Hypervalent Organoiodine Compounds: Radical Fragmentation of Oxabicyclic Hemiacetals. Convenient Synthesis of Medium-sized and Spiro Lactones

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Photolysis of steroidal models of oxyabicyclic hemiacetals such as 2-oxabicyclo[4.4.0]decan-1-ol, 9-oxabicyclo[4.3.0]nonan-1-ol and 2-oxabicyclo[3.3.0]octan-1-ol, in the presence of (diacetoxyiodo)benzene and iodine afforded, through ring expansion, ten-, nine- and eight-membered lactones, respectively. Spiro lactones of dihydropyran-5-spirocyclohexan-2(3*H*)-one and dihydrofuran-4-spirocyclohexan-2(3*H*)-one types were obtained by photolysis of steroidal models of 2-oxabicyclo[2.2.2]octan-1-ol and 7-oxabicyclo[3.2.1]octan-1-ol, respectively.

Medium- and large-ring lactones are of interest both with regard to the chemistry of natural products and to the immense pharmacological importance of many macrolide antibiotics containing these groups.[1]

A macrolide synthesis inevitably faces two major problems: the formation of the medium- or large-lactone ring and the stereochemical control of the chiral centres fixed on the ring system. This made the ring expansion methodology attractive for the resolution of the aforementioned problems. Although the concept of cleaving fused bonds in bicyclic [*n.m.*0] structures to create large rings has been applied with some success to the synthesis of macrocyclic lactones,[2] the scope of the concept has by no means been fully explored.

Continuing our studies on the synthetic applications of the β-fragmentation of alkoxyl radicals generated from cyclic alcohols by reaction with hypervalent iodo compounds,[3] we describe in detail the β-fragmentation of alkoxyl radicals generated from oxabicyclic hemiacetals of [*n.m.*0], [2.2.2] and [3.2.1] types, in order to achieve, through ring opening, the synthesis of medium-sized lactones as well as spiro lactones. Other syntheses of lactones by oxidative ring expansion fragmentation reactions have been reported[4,5] while our work was underway or after publication of our preliminary communication.[6a]

The different types of starting materials and the expected β-fragmentation products are outlined in Scheme 1. The reaction has been studied on steroidal models with special attention being paid to the regioselectivity of the process. Preliminary results to ascertain the feasibility of this approach have been reported earlier.[6]

Results and Discussion

Fragmentation of Oxabicycles [n.m.0].—The β-fragmentations were expected to occur through the mechanism shown in Scheme 1. Models **1** and **2** were selected because in the ring-chain tautomerism of the keto alcohols, the hemiacetal form (five- and six-membered rings)[7] is preferred. Moreover, the stability of the C-radical **A** (R = Me) will be favoured, which should be important in the regioselectivity of the ring opening process. The model compound **22** was prepared in order to study during the fragmentation the formation of a secondary *versus* a primary C-radical intermediate **A** (R = H) and to see how this influenced the regioselectivity.

Steroidal models **1** and **2** were prepared from the known keto acids **3**[8] and **5**[9] as follows. Methylation of the latter gave esters **4** and **6** which were treated with ethylene glycol and catalytic amounts of PTSA (toluene-*p*-sulphonic acid) to afford the ethylenedioxy derivatives **7** and **9**. These compounds were then reduced with LAH (lithium aluminium hydride) to give the alcohols **8** and **10** which after hydrolysis gave the hemiacetals **1** and **2**,[10] respectively.

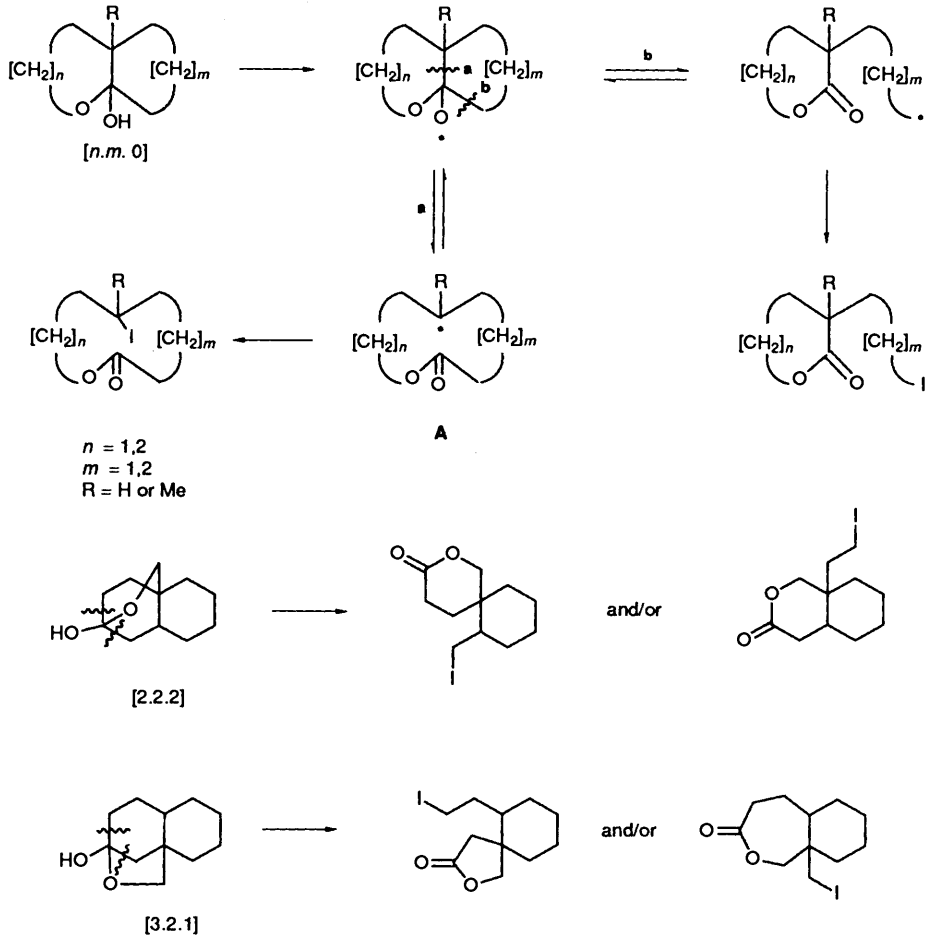
In the case of the hemiacetal **1** the spectroscopic data (see Experimental section) indicate that the ring-chain tautomerism between the hydroxy ketone and the cyclic hemiacetal is strongly displaced to the ring form. On the other hand, the complex ^{13}C NMR spectrum displayed by hemiacetal **2** indicates a slow equilibrium between the tautomers.[11]

The reaction of hemiacetals **1** and **2** with (diacetoxyiodo)-benzene (DIB) in the presence of iodine was performed by photolysis, after careful deoxygenation, with visible light (2 × 100 W tungsten-filament lamps) in cyclohexane under the conditions summarized in Table 1 (entries 1–4). The reaction gave good yields (*ca.* 80%) of medium-sized lactones when approximately stoichiometric amounts of DIB and iodine were used (entries 1 and 4). The presence of iodine was shown to be necessary for the reaction to take place (entry 2). When a catalytic amount of iodine was used only 30% of the hemiacetal was transformed after 2 h at 40 °C (entry 3).

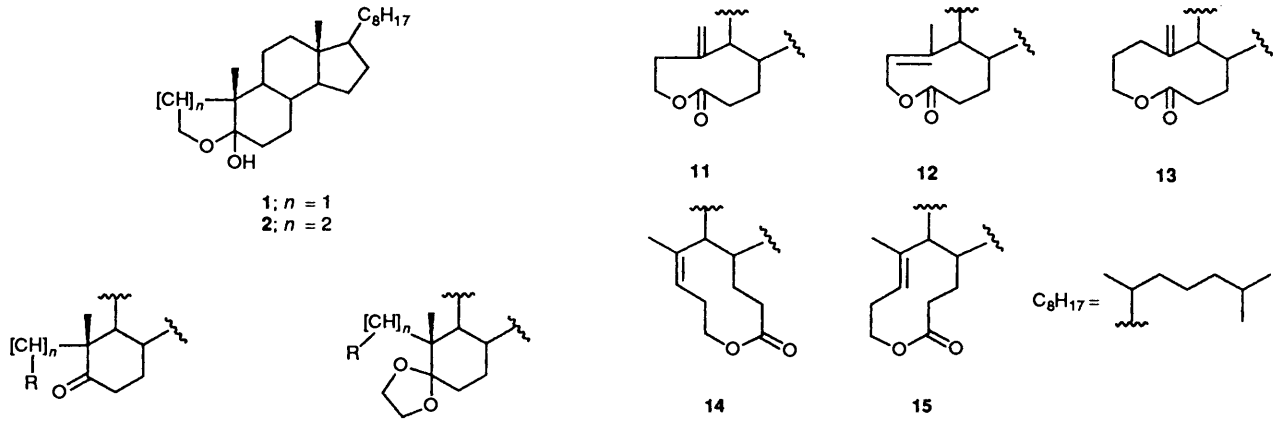
The structures of lactones **11**–**15** were determined on the basis of spectral evidence. Lactone **11** shows in its ^1H NMR spectrum broad signals for 19-H and 2-H, and its ^{13}C NMR spectrum is also complex due to the slow conformational equilibrium of the nine-membered ring lactone. A similar situation is observed for the NMR spectra of lactone **13**, in contrast with the neat and well resolved NMR spectra observed for lactones **12**, **14** and **15**.

The stereochemistries of the double bonds in lactones **14** and **15** were determined as *Z* and *E*, respectively, as deduced from the observed shielding of the C-10 methyl group signals in their ^{13}C NMR spectra (18.70 ppm for **14** and 13.14 ppm for **15**).[12] Recently, Suginome *et al.*[5b] have published details of the fragmentation of the hemiacetal **2** upon irradiation with a 100 W high pressure mercury lamp in benzene containing mercury(II) oxide and iodine, to give lactones **14** and **15** as the sole products.

The steroidal model of 2-oxabicyclo[3.3.0]octan-1-ol was prepared starting from the known lactone **16**[13] which was methylated to give **17** and reduced with LAH to afford diol **18**. Partial acetylation of **18** gave monoacetate **19** which was oxidized with an excess of Jones' reagent to give the ketone **21**. Hydrolysis of **21** provided the required hemiacetal **22**. This



Scheme 1



3; n = 1; R = CO_2H
4; n = 1; R = CO_2Me
5; n = 2; R = CO_2H
6; n = 2; R = CO_2Me

7; n = 1; R = CO_2Me
8; n = 1; R = CH_2OH
9; n = 2; R = CO_2Me
10; n = 2; R = CH_2OH

compound was in equilibrium with the open form, as shown by the complex ^1H and ^{13}C NMR spectra observed. Further characterization was achieved by means of the methyl acetal **23**, as shown in the Experimental section.

The photolysis of the hemiacetal **22** was realized analogously, as indicated in Table 1 (entry 5), to give the iodo lactone **24** as a single stereoisomer. AM parts of AMX systems were observed for 15-H and 22-H in its ^1H NMR spectrum, and the signal for the methine proton at C-17 appears as a singlet at 3.92 ppm. The structure and stereochemistry of the eight-membered lactone **24** was determined by X-ray crystallographic analysis (Fig. 1). The radical intermediate at C-17 is trapped by an iodo radical in a stereoselective manner to give an iodo derivative with *R* stereochemistry.

In the three models studied, **1**, **2** and **22**, β-fragmentation takes place with total regioselectivity to cleave the more substituted bond, in every case.

Fragmentation of [2.2.2] *Oxabicycles.*—A steroidal model of 2-oxabicyclo[2.2.2]octan-1-ol **31** was obtained starting from the known bromo ether **26**[14] essentially following reactions described in other steroid series.[15] Oxidation of the 3β-alcohol with Jones' reagent led to the ketone **27** which was reduced with Zn dust in acetic acid to give the enone **28**. After protection of the primary alcohol by reaction with dihydropyran, the

Table 1 Fragmentation of hemiacetals

Entry	Hemiacetal	DIB[a] (mmol)	Iodine[a] (mmol)	Conditions[b] (T/°C; t/h)	Products (yield %)
1	**1**	1.1	1	40; 1	**11** (45), **12** (40)
2	**1**	1.1	0	40; 1	No reaction
3	**1**	1.1	0.1	40; 2	**11** (13), **12** (12), **1** (70)
4	**2**	1.2	1.4	35–40; 6	**13** (33), **14** (17), **15** (33)
5	**22**	1.1	1	40; 1.6	**24** (82)
6	**31**	1.5	1	40–45; 2	**32** (35), **33** (27)
7	**35**	4.4	1	40–45; 5	**37** (50)
8	**39**	1.5	1	40–45; 3	**40** (84)
9	**49**	1.35	1.3	40; 5.5	**50** (77)
10	**51**	1.1	1	40; 3	**52** (72)

[a] Per mmol of hemiacetal. [b] All reactions under irradiation with two 100 W tungsten-filament lamps after careful deoxygenation.

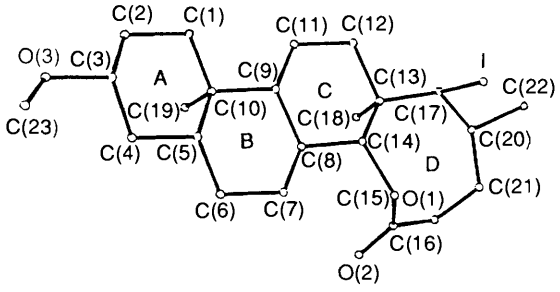
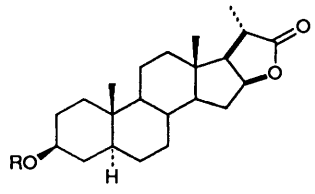
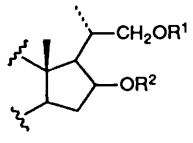


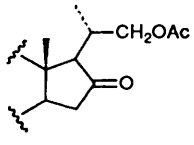
Fig. 1 X-Ray crystal structure of tactone **24** (hydrogen atoms omitted)



16; R = H
17; R = Me



18; R^1 = H; R^2 = H
19; R^1 = Ac; R^2 = H
20; R^1 = Ac; R^2 = Ac



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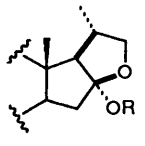
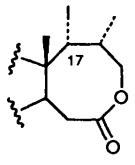


22; R = H
23; R = Me



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resulting tetrahydropyranyl (THP) ether **29** was reduced with lithium in liquid ammonia to the ketone **30**. Cleavage of the THP ether afforded the desired hemiacetal **31**.[16]

The photolysis of the oxabicyclo **31** under the conditions shown in Table 1 (entry 6) afforded a mixture of the regioisomeric iodo lactones **32** and **33**. The structures of both compounds were established by spectroscopic means. The ^{13}C NMR spectra of **32** and **33** show the carbon bearing the iodine atom at 10.28 and −3.5 ppm, respectively. Additional proof of these structures came from their ^1H NMR spectra (see Experimental section). The observed long range coupling (W coupling) between protons 5α and 19α in the ^1H NMR spectrum of lactone **33** confirms its structure.

These lactones may be synthetically useful since both types are present in the structure of important natural products. For instance, the formation of the spiro lactone **32** is the key step in the synthesis of limonin,[17] and the main structural features of the sesquiterpene vernolepin[18] are present in the lactone **33**.

In order to improve the regioselectivity of the reaction two other related models of 2-oxabicyclo[2.2.2]octan-1-ol, the hemiacetals **35** and **39**, were prepared. Methylation of the enone **29** with methyl iodide and potassium *tert*-butoxide afforded the dimethyl ketone **34** and subsequent hydrolysis of the THP ether gave the hemiacetal **35**.[17a] Formation of the methyl acetal **36**, followed by hydrogenation of the double bond over palladium-on-carbon gave, after hydrolysis, the hemiacetal **39**. The observed stereoselectivity in the hydrogenation arises from the strong steric hindrance produced by the methyl acetal group on the β-face of the molecule.[17a]

Photolysis of the hemiacetals **35** and **39** with DIB and iodine gave, under the conditions and in the yields shown in Table 1 (entries 7 and 8), the corresponding spiro lactones **37** and **40**.

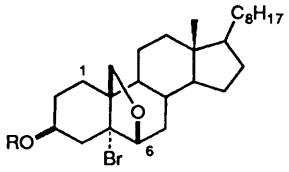
An analogue of the hemiacetal **39** has been transformed into the lactone **40** during the synthesis of rings A and A′ of limonin[17b] in several steps and low overall yield, using a Beckmann fragmentation for ring cleavage.

Fragmentation of [3.2.1] *Oxabicycles*.—The synthesis of the steroidal models of the 7-oxabicyclo[3.2.1]octan-1-ol **49** and **51** was realized as follows: the known 3-oxocholestane-5α- and -5β-carbonitrile **41** and **42**[19] were reduced, after protection of the carbonyl group, with diisobutylaluminium hydride in toluene, to afford the aldehydes **45** and **46**; further reduction with LAH and deprotection gave the desired isomeric hemiacetals **49** and **51**, respectively.

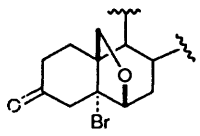
Fragmentation of these hemiacetals promoted by DIB and iodine (Table 1, entries 9 and 10) gave the iodo spiro-γ-lactones **50** and **52**. The structures were confirmed by NMR spectroscopy, the iodine-bearing carbon appearing at 1.99 ppm in the ^{13}C NMR spectrum of **50** and at 2.19 ppm in that of **52**. The stereochemistry at C-5 was confirmed by nuclear Overhauser effect (NOE) spectroscopy. Thus irradiation of 10-Me methyl group resulted in a strong enhancement of the AB system at C-4 in lactone **50** and of that at C-1′ in lactone **52**. Further evidence comes from the long range coupling (J_w 1.4 Hz) between the 6β-H and the proton 1′-*pro-S* in lactone **50** and the same 6β-H and the proton 4-*pro-S* in lactone **52**.

This study of the stereochemistry at C-5 is necessary because the stereochemistry of the starting cyano ketones has been determined exclusively on the basis of molecular rotations.[19] The fragmentation of these hemiacetals proceeded with total regioselectivity to give the smallest ring lactone. No products arising from the cleavage of the C(2)–C(3) bond have been detected.

We conclude that the use of the hypervalent iodo reagent DIB in the presence of iodine seems to be a good method for the generation and β-fragmentation of alkoxy radicals. The reaction is smooth and proceeds under mild conditions in good yields.



25; R = H
26; R = Ac



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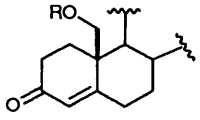
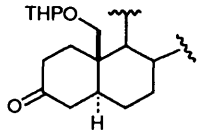


28; R = H
29; R = THP



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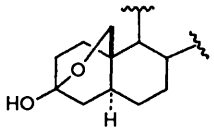

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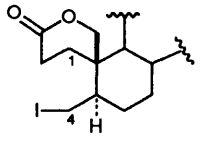

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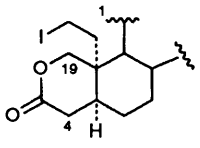

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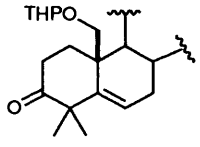

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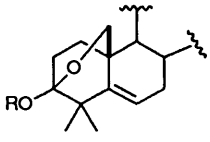
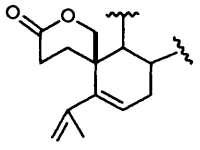


35; R = H
36; R = Me



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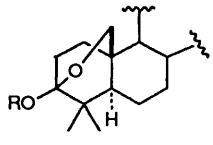
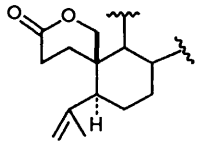


38; R = Me
39; R = H



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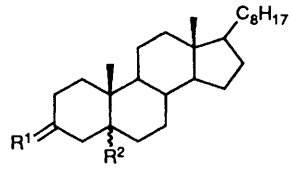
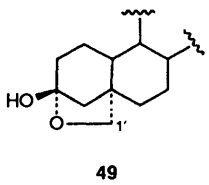


41; R^1 = O; R^2 = α-CN
42; R^1 = O; R^2 = β-CN
43; R^1 = $O(CH_2)_2O$; R^2 = α-CN
44; R^1 = $O(CH_2)_2O$; R^2 = β-CN
45; R^1 = $O(CH_2)_2O$; R^2 = α-CHO
46; R^1 = $O(CH_2)_2O$; R^2 = β-CHO
47; R^1 = $O(CH_2)_2O$; R^2 = α-CH_2OH
48; R^1 = $O(CH_2)_2O$; R^2 = β-CH_2OH



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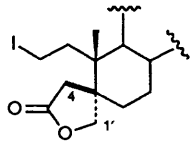

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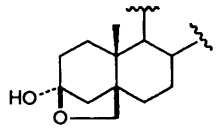

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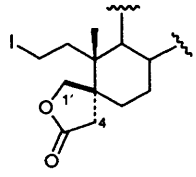

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Since our preliminary communication,[6] we have used hypervalent iodo compounds as reagents in the β-fragmentation of carbinolamides,[3b] lactols,[3c] and unsaturated lactols,[3a] and some applications of this reaction to the synthesis of natural products have also been published.[6b,c] This methodology has recently been used by Stork[20] and Yamamoto[21] for the fragmentation of different types of intramolecular hemiacetals.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotation measurements (α) were recorded at room temperature for solutions in $CHCl_3$ on Perkin-Elmer 141 and 142 polarimeters and are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded on Perkin-Elmer 257 and 681 spectrometers in $CHCl_3$ solutions. ^1H NMR spectra were recorded on a Bruker WP 200 SY (200 MHz) or a Bruker AC80 (80 MHz) spectrometer and ^{13}C NMR spectra on a Bruker WP 200 SY (50.3 MHz) or a Bruker AC80 (20.1 MHz) for solutions in $CDCl_3$ with Me_4Si as internal standard, *J* values are given in Hz. Low-resolution mass spectra were determined with Hewlett Packard 5930 A and VG Micromass ZAB-2F spectrometers and high-resolution mass spectra on a VG Micromass ZAB-2F spectrometer. Merck silica gels 60 and 0.063–0.2 mm were used for preparative thin layer chromatography and column chromatography respectively. Circular layers of 1 mm of Merck silica gel 60 PF 254 were used on a Harrison Chromatotron for centrifugally assisted chromatography. Commercial reagents and solvents were analytical grade or were purified by standard procedures prior to use. The spray reagent for TLC was vanillin (1 g) in H_2SO_4–EtOH (4:1; 200 cm^3). (Diacetoxyiodo)benzene (DIB) 98% was purchased from Aldrich.

5-Oxo-3,4-dinor-2,3-secocholestan-2-oic Acid **3**.—Preparation of this compound followed essentially a previously reported procedure; m.p. 166–167 °C (from MeOH); $[\alpha]_D$ +30 (*c* 0.2) (lit.,[8] m.p. 166.5–167.5 °C; $[\alpha]_D$ +29.8); ν_{max}/cm^{-1} 3580 and 1770; δ_H 0.65 (3 H, s, 13-Me), 0.83 (6 H, d, *J* 6.7, 25-Me_2), 0.86 (3 H, d, *J* 7.2, 20-Me), 1.08 (3 H, s, 10-Me), and 2.35 and 2.63 (2 H, AB, J_{AB} 16.8, 1-H_2); δ_C complex spectrum due to the ring-chain tautomerism; *m/z* 390 (*M*, 2%), 375 (*M* − Me, 6), 372 (*M* − H_2O, 41), 362 (4), 357 (11), 331 (100), 227 (3), 259 (8), 249 (6), 233 (5) and 217 (38).

Methyl 5-Oxo-3,4-dinor-2,3-secocholestan-2-oate **4**.—A solution of 5-oxo-3,4-dinor-2,3-secocholestan-2-oic acid **3** (1.0 g) in diethyl ether (50 cm^3) was treated with an excess of a diethyl ether solution of diazomethane and the mixture was stirred at ambient temperature for 1 h. After concentration the residue was purified by column chromatography (benzene–ethyl acetate; 95:5) to yield the *title compound* **4** (1.015 g, 98%), amorphous; ν_{max}/cm^{-1} 1725; δ_H 0.70 (3 H, s, 13-Me), 0.82 (3 H, d, *J* 8, 20-Me), 0.84 (6 H, d, *J* 6.7, 25-Me_2), 1.14 (3 H, s, 10-Me), 2.33 and 2.73 (2 H, AB, *J* 16.7, 1-H_2) and 3.62 (3 H, s, MeO); *m/z* 404.3292 (1%, M^+. $C_{26}H_{44}O_3$ requires *M*, 404.3288), 389.3026 (4. $C_{25}H_{41}O_3$ requires *M*, 389.3054),

373.3062 (4. $C_{25}H_{41}O_2$ requires *M*, 373.3105), 217.1937 (5. $C_{16}H_{25}$ requires *M*, 217.1955) and 191.1448 (5. $C_{13}H_{19}O$ requires *M*, 191.1435).

Methyl 5,5-*Ethylenedioxy*-3,4-*dinor*-2,3-*secocholestan*-2-*oate* **7**.—To a solution of compound **4** (1.0 g, 2.48 mmol) in benzene (50 cm^3), PTSA (toluene-*p*-sulphonic acid) (33 mg, 0.17 mmol) and ethane-1,2-diol (1.3 cm^3, 23.3 mmol) were added and the mixture was refluxed in a Dean–Stark apparatus for 4 h. The organic solution was washed with brine and saturated aqueous $NaHCO_3$, dried (Na_2SO_4) and evaporated under reduced pressure. Silica gel column chromatography of the residue (benzene–ethyl acetate; 95:5) gave the *title compound* **7** (1.1 g, 99%), m.p. 66.5–67.0 °C (MeOH), $[\alpha]_D$ +33 (*c* 0.116); ν_{max}/cm^{-1} 1725; δ_H 0.64 (3 H, s, 13-Me), 0.85 (6 H, d, *J* 6.7, 25-Me_2), 0.87 (3 H, d, *J* 7.4, 20-Me), 1.08 (3 H, s, 10-Me), 2.31 and 2.18 (2 H, AB, J_{AB} 13.5, 1-H_2), 3.59 (3 H, s, MeO) and 3.89 (4 H, m, $W_{1/2}$ 5 Hz, 5,5-ethylenedioxy); *m/z* 448.3565 (35%, M^+. $C_{28}H_{48}O_4$ requires *M*, 448.3552), 433.3344 (1; $C_{27}H_{45}O_4$ requires *M*, 433.3315), 417.3365, (3; $C_{27}H_{45}O_3$ requires *M*, 417.3365), 360.3020 (5; $C_{24}H_{40}O_2$ requires *M*, 360.2982), 386.3199 (10; $C_{26}H_{42}O_2$ requires *M*, 386.3138) and 285.2503 (9; $C_{17}H_{33}O_3$ requires *M*, 285.2429).

5,5-*Ethylenedioxy*-3,4-*dinor*-2,3-*secocholestan*-2-*ol* **8**.—A solution of the methyl ester **7** (637 mg, 1.42 mmol) in dry diethyl ether (100 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (510 mg, 13.4 mmol) in dry diethyl ether (80 cm^3) at 0 °C. The mixture was stirred at room temperature for 2 h, and treated dropwise with saturated aqueous Na_2SO_4. The precipitate was filtered off and washed thoroughly with diethyl ether and the filtrate and the washing were combined, dried (Na_2SO_4) and evaporated under reduced pressure. Silica gel column chromatography of the residue (benzene–ethyl acetate; 70:30) gave *alcohol* **8** (491 mg, 82%), m.p. 64–66 °C (MeOH); $[\alpha]_D$ +37 (*c* 0.134); ν_{max}/cm^{-1} 3600 and 3540–3300; δ_H 0.64 (3 H, s, 13-Me), 0.84 (6 H, d, *J* 6.7, 25-Me_2), 0.87 (3 H, d, *J* 6.4, 20-Me), 1.00 (3 H, s, 10-Me), 3.77 (2 H, m, $W_{1/2}$ 25 Hz, 2-H_2) and 3.95 (4 H, m, $W_{1/2}$ 5 Hz, 5,5-ethylenedioxy); δ_C 113.27 (s, C-5), 63.98 (t), 63.86 (t), 59.79 (t), 56.29 (d), 56.07 (d), 47.12 (d), 43.63 (s), 42.62 (s), 39.92 (t), 39.52 (t), 37.93 (t), 36.21 (t), 35.86 (d), 34.81 (d), 29.57 (t), 28.27 (t), 28.04 (t), 28.04 (d), 24.25 (t), 23.94 (t), 22.87 (q), 22.62 (q), 22.07 (t), 18.67 (q), 18.09 (q) and 12.17 (q); *m/z* 420.3578 (5%, M^+. $C_{27}H_{48}O_3$ requires *M*, 420.3602), 402.3437 (1; $C_{27}H_{46}O_2$ requires *M*, 402.3497), 358.3267 (60; $C_{25}H_{42}O$ requires *M*, 358.3233), 347.2869 (5; $C_{23}H_{39}O_2$ requires *M*, 347.2948), 343.2966 (5; $C_{24}H_{39}O$ requires *M*, 343.2999), 285.2587 (7; $C_{21}H_{33}$ requires *M*, 285.2580) and 203.1441 (6; $C_{14}H_{19}O$ requires *M*, 203.1434).

2-*Hydroxy*-3,4-*dinor*-2,3-*secocholestan*-5-*one* 2,5-*Hemiacetal* **1**.—A solution of the alcohol **8** (276 mg, 0.66 mmol) in acetone (138 cm^3) containing PTSA (344 mg, 1.81 mmol) was stirred at room temperature for 30 min. The reaction mixture was then poured into water and extracted with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4) and evaporated under reduced pressure. Silica gel column chromatography of the residue (benzene–ethyl acetate; 80:20) gave *compound* **1** (210 mg, 85%), m.p. 113–115 °C (MeOH), $[\alpha]_D$ +63 (*c* 0.126); ν_{max}/cm^{-1} 3600 and 3540–3210; δ_H 0.65 (3 H, s, 13-Me), 0.84 (6 H, d, *J* 6.7, 25-Me_2), 0.88 (3 H, d, *J* 6.6, 20-Me), 0.99 (3 H, s, 10-Me), and 3.88 (2 H, m, $W_{1/2}$ 25 Hz, 2-H_2); δ_C 105.81 (s), 64.08 (t), 56.23 (d), 56.16 (d), 47.06 (s), 46.26 (d), 42.64 (s), 40.09 (t), 39.54 (t), 36.18 (t), 35.78 (d), 35.36 (d), 34.51 (t), 32.58 (t), 28.26 (t), 28.01 (d), 27.98 (t), 24.21 (t), 23.87 (t), 22.80 (t), 22.80 (q), 22.56 (q), 18.70 (q), 14.53 (q) and 12.08 (q); *m/z* 376.3307 (1%, M^+. $C_{25}H_{44}O_2$ requires *M*, 376.3340), 358.3109 (100; $C_{25}H_{42}O$ requires *M*, 358.3234), 343.2991 (15. $C_{24}H_{39}O$ requires *M*, 343.3000), 332.3035 (3; $C_{23}H_{40}O$ requires *M*, 332.3078), 247.2468 (3. $C_{18}H_{31}$ requires *M*, 247.2424) and 245.1904 (3. $C_{17}H_{25}O$ requires *M*, 245.1904).

Reaction of Compound **1** *with* DIB–I_2.—A solution of the hemiacetal **1** (200 mg, 0.53 mmol) in cyclohexane (53 cm^3) containing DIB (188 mg, 0.58 mmol) and iodine (135 mg, 0.53 mmol), after careful deoxygenation by several cycles of pumping followed by filling with argon was irradiated with two 100 W tungsten-filament lamps at 40 °C for 1 h. The reaction mixture was then poured into water and extracted with dichloromethane. The organic layer was washed successively with aqueous sodium thiosulphate and water, dried (Na_2SO_4) and concentrated under reduced pressure. Silica gel chromatography of the residue (benzene–hexane; 80:20) gave a mixture (169 mg, 85%) of *lactones* **11** (90 mg, 53%) and **12** (79 mg, 47%). The lactone **11**, amorphous; ν_{max}/cm^{-1} 3060 (C=CH_2), 1720, 1630 and 895 (C=CH_2); δ_H 0.69 (3 H, s, 13-Me), 0.84 (6 H, d, *J* 6.6, 25-Me_2), 0.87 (3 H, d, *J* 6.5, 20-Me), 4.25 (1 H, m, $W_{1/2}$ 25 Hz, 2-H), 4.49 (1 H, m, $W_{1/2}$ 30 Hz, 2-H) and 4.93 and 4.96 (each 1 H, s, br s, 19-H_2); δ_C complex spectrum due to slow conformational equilibrium of the nine-membered ring; *m/z* 374.3166 (15%, M^+. $C_{25}H_{42}O_2$ requires *M*, 374.3182), 346.2839 (2. $C_{23}H_{38}O_2$ requires *M*, 346.2870), 330.2856 (3. $C_{23}H_{38}O$ requires *M*, 330.2921), 290.2190 (4. $C_{19}H_{30}O_2$ requires *M*, 290.2244), 261.1844 (21. $C_{17}H_{25}O_2$ requires *M*, 261.1853) and 243.1750 (4. $C_{17}H_{23}O$ requires *M*, 243.1748). Lactone **12**, amorphous; ν_{max}/cm^{-1} 1720 and 1635 (CH=C); δ_H 0.68 (3 H, s, 13-Me), 0.84 (6 H, d, *J* 6.6, 25-Me_2), 0.88 (3 H, d, *J* 6.6, 20-Me), 1.66 (3 H, s, 10-Me), 4.31 and 4.89 (2 H, AMX, J_{AM} 6.2, J_{AX} 6.6, J_{MX} 12.8, 2-H_2) and 5.66 (1 H. AMX, 1-H); δ_C 179.01 (s, 5-C), 147.14 (s, 10-C), 122.74 (d, 1-C), 62.77 (t, 2-C), 56.32 (d), 50.81 (d), 43.82 (d), 43.17 (s), 39.75 (t), 39.70 (t), 37.64 (d), 36.28 (t), 35.87 (d), 29.50 (t), 28.18 (d), 28.03 (t), 27.09 (t), 25.67 (t), 24.87 (t), 23.86 (t), 22.94 (q), 22.70 (q), 18.83 (q), 18.79 (q) and 12.19 (q); *m/z* 374.3213 (11%, M^+. $C_{25}H_{42}O_2$ requires *M*, 374.3243), 359.2949 (21. $C_{24}H_{39}O_2$ requires *M*, 359.2949), 356.3029 (5. $C_{25}H_{40}O$ requires *M*, 356.3077), 304.2774 (15. $C_{21}H_{36}O$ requires *M*, 304.2765), 301.2919 (8. $C_{22}H_{37}$ requires *M*, 301.2894), 293.2416 (13. $C_{19}H_{33}O_2$ requires *M*, 293.2353), 277.2213 (25. $C_{18}H_{29}O_2$ requires *M*, 277.2166) and 261.1877 (49. $C_{17}H_{25}O_2$ requires *M*, 261.1853). When the reaction was carried out under the same conditions but without iodine starting material was recovered unchanged. With a catalytic amount of iodine (0.1 mmol per mmol of **1**) only 30% of the hemiacetal was transformed after 2 h at 40 °C.

3-*Hydroxy*-4-*nor*-3,4-*secocholestan*-5-*one* 3,5-*Hemiacetal* **2**.—A solution of the alcohol **10**[9] (394 mg, 0.91 mmol) in acetone (200 cm^3) containing PTSA (473 mg, 2.49 mmol) was stirred at room temperature for 30 min. Work-up and column chromatography of the residue (benzene–ethyl acetate; 85:15) gave *compound* **2** (303 mg, 85%), amorphous; ν_{max}/cm^{-1} 3580, 3500–3300 and 1690; δ_H 0.63 (3 H, s, 13-Me), 0.84 (6 H, d, *J* 6.9, 25-Me_2), 0.88 (3 H, d, *J* 6.6, 20-Me), 0.90 (3 H, s, 10-Me), 3.60 (1 H, m, $W_{1/2}$ 20 Hz, 3-H) and 3.90 (1 H, m, $W_{1/2}$ 25 Hz, 3-H); δ_C complex spectrum due to the ring-chain tautomerism; *m/z* 390.3512 (2%, M^+. $C_{26}H_{46}O_2$ requires *M*, 390.3497), 375 (*M* − Me, 2), 373 (24), 372 (83), 359 (3), 358 (16), 357 (53), 315 (9), 287 (7), 259 (8) and 217 (10).

Reaction of Compound **2** *with* DIB–I_2.—A solution of the hemiacetal **2** (200 mg, 0.51 mmol) in cyclohexane (50 cm^3) containing DIB (202 mg, 0.63 mmol) and iodine (181 mg, 0.71 mmol), after careful deoxygenation by several cycles of pumping followed by filling with argon was irradiated with two 100 W tungsten-filament lamps for 6 h at 35–40 °C. Work-up as

described previously gave a mixture of lactones (164 mg, 82%) which was separated after careful column chromatography (hexane) and PLC (benzene). 10-*Methylene*-4-*oxa*-5,10-*seco*-*cholestan*-5-*one* **13** (65 mg, 40%), amorphous; ν_{max}/cm^{-1} 3060 ($C{=}CH_2$), 1712, 1630 and 885 ($C{=}CH_2$); δ_H 0.71 (3 H, s, 13-Me), 0.85 (6 H, d, *J* 6.5, 25-Me_2), 0.89 (3 H, d, *J* 5.3, 20-Me), 3.86 (1 H, m, $W_{1/2}$ 25 Hz, 3-H), 4.62 (1 H, m, $W_{1/2}$ 30 Hz, 3-H) and 4.74 and 4.83 (each 1 H, s, s, 19-H_2); δ_C complex spectrum due to slow conformational equilibrium of the ten-membered ring; *m/z* 388.3361 (24%, M^+. $C_{26}H_{44}O_2$ requires *M*, 388.3382), 373.3123 (10. $C_{25}H_{41}O_2$ requires *M*, 373.3141), 347.2990 (5. $C_{23}H_{39}O_2$ requires *M*, 347.3032), 319.2597 (6. $C_{21}H_{35}O_2$ requires *M*, 319.2636), 315.3040 (5. $C_{23}H_{39}$ requires *M*, 315.3050), 275 (44) and 247 (11).

Lactone **14** (33 mg, 20%), amorphous, ν_{max}/cm^{-1} 1715; δ_H 0.70 (3 H, s, 13-Me), 0.88 (6 H, d, *J* 7.1, 25-Me_2), 0.91 (3 H, d, *J* 6.5, 20-Me), 1.67 (3 H, s, 10-Me), 2.57 (2 H, m, $W_{1/2}$ 25 Hz, 2-H), 3.63 (1 H, m, $W_{1/2}$ 30 Hz, 3-H), 4.60 (1 H, m, $W_{1/2}$ 20 Hz, 3-H) and 5.19 (1 H, m, $W_{1/2}$ 20 Hz, 1-H); δ_C 175.06 (s, C-5), 143.09 (s, C-10), 120.46 (d, C-1), 61.97 (t, C-3), 56.03 (d), 50.48 (d), 42.89 (s), 41.50 (d), 39.59 (t), 39.54 (t), 36.41 (d), 36.19 (t), 35.73 (d), 30.51 (t), 28.07 (d), 27.97 (t), 27.41 (t), 25.78 (t), 25.40 (t), 24.21 (t), 23.72 (t), 22.83 (q), 22.61 (q), 18.87 (q), 18.70 (q) and 11.96 (q); *m/z* 388.3323 (13%, M^+. $C_{26}H_{44}O_2$ requires *M*, 388.3340), 373.3071 (9. $C_{25}H_{41}O_2$ requires *M*, 373.3105), 347.2955 (3. $C_{23}H_{39}O_2$ requires *M*, 347.2962), 319.2685 (15. $C_{21}H_{35}O_2$ requires *M*, 319.2735), 315.3052 (12. $C_{23}H_{39}$ requires *M*, 315.3054), 305.2467 (6. $C_{20}H_{33}O_2$ requires *M*, 305.2479), 275 (38) and 247 (26).

Lactone **15** (64 mg, 40%), amorphous; ν_{max}/cm^{-1} 1718; δ_H 0.71 (3 H, s, 13-Me), 0.85 (6 H, d, *J* 7.4, 25-Me_2), 0.88 (3 H, d, *J* 7.3, 20-Me), 1.62 (3 H, s, 10-Me), 4.00 (1 H, m, $W_{1/2}$ 20 Hz, 3-H), 4.90 (1 H, m, $W_{1/2}$ 30 Hz, 3-H) and 5.05 (1 H, m, $W_{1/2}$ 20 Hz, 1-H); δ_C 176.61 (s, C-5), 143.13 (s, C-10), 123.92 (d, C-1), 65.17 (t, C-3), 56.52 (d), 55.64 (d), 55.21 (d), 42.83 (s), 40.28 (d), 39.68 (t), 39.46 (t), 36.26 (t), 35.92 (d), 33.66 (t), 30.22 (t), 29.38 (t), 28.17 (d), 28.11 (t), 27.94 (t), 25.63 (t), 23.98 (t), 22.96 (q), 22.71 (q), 18.89 (q), 13.14 (q) and 12.10 (q); *m/z* 388.3290 (18%; M^+, $C_{26}H_{44}O_2$ requires *M*, 388.3339), 373.3166 (7. $C_{25}H_{41}O_2$ requires *M*, 373.3228), 370.3337 (6. $C_{26}H_{42}O$ requires *M*, 370.3440), 347.2865 (10. $C_{23}H_{39}O_2$ requires *M*, 347.2947), 319.2548 (11. $C_{21}H_{35}O_2$ requires *M*, 319.2636), 315.3090 (9. $C_{23}H_{39}$ requires *M*, 315.3130), 305.2740 (5. $C_{21}H_{37}O$ requires *M*, 305. 2844), 275 (34) and 247 (20).

3β-*Methoxy*-23,24-*dinor*-5α-*cholano*-22,16β-*lactone* **17**.—Prepared from 3β-hydroxy-23,24-dinor 5α-cholano-22,16β-lactone **16**[13] essentially as described[22] for 3β-methoxy-5α-cholestane in 97% yield, m.p. 176–178 °C (acetone); $[\alpha]_D$ −42 (*c* 0.53); ν_{max}/cm^{-1} 1785; δ_H 0.66 (3 H, s, 13-Me), 0.76 (3 H, s, 10-Me), 1.26 (3 H, d, *J* 7.5, 20-Me), 2.53 (1 H, m, $W_{1/2}$ 25 Hz, 20β-H), 3.07 (1 H, m $W_{1/2}$ 30 Hz, 3α-H), 3.29 (3 H, s, 3β-OMe) and 4.89 (1 H, m, $W_{1/2}$ 22 Hz, 16a-H); δ_C 12.29 (q), 13.89 (q), 17.97 (q), 20.56 (t), 27.84 (t), 28.62 (t), 32.21 (t), 33.03 (t), 34.29 (t), 34.92 (d), 35.92 (s), 36.06 (d), 36.94 (t), 38.39 (t), 41.77 (s), 44.75 (d), 54.50 (d), 54.62 (d), 55.49 (q), 59.08 (d), 79.68 (d), 82.71 (d) and 181.23 (s); *m/z* 360.2659 (17%, M^+. $C_{23}H_{36}O_3$ requires *M*, 360.2665), 328.2349 (100. $C_{22}H_{32}O_2$ requires *M*, 328.2403), 313.2212 (46. $C_{21}H_{29}O_2$ requires *M*, 313.2168), 274.1986 (16. $C_{18}H_{26}O_2$ requires *M*, 274.1933) and 215 (44).

3β-*Methoxy*-23,24-*dinor*-5α-*cholane*-16β,22-*diol* **18**.—A solution of lactone **17** (2.28 g, 6.33 mmol) in anhydrous tetrahydrofuran (THF) (43 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (2.04 g, 53.7 mmol) in THF (40 cm^3) at 0 °C. The mixture was stirred at reflux temperature for 45 min, cooled at room temperature and treated dropwise with saturated aqueous Na_2SO_4, and the reaction mixture was then processed as described in a previous experiment. Column chromatography of the residue gave *diol* **18** (2.24 g, 97%), m.p. 187–190 °C (dichloromethane); $[\alpha]_D$ +4 (*c* 0.42); ν_{max}/cm^{-1} 3610 and 3530–3200; δ_H 0.78 (3 H, s, 13-Me), 0.87 (3 H, s, 10-Me), 0.93 (3 H, d, *J* 7, 20-Me), 3.12 (1 H, m, $W_{1/2}$ 30 Hz, 3α-H), 3.32 (3 H, s, 3β-OMe), 3.53 (2 H, d, *J* 5.4, 22-H_2), 3.75 (2 H, m, $W_{1/2}$ 30 Hz, OH) and 4.35 (1 H, m, $W_{1/2}$ 20 Hz, 16α-H); δ_C 12.40 (q), 13.46 (q), 17.07 (q), 21.10 (t), 27.99 (t), 28.93 (t), 32.21 (t), 32.76 (d), 34.44 (t), 35.23 (d), 35.76 (t), 35.94 (s), 37.03 (t), 40.48 (t), 43.06 (s), 44.94 (d), 54.45 (d), 54.57 (d), 55.62 (q), 62.41 (d), 70.68 (t), 72.68 (d) and 80.06 (d); *m/z* 346.2877 (1%, $M^+ - H_2O$. $C_{23}H_{38}O_2$ requires *M*, 346.2871), 331.2565 (14. $C_{22}H_{35}O_2$ requires *M*, 331.2637), 316.2665 (50. $C_{22}H_{36}O$ requires *M*, 316.2706), 301.2533 (23. $C_{21}H_{33}O$ requires *M*, 301.2531), 288.2314 (18. $C_{20}H_{32}O$ requires *M*, 288.2408) and 248.2125 (100. $C_{17}H_{28}O$ requires *M*, 248.2140).

3β-*Methoxy*-23,24-*dinor*-5α-*cholane*-16β,22-*diol* 22-*Acetate* **19**.—To a solution of diol **18** (2.1 g, 5.8 mmol) in pyridine (300 cm^3) was added dropwise acetic anhydride (12 cm^3). The mixture was stirred at room temperature for 5 h, poured into water, neutralized with $NaHCO_3$ and extracted with dichloromethane. The organic layer was washed successively with dil. HCl, saturated aqueous $NaHCO_3$ and water, and concentrated under reduced pressure. Silica gel column chromatography of the residue gave the *monoacetate* **19** (1.84 g, 75%) and a small amount of the diacetate **20** (0.225 g, 8%). Compound **19**, m.p. 161–162 °C (MeOH); $[\alpha]_D$ +23 (*c* 0.70); ν_{max}/cm^{-1} 3600, 3560–3320, and 1715; δ_H 0.79 (3 H, s, 13-Me), 0.87 (3 H, s, 10-Me), 1.06 (3 H, d, *J* 6.7, 20-Me), 2.07 (3 H, s, 22-OAc), 2.80 (1 H, m, $W_{1/2}$ 24 Hz, OH), 3.11 (1 H, m, $W_{1/2}$ 30 Hz, 3α-H), 3.33 (3 H, s, 3β-OMe), 3.63 (1 H, dd, *J* 7.9, 16α-H) and 4.33 (2 H, m, $W_{1/2}$ 19 Hz, 22-H_2); δ_C 12.32 (q), 13.24 (q), 16.95 (q), 20.93 (t), 21.07 (q), 27.91 (t), 28.84 (t), 30.63 (d), 32.09 (t), 34.36 (t), 35.14 (d), 35.87 (s), 36.18 (t), 36.96 (t), 40.10 (t), 42.66 (s), 44.84 (d), 54.30 (q), 54.48 (d), 55.54 (d), 58.28 (d), 70.19 (t), 71.94 (d), 79.90 (d) and 171.88 (s); *m/z* 388.2961 (1%, $M^+ - H_2O$. $C_{25}H_{40}O_3$ requires *M*, 388.2975), 346.2880 (34. $C_{23}H_{38}O_2$ requires *M*, 346.2869), 331.2618 (22. $C_{22}H_{35}O_2$ requires *M*, 331.2635), 329.2487 (15. $C_{22}H_{33}O_2$ requires *M*, 329.2478), 328.2750 (20. $C_{23}H_{36}O$ requires *M*, 328.2764), 316.2740 (38. $C_{22}H_{36}O$ requires *M*, 316.2764), 289.2485 (39. $C_{20}H_{33}O$ requires *M*, 289.2520) and 248.2156 (100. $C_{17}H_{28}O$ requires *M*, 248.2139).

22-*Acetoxy*-3β-*methoxy*-23,24-*dinor*-5α-*cholan*-16-*one* **21**.—To a stirred solution of compound **19** (1.7 g, 4.18 mmol) in acetone (170 cm^3) was added dropwise an excess of Jones' reagent at room temperature. The excess of reagent was destroyed with methanol and the mixture was poured into water and extracted with ethyl acetate. The extract was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (benzene–ethyl acetate; 90:10) to give *ketone* **21** (1.55 g, 92%), m.p. 136–138 °C (pentane–acetone); $[\alpha]_D$ −117° (*c* 0.88); ν_{max}/cm^{-1} 1720; δ_H 0.82 (6 H, s, 10-Me, 13-Me), 1.03 (3 H, d, *J* 6.9, 20-Me), 2.04 (3 H, s, 22-OAc), 3.14 (1 H, m, $W_{1/2}$ 23 Hz, 3α-H), 3.34 (3 H, s, 3β-OMe) and 4.20 and 4.33 (2 H, AMX, J_{AM} 10.6, J_{AX} 4.1, J_{MX} 6.9, 22-H_2); δ_C 12.38 (q), 13.69 (q), 16.76 (q), 20.85 (t), 21.06 (q), 27.94 (t), 28.68 (t), 31.24 (d), 32.24 (t), 34.37 (t), 34.51 (d), 36.02 (s), 36.76 (t), 38.82 (t), 39.11 (t), 43.15 (s), 44.84 (d), 50.91 (d), 54.29 (d), 55.68 (q), 64.33 (d), 68.29 (t), 79.83 (d), 171.23 (s) and 218.04 (s); *m/z* 404.2900 (0.4%, M^+. $C_{25}H_{40}O_4$ requires *M*, 404.2924), 389.2724 (11. $C_{24}H_{37}O_4$ requires *M*, 389.2690), 344.2699 (17. $C_{23}H_{36}O_2$ requires *M*, 344.2712), 329.2481 (100. $C_{22}H_{33}O_2$ requires *M*, 329.2478) and 289.2181 (86. $C_{19}H_{29}O_2$ requires *M*, 289.2166).

22-*Hydroxy*-3β-*methoxy*-23,24-*dinor*-5α-*cholan*-16-*one* 16,22-*Hemiacetal* **22**.—A solution of sodium hydroxide in methanol (0.6%; 28 cm^3) was added to compound **21** (1.55 g) in methanol (28 cm^3). The mixture was stirred at room temperature for 24 h, poured into water and extracted with ethyl acetate. The organic layer was washed with dil. HCl and water, dried (Na_2SO_4) and concentrated under reduced pressure to give *hemiacetal* **22**, m.p. 131–133 °C (acetone); $[\alpha]_D$ −52° (*c* 0.206); ν_{max}/cm^{-1} 3565, 3500–3300 and 1720; δ_H 0.64 (3 H, s, 13-Me), 0.69 (3 H, s, 13-Me), 0.71 (3 H, s, 10-Me), 0.93 (3 H, d, *J* 6.4, 20-Me), 0.96 (3 H, d, *J* 6.9, 20-Me), 3.22 (3 H, s, 3β-OMe), 3.55 (2 H, m, $W_{1/2}$ 7.5 Hz, 22-H_2, chain form) and 3.60 and 4.10 (2 H, AMX, 22-H_2, ring form); δ_C complex spectrum due to the ring-chain tautomerism; *m/z* 362.2804 (3%, M^+. $C_{23}H_{38}O_3$ requires *M*, 362.2818), 344.2727 (7. $C_{23}H_{36}O_2$ requires *M*, 344.2740), 332.2716 (20. $C_{22}H_{36}O_2$ requires *M*, 332.2720), 329.2481 (40. $C_{22}H_{33}O_2$ requires *M*, 329.2484) and 289.2135 (100. $C_{19}H_{29}O_2$ requires *M*, 289.2166). Further characterization was achieved by treatment of a solution of compound **22** (31 mg, 0.086 mmol) in methanol (6 cm^3) with catalytic amounts of PTSA at room temperature for 1 h, when the *methyl acetal* **23** (32 mg, 99%) was obtained, m.p. 154–156 °C (MeOH); $[\alpha]_D$ −46° (*c* 0.292); ν_{max}/cm^{-1} 1090; δ_H 0.72 (3 H, s, 10-Me), 0.76 (3 H, s, 13-Me), 1.00 (3 H, d, *J* 6.8, 20-Me), 3.10 (1 H, m, $W_{1/2}$ 20 Hz, 3-H), 3.16 (3 H, s, 3-OMe), 3.30 (3 H, s, 16-OMe) and 3.45 and 4.11 (2 H, AMX, J_{AM} J_{MX} J_{AX} 8.3, 22-H_2); δ_C 79.94 (d, C-3), 77.74 (t, C-22), 71.09 (d, C-21), 55.98 (d), 55.66 (q, 3-OMe), 54.50 (d), 49.36 (q, 16-OMe), 44.94 (d), 41.13 (s), 39.36 (t), 37.01 (t), 36.01 (s), 35.19 (d), 34.50 (t), 33.69 (t), 32.20 (t), 31.60 (d), 28.88 (t), 28.03 (t), 20.88 (t), 20.01 (q), 14.74 (q) and 12.44 (q), one quaternary carbon atom is not distinguished; *m/z* 376.2959 (17%, M^+. $C_{24}H_{40}O_3$ requires *M*, 376.2975), 361.2675 (4. $C_{23}H_{37}O_3$ requires *M*, 361.2740) and 329.2495 (47. $C_{22}H_{33}O_2$ requires *M*, 329.2511).

Reaction of Compound **22** *with* DIB–I_2.—A solution of the hemiacetal **22** (100 mg, 0.27 mmol) in cyclohexane (28 cm^3) containing DIB (100 mg, 0.31 mmol) and iodine (71 mg, 0.28 mmol), after careful deoxygenation by several cycles of pumping followed by filling with argon was irradiated with two 100 W tungsten-filament lamps at 40 °C for 100 min. Work-up as described in a previous experiment gave *lactone* **24** (111 mg, 82%) after purification by column chromatography (benzene–ethyl acetate; 95:5), m.p. 180–182 °C (pentane–ethyl acetate), $[\alpha]_D$ −55° (*c* 0.206); ν_{max}/cm^{-1} 1730; δ_H 0.66 (3 H, s, 13-Me), 0.86 (3 H, d, *J* 6.6, 20-Me), 1.00 (3 H, s, 10-Me), 2.06 (1 H, AMX, J_{AM} 14.0, J_{MX} 5.9, 15-H), 2.84 (1 H, AMX, J_{AM} 14.0, J_{AX} 6.6, 15-H), 3.00 (1 H, m, $W_{1/2}$ 21.1 Hz, 3-H), 3.22 (3 H, s, 3β-OMe), 3.83 (1 H, AMX, J_{AM} 12.1, J_{MX} 0, 22-H), 4.07 (1 H, AMX, J_{AM} 12.3, J_{AX} 3.8, 22-H) and 3.92 (1 H, s, 17-H); δ_C 176.27 (s, 16-C), 79.77 (d, 3-C), 71.40 (t, 22-C), 68.45 (d, 21-C), 55.66 (q, 3-OMe), 53.16 (d), 49.50 (d), 44.31 (t), 43.50 (d), 42.56 (s), 36.84 (d), 36.80 (t), 36.06 (d), 36.06 (s), 34.15 (t), 31.77 (t), 31.68 (t), 28.86 (t), 27.89 (t), 21.31 (t), 21.08 (q), 17.58 (q) and 12.34 (q); *m/z* 488.1725 (1; M^+, $C_{23}H_{37}IO_3$ requires *M*, 488.1788), 441.1462 ($C_{21}H_{30}IO_2$ requires *M*, 441.1290), 361.2607 (15. $C_{23}H_{37}O_3$ requires *M*, 361.2741), 345.2496 (15. $C_{22}H_{33}O_3$ requires *M*, 345.2428), 329.2433 (100. $C_{22}H_{33}O_2$ requires *M*, 329.2433), 289.2433 (50. $C_{19}H_{29}O_2$ requires *M*, 289.2166) and 215.1765 (40. $C_{16}H_{23}$ requires *M*, 215.1798).

Crystallographic Data for Compound **24**.—A suitable crystal of 0.22 × 0.30 × 0.20 mm^3 was selected for X-ray analysis. Cell parameters obtained by least squares analysis of diffractometer measurements of 44 centred reflections with $10 < \theta < 45°$. The crystals are monoclinic space group $P2_1$: a = 11.956(1), b = 12.566(1), c = 7.2900(3) Å, β = 96.772(4)°. Data collected on a Philips PW 1100 four-circle diffractometer with graphite monochromated Cu-K_α radiation, $\omega/2\theta$ scan technique, scan speed 0.055° s^{-1}, scan width 1.50°, θ_{max} 65°. Two standard reflections (2 2 0, −2 −2 0) measured every 90 min showed no variation in the intensity. 1959 Independent reflections were measured, 1825 observed [$I > 2\sigma(I)$]. Corrections of Lorentz and polarization were applied. The structure was solved by Patterson and direct methods (MULTAN).[23] An absorption correction (μ = 118.257 cm^{-1}) following the DIFABS[24] procedure was applied on isotropically refined data. Full-matrix least-squares anisotropic refinement (on *F*) of all non-hydrogen atoms and subsequent difference Fourier synthesis revealed positions for all H atoms; they were included in the last cycles of refinement as fixed contributors. Neutral-atom scattering factors and anomalous dispersion corrections were taken from International Tables of Crystallography.[25] A weighting scheme was applied so as not to give trends in $\langle w\Delta^2F \rangle$ *vs.* $\langle F_o \rangle$ and *vs.* $\langle \sin\theta/\lambda \rangle$. Final *R* and R_w values are 6.7 and 8.7, respectively. The non-hydrogen atom numbering is shown in the molecular projection (Fig. 1); the more significant results (non-H co-ordinates, bond lengths and angles) are given in Tables 2–4. Full lists of bond lengths and angles, hydrogen coordinates and anisotropic thermal parameters have been deposited at the C.C.D.C.*

5-*Bromo*-6β,19-*epoxy*-5α-*cholestan*-3β-*ol* **25**.—Preparation of 5-bromo-6β,19-epoxy-5α-cholestan-3β-yl acetate **26** followed essentially the procedure described by Kalvoda *et al.*,[14] m.p. 152–153 °C; $[\alpha]_D$ +6° (*c* 0.246) (lit.,[13] 149 °C; $[\alpha]_D$ ±0°); ν_{max}/cm^{-1} 1725; δ_H 0.69 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.5, 25-Me_2), 0.89 (3 H, d, *J* 6.5, 20-Me), 2.03 (3 H, s, 3β-OAc), 3.74, 3.92 (2 H, AB, J_{AB} 8.3, 19-H_2), 4.06 (1 H, d, *J* 4.3, 6-H) and 5.20 (1 H, m, $W_{1/2}$ 20 Hz, 3α-H); δ_C 170.35 (s, 3-OAc), 82.47 (d, C-3), 74.70 (s, C-5), 70.12 (d, C-6), 67.60 (t, C-19), 56.17 (d), 54.52 (d), 48.83 (d), 45.99 (s), 43.32 (s), 41.50 (t), 39.92 (t), 39.63 (t), 36.26 (t), 35.84 (d), 33.44 (d), 33.98 (t), 28.38 (t), 28.13 (d), 27.02 (t), 23.91 (t), 23.60 (t), 23.40 (t), 22.92 (q), 22.82 (t), 22.67 (q), 21.39 (q), 18.74 (q) and 12.54 (q); *m/z* 443 (M^+ −Br, 7), 400 (*M* − Br − C_3H_7, m 2), 383 (*M* − Br − $C_2H_4O_2$, 69), 353 (46) and 341 (17). Hydrolysis of ester **26** with sodium carbonate in methanol at room temperature overnight gave the *title alcohol* **25**, m.p. 146–147 °C (hexane), $[\alpha]_D$ +1° (*c* 0.364); ν_{max}/cm^{-1} 3600 and 3500–3300; δ_H 0.70 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.6, 25-Me_2), 0.89 (3 H, d, *J* 6.5, 20-Me), 3.72, 3.91 (2 H, AB, J_{AB} 8.3, 19-H_2), 4.06 (1 H, d, *J* 4.3, 6-H) and 4.14 (1 H, m, $W_{1/2}$ 20 Hz, 3-H); *m/z* 401.3378 (4%, M^+ − Br. $C_{27}H_{45}O_2$ requires *M*, 401.3419), 400 (6), 383 (5), 370 (5), 354 (22) and 341 (16).

19-*Hydroxycholest*-4-*en*-3-*one* **28**.—The alcohol **25** (500 mg) in acetone (100 cm^3) at 0 °C was treated dropwise with Jones' reagent until permanently orange in colour; the excess of reagent was then destroyed by adding methanol. The mixture was poured into water and extracted with diethyl ether, which was washed with water, dried (Na_2SO_4) and evaporated under reduced pressure to give the unstable ketone **27** which was used in the next step without purification.

The crude ketone **27** in propan-2-ol (30 cm^3) and acetic acid (3.4 cm^3) was stirred and heated at 80–90 °C for 3 h with zinc dust (3.2 g, previously activated by brief washing with 5% hydrochloric acid, water, methanol, and diether ether). The filtered solution was then poured into water and extracted with chloroform, which was washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated under

* For full details of the Cambridge Crystallographic Data Centre deposition scheme see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1991, issue 1.

Table 2 Non-hydrogen atom fractional co-ordinates

Atom	*x*	*y*	*z*
I	0.2821(1)	0.2500(0)	0.0237(1)
O(1)	0.4534(11)	0.1782(10)	0.6004(15)
O(2)	0.6165(12)	0.1024(10)	0.5913(18)
O(3)	1.0870(12)	0.1510(10)	−0.3850(23)
C(1)	0.8508(15)	0.3075(12)	−0.2224(24)
C(2)	0.9638(14)	0.2826(13)	−0.2940(27)
C(3)	0.9778(14)	0.1681(14)	−0.3206(24)
C(4)	0.9690(13)	0.1081(11)	−0.1414(23)
C(5)	0.8548(13)	0.1292(10)	−0.0724(26)
C(6)	0.8351(14)	0.0648(11)	0.0959(28)
C(7)	0.7164(13)	0.0769(11)	0.1434(23)
C(8)	0.6815(12)	0.1942(10)	0.1679(19)
C(9)	0.7108(10)	0.2617(18)	−0.0010(18)
C(10)	0.8350(10)	0.2525(18)	−0.0374(17)
C(11)	0.6729(14)	0.3766(12)	0.0124(26)
C(12)	0.5510(15)	0.3873(12)	0.0504(27)
C(13)	0.5198(13)	0.3199(12)	0.2268(26)
C(14)	0.5549(14)	0.2034(11)	0.1858(21)
C(15)	0.5046(12)	0.1179(10)	0.3019(20)
C(16)	0.5314(15)	0.1313(11)	0.5042(22)
C(17)	0.3947(13)	0.3396(12)	0.2440(22)
C(18)	0.5904(14)	0.3658(11)	0.4012(26)
C(19)	0.9169(15)	0.2954(13)	0.1210(26)
C(20)	0.3461(13)	0.3240(12)	0.4325(22)
C(21)	0.3438(15)	0.2145(12)	0.5159(24)
C(22)	0.2275(15)	0.3723(15)	0.4272(28)
C(23)	1.0989(20)	0.0494(15)	−0.4662(37)

Table 3 Non-hydrogen interatomic distances (Å)

Bond	Distance/Å	Bond	Distance/Å
I–C(17)	2.2677(16)	C(8)–C(9)	1.5500(25)
O(1)–C(16)	1.3871(23)	C(8)–C(14)	1.5397(24)
O(1)–C(21)	1.4375(24)	C(9)–C(10)	1.5289(20)
O(2)–C(16)	1.1960(22)	C(9)–C(11)	1.5472(33)
O(3)–C(3)	1.4687(24)	C(10)–C(19)	1.4913(24)
O(3)–C(23)	1.4298(26)	C(11)–C(12)	1.5544(27)
C(1)–C(2)	1.5318(28)	C(12)–C(13)	1.6025(28)
C(1)–C(10)	1.5829(25)	C(13)–C(14)	1.5547(24)
C(2)–C(3)	1.4581(25)	C(13)–C(17)	1.5667(24)
C(3)–C(4)	1.4944(27)	C(13)–C(18)	1.5523(26)
C(4)–C(5)	1.5403(27)	C(14)–C(15)	1.5314(24)
C(5)–C(6)	1.4604(29)	C(15)–C(16)	1.4962(24)
C(5)–C(10)	1.5620(30)	C(17)–C(20)	1.5824(25)
C(6)–C(7)	1.5284(27)	C(20)–C(21)	1.5192(25)
C(7)–C(8)	1.5550(22)	C(20)–C(22)	1.5310(27)

Table 4 Non-hydrogen interbond angles (°)

Bond	Angle/°	Bond	Angle/°
C(16–O(1)–C(21)	123.48(1)	C(1)–C(10)–C(19)	109.47(1)
C(3)–O(3)–C(23)	115.14(2)	C(9)–C(11)–C(12)	112.93(1)
C(2)–C(1)–C(10)	112.05(2)	C(11)–C(12)–C(13)	112.83(2)
C(1)–C(2)–C(3)	112.15(2)	C(12)–C(13)–C(18)	108.56(1)
O(3)–C(3)–C(2)	108.19(1)	C(12)–C(13)–C(17)	105.04(1)
C(2)–C(3)–C(4)	110.73(2)	C(12)–C(13)–C(14)	105.54(1)
O(3)–C(3)–C(4)	111.49(2)	C(17)–C(13)–C(18)	107.55(1)
C(3)–C(4)–C(5)	111.66(2)	C(14)–C(13)–C(18)	112.10(1)
C(4)–C(5)–C(10)	112.90(1)	C(14)–C(13)–C(17)	117.52(1)
C(4)–C(5)–C(6)	114.67(2)	C(8)–C(14)–C(13)	111.48(1)
C(6)–C(5)–C(10)	111.27(2)	C(13)–C(14)–C(15)	115.63(1)
C(5)–C(6)–C(7)	111.77(2)	C(8)–C(14)–C(15)	117.00(1)
C(6)–C(7)–C(8)	112.53(1)	C(14)–C(15)–C(16)	113.37(1)
C(7)–C(8)–C(14)	110.12(1)	O(2)–C(16)–C(15)	125.54(2)
C(7)–C(8)–C(9)	107.91(1)	O(1)–C(16)–C(15)	119.01(2)
C(9)–C(8)–C(14)	109.50(1)	O(1)–C(16)–O(2)	115.42(2)
C(8)–C(9)–C(11)	111.12(1)	I–C(17)–C(13)	110.77(1)
C(8)–C(9)–C(10)	112.93(1)	C(13)–C(17)–C(20)	120.36(1)
C(10)–C(9)–C(11)	112.21(2)	I–C(17)–C(20)	107.37(1)
C(5)–C(10)–C(9)	105.99(2)	C(17)–C(20)–C(21)	120.55(1)
C(1)–C(10)–C(9)	108.12(1)	C(17)–C(20)–C(22)	110.59(1)
C(1)–C(10)–C(5)	105.81(1)	C(22)–C(20)–C(21)	108.99(2)
C(9)–C(10)–C(19)	115.08(1)	O(1)–C(21)–C(20)	114.34(2)
C(5)–C(10)–C(19)	111.90(2)		

reduced pressure. Silica gel column chromatography of the residue (benzene–ethyl acetate; 80:20) gave the 19-*hydroxy compound* **28** (320 mg, 77%), m.p. 144.5–145.5 °C; $[\alpha]_D$ +82 (*c* 0.302); ν_{max}/cm^{-1} 3620, 3560–3160 and 1655; δ_H 0.70 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.8, 25-Me$_2$), 0.90 (3 H, d, *J* 7.1, 20-Me), 3.89, 4.07 (2 H, AB, J_{AB} 10.9, 19-H$_2$) and 5.94 (1 H, s, 4-H); δ_C 184.25 (s, C-3), 168.32 (s, C-5), 126.52 (d, C-4), 65.80 (t, C-19), 56.35 (d), 56.17 (d), 54.16 (d), 44.07 (s), 42.56 (s), 40.11 (t), 39.55 (t), 39.55 (t), 36.33 (d), 35.78 (d), 35.10 (t), 33.71 (t), 33.47 (t), 32.40 (t), 28.21 (t), 28.04 (d), 24.15 (t), 23.89 (t), 22.87 (q), 22.62 (q), 21.66 (t), 18.70 (q) and 12.14 (q); *m/z* 400.3304 (2%, M$^+$. $C_{27}H_{44}O_2$ requires *M*, 400.3341), 382 (*M* − H_2O, 6), 370.3206 (100. $C_{26}H_{42}O$ requires *M*, 370.3235), 355 (20) and 257 (37).

3,19-*Epoxy*-5α-*cholestan*-3-*ol* **31**.—To a solution of the alcohol **28** (0.5 g, 1.25 mmol) in diethyl ether (5 cm^3) and dichloromethane (7 cm^3), was added dihydropyran (0.4 cm^3, 4.4 mmol) and PTSA (10 mg, 0.053 mmol). The reaction mixture was stirred overnight at room temperature and then poured into water and extracted with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated under reduced pressure, to give the crude tetrahydropyranyl ether **29** which was used without purification in the next reaction.

A solution of the crude tetrahydropyranyl ether **29** (0.56 g) in anhydrous THF (10 cm^3) was added with stirring to a solution of lithium (60 mg) in distilled liquid ammonia (20 cm^3). After 10 min the lithium excess was destroyed with solid ammonium chloride. The residue obtained after evaporation of the ammonia was treated with water and the resulting mixture was extracted with ethyl acetate, and the extract was washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was stirred in dioxane containing hydrochloric acid (0.5 mol dm^{-3}; 5 cm^3) for 24 h at room temperature. The usual processing gave a crude product which was purified by column chromatography (hexane–ethyl acetate; 90:10) to give the *title compound* **31** (420 mg, 83%), m.p. 146–147 °C (hexane–acetone); $[\alpha]_D$ +49° (*c* 0.20); ν_{max}/cm^{-1} 3610–3570, 3500–3200 and 1700; δ_H 0.85 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.31, 25-Me$_2$), 0.89 (3 H, d, *J* 6.21, 20-Me) and, 4.02 (1 H, m, $W_{1/2}$ 75 Hz, 3-H); δ_C complex spectrum due to the ring-chain tautomerism; *m/z* 402.3475 (30%, M$^+$. $C_{27}H_{46}O_2$ requires *M*, 402.3496), 384 (*M* − H_2O, 6), 371 (*M* − CH_3O, 43), 355 (25) and 314 (12).

Reaction of Compound **31** *with* DIB–I_2.—A solution of compound **31** (157 mg, 0.39 mmol) in cyclohexane (50 cm^3) containing DIB (189 mg, 0.58 mmol) and iodine (99 mg, 0.39 mmol), after careful deoxygenation, was irradiated with two 100 W tungsten-filament lamps at 40–45 °C for 2 h. The usual processing gave a residue, which was purified by Chromatotron (hexane–ethyl acetate; 97:3) to give *lactone* **32** (72 mg, 35%) and *lactone* **33** (56 mg, 27%). 4-*Iodo*-3-*nor*-2,3-*secocholestane* 2,19-*lactone* **32**, amorphous, ν_{max}/cm^{-1} 1735; δ_H 0.66 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.6, 25-Me$_2$), 0.89 (3 H, d, *J* 6.3, 20-Me), 2.49 (2 H, m, $W_{1/2}$ 20 Hz, 2-H$_2$), 2.92, 3.52 (2 H, AMX, J_{AM} 10.3, J_{MX} 0, J_{AX} 1.6, 4-H$_2$) and 4.26 (2 H, s, 19-H$_2$); δ_C 173.60 (s, C-3), 66.50 (t, C-19), 56.70 (d), 56.22 (d), 53.86 (d, 52.03 (d), 42.41 (s), 40.62 (s), 40.09 (t), 39.60 (t), 36.48 (d), 36.21 (t), 35.82 (d), 31.37 (t), 29.94 (t), 29.44 (t), 28.25 (d), 28.13 (t), 27.84 (t), 24.16 (t), 23.93 (t), 22.94 (q), 22.76 (t), 22.67 (q), 18.77 (q), 12.17 (q) and 10.28 (t, C-4); *m/z* 528.2460 (1%, M$^+$. $C_{27}H_{45}IO_2$ requires *M*, 528.2464), 497.2264 (1. $C_{26}H_{42}IO$ requires *M*, 497.2280),

401.3457 (64. $C_{27}H_{45}O_2$ requires *M*, 401.3496) and 383.3279 (17. $C_{27}H_{43}O$ requires *M*, 383.3311).

2-*Iodo*-3-*nor*-3,4-*secocholestane* 4,19-*lactone* **33**, m.p. 152.6–153.3 °C (pentane); $[\alpha]_D$ +32° (*c* 0.122); ν_{max}/cm^{-1} 1720; δ_H, 0.64 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.4, 25-Me_2), 0.89 (3 H, d, *J* 6.3, 20-Me), 2.26 (1 H, AMX, dd, J_{MX} 0.7, J_{AM} 18.5, 4β-H), 2.79 (1 H, AMX, dd, J_{AX} 6.7, 4α-H), 2.30 (2 H, apparent q, ABX_2, 1-H_2), 3.09 (2 H, apparent ABX_2, 2-H_2), 4.01 (1 H, AB, J_{AB} 11.7, $J_{W5,19\alpha}$ 1.4, 19α-H) and 4.62 (1 H, AB, 19β-H); δ_C 169.99 (s, C-3), 72.64 (t, C-19), 56.58 (d), 56.37 (d), 45.38 (d), 42.47 (s), 40.07 (t), 39.60 (t), 39.39 (s), 37.93 (t), 36.21 (t), 35.80 (d), 35.36 (d), 34.39 (d), 34.39 (t), 30.37 (t), 29.61 (t), 28.25 (t), 28.11 (d), 24.08 (t), 23.94 (t), 22.92 (q), 22.67 (q), 21.72 (t), 18.77 (q), 12.16 (q) and −3.50 (t, C-2); *m/z* 528.2440 (2%, M^+. $C_{27}H_{45}IO_2$ requires *M*, 528.2466), 401.3385 (9. $C_{27}H_{45}O_2$ requires *M*, 401.3417), 400.3276 (13. $C_{27}H_{44}O_2$ requires *M*, 400.3338), 385.3125 (6. $C_{26}H_{41}O_2$ requires *M*, 385.3145), 373.3108 (8. $C_{25}H_{41}O_2$ requires *M*, 373.3111) and 342.3230 (9. $C_{25}H_{42}$ requires *M*, 342.3285).

4,4-*Dimethyl*-19,3-*epoxycholest*-5-*en*-3-*ol* **35**.—Ketone **29** (0.46 g, 0.95 mmol) in *tert*-butyl alcohol (4 cm^3) was added to a solution of potassium *tert*-butoxide (1.3 g, 12 mmol) in *tert*-butyl alcohol (17 cm^3). The mixture was stirred under argon for 10 min at 65 °C, and a solution of iodomethane (0.63 cm^3, 10 mmol) in benzene (14 cm^3) was added dropwise over 2.5 h. The reaction mixture was then poured into water and processed in the usual way to give the crude ketone **34** (0.4 g). This crude compound was stirred overnight at room temperature in dioxane (20 cm^3) containing hydrochloric acid (1 cm^3) to give, after work-up and column chromatography (hexane–ethyl acetate; 96:4), the *title compound* **35** (223 mg, 55%), m.p. 173–175 °C (pentane); $[\alpha]_D$ −41° (*c* 0.084); ν_{max}/cm^{-1} 3590 and 3570–3140; δ_H 0.65 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.01, 25-Me_2), 1.13 (6 H, s, 4-Me_2), 3.69 (1 H, dd, *J* 7.41, $J_{W1\alpha-19\beta}$ 2.8, 19β-H), 3.99 (1 H, d, *J* 7.52, 19α-H) and 5.60 (1 H, m, $W_{1/2}$ 12.8 Hz, 6-H); δ_C complex spectrum due to the ring-chain tautomerism; *m/z* 428.3638 (25%, M^+. $C_{29}H_{48}O_2$ requires *M*, 428.3651), 413.3439 (10. $C_{28}H_{45}O_2$ requires *M*, 413.3460), 410.3586 (5. $C_{29}H_{46}O$ requires *M*, 410.3626), 398.3577 (68. $C_{28}H_{46}O$ requires *M*, 398.3607), 381.3465 (43. $C_{28}H_{45}$ requires *M*, 381.3519), 355.3291 (16. $C_{26}H_{43}$ requires *M*, 355.3363) and 342.2945 (26. $C_{24}H_{38}O$ requires *M*, 342.2969).

Reaction of Compound **35** *with* DIB–I_2.—A solution of compound **35** (34 mg, 0.079 mmol) in cyclohexane (12 cm^3) containing DIB (114 mg, 0.35 mmol) and iodine (20 mg, 0.079 mmol) was deoxygenated and irradiated as described previously at 40–45 °C for 5 h. Work-up and Chromatotron chromatography (hexane–ethyl acetate; 92:8) gave 4-*methyl*-4-*methylene*-3-*nor*-2,3-*secocholestane* 2,19-*lactone* **37** (17 mg, 50%), m.p. 109–111 °C (MeOH); ν_{max}/cm^{-1} 3060, 1660 and 900 (C=CH_2) and 1735; δ_H 0.73 (3 H, s, 13-Me), 0.87 (6 H, d, *J* 6.73, 25-Me_2), 0.92 (3 H, d, *J* 7.39, 20-Me), 1.97 (3 H, s, 4-Me), 4.23, 4.36 (2 H, AB, J_{AB} 12.37, 19-H_2), 4.74, 5.04 (2 H, s, 4=CH_2) and 5.54 (1 H, m, $W_{1/2}$ 10 Hz, 6-H); δ_C 174.28 (s, C-3), 146.53 (s, C-4), 143.42 (s, C-5), 127.68 (d, C-6), 116.96 (t, 4=CH_2), 69.99 (t, C-19), 56.78 (d), 56.29 (d), 49.17 (d), 42.54 (s), 40.14 (s), 40.08 (t), 39.66 (t), 36.30 (t), 35.89 (d), 32.23 (d), 31.14 (t), 29.86 (t), 28.39 (t), 28.16 (d), 27.81 (t), 27.51 (q), 24.23 (t), 23.98 (t), 22.96 (q), 22.84 (t), 22.69 (q), 18.81 (q) and 12.24 (q); *m/z* 426.3491 (69%, M^+. $C_{29}H_{46}O_2$ requires *M*, 426.3496), 411.3271 (21. $C_{28}H_{43}O_2$ requires *M*, 411.3281), 397.3612 (27. $C_{28}H_{45}O$ requires *M*, 397.3755), 381.3295 (13. $C_{27}H_{41}O$ requires *M*, 381.3434) and 313.2171 (15. $C_{21}H_{29}O_2$ requires *M*, 313.2175).

3α-*Methoxy*-4,4-*dimethyl*-3,19-*epoxycholest*-5-*ene* **36**.—To a solution of compound **34** (4.5 g, 8.8 mmol) in methanol (300 cm^3) was added hydrochloric acid in methanol (1.5 mol dm^{-3}; 180 cm^3) and the mixture stirred at room temperature overnight. Work-up gave a crude product which was purified by column chromatography (hexane–ethyl acetate; 96:4) to give the *title compound* **36** (1.73 g, 45%), m.p. 111–112 °C (MeOH); $[\alpha]_D$ −28° (*c* 0.218); ν_{max}/cm^{-1} 1130, 1085, 1030 and 840 (C=CH); δ_H 0.65 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.8, 25-Me_2), 0.90 (3 H, d, *J* 7.1, 20-Me), 1.07, 1.09 (6 H, s, 4-Me_2), 3.31 (3 H, s, 3-OMe), 3.74 (1 H, dd, *J* 7.9, $J_{W1\alpha-19\beta}$ 2.9, 19β-H), 3.94 (1 H, d, *J* 7.9, 19α-H) and 5.56 (1 H, d, *J* 4.9, 6-H); *m/z* 442.3783 (48%, M^+. $C_{30}H_{50}O_2$ requires *M*, 442.3810), 427 (*M* − CH_3, 19), 412 (4), 399.3561 (59. $C_{28}H_{47}O$ requires *M*, 399.3627), 367 (15), 355 (21) and 329 (18).

3α-*Methoxy*-4,4-*dimethyl*-3,19-*epoxycholestane* **38**.—A solution of the olefin **36** (1.50 g) in ethanol (190 cm^3) was hydrogenated over palladium on carbon 10% (1.94 g) at atmospheric pressure for 14 h. After filtration over Celite the crude product was isolated in the usual manner and purified by column chromatography (benzene–ethyl acetate; 98:2) to give the *title compound* **38** (1.40 g, 93%), m.p. 123–124 °C (MeOH); $[\alpha]_D$ +61 (*c* 0.206); ν_{max}/cm^{-1} 1060, 1040 and 1020; δ_H 0.61 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.2, 25-Me_2), 0.89 (3 H, d, *J* 6.2, 20-Me), 0.93, 0.97 (6 H, s, 4-Me_2), 3.26 (3 H, s, 3-OMe), 3.83 (1 H, dd, *J* 8.8, J_W 1.4, 19-H) and 4.06 (1 H, dd, *J* 10.3, J_W 3.1, 19-H); *m/z* 444.3924 (46%, M^+. $C_{30}H_{52}O_2$ requires *M*, 444.3967), 429 (*M* − CH_3, 4), 401 (3), 388 (12), 383 (15) and 357 (24).

4,4-*Dimethyl*-3,19-*epoxy*-5α-*cholestan*-3-*ol* **39**.—Compound **38** (1.40 g, 3.15 mmol) in acetone (280 cm^3) was treated with PTSA (120 mg, 0.63 mmol) and stirred at reflux temperature for 12 h. Work-up gave, after column chromatography (benzene–ethyl acetate; 90:10), the *title compound* **39** (1.31 g, 97%), m.p. 163.5–164.5 °C (pentane); $[\alpha]_D$ +55° (*c* 0.272); ν_{max}/cm^{-1} 3590 and 3500–3200; δ_H 0.61 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.0, 25-Me_2), 0.96, 1.03 (6 H, s, 4-Me_2), 3.86 (1 H, d, *J* 9.2, 19α-H) and 4.08 (1 H, dd, *J* 9.2, $J_{W1\alpha-19\beta}$ 2.6, 19β-H); δ_C 98.45 (s, C-3), 67.15 (t, C-19), 56.61 (d), 56.45 (d), 51.41 (d), 49.80 (d), 42.56 (s), 40.43 (s), 40.36 (t), 39.62 (t), 36.28 (t), 36.21 (d), 35.87 (d), 35.26 (s), 32.05 (t), 31.64 (t), 29.55 (t), 28.38 (t), 28.12 (q), 28.12 (d), 24.33 (t), 24.22 (t), 23.96 (t), 22.94 (q), 22.68 (q), 22.02 (t), 18.78 (q), 18.13 (q) and 12.13 (q); *m/z* 430.3792 (53%, M^+. $C_{29}H_{50}O_2$ requires *M*, 430.3808), 412 (*M* − H_2O, 6), 399 (*M* − CH_3O, 31), 383 (20), 357 (13) and 317 (17).

Reaction of Compound **39** *with* DIB–I_2.—A solution of compound **39** (50 mg, 0.116 mmol) in cyclohexane (15 cm^3) containing DIB (56.2 mg, 0.174 mmol) and iodine (29.5 mg, 0.116 mmol) was deoxygenated and irradiated as described previously at 40–45 °C for 3 h. Work-up gave a crude product which was purified by Chromatotron chromatography to yield 4-*methyl*-4-*methylene*-3-*nor*-2,3-*secocholestane* 2,19-*lactone* **40** (41.8 mg, 84%), m.p. 106–108 °C (pentane); $[\alpha]_D$ +49 (*c* 0.568); ν_{max}/cm^{-1} 3060, 1625 and 895 (C=CH_2) and 1735; δ_H 0.68 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.35, 25-Me_2), 0.89 (3 H, d, *J* 6.4, 20-Me), 1.80 (3 H, s, 4-Me), 4.29, 4.48 (2 H, AB, J_{AB} 12.3, 19-H_2) and 4.76, 4.95 (2 H, s, 4=CH_2); δ_C 174.38 (s, C-3), 146.77 (s, C-4), 115.97 (t, C=4), 67.28 (t, C-19), 56.75 (d), 56.44 (d), 55.95 (d), 54.47 (d), 42.59 (s), 40.33 (t), 39.68 (t), 39.17 (t), 36.40 (d), 36.30 (t), 35.89 (d), 31.87 (t), 29.82 (t), 28.44 (t), 28.33 (t), 28.15 (d), 27.88 (t), 24.27 (t), 23.99 (s), 23.21 (t), 22.93 (q), 22.69 (q), 22.50 (q), 18.79 (q) and 12.27 (q); *m/z* 428.3610 (34%, M^+. $C_{29}H_{48}O_2$ requires *M*, 428.3652), 413.3424 (13. $C_{28}H_{45}O_2$ requires *M*, 413.3431), 385.2968 (8. $C_{26}H_{41}O_2$ requires *M*, 385.3104), 372.3052 (14. $C_{25}H_{40}O_2$ requires *M*, 372.3077), 359.2946 (36. $C_{24}H_{39}O_2$ requires *M*, 359.2949) and 315.2290 (42. $C_{21}H_{31}O_2$ requires *M*, 315.2322).

3-Oxocholestane-5α-carbonitrile, **41** *and -5β-carbonitrile*, **42**.—Preparation of these compounds followed essentially a previously reported procedure. Compound **41**, m.p. 181–183 °C (MeOH); $[\alpha]_D$ +46 (*c* 0.264) (lit.,[19] m.p. 181–184 °C, $[\alpha]_D$ +47); ν_{max}/cm^{-1} 2225 and 1715; δ_H 0.69 (3 H, s, 13-Me), 0.87 (6 H, d, *J* 6.6, 25-Me_2), 0.91 (3 H, d, *J* 6.6, 20-Me), 1.14 (3 H, s, 10-Me) and 2.46 and 2.52 (2 H, AB, J_{AB} 16.0, 4-H_2); δ_C 12.17 (q), 12.46 (q), 18.78 (q, C-21), 21.61 (t), 22.68 (q, C-26), 22.94 (q, C-27), 23.97 (t, C-23), 24.19 (t, C-15), 28.12 (d, C-25), 28.19 (t, C-16), 28.30 (t), 31.72 (t), 34.26 (t), 34.92 (d), 35.87 (d, C-20), 36.23 (t, C-22), 37.28 (t), 37.97 (s), 39.61 (double t, C-24), 42.67 (s), 47.38 (s), 47.49 (t), 49.47 (d), 55.68 (d), 56.24 (d), 122.32 (s, C-1′) and 206.41 (s, C-3); *m/z* 411.3496 (61%, M^+; Calc. for $C_{28}H_{45}NO$ *M*, 411.3499), 396.3389 (5. Calc. for $C_{27}H_{42}NO$ *M*, 396.3391) and 256.1691 (100. Calc. for $C_{17}H_{22}NO$ *M*, 256.1699). Compound **42**, m.p. 125–127 °C (MeOH); $[\alpha]_D$ +26 (*c* 0.248) (lit.,[19] m.p. 127–128 °C, $[\alpha]_D$ +27.4); ν_{max}/cm^{-1} 2230 and 1715; δ_H 0.69 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.4, 25-Me_2), 0.91 (3 H, d, *J* 6.5, 20-Me), 1.26 (3 H, s, 10-Me), 2.37 and 3.00 (2 H, AB, J_{AB} 15.9, 4-H_2); δ_C 12.00 (q), 18.66 (q, C-21), 19.48 (q), 21.36 (t), 22.53 (q, C-26), 22.76 (q, C-27), 23.79 (t), 24.00 (t), 25.59 (t), 27.95 (d, C-25), 28.14 (t, C-16), 31.26 (t), 33.43 (t), 34.43 (d), 35.67 (d, C-20), 36.10 (t, C-22), 36.54 (t), 37.13 (s), 39.47 (t), 39.78 (t, C-24), 40.22 (d), 42.53 (s), 44.24 (t), 45.82 (s), 56.14 (d), 56.22 (d), 122.72 (s, C-1′) and 206.72 (s, C-3); *m/z* 411.3483 (64%, M^+. Calc. for $C_{28}H_{45}NO$ *M*, 411.3498), 396.3280 (8. Calc. for $C_{27}H_{42}NO$ *M*, 396.3265), 383.3200 (12. Calc. for $C_{27}H_{43}O$ *M*, 383.3267) and 256.1696 (100. Calc. for $C_{17}H_{22}NO$ *M*, 256.1699).

3,3-Ethylenedioxycholestane-5α-carbonitrile **43**.—To a solution of compound **41** (500 mg, 1.2 mmol) in benzene (28 cm^3) was added PTSA (19 mg, 0.1 mmol) and ethylene glycol (0.7 cm^3, 12.5 mmol) and the mixture was refluxed in a Dean–Stark apparatus for 4 h. Work-up and column chromatography (hexane–ethyl acetate; 85:15) gave compound **43**, m.p. 149–149.8 °C (MeOH); $[\alpha]_D$ +29.41 (*c* 0.2) (lit.,[26] m.p. 144–145 °C, $[\alpha]_D$ +30.2); ν_{max}/cm^{-1} 2200; δ_H 0.64 (3 H, s, 13-Me), 0.85 (6 H, d, *J* 6.5, 25-Me_2), 0.89 (3 H, d, *J* 6.52, 20-Me), 0.95 (3 H, s, 10-Me) and 4 (4 H, m, $W_{1/2}$ 40 Hz, 3,3-ethylenedioxy); δ_C 12.20 (q), 12.72 (q), 18.72 (q, C-21), 21.47 (t), 22.64 (q, C-26), 22.89 (q, C-27), 23.93 (t), 24.06 (t), 27.35 (t), 28.07 (d, C-25), 28.28 (t, C-16), 31.13 (t), 32.00 (t), 32.31 (t), 34.78 (d), 35.88 (d, C-20), 36.20 (t, C-22), 37.88 (s), 39.58 (t), 39.68 (t, C-24), 40.01 (t), 42.73 (s), 45.17 (s), 48.78 (d), 55.71 (d), 56.16 (d, C-17), 64.18 (t), 64.76 (t), 107.11 (s, C-3) and 123.31 (s, C-1′); *m/z* 455.3763 (10%, M^+. Calc. for $C_{30}H_{49}NO_2$ *M*, 455.3763), 440.3519 (4. Calc. for $C_{29}H_{46}NO_2$ *M*, 440.3528), 401.3409 (2. Calc. for $C_{27}H_{45}O_2$ *M*, 401.3419), 398.3075 (2. Calc. for $C_{26}H_{40}NO_2$ *M*, 398.3059) and 342.2455 (2. Calc. for $C_{22}H_{32}NO_2$ *M*, 342.2433).

3,3-Ethylenedioxycholestane-5α-carbaldehyde **45**.—To a solution of compound **43** (51 mg, 0.11 mmol) in toluene (1 cm^3) was added slowly at 0 °C, under argon, a solution of diisobutylaluminium hydride (DIBAL) in toluene (1 mol dm^{-3}; 0.22 cm^3). The mixture was stirred at room temperature for 2 h and then poured into brine and extracted with dichloromethane. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was hydrolysed by absorption in a short silica gel 40 (Merck 0.063–0.2 mm) column for 18 h. Elution with ethyl acetate gave compound **45** (41 mg, 80%), m.p. 109.4–111.7 °C (MeOH); $[\alpha]_D$ +2 (*c* 0.30) (lit.,[26] m.p. 115–117 °C, $[\alpha]_D$ +4.6); ν_{max}/cm^{-1} 1693; δ_H 0.65 (3 H, s, 13-Me), 0.85 (6 H, d, *J* 6.9, 25-Me_2), 0.89 (3 H, d, *J* 6.9, 20-Me), 1.05 (3 H, s, 10-Me), 3.85 (4 H, m, $W_{1/2}$ 33 Hz, 3,3-ethylenedioxy) and 9.91 (1 H, s, 1′-H); δ_C 12.15 (q), 15.18 (q), 18.66 (q, C-21), 21.41 (t), 22.49 (q, C-26), 22.72 (q, C-27), 23.84 (t, C-23), 23.97 (t, C-15), 27.33 (t), 27.97 (d, C-25), 28.14 (t, C-16), 29.32 (t), 29.41 (t), 31.10 (t), 34.90 (d), 35.75 (d, C-20), 36.17 (t, C-22), 36.75 (s), 39.51 (t, C-24), 39.91 (t), 40.90 (t), 42.73 (s), 47.30 (d), 52.69 (s), 56.24 (double d, C-17), 63.59 (t), 64.47 (t), 108.24 (s, C-3) and 207.46 (d, C-1′); *m/z* 458.3755 (<1%, M^+. Calc. for $C_{30}H_{50}O_3$ *M*, 458.3760), 430.3820 (57. Calc. for $C_{29}H_{50}O_2$ *M*, 430.3811), 401.3426 (6. Calc. for $C_{27}H_{45}O_2$ *M*, 401.3419), 387.3643 (14. Calc. for $C_{27}H_{47}O$ *M*, 387.3627), 369.3538 (8. Calc. for $C_{27}H_{45}$ *M*, 369.3522) and 316.3102 (7. Calc. for $C_{23}H_{40}$ *M*, 316.3130).

3,3-Ethylenedioxycholestan-5α-ylmethanol **47**.—A solution of compound **45** (17 mg, 0.037 mmol) in dry THF (2 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (10 mg, 0.26 mmol) in dry THF (2 cm^3). The mixture was stirred at room temperature for 30 min, and treated dropwise with saturated aqueous Na_2SO_4. Work-up and Chromatotron chromatography (hexane–ethyl acetate; 85:15) gave *compound* **47** (10.4 mg, 60%), amorphous; ν_{max}/cm^{-1} 3540; δ_H 0.63 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.2, 25-Me_2), 0.89 (3 H, d, *J* 6, 20-Me), 1.02 (3 H, s, 10-Me) and 3.9 (6 H, m, $W_{1/2}$ 35 Hz, 3,3-ethylenedioxy and 1′-H_2); δ_C 12.38 (q), 14.88 (q), 18.79 (q, C-21), 21.62 (t), 22.67 (q, C-26), 22.93 (q, C-27), 23.95 (t, C-23), 24.10 (t, C-15), 28.09 (d and t, C-25), 28.36 (t, C-16), 29.69 (t), 29.82 (t), 30.92 (t), 34.71 (d), 35.89 (d, C-20), 36.29 (t, C-22), 37.55 (s), 38.08 (t), 39.63 (t, C-24), 40.16 (t), 41.25 (s), 42.94 (s), 45.21 (d), 56.32 (d, C-17), 56.89 (d), 61.25 (t, C-1′), 63.72 (t), 64.79 (t) and 109.50 (s, C-3); *m/z* 460.3931 (24%, M^+. $C_{30}H_{52}O_3$ requires *M*, 460.3917), 445.3684 (2. $C_{29}H_{49}O_3$ requires *M*, 445.3681) and 430.3844 (14. $C_{29}H_{50}O_2$ requires *M*, 430.3811).

5α-Hydroxymethylcholestan-3-one 3,5α-Hemiacetal **49**.—A solution of compound **47** (10 mg, 0.02 mmol) in THF (0.8 cm^3) was treated with 10% aqueous hydrochloric acid (0.4 cm^3). After 42 h at room temperature the mixture was poured into brine and extracted and worked up. Chromatotron chromatography of the residue (hexane–ethyl acetate; 75:25) gave *compound* **49** (7.5 mg, 83%), m.p. 195.6–198.4 °C (MeOH); $[\alpha]_D$ +32 (*c* 0.30); ν_{max}/cm^{-1} 3570 and 3400; δ_H 0.65 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.6, 25-Me_2), 0.89 (3 H, d, *J* 8.2, 20-Me), 0.95 (3 H, s, 10-Me), 2.77 (1 H, m, $W_{1/2}$ 15 Hz, 3-OH) and 3.59 and 4.19 (2 H, AB, J_{AB} 8.2, 1′-H_2); δ_C 12.19 (q), 15.25 (q), 18.85 (q, C-21), 21.70 (t), 22.72 (q, C-26), 22.96 (q, C-27), 24.00 (t, C-23), 24.35 (t, C-15), 28.17 (d, C-25), 28.35 (t, C-16), 29.86 (t), 31.69 (t), 33.71 (t), 35.14 (t), 35.75 (d), 35.94 (d, C-20), 36.33 (t, C-22), 37.51 (s), 39.68 (t, C-24), 40.20 (t), 42.75 (s), 44.79 (t), 48.99 (d), 56.36 (d), 56.43 (d, C-17), 74.94 (t, C-1′) and 105.84 (s, C-3); one quaternary carbon atom is not distinguished; *m/z* 416.3655 (31%, M^+. $C_{28}H_{48}O_2$ requires *M*, 416.3654), 401.3441 (2. $C_{27}H_{45}O_2$ requires *M*, 401.3419), 386.3560 (5. $C_{27}H_{46}O$ requires *M*, 386.3549), 359.2937 (20. $C_{24}H_{39}O_2$ requires *M*, 359.2950), 319.3375 (6. $C_{23}H_{43}$ requires *M*, 319.3364) and 111.0463 (100. $C_6H_7O_2$ requires *M*, 111.0446).

Reaction of Compound **49** *with* DIB–I_2.—A solution of compound **49** (22 mg, 0.052 mmol) in cyclohexane (6 cm^3) containing DIB (23 mg, 0.07 mmol) and iodine (17 mg, 0.067), after careful deoxygenation, was irradiated with two 100 W tungsten-filament lamps at 40 °C for 5.5 h. Work-up gave a residue which was purified by Chromatotron chromatography (benzene) to give *2-iodo-3-nor-2,3-secocholestane 4β,1′-lactone* **50** (22 mg, 77%), m.p. 146–149 °C (MeOH); $[\alpha]_D$ +6 (*c* 0.30); ν_{max}/cm^{-1} 1770; δ_H 0.65 (3 H, s, 13-Me), 0.85 (6 H, d, *J* 6.8, 25-Me_2), 0.89 (3 H, d, *J* 7.4, 20-Me), 0.89 (3 H, s, 10-Me), 2.05 and 2.66 (2 H, AX, J_{AX} 18, 4-H_2), 3.2 (2 H, m, $W_{1/2}$ 25 Hz, 2-H_2), 4.14 (1 H, AB, J_{AB} 9.6, 1′-H) and 4.26 (1 H, AB, J_{AB} 9.6, $J_{W1'\text{-}proS\text{-}6\beta}$ 0.9, 1′-H); δ_C 1.99 (t, C-2), 12.10 (q), 14.55 (q),

18.76 (q, C-21), 22.68 (q, C-26), 22.93 (q, C-27), 23.10 (t), 23.96 (t, C-23), 24.23 (t, C-15), 27.55 (t), 28.14 (d, C-25), 28.24 (t, C-16), 33.50 (t), 34.55 (d), 35.87 (d, C-20), 36.24 (t, C-22), 39.27 (t), 39.62 (t, C-24), 40.03 (t), 42.39 (s), 42.96 (s), 43.18 (t), 47.84 (s), 49.44 (d), 56.28 (d), 56.38 (d, C-17), 72.61 (t, C-1′) and 176.5 (s, C-3); *m/z* 542.2622 (1%, M^+. $C_{28}H_{47}IO_2$ requires *M*, 542.2623), 527.2375 (1. $C_{27}H_{44}IO_2$ requires *M*, 527.2388), 415.3557 (100. $C_{28}H_{47}O_2$ requires *M*, 415.3576), 387.3268 (34. $C_{26}H_{43}O_2$ requires *M*, 387.3263), 373.3441 (7. $C_{26}H_{45}O$ requires *M*, 373.3470), 261.1897 (12. $C_{17}H_{25}O_2$ requires *M*, 261.1854) and 233.1551 (10. $C_{15}H_{21}O_2$ requires *M*, 233.1541).

3,3-*Ethylenedioxycholestane*-5β-*carbonitrile* **44**.—To a solution of compound **42** (580 mg, 1.4 mmol) in benzene (32 cm^3) was added PTSA (22 mg, 0.1 mmol) and ethylene glycol (0.8 cm^3, 14.4 mmol) and the mixture was refluxed in a Dean–Stark apparatus for 3 h. Work-up and silica gel column chromatography of the residue (hexane–ethyl acetate; 85:15) gave compound **44** (545 mg, 85%), m.p. 151.5–152 °C (benzene–pentane); $[\alpha]_D$ +14.3 (*c* 0.272) (lit.,[26] m.p. 156–156.5 °C, $[\alpha]_D$ +14.8); ν_{max}/cm^{-1} 2210; δ_H 0.64 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.3, 25-Me_2), 0.88 (3 H, d, *J* 5.9, 20-Me), 1.18 (3 H, s, 10-Me) and 4.0 (4 H, m, $W_{1/2}$ 45 Hz, 3,3-ethylenedioxy); δ_C 11.99 (q), 18.71 (q, C-21), 19.69 (q), 21.06 (t), 22.63 (q, C-26), 22.88 (q, C-27), 23.91 (t), 24.16 (t), 26.09 (t), 28.06 (d, C-25), 28.27 (t, C-16), 29.84 (t), 31.89 (t), 32.63 (t), 34.45 (d), 35.80 (d, C-20), 36.19 (t, C-22), 36.82 (s), 36.88 (t), 39.56 (t), 39.73 (d), 39.89 (t, C-24), 42.49 (s), 42.80 (s), 56.25 (d), 56.29 (d), 64.33 (t), 64.69 (t), 107.9 (s, C-3) and 124.28 (s, C-1′); *m/z* 455.3789 (5%, M^+. Calc. for $C_{30}H_{49}NO_2$ *M*, 455.3789), 440.3544 (1. Calc. for $C_{29}H_{46}NO_2$ *M*, 440.3529) and 398.3075 (2. Calc. for $C_{26}H_{40}NO_2$ *M*, 398.3059).

3,3-*Ethylenedioxycholestane*-5β-*carbaldehyde* **46**.—To a solution of compound **44** (250 mg, 0.55 mmol) in toluene (14 cm^3) was added slowly at 0 °C, under argon, a solution of DIBAL in toluene (1 mol dm^{-3}; 1.14 cm^3). The mixture was stirred at room temperature for 2.5 h. Work-up as described previously for the 5α-isomer gave, after silica gel hydrolysis and column chromatography, compound **46** (167 mg, 66%), m.p. 121.2–124.2 °C (MeOH); $[\alpha]_D$ +21.76 (*c* 0.17) (lit.,[26] m.p. 125–130 C); ν_{max}/cm^{-1} 1705; δ_H 0.63 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.7, 25-Me_2), 0.89 (3 H, d, *J* 7, 20-Me), 0.99 (3 H, s, 10-Me), 3.9 (4 H, m, $W_{1/2}$ 23 Hz, 3,3-ethylenedioxy) and 9.99 (1 H, s, 1′-CHO); δ_C 12.12 (q), 17.68 (q), 18.87 (q, C-21), 20.38 (t), 22.71 (q, C-26), 22.95 (q, C-27), 24.07 (t, C-23), 24.34 (t, C-15), 26.67 (t), 27.73 (t), 28.17 (d, C-25), 28.43 (t, C-16), 29.86 (s), 30.18 (t), 30.49 (t), 35.02 (d), 35.96 (d, C-20), 36.38 (t, C-22), 37.90 (t), 39.73 (t, C-24), 40.14 (t), 41.55 (d), 42.66 (s), 51.72 (s), 56.54 (d, C-17), 56.79 (d), 64.16 (t), 64.71 (t), 109.31 (s, C-3) and 208.41 (d, C-1′); *m/z* 458.3760 (1%, M^+. Calc. for $C_{30}H_{50}O_3$ *M*, 458.3751), 430.3816 (74. Calc. for $C_{29}H_{50}O_2$ *M*, 430.3811), 401.3405 (10. Calc. for $C_{27}H_{45}O_2$ *M*, 401.3420), 387.3632 (14. Calc. for $C_{27}H_{47}O$ *M*, 387.3627) and 369.3509 (10. Calc. for $C_{27}H_{45}$ *M*, 369.3521).

3,3-*Ethylenedioxycholestan*-5β-*ylmethanol* **48**.—A solution of the aldehyde **46** (178 mg, 0.39 mmol) in dry THF (20 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (105 mg, 2.7 mmol) in dry THF (20 cm^3). The mixture was stirred at room temperature for 20 min. Work-up as described previously and Chromatotron chromatography of the residue (hexane–ethyl acetate; 80:20) gave the *alcohol* **48** (74 mg, 41%), m.p. 117.2–118.9 C (MeOH); $[\alpha]_D$ +32.8 (*c* 0.174); ν_{max}/cm^{-1} 3540 and 3450; δ_H 0.63 (3 H, s, 13-Me), 0.84 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 7.4, 25-Me_2), 0.89 (3 H, d, *J* 6.2, 20-Me), 2.69 (1 H, dd, *J* 7.5, 7.5, 1′-OH), 3.2 (1 H, dd, *J* 7.5, 11.3, 1′-H) and 3.97 (5 H, m, $W_{1/2}$ 26 Hz, 1′-H and 3,3-ethylenedioxy), [after D_2O 3.2 and 3.9 (2 H, AX, J_{AX} 11.4, 1′-H_2)]; δ_C 12.05 (q), 16.29 (q), 18.83 (q, C-21), 20.72 (t), 22.71 (q, C-26), 22.96 (q, C-27), 24.04 (t, C-23), 24.42 (t, C-15), 27.12 (t), 28.16 (d, C-25), 28.46 (t, C-16), 29.62 (t), 29.77 (t), 31.97 (t), 35.42 (d), 35.76 (t), 35.97 (d, C-20), 36.33 (t, C-22), 37.16 (s), 39.68 (t, C-24), 40.26 (t), 41.72 (d), 42.49 (s), 56.47 (d, C-17), 56.94 (d), 63.99 (t), 64.80 (t), 70.42 (t, C-1′) and 110.54 (s, C-3), one quaternary carbon atom is not distinguished; *m/z* 460.3901 (25%, M^+; $C_{30}H_{52}O_3$ requires *M*, 460.3916), 445.3690 (1. $C_{29}H_{49}O_3$ requires *M*, 445.3681), 429.3722 (79. $C_{29}H_{49}O_2$ requires *M*, 429.3732), 401.3448 (3. $C_{27}H_{45}O_2$ requires *M*, 401.3419), 387.3611 (6. $C_{27}H_{47}O$ requires *M*, 387.3627) and 367.3391 (12. $C_{27}H_{43}$ requires *M*, 367.3365).

5β-*Hydroxymethylcholestan*-3-*one* 3,5β-*Hemiacetal* **51**.—A solution of compound **48** (70 mg, 0.15 mmol) in acetone (34 cm^3) was treated with PTSA (79 mg, 0.4 mmol) and stirred at room temperature for 1 h. Work-up and Chromatotron chromatography (hexane–ethyl acetate; 70:30) gave *compound* **51** (55 mg, 87%), m.p. 120.5–121.8 °C (MeOH); $[\alpha]_D$ +39.3 (*c* 0.244); ν_{max}/cm^{-1} 3580, 3365 and 1700; δ_H 0.66 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.6, 25-Me_2), 0.89 (3 H, d, *J* 8.9, 20-Me) 0.88 and 0.96 (3 H, s, 10-Me), the remainder of the signals are complex due to the ring-chain tautomerism; δ_C complex spectrum due to the ring-chain tautomerism, only the following signals are distinguished: 18.88 (q, C-21), 22.71 (q, C-26), 22.93 (q, C-27), 24.05 (t, C-23), 24.38 (t, C-15), 28.19 (d, C-25), 28.46 (t, C-16), 35.97 (d, C-20), 36.39 (t, C-22), 39.74 (t, C-24) and 56.56 (d, C-17); *m/z* 416.3657 (21%, M^+. $C_{28}H_{48}O_2$ requires *M*, 416.3654), 401.3405 (3. $C_{27}H_{45}O_2$ requires *M*, 401.3420), 386.3519 (100. $C_{27}H_{46}O$ requires *M*, 386.3548), 367.3365 (14. $C_{27}H_{43}$ requires *M*, 367.3364), 359.2961 (19. $C_{24}H_{39}O_2$ requires *M*, 359.2950) and 316.3080 (14. $C_{23}H_{40}$ requires *M*, 316.3130).

Reaction of Compound **51** *with* DIB–I_2.—A solution of the compound **51** (33 mg, 0.079 mmol) in cyclohexane (8 cm^3) containing DIB (28 mg, 0.087 mmol) and iodine (20 mg, 0.079 mmol), was irradiated, after careful deoxygenation, with two 100 W tungsten-filament lamps at 40 °C for 3 h. Work-up gave a residue, which was purified by Chromatotron chromatography (hexane–ethyl acetate; 90:10) to give 2-*iodo*-3-*nor*-2,3-*secocholestane* 4α,1′-*lactone* **52** (31 mg, 72%), amorphous; ν_{max}/cm^{-1} 1770; δ_H 0.65 (3 H, s, 13-Me), 0.85 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 5.4, 25-Me_2), 0.90 (3 H, d, *J* 7.3, 20-Me), 2.36 (1 H, AB, J_{AB} 18, 4-H), 2.54 (1 H, AB, J_{AB} 18, $J_{W-4proS-6\beta}$ 1.4, 4-H), 3.2 (2 H, m, $W_{1/2}$ 25 Hz, 2-H_2) and 3.8 and 4.29 (2 H, AX, J_{AX} 9.5, 1′-H_2); δ_C 2.12 (t, C-2), 12.11 (q), 12.83 (q), 18.78 (q, C-21), 22.68 (q, C-26), 22.91 (q, C-27), 22.97 (t), 23.97 C-23), 24.28 (t, C-15), 27.37 (t), 28.14 (d, C-25), 28.24 (t, C-16), 33.44 (t), 34.93 (d), 34.99 (t), 35.88 (d, C-20), 36.28 (t, C-22), 39.66 (t, C-24), 40.05 (t), 42.44 (s), 42.58 (s), 43.47 (t), 47.77 (s), 50.84 (d), 56.18 (d), 56.43 (d, C-17), 76.73 (t, C-1′) and 176.35 (s, C-3); *m/z* 542.2620 (< 1%, M^+. $C_{28}H_{47}IO_2$ requires *M*, 542.2623), 415.3560 (100. $C_{28}H_{47}O_2$ requires *M*, 415.3576), 397.3444 (13. $C_{28}H_{45}O$ requires *M*, 397.3471), 387.3282 (64. $C_{26}H_{43}O_2$ requires *M*, 387.3262), 303.2333 (12. $C_{20}H_{31}O_2$ requires *M*, 303.2324), 289.2153 (20. $C_{19}H_{29}O_2$ requires *M*, 289.2167), 275.2012 (24. $C_{18}H_{27}O_2$ requires *M*, 275.2011), 261.1840 (47. $C_{17}H_{25}O_2$ requires *M*, 261.1855), 233.1556 (53. $C_{15}H_{21}O_2$ requires *M*, 233.1541) and 207.1379 (32. $C_{13}H_{19}O_2$ requires *M*, 207.1385).

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