperature CD) 2β-methyl-5α-cholestan-3-one (1), 2α-methyl-5α-cholestan-2-one (4), 3α-methyl-5α-cholestan-2-one (3), 3β-methyl-5α-cholestan-2-one (4), 2β-methoxy-5α-cholestan-3-one (5), 2α-methoxy-5α-cholestan-3-one (6), 3α-methoxy-5α-cholestan-2-one (7), 3β-methoxy-5α-cholestan-2-one (8), and the corres-

ponding unsubstituted ketones, 5α-cholestan-3-one (9) and 5α-cholestan-2-one (10). The CD data and their analysis is reported herein.





1: X=H, Y=CH_3
2: X=CH_3, Y=H
5: X=H, Y=OCH_3
6: X=OCH_3, Y=H
9: X=Y=H

3: X=CH_3, Y=H
4: X=H, Y=CH_3
7: X=OCH_3, Y=H
8: X=H, Y=OCH_3
10: X=Y=H

Synthesis and Results

Compounds 1-8 were synthesized using known procedures [9,10] *via* opening of 2,3-epoxide. Thus, treatment of the 2α,3α-epoxide with lithio 1,3-dithiane followed by Ni(R) desulfurization gave 2β-methyl-5α-cholestan-3α-ol, which yielded 1 upon careful oxidation [9]. The more stable equatorial isomer (2) was obtained quantitatively by acid catalyzed epimerization of 1. Similarly, 3 and 4 were prepared [9] *via* lithio 1,3-dithiane opening of 2β,3β-oxido-5α-cholestane, which was conveniently synthesized in 75% yield from 5α-cholest-2-ene using a modification of the procedure of Adinolfi *et al.* [11]. Preparation of the methoxyketones was achieved *via* acid-catalyzed opening of the epoxides in methanol [10]. Thus, 2α,3α-oxido-5α-cholestane gave first the axial methoxyketone (5), which could be epimerized to the more stable equatorial isomer (6). Similarly, 2β,3β-oxido-5α-cholestane yielded 7 and 8. Parent ketone 9 was prepared by dichromate oxidation of cholestan-3β-ol; 8 was prepared by oxidation of 5α-cholestan-2β-ol, which was obtained following $LiAlH_4$

treatment of 2β,3β-oxido-5α-cholestane.

Results

The CD spectra for the n-π* transitions of 3-ketones 1, 2, 5, 6 and 9 are shown in Figure 1; the CD spectra of 2-ketones 3, 4, 7, 8 and 10 are shown in Figure 2. The bathochromic λ_{max} shifts of the axial OCH_3 ketones (6, Figure 1 and 7, Figure 2) are easily recognizable. Rotatory strengths (R) from the variable temperature CD spectra are presented in Table 1. The change in R between 25°C and -175°C is small, and the CD Cotton effect (CE) sign remains invariant. At -175°C vibrational structure becomes more recognizable on the CD curves. As is revealed especially at -175°C, unsubstituted and methyl-substituted ketones have an average vibrational spacing of ca 1100 cm^{-1}; the methoxyketones have an average value of 1150 cm^{-1}. The spacings correspond roughly to the lowest vibrational transition of the n-π* excited state of the ketone. The influence of solvent on the n-π* CD transition can be seen in Tables 2 and 3 which compare λ_{max}, $\Delta\varepsilon$ and R values in n-heptane and EPA (ethyl ether-isopentane-ethanol 5:5:2). As expected, EPA causes an hypsochromic λ_{max} shift relative to n-heptane. In most cases the $\Delta\varepsilon$ values are larger in EPA, as might be expected from previously observed solvent-dependent rotatory strength data on cholestan-3-one [12] and other steroidal ketones [13].

Discussion

The contribution of the substituent CH_3 or OCH_3 group to the CD CE may be approximated by substracting the $\Delta\varepsilon$ or R value associated with the unsubstituted ketone from that of the substituted ketone [2]. Inherent to this approximation is the assumption that the ring geometries remain substituent invariant and the realization that one is comparing H as a substituent to CH_3 or OCH_3 as a substituent. Substituent contributions

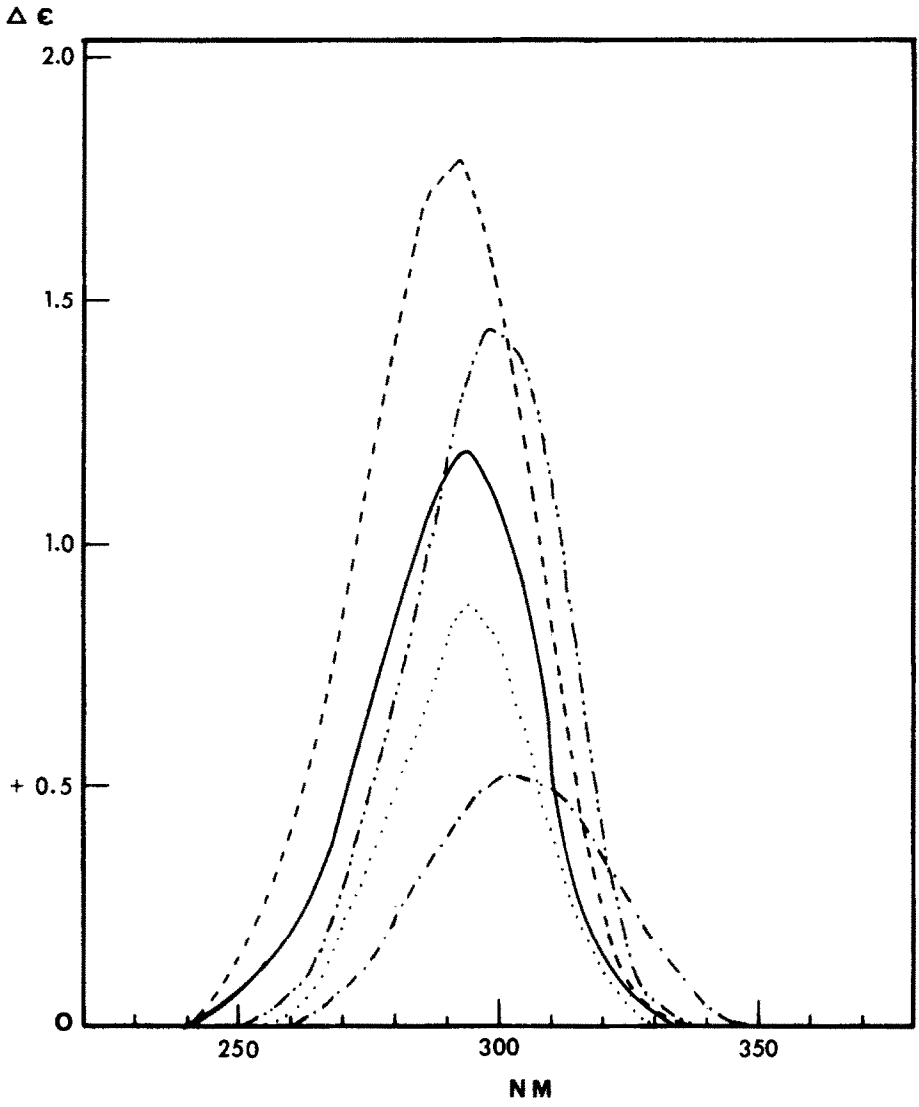


Figure 1 Circular dichroism spectra of 5α-cholestan-3-one (————), 2β-methyl-5α-cholestan-3-one (- - - - - -), 2α-methyl-5α-cholestan-3-one (. . . . . .), 2β-methoxy-5α-cholestan-3-one (- . - . - .), and 2α-methoxy-5α-cholestan-3-one (- .. - .. - ..) in ethanol-isopentane-diethyl ether [2:5:5] (EPA) at 25° C.

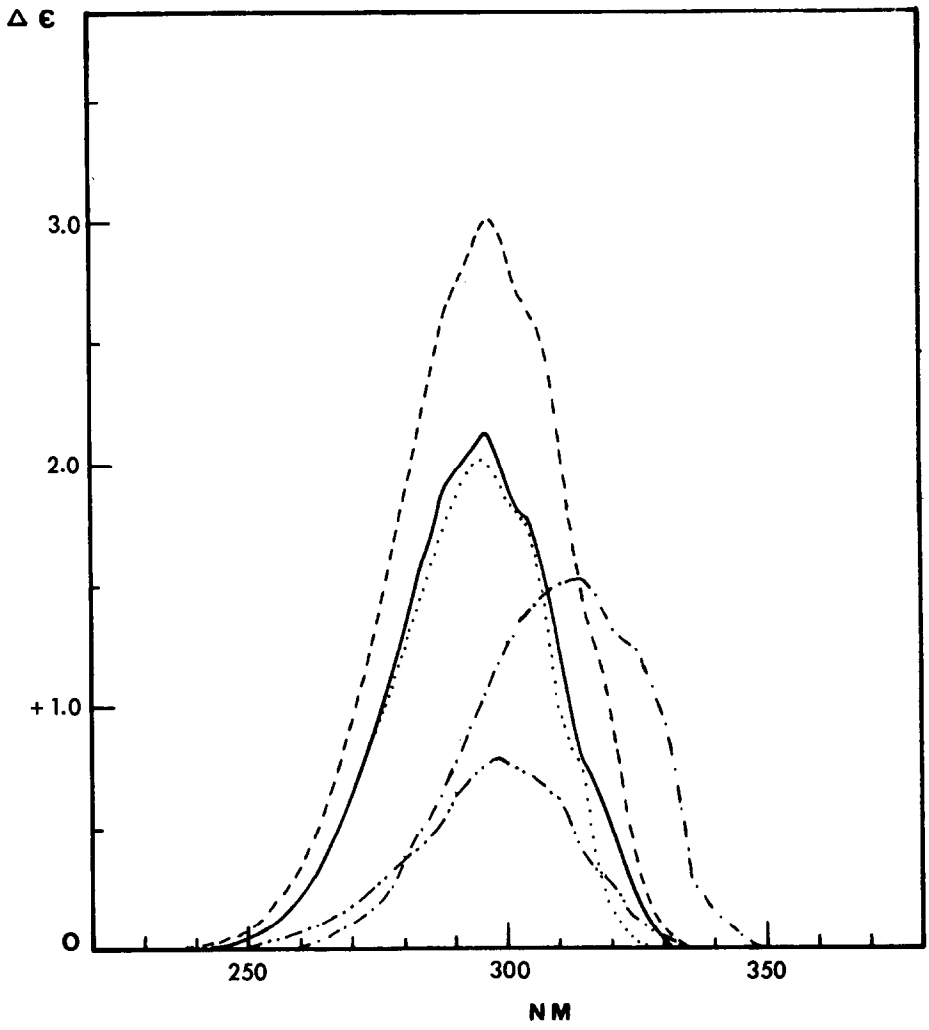


Figure 2 Circular dichroism spectra of 5α-cholestan-2-one (————), 3α-methyl-5α-cholestan-2-one (- - - - - -), 3β-methyl-5α-cholestan-2-one (. . . . . .), 3α-methoxy-5α-cholestan-2-one (- · - · - · -), and 3β methoxy-5α-cholestan-2-one (- ·· - ·· - ··) in ethanol-isopentane-diethyl ether [2:5:5] (EPA) at 25° C.

Table 1. Reduced Rotational Strengths, $[R]^T$, in EPA at Various Temperatures for Steroidal Ketones with the 5α-Configuration

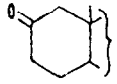
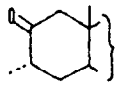
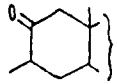
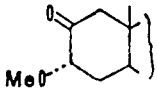
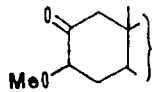
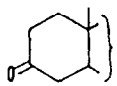
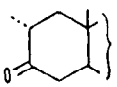
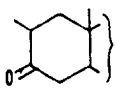
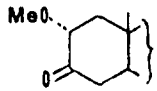
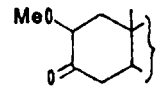
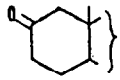
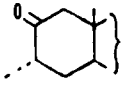
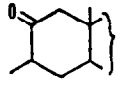
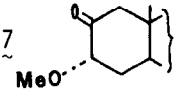
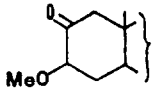
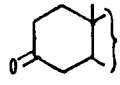
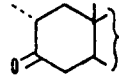
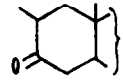
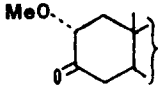
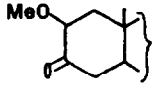
		25°	-25°	-100°	-175°	% Change between 25° and -175°
10		+6.62	+6.51	+6.37	+6.38	-4%
3		+9.47	+9.60	+9.77	+10.23	+8%
4		+6.07	+5.87	+5.68	+5.68	-6%
7		+4.96	+4.49	+4.11	+3.76	-24%
8		+2.30	+2.49	+2.53	+2.61	+13%
9		+3.99	+4.07	+4.11	+4.18	+5%
2		+2.40	+2.43	+2.46	+2.65	+10%
1		+5.65	+5.74	+6.21	+6.57	+16%
6		+4.49	+4.55	+4.83	+5.40	+20%
5		+1.75	+1.79	+1.89	+2.12	+20%

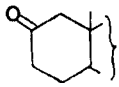
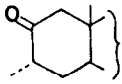
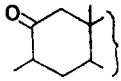
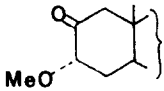
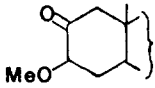
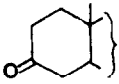
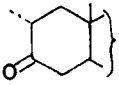
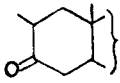
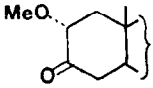
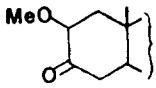
Table 2. Comparison of $\Delta\varepsilon$ of the CD Curves of the 5α-Cholestanones in EPA and n-Heptane at 25°

		EPA		n-Heptane		Solvent Effect	
		λ(nm)	Δε	λ(nm)	Δε	ΔΔε*	Δλ(nm)**
10		296	+2.133	297.5	+1.263	+0.870	+1.5
3		296.5	+2.990	298	+2.785	+0.205	+1.5
4		295	+2.017	296.5	+1.513	+0.504	+1.5
7		314	+1.526	316	+1.222	+0.304	+2.0
8		298	+0.771	--	--	--	--
9		293	+1.189	296.5	+0.819	+0.370	+3.5
2		294	+0.871	302	+0.689	+0.182	+8.0
1		292	+1.786	294.5	+1.700	+0.086	+2.5
6		297	+1.440	305	+1.552	-0.112	+8.0
5		303.5	+0.517	--	--	--	--

*$\Delta\Delta\varepsilon$ = $\Delta\varepsilon$ (in EPA) - $\Delta\varepsilon$ (in n-Heptane)

**$\Delta\lambda$ = λ (in n-Heptane) - λ (in EPA)

Table 3. Comparison of $[R]^{25}$ in EPA and n-Heptane for 5α-Cholestanones

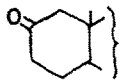
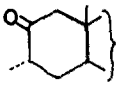
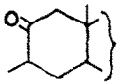
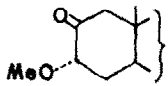
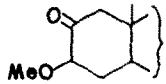
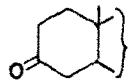
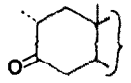
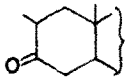
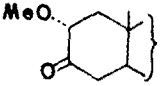
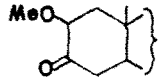
		EPA	n-Heptane	Solvent Effect $\Delta[R]^T$ *
10		+6.62	+4.08	+2.54
3		+9.47	+9.35	+0.12
4		+6.07	+4.70	+1.37
7		+4.96	+4.10	+0.86
8		+2.30	--	--
9		+3.99	+2.73	+1.26
2		+2.40	+2.08	+0.32
1		+5.65	+5.78	-0.13
6		+4.49	+5.34	-0.85
5		+1.75	--	--

*$\Delta[R]^T = [R]^T$ (in EPA) - $[R]^T$ (in n-Heptane)

are summarized in Table 4 as $\Delta\Delta\varepsilon$ or ΔR. The data reveal that, expectedly, α-axial CH_3 has a larger octant contribution than α-equatorial CH_3. Axial CH_3 groups follow the Octant Rule [7] in both EPA and n-heptane, but equatorial groups do not always. In EPA their contributions are consignate, but in n-heptane the 3(e) -CH_3 of 4 makes a dissignate contribution. This peculiar solvent (solvation [12,13]?)effect was unanticipated. However, it is worth noting that calculations [8] predict a (+) CE contribution from the equatorial CH_3's of both 2 and 4. Insofar as CD spectra in hydrocarbon solvents approximate gas phase spectra (and, e.g., those calculated by theory), the data seem to provide the first example of "anti-octant" or dissignate behavior for an α-equatorial CH_3. And they clearly indicate the rather significant environmental and, presumably, stereochemical sensitivity of the inherently small $\Delta\varepsilon$ (R) values for equatorial CH_3 groups, which do after all lie close to an extended carbonyl (octant) symmetry plane. But it must be stressed that the consignate-dissignate behavior of an equatorial CH_3 group presupposes that the position of such a group is known, and that, in the case of 4, it is located above the octant symmetry plane.

Curiously, the magnitudes of the contributions for axial and equatorial CH_3 groups are different when derived from 2-keto and 3-keto-5α-cholestanes. The R values at -175°C derived from the substituted 5α-cholestan-2-ones are twice as large for axial CH_3 but only one-half as large for equatorial CH_3 when compared with 5α-cholestan-3-ones. One might attribute differences in the axial CH_3 values to differing ring geometries in the parent and unsubstituted 3-oxo system (due to 1,3-diaxial CH_3-CH_3 interaction between CH_3 groups at C-2 and C-10); however, such a rationalization seems to be less applicable to the equatorial CH_3 ketones.

Table 4. Comparison of $\Delta[R]^{T*}$ and $\Delta\Delta\varepsilon^{**}$ of Keto-5α-steroids in EPA (Upper Entry) and n-Heptane (Lower Entry).

		$\Delta[R]^{25}$	$\Delta\Delta\varepsilon$ (25°C)	$\Delta[R]^{-175}$	$\Delta\Delta\varepsilon$ (-175°C)
10		0	0	0	0
3		+2.85 +5.27	+0.857 +1.522	+3.85	+1.116
4		-0.55 +0.62	-0.116 +0.250	-0.70	-0.092
7		-1.66 +0.02	-0.607 -0.041	-2.62	-0.700
8		-4.32 †	-1.362 †	-3.77	-1.212
9		0	0	0	0
2		-1.59 -0.65	-0.318 -0.130	-1.53	-0.400
1		+1.66 +3.05	+0.597 +0.881	+2.39	+0.732
6		+0.50 +2.61	+0.251 +0.733	+1.22	+0.329
5		-2.24 †	-0.672 †	-2.06	-0.724

*$\Delta[R]^T = [R]^T$ (α-substituted 2- or 3-keto steroids) $-[R]^T$ (parent ketone), where [R] is the reduced rotatory strength.

**$\Delta\Delta\varepsilon = \Delta\varepsilon$ (α-substituted 2- or 3-keto steroids) - $\Delta\varepsilon$ (parent ketone).

† Sample insoluble in n-heptane.

CH_3 and OCH_3 substituents behave strikingly differently but both exhibit pronounced solvent effects (Table 4). The axial OCH_3 groups exhibit dissignate behavior in EPA, but the equatorial OCH_3 groups do not behave in a uniform way: the 2(e)-OCH_3 group gives a dissignate contribution in both EPA and n-heptane but the 3(e)-OCH_3 group gives a consignate contribution in EPA. Curiously, the (3a)-OCH_3 group has essentially a zero contribution to the R in n-heptane. In other systems, axial-like α-*endo* OH and OAc substituted bornan-2-one and bornan-3-one exhibit "anti-octant" effects [14]. However, in those systems, the equatorial-like α-*exo* OH and OAc groups also give "anti-octant" contributions [14]. Examples of steroid α-acetoxyketones and α-hydroxyketones reveal no consistent consignate or dissignate behavior [15,16]. Similar dissignate effects found among α-amino ketones have been noted and explained [17] on the basis of interaction of the lone pair heteroatom electrons with the carbonyl group [17]. As has been shown previously the nature and shape of the octant surfaces of the Octant Rule will be governed by the nature of the substituent. More electron-rich or electron-diffuse substituents such as OCH_3, OH or OAc need not *a priori* follow the same rule as a CH_3 substituent, or even a Cl substituent. A particularly cogent discussion is that offered for α-NH_2 ketones. In an analysis of the influence on R of the relative orientation of the N lone pair and the carbonyl group, R varied between +1 and +30 for torsional angles 0 to 315°; whereas, when CH_3 replaced NH_2, R varied only between +19.8 and +20.6 [8].

Conclusions

Cotton effect contributions of axial CH_3 or OCH_3 groups are generally larger in magnitude than those of the corresponding equatorial substituents. Axial CH_3 groups follow the classical Octant Rule but axial OCH_3 groups exhibit "anti-octant" behavior. Equatorial CH_3 and OCH_3 groups exhibit less consistent behavior and may or may not obey the classical Octant Rule. We urge caution in applying the Octant Rule to equatorial substituents until a more detailed experimental and theoretical knowledge of the parameters influencing their octant contributions can be achieved.

Experimental Part

All circular dichroism spectra were obtained in MCB spectroscopic grade n-heptane or EPA (ether,isopentane,ethylalcohol-5:5:2 v/v/v) on a JASCO J-40 spectrophotometer equipped with piezoelectric modulator and lock-in amplifier. Variable temperature CD spectra were obtained using a cryoscopic dewar as described by E. L. Docks [18]. Nuclear magnetic resonance (nmr) spectra were measured in deuteriochloroform on a Varian A-60 or Perkin-Elmer R-24B instrument. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 137 (Infracord) spectrophotometer. Mass spectra were recorded on a Jeolco JMS-07 mass spectrometer. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Sodium D-line rotations were measured on a Perkin-Elmer 141 polarimeter. Spectroscopic solvents (EPA and n-heptane) were from Matheson and were used as obtained. Tetrahydrofuran (THF) and ether were dried by heating at reflux over sodium metal wire using benzophenone as indicator. Standard Jones reagent was prepared by dissolving 26.72g of chromium trioxide (Baker Analyzed) in 23 ml of concentrated sulfuric acid diluted with water to a volume of 100 ml for Jones oxidation [19]. The silica gel used for thin layer chromatography was silica gel F, M. Woelm, Eschwege. The plates used for preparative thin layer chromatography (p.t.l.c.) (20 x 20 cm) were 1 mm thick in adsorbent, whereas the analytical thin layer chromatography plates (5 x 20 cm) were 0.250 mm thick. Silica gel for column chromatography was also Woelm. All steroids below are of the 5α-series.

Cholest-2-ene. This was prepared in 70% yield, mp 72.5-73.5° by basic Al_2O_3 catalyzed elimination of cholestanyl tosylate, according to the procedure of Nakano, Hasegawa and Djerassi [20].

2α,3α-Oxidocholestane. Cholest-2-ene (2.491 g, 6.7 mmol) was dissolved in methylene chloride (25 mL) and the solution was chilled to -5° in a

250 mL rb flask fitted with a condenser and a calcium chloride tube. Then m-chloroperbenzoic acid (Aldrich) (1.991 g, 11.5 mmol) in methylene chloride (25 mL), pre-cooled to 0°, was added to the flask. The mixture was stirred and allowed to warm to room temperature. After 48 h. the solution was diluted with 100 mL of methylene chloride and was washed in sequence with 10% sodium sulfite (100 mLO, 10% sodium thiosulfate (100 mL), 1 M sodium bicarbonate (200 mL) and water (200 mL). The methylene chloride extract was dried over sodium sulfate (anhydrous) and evaporated (rotary) to a volume of ca. 10 mL. Addition of methanol (10 mL) followed by cooling in ice-acetone bath yielded 1.60 g (62%) of 2α,3α-oxido-5α-cholestane, m.p. 103-103.5°, $[\alpha]_D^{25}$ +34.4° (c. 1.54, chloroform) (Lit. [21] $[\alpha]_D^{25}$ +35.1° (chloroform)).

2β,3β-Oxidocholestane [11]. Glacial acetic acid (350 mL) was added to a mixture of Δ^2-cholestene (5.80 g, 15.6 mmol), iodine (1.98 g, 7.8 mmol) and potassium iodate (0.8359). The mixture was then stirred and treated in an oil bath (62°) for 2.5 h. After cooling, the mixture was poured into water (200 mL) and was extracted with hexane (5 x 150 mL). The combined extract was then washed with 5% sodium bicarbonate (3 x 150 mL) 5 N sodium thiosulfate (2 x 150 mL) and water (2 x 100 mL). After evaporation of hexane, acetone-methanol (1:1) was added to crystallize the desired product. Recrystallization from acetone-methanol (1:1) yielded 6.76 g (78%) of 3α-iodo-5α-cholestan-2β-yl acetate, m.p. 85-88°.

Sodium hydroxide (0.546 g, 13.6 mmol) in methanol (500 mL) was added to a mixture of 3α-iodo-5α-cholestan-2β-yl acetate (3.80 g, 6.8 mmol) and tetrahydrofuran (150 mL). The reaction solution was stirred on a steam bath for 2 h. Then the solution was poured into water (400 mL) with crushed ice. Crystals formed and were filtered. Recrystallized from methanol-ether (5:1) yielded 2.50 g (96%) of 2β,3β-oxido-5α-cholestane, m.p. 84.5-86.5°, $[\alpha]_D^{25}$ + 50.0° (c. 1.53, chloroform), (Lit. [22] $[\alpha]_D^{25}$ +50.1° (chloroform)). The preparation is indicated as follows.

2β-Methylcholestan-3-one(1). This substance was prepared in overall 17% yield from 2α,3α-oxidocholestane by treatment with 2-lithio-1,3-dithiane, Ni(R) desulfurization and careful Jones oxidation by modification of the procedure of Jones and Grayshan [10].

2β-(2-(1,3-Dithianyl))-5α-cholestan-3α-ol. 2-Lithio-1,3-dithane was prepared by slow addition of n-butyllithium (15.0 mL of a 1.46 M hexane solution, 22 mmol) to 1,3-dithiane (2.59 g, 22 mmol) in freshly distilled tetrahydrofuran (55 mL) at -23° (Dry Ice in CCl_4) under nitrogen. After stirring for one hour, a -23° solution of 2α,3α-oxido-5α-cholestane (1.10 g, 2.8 mmol) in dry tetrahydrofuran (10 mL) was added. Then the reaction mixture was allowed to stand in the refrigerator (-3°C) for one week. Afterward, the solution was poured into water (500 mL) and extracted with ether (5 x 50 mL). The combined ether extract was washed with water (2 x 25 mL), dried with anhydrous sodium sulfate and the ether was evaporated. A yellowish gum obtained was purified on a column of silica gel using a gradient elution with hexane-benzene-ether. Crude 2β(2-(1,3-dithianyl))-5α-cholestan-3α-ol (650 mg, 46%) was collected, m.p. 88-106°; nmr ($CDCl_3$) δ 0.64 (C-18 CH_3), 4.25 (m, H C $S_2C_3H_6$, C-3H) ppm.

2β-Methyl-5α-cholestan-3α-ol. 2β-(2-(1,3-Dithianyl))-5α-cholestan-3α-ol (476 mg, 0.9 mmol), absolute ethanol (110 mLO and freshly prepared W-2 Raney nickel [22] (6.5 g) were heated at reflux for 4 h. in a 250 mL, 3-N RB flask. Then the nickel was removed by filtration and the residue was crystallized from ether-methanol (1:5). The crude product was further purified by p.t.l.c. using benzene as the developing solvent. The 2β-methyl-5α-cholestan-3α-ol obtained was recrystallized from ether-methanol (1:5) as needles, 184 mg (51%), m.p. 110-113°, nmr ($CDCl_3$) δ 0.64 (C-18 CH_3), 0.83 (C-19 CH_3), 1.10 (3H, d, J - 7 Hz, 2β CH_3), 3.66 (1H, m, C-3βH) ppm.

2β-Methyl-5α-cholestan-3-one(1). 2β-Methyl-5α-cholestan-3α-ol (79 mg, 0.20 mmol) in acetone (14 mL) was stirred at 0° for 3 min with Jones reagent (8 N chromic acid) (0.07 mL). The mixture was then immediately poured into water (100 mL) and extracted with ether 3 x 50 mL) followed by evaporation of the dried (using anhydrous magnesium sulfate) combined extract yielding crude 2β-methyl-5α-cholestan-3-one. Purification by p.t.l.c. with benzene development followed by recrystallization from ether-methanol (1:5) gave the pure product as needles, 57 mg (71%); m.p. 95.5-96.5°; ir (CCl_4) 1715 cm^{-1} (carbonyl); UV (EPA) λ_{max} 284 (ε 27.7); nmr ($CDCl_3$) δ 0.65 (C-18 CH_3), 0.75 (C-19 CH_3), 1.02 (3H, d J - 7.5 Hz, 2 CH_3) ppm; and $[\alpha]_D^{25}$ +96.1° (c·0.80, chloroform) (Lit. [23] $[\alpha]_D^{25}$ +86° (c·0.88, chloroform)). CD reported as Δε(λ,nm) in n-heptane (c·1.46) at 25°C: 0(340), +0.648(317), +0.778(314), +1.008(310), +1.477 (303), +1.498(300), +1.700(294.5), +1.527(289), +1.484(286), +1.160(280), +0.274(260), 0(240); in EPA (c·0.96) at 25°C: 0(335), +0.066(325), +0.515(315), +0.811(310), +1.210(305), +1.588(298), +1.786(292), +1.665 (285), +0.854(270), 0(240); in EPA at -25°C: 0(335), +0.479(315), +0.754 (310), +1.126(305), +1.539(298), +1.804(292), +1.702(285), +0.866(270), 0(240); in EPA at -100°C: 0(335), +0.757(310), +1.524(302), +1.570(300), +1.655(297), +1.949(292), +1.813(287), +1.799(285), +0.893(270), 0(240); in EPA at -175°C: 0(320), +0.327(315), +0.760(310), +0.756(308), +1.699 (299), +1.575(296), +2.030(290), +1.730(285), +1.752(283), +1.619(280), +0.938(270), 0(240). Values are corrected for solvent contraction.

2α-Methyl-5α-cholestan-3-one(2). 2β-Methyl-5α-cholestan-3-one (34 mg, 0.08 mmol) in ethanol (5 mL) containing 20% aqueous sulfuric acid (0.1 mL) was heated at reflux for 2 h. The mixture was diluted with water (200 mL), extracted with ether (3 x 50 mL) and the dried (anhydrous magnesium sulfate) ether extract evaporated to give a 2α-methyl-5α-cholestan-3-one. Purification by p.t.l.c. with benzene development followed by recrystallization from ether-methanol (1:5) gave the pure product as needles, 26 mg (76%): (m.p. 115-117°; UV (EPA) λ_{max} 285 (ε 22.7); nmr ($CDCl_3$) δ 0.66 (C-18 CH_3), 0.97 (3H, d, J - 8 Hz, 2α CH_3), 1.04 (C-19 CH_3) ppm; and $[\alpha]_D^{25}$ +36.3° (c·0.89, chloroform) (Lit. [23,24] $[\alpha]_D^{25}$ +33° (c·0.9, chloroform); $[\alpha]_D^{25}$ +44° (c·0.93, chloroform)). CD reported as Δε(λ,nm) in n-heptane (c.2.52) at 25°C: 0(340), +0.075(325), +0.196(320), +0.451(313), +0.497(310), +0.689(302), +0.659(298), +0.661 (295), +0.563(290), +0.480(286), +0.136(270), 0(250); in EPA (c·0.96) at 25°C: 0(330), +0.110(320), +0.460(310), +0.811(299), +0.871(294), +0.822 (290), +2.19(270), 0(255); in EPA at -25°C: 0(330), +0.255(315), +0.449 (310), +0.800(300), +0.815(298), +0.856(292.5), +0.821(290), +0.255(270),

O(255); in EPA at -100°C: O(330), 0.402(312), 0.495(308), +0.804(299), +0.799(297), +0.837(292),+0.668(284), +0.524(280), O(255); in EPA at -175°C: O(330), +0.283(315), +0.526(310), +0.566(306), +0.898(300), +0.818(296), +0.871(291.5), +0.650(284), +0.221(270), O(255). Values are corrected for solvent contraction.

3α-Methylcholestan-2-one(3). This substance was prepared as in 1, above, to give an overall 58% yield with m.p. 127-128°; ir (CCl_4) 1705 cm^{-1} (carbonyl); UV (EAP) λ_{max}288 (ε 30.5); nmr ($CDCl_3$) δ 0.63 (C-18 CH_3), 0.73(C-19 CH_3), 1.18 (3H, d, J = 8 Hz, 3 CH_3) ppm; and $[\alpha]_D^{25}$ +83.6° (c·0.87, chloroform) (Lit. [25] $[\alpha]_D^{25}$ +88°, chloroform)). CD reported as Δε(λ,nm) in n-heptane (c·2.16) at 25°C: O(340), +0.643(325), +1.431 (319), +1.461(317), +2.629(308), +2.493(304), +2.785(298), +2.356(292), +2.288(290), +0.701(270), +0.253(260), O(235); in EPA (c·0.96) at 25°C: O(335), +0.044(330), +0.876(320), +1.336(315), +2.519(306), +2.629(303), +2.990(296.5), +2.717(290), +1.873(280), +0.394(260), O(240); in EPA at -25°C: O(335), +0.265(325), +1.121(318), +1.244(316), +2.589(306), +2.630(303), +3.027(297), +2.691(290), +1.845(280), +0.367(260), O(240); in EPA at -100°C: O(335), +1.271(318), +1.309(316), +2.683(306.5), +2.571(303), +3.029(297), +2.580(290), +2.496(288), +1.701(280), +0.841 (270), +0.337(260), O(240); in EPA at -175°C: O(335), +0.124(325), +1.690(316.5), +1.451(313), +3.061(305.5), +2.566(301), +3.132(295.5), +2.451(289),+2.459(288), +1.672(280), +0.319(260), O(240). Values are corrected for solvent contraction.

3β-Methylcholestan-2-one(4). This ketone was prepared as for 2 by acid-catalyzed epimerization of 3 in 72% isolated yield, m.p. 148-149.5°; ir (CCl_4) 1705 cm^{-1} (carbonyl); UV (EPA) λ_{max}285 (ε 30.7); nmr ($CDCl_3$) δ 0.62 (C-18 CH_3), 0.68 (C-19 CH_3), 0.88 (3H, d, 3β CH_3) ppm; and $[\alpha]_D^{25}$ +50.0° (c·1.24, chloroform) (Lit. [25] $[\alpha]_D^{25}$ +49° (chloroform)). CD reported as Δε(λ, nm) in n-heptane (c·1.38) at 25°C: O(335), +0.880 (315.5), +0.846(313), +1.501(305.5), +1.341(301), +1.513(296.5), +1.242 (291), +1.219(290), +1.143(287), +0.777(280), +0.122(260), O(240); in EPA (c·1.0) at 25°C: O(330), +0.300(320), +0.794(315), +1.095 (310), +1.695(305), +1.813(302), +1.846(300), +2.017(295), +1.771(288), +1.277(280), +0.279(260), O(240); in EPA at -25°C: O(330), +0.719(315), +1.018(310), +1.767(302), +1.757(300), +1.967(293.5), +1.797(290), +1.657 (286), +1.248(280), +0.260(260), O(240); in EPA at -100°C: O(330), +0.751(315), +0.897(312), +0.879(310), +1.776(302), +1.648(298), +1.895 (293), +1.602(288), +1.538(285), +1.145(280), +0.238(260), O(240); in EPA at -175°C: O(330), +0.711(315), +1.118(311.5), +0.844(307.5), +1.924 (301), +1.508(276.5), +1.855(292), +1.409(286), +1.413(285), +1.083(280) +0.225(260), O(240). Values are corrected for solvent contraction.

2β-Methoxycholestan-3-one(5) [10]. 2α,3α-Oxido-5α-cholestane (0.515 g, 1.33 mmol) was dissolved in anhydrous methanol (550 mL), and to this solution were added a few crystals of *p*-toluenesulfonic acid. The resulting solution was stirred for 30 h. in a dry nitrogen atmosphere at 28°. The catalyst was then neutralized with barium carbonate, and the mixture was filtered. Evaporation of the solvent to near dryness produced a white crystalline compound. Purification by p.t.l.c. (developing solvent, benzene:ether (5:1)) and recrystallization from ether-methanol (1:5) gave pure 2β-methoxy-5α-cholestan-3α-ol, 285 mg (51%), m.p. 156-

157°; ir (CCl_4) 1022 cm^{-1} (C-OH), 1098 cm^{-1} (C-OCH_3), 3600 cm^{-1} (sharp, unassociate -OH stretch); and nmr ($CDCl_3$) δ 0.64 (C-18 CH_3), 326 (CH_3O-) ppm.

2β-Methoxy-5α-cholestan-3α-ol (100 mg, 0.24 mmol) in acetone (15 mL) was stirred at room temperature for 2 min with Jones reagent (8 N chromic acid) (0.06 mL. The mixture was then immediately poured into water (50 mL) and extracted with ether (3 x 20 mL). The combined extract was dried (anhydrous sodium sulfate) and the solvent was evaporated to give pure 2β-methoxy-5α-cholestan-3-one, 81 mg (81%), m.p. 71-73.5°; ir (CCl_4) 1093 cm^{-1} (C-OCH_3), 1715 cm^{-1} (carbonyl); nmr ($CDCl_3$) δ 0.66 (C-18 CH_3), 1.00 (C-19 CH_3), 3.24 (CH_3O-) ppm; and $[\alpha]_D^{25}$ +59.9° (c·0.85, chloroform). CD reported as Δε(λ,nm) in EPA (c·0.96) at 25°C: 0(350), +0.039(340), +0.257(325), +0.346(320), +0.465(313), +0.488(310), +0.517 (303.5), +0.508(300), +0.501(298), +0.474(295), +0.246(280), 0(260); in EPA at -25°C: 0(350), +0.182(330), +0.265(325), +0.339(320), +0.443 (314.5), +0.469(310), +0.496(303.5), +0.479(300), +0.466(298), +0.441 (295), +0.229(280), 0(260); in EPA at -100°C: 0(350), +0.321(325), +0.350(321), +0.369(320), +0.472(313), +0.461(310), +0.459(309), +0.471 (303.5), +0.443(300), +0.428(298), +0.404(295), 0(260); in EPA at -175°C: 0(350), +0.416(323), +0.412(321), +0.431(320), +0.574(314.5), +0.497(310), +0.477(307.5), +0.519(303.5), +0.462(300), +0.423(298), +0.394(295), 0(260). Values are corrected for solvent contraction.

2α-Methoxy-5α-cholestan-3-one(6). 2β-Methoxy-5α-cholestan-3-one (250 mg, 0.600 mmol) was dissolved in 140 mL of a 4% solution (by weight) of potassium hydroxide in distilled methanol. The mixture solution was stirred at room temperature for 3 h. in a nitrogen atmosphere. Then the solution was neutralized with dilute (10%) hydrochloric acid. Afterward, the mixture solution was filtered and the solvent was evaporated by rotary evaporator. The crude product was purified by p.t.l.c. (developing solvent, benzene:ether (5:1)). Pure 2α-methoxy-5α-cholestan-3-one, 124 mg (50%), m.p. 126-128°, was collected. It had ir (CCl_4) 1131 cm^{-1} (C-OCH_3), 1723 cm^{-1} (carbonyl); nmr ($CDCl_3$) δ 0.65 (C-18 CH_3), 1.04 (C-19 CH_3), 3.37 (CH_3O-) ppm; and $[\alpha]_D^{25}$ +64.9° (c·0.90, chloroform). CD reported as Δε(λ,nm) in n-heptane (c·1.48) at 25°C: 0(350), +1.049(317), +1.108(315), +1.389(310), +1.552(305), +1.531(303), +1.530(300), +1.515 (298), +1.419(295), +0.724(280), +0.118(260), 0(245); in EPA (c·0.98) at 25°C: 0(350), +0.223(325), +0.502(320), +0.848(315), +1.122(310), +1.361 (305), +1.434(300), +1.440(297), +1.400(295), +0.770(280), 0(245); in EPA at -25°C: 0(330), +0.467(320), +0.789(315), +1.101(310), +1.350(305), +1.443(300), +1.454(297), +1.433(295), +1.277(290), +0.779(280), 0(240); in EPA at -100°C: 0(330), +0.429(320), +0.809(315), +0.900(313), +1.109 (310), +1.447(305), +1.519(300), +1.547(297), +1.524(295), +0.838(280), +0.086(260), 0(250); in EPA at -175°C: 0(330), +0.415(320), +0.874(315), +0.951(313), +1.077(310), +1.523(305), +1.600(302), +1.604(300), +1.600 (299), +1.627(295), +0.892(280), 0(250). Values are corrected for solvent contraction.

3α-Methoxy-5α-cholestan-2-one(7) [10]. 2β,3β-Oxido-5α-cholestane (0.80 g, 2.07 mmol) was dissolved in anhydrous methanol (700 mL), and to this solution were added a few crystals of *p*-toluenesulfonic acid. The resulting solution was stirred for 12 h. in a dry nitrogen atmosphere at 32°. The catalyst was then neutralized with barium carbonate, and the

mixture was filtered. After evaporation of the solvent, purification by p.t.l.c. (developing solvent, benzene:ether (5:1)), and recrystallization from ether-methanol (1:5), pure 3α-methoxy-5α-cholestan-2β-ol, 488 mg (56%), m.p. 151.5-153°, was collected. It had ir (CCl_4) 1023 cm^{-1} (C-OH), 1095 cm^{-1} (C-OCH_3), 3600 cm^{-1} (C-OH); and nmr ($CDCl_3$) δ 0.64 (C-18 CH_3), 0.74 (C-19 CH_3), 3.28 (CH_3O-) ppm.

3α-Methoxy-5α-cholestan-2β-ol (400 mg, 0.95 mmol) in acetone (55 mL) was stirred at room temperature for 2 min with Jones reagent (8 N chromic acid). The mixture was then immediately poured into water (50 mL) and extracted with ether (3 x 20 mL). The combined extract was dried (anhydroud sodium sulfate) and the solvent was evaporated to give pure 3α-methoxy-5α-cholestan-2-one, 360 mg (91%), m.p. 124-125°; ir (CCl_4) 1087 cm^{-1} (C-OCH_3), 1713 cm^{-1} (carbonyl); UV (EPA) λ_{max}307 (ε 37.0); nmr ($CDCl_3$) δ 0.64 (C-18 CH_3), 0.72 (C-19 CH_3), 3.21 (CH_3O-) ppm; and $[\alpha]_D^{25}$ +58.6° (c·0.84, chloroform). CD reported as Δε(λ,nm) in n-heptane (c·1.48) at 25°C: 0(350), +0.359(335), +0.816(328), +0.854(325), +1.222 (316), +1.128(310), +1.115(307), +1.081(305), +0.906(300), +0.555(290), +0.103(270), 0(250); in EPA (c·1.0) at 25°C: 0(350),+0.328(335),+0.760(330), +1.017(325), +1.312(320), +1.526(314), +1.504(310), +1.444(305), +1.258 (300), +0.372(280), 0(260); in EPA at -25°C: 0(350), +0.295(335), +0.895 (328), +0.987(325), +1.450(316), +1.384(310), +1.343(306), +1.140(300), +0.682(290), +0.295(280), 0(260); in EPA at -100°C: 0(350), +0.252(335), +0.933(327), +0.919(325), +1.349(316.5), +1.167(309), +1.176(307), +0.933 (300), +0.523(290), +0.187(280), 0(260); in EPA at -175°C: 0(350), +0.124(335), +0.980(328), +0.782(322), +1.316(315.5), +0.936(308), +1.025 (304.8), +0.804(300), +0.177(280), 0(260). Values are corrected for solvent contraction.

3β-Methoxy-5α-cholestan-2-one(8). 3α-Methoxy-5α-cholestan-2-one (160 mg, 0.38 mmol) was dissolved in 65 mL of a 4% solution (by weight) of potassium hydroxide in distilled methanol. The mixture solution was stirred at room temperature for 3 h. in a nitrogen atmosphere. Then the solution was neutralized with dilute (10%) hydrochloric acid. Afterward, the mixture solution was filtered and the solvent was evaporated by rotary evaporator. The crude product was purified by p.t.l.c. (developing solvent, benzene:ether (5:1)). Pure 3β-methoxy-5α-cholestan-2-one, 81 mg (51%), m.p. 106-108°, was collected. It had ir (CCl_4) 1129 cm^{-1} (C-OCH_3) 1720 cm^{-1} (carbonyl); nmr ($CDCl_3$) δ 0.64 (C-18 CH_3), 0.74 (C-19 CH_3), 3.37 (CH_3O-) ppm; and $[\alpha]_D^{25}$ +36.9° (c·1.30, chloroform). CD reported as Δε(λ,nm) in EPA (c·1.0) at 25°C: 0(335), +0.153(323), +0.306(319), +0.476(313), +0.612(310), +0.711(305), +0.771(298), +0.634(290), +0.175 (270), 0(250); in EPA at -25°C: 0(335), +0.214(325), +0.529(315), +0.773(305), +0.778(303), +0.794(298), +0.672(290), +0.214(279), 0(250); in EPA at -100°C: 0(335), +0.084(325), +0.401(317), +0.429(315), +0.747 (305), +0.747(303), +0.789(296.5), +0.681(290), +0.196(270), 0(250); in EPA at -175°C: 0(335), +0.062(323), +0.247(319), +0.442(315), +0.446 (313), +0.495(310), +0.777(302.5), +0.764(300), +0.804(295), +0.455(280), 0(250). Values are corrected for solvent contraction.

Cholestan-3-one(9). Prepared from cholestan-3β-ol (Winthrop) by oxidation with $K_2Cr_2O_7$ in glacial acetic acid [26]. It had m.p. 126.5-127° (Lit. [27] m.p. 128-129°); UV (EPA) λ_{max}285 (ε 17.2); $[\alpha]_D^{25}$ 41.4°,

(chloroform)); and nmr ($CDCl_3$) δ 0.67 (C-18 CH_3), 0.99 (C-19 CH_3) ppm. CD reported as Δε(λ,nm) in n-heptane (c·1.94) at 25°C: 0(340),+0.277(320), +0.392(317), +0.481(313), +0.586(310), +0.756(304), +0.769(302), +0.819 (296.5), +0.696(288), +0.487(280), +0.089(260), 0(240); in EPA (c·1.02) at 25°C: 0(335), +0.179(320), +0.592(310), +0.886(305), +1.045(300), +1.189(293), +1.159(290), +0.895(280), +0.239(260), 0(240); in EPA at -25°C: 0(340), +0.616(310), +0.940(304), +1.055(300), +1.194(293.5), +1.180(290), +0.907(280), +0.528(270), +0.241(260), 0(240); in EPA at -100°C: 0(340), +0.212(320), +0.484(315), +0.637(310), +1.053(303), +1.112(300), +1.257(293.5), +1.129(286), +0.900(280), +0.221(260), 0(240); in EPA at -175°C: 0(340), +0.229(320), +0.623(313), +0.631(312), +1.165(302), +1.149(300), +1.298(293.5), +1.189(290), +1.113(286), +0.474 (270), 0(240). Values are corrected for solvent.

Cholestan-2-one(10). 2β,3β-Oxido-5α-cholestane (800 mg, 2 mmol) was dissolved in anhydrous ether (20 mL). Then lithium aluminum hydride (115 mg, 3 mmol) in anhydrous ether (5 mL) was added to the solution slowly. Afterward, the reaction mixture was stirred and heated at reflux for 4.5 h. Then 1 mL of water was added dropwise and followed by 0.5 mL of 15% sodium hydroxide. Finally, 5 more mL of water were added and the reaction mixture was filtered and dried (anhydrous magnesium sulfate). Methanol was added to the ether solution to crystallize the final product. Crude 2β-hydroxy-5α-cholestane, 615 mg (79%) was collected. The crude product was purified by p.t.l.c. (developing solvent, benzene:ether (40:20)), m.p. 149.5-151° (Lit. [28] m.p. 153-155°).

Crude 2β-hydroxy-5α-cholestane (250 mg, 0.6 mmol) in acetone (40 mL) was stirred at 0°C for 2 min with Jones reagent (8 N chromic acid, oxidation was carried out by titration). Then the reaction solution was poured into 200 mL of water and extracted with ether (3 x 60 mL). After the evaporation of ether, the crude product was purified by p.t.l.c. (developing solvent, benzene:ether (5:1)). Pure 5α-cholestan-2-one, 207 mg (89%), m.p. 125-127° (Lit. [29] m.p. 126-128°), was collected. It had ir (CCl_4) 1701 cm^{-1} (carbonyl); UV (EPA) λ_{max}285 (ε 30.0); $[\alpha]_D^{25}$ +46.1° (c·1.12, chloroform) (Lit. [29] $[\alpha]_D^{25}$ +48° (c·1.00, chloroform)); and nmr ($CDCl_3$) δ 0.65 (C-18 CH_3), 0.75 (C-19 CH_3) ppm. CD reported as Δε(λ,nm) in n-heptane (c·2.54) at 25°C: 0(335), +0.160(325), +0.631(318), +0.607 (315.5), +1.175(307), +1.067(303), +1.263(297.5), +1.071(292), +1.063 (290), +1.007(288), +0.128(260), 0(240); in EPA (c·0.98) at 25°C: 0(330), +0.725(317), +0.797(315), +1.274(310), +1.750(305), +1.792(303), +2.133 (296), +2.019(291), +1.947(288.5), +1.408(280), +0.290(260), 0(235); in EPA at -25°C: 0(330), +0.675(317), +0.819(313), +1.127(310), +1.715 (304.5), +1.744(302), +2.091(295.5), +1.966(291), +1.908(288.5), +1.407 (280), +0.308(260), 0(235); in EPA at -100°C: 0(327), +0.760(315), +0.751(314), +1.034(310), +1.688(304.5), +1.644(301.5), +1.997(295.5), +1.803(291), +1.776(288.5), +1.246(280), +0.265(260), 0(235); in EPA at -175°C: 0(325), +0.979(314.5), +0.828(311), +1.882(303.5), +1.597(299.5), +2.016(294.5), +1.706(291), +1.631(288.5), +1.656(287), +1.221(280), +0.251(260), 0(235). Values are corrected for solvent contraction.

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