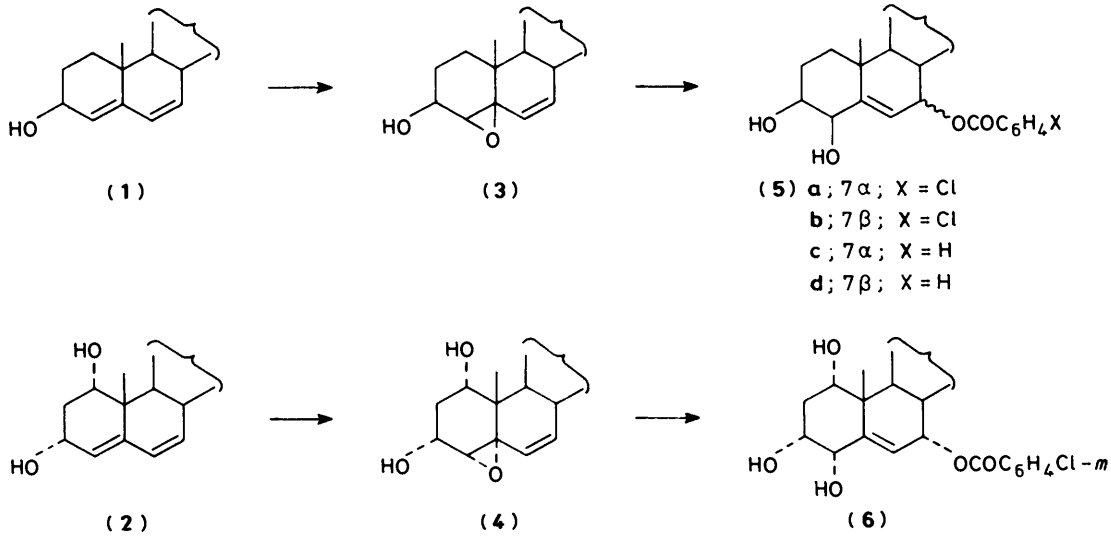
Steroidal Allylic Epoxides

Erwin Glotter* and Michael Zviely
Faculty of Agriculture, The Hebrew University of Jerusalem, Rehovot 76–100, Israel

Two allylic epoxides, 4β,5β-epoxycholest-6-en-3β-ol and 4α,5α-epoxycholest-6-ene-1α,3α-diol, were obtained by reaction of the corresponding conjugated dienols with t-butyl hydroperoxide in the presence of bisacetylacetonato-oxovanadium as catalyst. The reductive opening of these epoxides and other related reactions are discussed.

We have recently reported[1] the results of an investigation on the behaviour of steroidal conjugated dienols (**1**) and (**2**) in the presence of *m*-chloroperbenzoic acid. Although there was evidence on the transient formation of the allylic epoxides (**3**) and (**4**), these could not be isolated because the initially formed epoxide ring was spontaneously opened by the weakly nucleophilic *m*-chlorobenzoate anion present in the medium, to give compounds (**5a**) and (**5b**) from (**1**) and compound (**6**) from (**2**). We expected therefore to change the outcome of the reaction by using an epoxidizing agent which would not lead to the formation of any nucleophilic by-product. t-Butyl hydroperoxide in the presence of a vanadium catalyst (Sharpless reagent[2]) in dry benzene as solvent, seemed to be a suitable reagent for such a purpose and, indeed, it made possible not only the formation, but also the isolation of the highly reactive allylic epoxides (**3**) and (**4**).



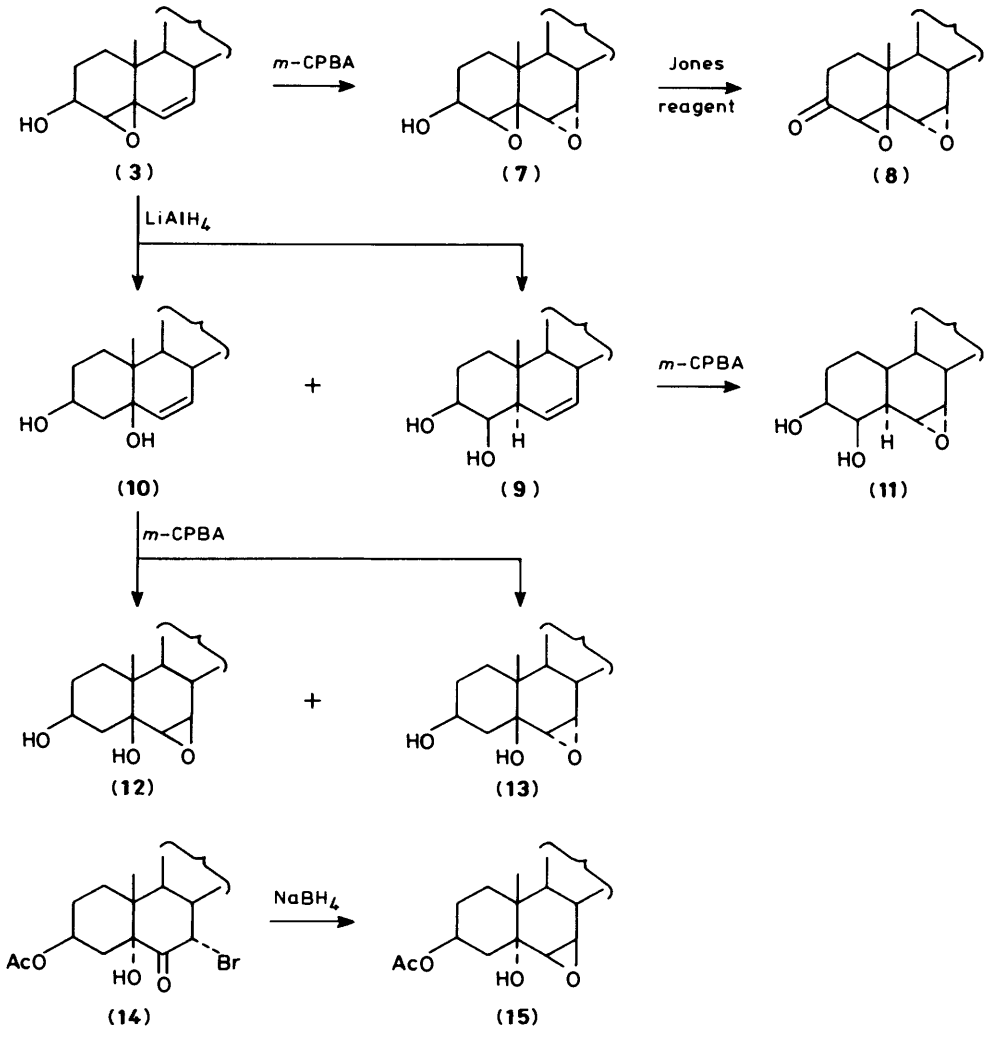
Allylic epoxides are stabilized when the double bond is conjugated to an electron withdrawing group, a ketonic carbonyl for instance. Steroidal 4α,5α- and 4β,5β-epoxy-2-en-1-ones[3] and an A-nor-5β,6β-epoxy-2-en-1-one[4] are such compounds. The last two are obtained in excellent yield by epoxidation of the corresponding dienones with perbenzoic acid; the first compound is indirectly obtained from a 3β-acetoxy-1α-hydroxy-4α,5α-epoxy derivative by CrO_3 oxidation and subsequent β-elimination.

4β,5β-Epoxycholest-6-ene-3β-ol (**3**) was characterized by its n.m.r. spectrum. The vinylic 6-H and 7-H give rise to two double doublets at δ 5.91 (*J* 9.4 and 0.8 Hz) and 4.92 (*J* 9.4 and 2.4 Hz), respectively; the epoxidic 4α-H appeared as a narrow doublet, δ 3.22 (*J* 0.8 Hz). The structure of (**3**) was demonstrated by epoxidation of the double bond with *m*-chloroperbenzoic acid to yield the diepoxy alcohol (**7**) which upon oxidation with CrO_3 gave 4β,5β;6α,7α-diepoxycholestan-3-one (**8**). The n.m.r. signals of the relevant protons in (**8**) were identical to those reported for a similarly substituted 17β-acetoxyandrostane.[5]

The isolation of the allylic epoxide (**3**) offered the possibility of confirming its involvement in the formation of the mixture of stereoisomeric *m*-chlorobenzoates (**5a**) and (**5b**).[1] Treatment of compound (**3**) with benzoic acid in benzene, in the presence of a trace of *m*-chloroperbenzoic acid,[6] gave a mixture of the 7α- and 7β-allylic benzoates (**5c**) and (**5d**); their n.m.r. spectra were similar (with the exception of the signals due to the aromatic protons) to those of the 7α- and 7β-*m*-chlorobenzoates (**5a**) and (**5b**), respectively.

Lithium aluminium hydride reduction of 4β,5β-epoxycholestan-3β-ol proceeded stereoselectively with cleavage of the C(4)–O bond to give cholestane-3β,5β-diol.[7] The presence of the allylic double bond in (**3**) was expected to change the course of opening of the epoxide ring by favouring cleavage of the C(5)–O bond. Indeed, this opening was bidirectional, leading to a roughly 1:1 mixture of 5α-cholest-6-ene-3β,4β-diol (**9**) and cholest-6-ene-3β,5β-diol (**10**). The latter was previously obtained[8] along with cholest-4-ene-3β,6β-diol by treatment of 5β,6β-epoxycholestan-3β-ol with lithium diethylamide. It is worth mentioning that although the 6,7-double bond had an obvious influence on the course of this reaction by allowing the cleavage of the C(5)–O bond, thus leading to compound (**9**), it did not participate in the reaction, as in the opening of the epoxide by the weakly nucleophilic benzoate anion (**3**) ⟶ (**5**).

The *trans* junction of rings A and B in compound (**9**) was



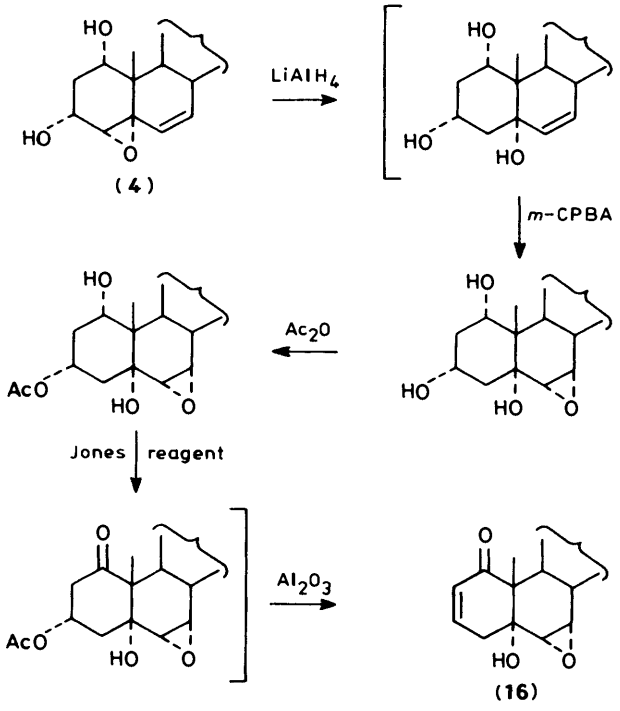
Scheme 1.

obvious from the n.m.r. pattern of the 3α-H signal (broad multiplet, δ 3.59, $W_{\frac{1}{2}}$ *ca.* 20 Hz). The alternative *cis* junction with an equatorial orientation of 3α-H would have required a significantly narrower signal of this proton, even less than that found in compound (**10**) (δ 4.05, multiplet, $W_{\frac{1}{2}}$ *ca.* 12 Hz). The structure assigned to compound (**9**) was further confirmed by epoxidation of the double bond with *m*-chloroperbenzoic acid, which led to the formation of the 6α,7α-epoxide (**11**). The signal of the 3α-H remained as a broad multiplet $W_{\frac{1}{2}}$ *ca* 20 Hz at δ 3.59, whereas the epoxidic protons appeared as a double doublet (*J* 4 and 1 Hz) at δ 3.23 for 6β-H and a double doublet (*J* 4 and 2.5 Hz) at δ 3.12 for 7β-H. The allylic alcohol (**10**) was unaffected by Sharpless reagent, behaviour easily rationalized by considering the wide dihedral angle between 5β-OH and Δ^6. Similar results were obtained on attempted use of this reagent for the epoxidation of 3β-acetoxy-5β-hydroxycholest-7-en-6-one.[9] The epoxidation of (**10**) proceeded in good yield, although slowly, with *m*-chloroperbenzoic acid to give a *ca.* 1:2 mixture of the 6β,7β-epoxide (**12**) and the 6α,7α-epoxide (**13**). The former was characterized by two doublets at δ 2.86 and 3.11 (*J* 4.2 Hz). In view of the relative position of 7α-H with respect to 8β-H, the lack of measurable coupling between these protons seems reasonable. In the stereoisomeric 6α,7α-epoxide (**13**), the signal of 6β-H appeared as a doublet, δ 2.95 (*J* 5.7 Hz) and that of 7β-H as a double doublet at δ 3.09 (*J* 5.7 and 2.4 Hz). The size of the coupling between 7β-H and 8β-H is comparable to that found in compound (**11**). The assignments are further supported by the chemical shifts of the 19-Me, at lower field in (**12**) (δ 1.01) and at higher field in (**13**) (δ 0.89).

The stereoisomeric *trans*-epoxy alcohol (**15**) (3β-acetoxy-6β,7β-epoxycholestan-5α-ol) was prepared by $NaBH_4$ reduction of the bromo ketone (**14**).[10] The intermediate *trans*-diaxial bromohydrin (7α-bromo-6β-hydroxy) was converted spontaneously into the epoxide (**15**).

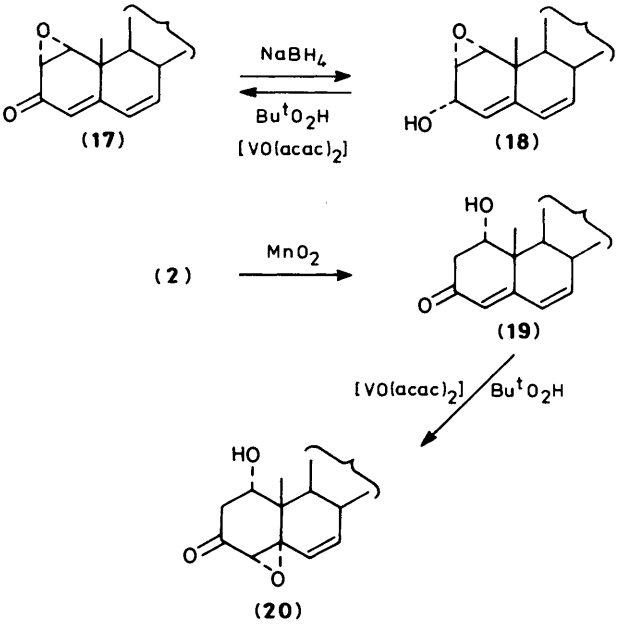
Treatment of the dienediol (**2**) with the Sharpless reagent afforded in good yield the expected allylic epoxide (**4**) which was even less stable than compound (**3**) and could be identified by n.m.r. as the major component of the crude product. The two vinylic protons gave rise to a doublet, δ 6.00 (*J* 10 Hz) for 6-H and a double doublet, δ 5.11 (*J* 10 and 2.5 Hz) for 7-H; the epoxidic 4β-H appeared at δ 3.47 as a doublet *J* 2.5 Hz. The compound decomposed into an intractable mixture during attempted crystallization or purification by chromatography on silica, neutral alumina or Florisil (a slightly basic magnesium silicate adsorbent). The crude product was therefore submitted to a series of reactions, as outlined in Scheme 2, without any purification of the products resulting in the intermediate steps. Side products which were undoubtedly obtained in this sequence are not shown in this scheme.

The substitution pattern of rings A and B as in (**16**) is found in



Scheme 2.

many naturally occurring ergostane-type steroids isolated from Nicandra spp., Datura spp. and also from certain varieties of Withania spp.; all of the *Solanaceae* family.[11] Several attempts to find alternative methods for the preparation of cholest-6-ene-1,3,5-triol failed. The ketone function in the known 1α,2α-epoxycholesta-4,6-dien-3-one (**17**) was reduced with $NaBH_4$ to the corresponding 3α-alcohol (**18**).[3] Attempted epoxidation of the latter with *m*-chloroperbenzoic acid led to intractable mixtures, whereas treatment with the Sharpless reagent resulted in re-oxidation to the original epoxy ketone (**17**), instead of epoxidation. Such oxidations are encountered with hindered allylic alcohols.[2,12] However, in contrast to the present case, the results reported heretofore refer to equatorially oriented allylic alcohols (Sharpless and Verhoeven mention in their review[2] a private communication from Y. Kishi on the oxidation of a strongly hindered axial allylic alcohol).



Oxidation of the dienediol (**2**) with MnO_2 afforded 1α-hydroxycholesta-4,6-dien-3-one (**19**).[13] In addition to the characteristic pattern of the vinylic protons of the 4,6-dien-3-one system (singlet at δ 5.74 for 4-H and an apparently two proton singlet at δ 6.14 for the practically equivalent 6-H and 7-H), the compound had a narrow multiplet at δ 4.18 for 1β-H. This hydroxy dienone was stereoselectively epoxidized with the Sharpless reagent to the 4α,5α-epoxy derivative (**20**), characterized by a singlet at δ 3.45 for the epoxidic 4β-H and by the upfield shift of the signal of 1β-H to δ 3.78.

The use of the Sharpless reagent for the epoxidation of α,β-unsaturated ketones possessing a hydroxy group two or three bonds away from the conjugated system will be reported in a forthcoming publication.[9] Compound (**20**) was not, however, more stable than the allylic epoxide (**4**). Although obtained in a yield of at least 70% (according to the n.m.r. spectrum of the crude product) it could not be purified and lithium aluminium hydride reduction afforded a product whose n.m.r. spectrum was much the same as that of the product obtained from compound (**4**).

Experimental

M.p.s were taken with a Fisher-Johns apparatus. Optical rotations were recorded with an automatic Perkin-Elmer 141 polarimeter. ^1H N.m.r. spectra were determined at 80 MHz on a Varian FT-80A and 200 or 300 MHz on Bruker WH instruments for *ca.* 5% solutions in deuteriochloroform containing $SiMe_4$. Flash chromatography was done on silica gel 60, 230—400 mesh (Merck); t.l.c. was carried out on plates of silica gel 60 F_{254} (Merck); preparative chromatoplates (1 mm thick) were prepared with silica gel PF_{254} (Merck). Light petroleum refers to the fraction of b.p. 60—80 °C; ether refers to diethyl ether. Mass spectra were taken with a Finnigan 4000 instrument. Analyses were performed in the microanalytical laboratory of the Hebrew University under the direction of Mrs. S. Blum.

4β,5β-*Epoxycholest*-6-*en*-6β-*ol* (**3**).—The reaction was performed in a dry three-necked flask, in nitrogen atmosphere, according to the usual procedure for reactions with t-butyl hydroperoxide in the presence of bisacetylacetonato-oxovanadium as catalyst.[2,12] A freshly prepare solution of the catalyst (0.75 mg) in dry benzene (0.5 ml) was introduced in the flask with a syringe through a rubber septum; this was followed by a solution of cholesta-4,6-dien-3β-ol[1,14] (200 mg) in dry benzene (10 ml) and a 3M-solution of t-butyl hydroperoxide in the same solvent (0.25 ml). After 24 h at 40 °C the solution was cooled and filtered through a short column of Florisil (*ca.* 5 g). The product was eluted first with light petroleum and then with ether. After removal of the solvent, the product (190 mg) was crystallized from acetone, m.p. 114—116 °C; $[\alpha]_D$ + 60° (*c* 0.1, $CHCl_3$) (Found: C, 77.35; H, 10.9. $C_{27}H_{44}O_2 \cdot H_2O$ requires C, 77.45; H, 11.1%).

4α,5α-*Epoxycholest*-6-*ene*-1α,3α-*diol* (**4**).—The epoxidation of cholesta-4,6-diene-1α,3α-diol (**2**)[15] (200 mg) was carried out as described above. Attempted isolation by filtration through Florisil [elution with dichloromethane–ethyl acetate (7:3)] resulted in only 31 mg of almost pure epoxide (**4**) which was characterized by its n.m.r. spectrum. For preparative purposes the crude product was used as obtained after evaporation of the solvent at room temperature, under reduced pressure.

Table. N.m.r. data*

Compd.	3-H	4-H	6-H	7-H	18-H	19-H	Other signals
(3)	3.94 m ($W_{\frac{1}{2}}$ 9)	3.22 d (0.8)	5.91 dd (9.4, 0.8)	4.92 dd (9.4, 2.4)	0.72 s	0.99 s	
(4)	4.18 m ($W_{\frac{1}{2}}$ 12)	3.47 d (2.5)	6.00 d (10.0)	5.11 dd (10.0, 2.5)	0.75 s	0.96 s	3.80 m ($W_{\frac{1}{2}}$ 6), 1-H
(5c)	3.53 m ($W_{\frac{1}{2}}$ 21)	4.13 d (3.5)	5.92 d (4.7)	5.24 t (4.7)	0.69 s	1.25 s	7.32—8.05 m, ArH
(5d)	3.54 m ($W_{\frac{1}{2}}$ 21)	4.12 d (3.1)	5.63 d (2.3)	5.26 dd (8.6, 2.3)	0.73 s	1.30 s	7.34—8.08 m, ArH
(7)	3.99 m ($W_{\frac{1}{2}}$ 16)	3.40 m ($W_{\frac{1}{2}}$ 4)	2.64 d (3.9)	3.20 d (3.5)	0.72 s	0.94 s	
(8)		3.30 s	2.65 d (3.8)	3.23 dd (4.0)	0.73 s	1.10 s	
(9)	3.59 m ($W_{\frac{1}{2}}$ 20)	3.94 d (1.6)	5.64 d (10.0)	5.53 d (10.0)	0.69 s	0.99 s	
(10)	4.05 m ($W_{\frac{1}{2}}$ 12)		5.47 dd (10.2, 1.2)	5.40 dd (10.2, 2.3)	0.69 s	0.94 s	
(11)	3.59 m ($W_{\frac{1}{2}}$ 20)	4.12 m ($W_{\frac{1}{2}}$ 7)	3.23 dd (4.0, 1.0)	3.12 dd (4.0, 2.5)	0.70 s	0.95 s	
(12)	4.08 m ($W_{\frac{1}{2}}$ 7)		2.86 d (4.2)	3.11 d (4.2)	0.68 s	1.01 s	
(13)	4.20 m ($W_{\frac{1}{2}}$ 12)		2.95 d (5.7)	3.09 dd (5.7, 2.4)	0.68 s	0.89 s	
(15)	5.19 m ($W_{\frac{1}{2}}$ 20)		2.80 d (3.8)	3.00 d (3.8)	0.69 s	1.08 s	2.02 s, COMe
(16)	6.57 ddd (10.0, 5.0, 2.4)		3.03 d (3.6)	3.31 dd (3.6, 1.9)	0.73 s	1.18 s	5.85 dd (10.0, 2.4), 2-H
(19)		5.74 s	6.14 s		0.69 s	1.06 s	4.18 m ($W_{\frac{1}{2}}$ 10), 1-H 2.70 dd (5.0, 2.5), 2-H
(20)		3.45 s	6.12 d (14.0)	5.03 dd (14.0, 2.8)	0.73 s	0.90 s	3.78 m ($W_{\frac{1}{2}}$ 9), 1-H

* Recorded in $CDCl_3$ at 200 or 300 MHz. The spectra of compounds (**4**), (**5c**), (**5d**), (**12**), (**15**), (**19**) and (**20**) were taken at 80 MHz. Signals recorded as δ values; coupling constants or signal widths ($W_{\frac{1}{2}}$, Hz) are in parentheses.

7α- and 7β-Benzoyloxycholest-5-ene-3β,4β-diol (**5c, d**).—To a solution of compound (**3**) (46 mg) in dry benzene (10 ml), benzoic acid (16 mg) and commercial 85% *m*-chloroperbenzoic acid (1.6 mg) were added; the reaction was kept overnight at room temperature. It was then washed consecutively with 5% aqueous ammonia, and water and then dried (Na_2SO_4). The crude product was separated on a preparative chromatoplate [ethyl acetate–toluene (1:2)]. Extraction of the lower band gave the 7α-benzoyloxy derivative (**5c**) (12 mg) and the upper gave the 7β-stereoisomer (**5d**) (14 mg). Characterization was done by n.m.r. and comparison with the spectra of compounds (**5a**) and (**5b**).[1]

4β,5β;6α,7α-Diepoxycholestan-3β-ol (**7**).—To a solution of compound (**3**) (85 mg) in dry benzene (5 ml), 85% *m*-chloroperbenzoic acid (44 mg) was added, and the solution was kept overnight at room temperature. After being washed with 5% aqueous ammonia and with water, the solution was dried (Na_2SO_4), the solvent was removed under reduced pressure, and the crude product (62 mg) was purified by flash chromatography [elution with light petroleum–ethyl acetate (5:2)]. The pure diepoxide (**7**) (39 mg) had m.p. 163—164 °C (from methanol) (Found: C, 76.2; H, 10.35. $C_{27}H_{44}O_3 \cdot 0.5H_2O$ requires C, 76.7; H, 10.6%).

4β,5β;6α,7α-Diepoxycholestan-3-one (**8**).—Compound (**7**) (30 mg) in acetone solution was oxidized with Jones reagent at 10 °C. Excess of the reagent was destroyed with methanol, water was added, and the product was extracted with dichloromethane. The crude product (28 mg) was purified on a chromatoplate. It was characterized by comparison of its n.m.r. spectrum with that of 17β-acetoxy-4β,5β;6α,7α-diepoxyandrostan-3-one.[5]

Reduction of Compound (**3**) *with Lithium Aluminium Hydride.*—A solution of (**3**) (100 mg) in dry tetrahydrofuran (10 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (70 mg) in the same solvent (10 ml). The product (90 mg) obtained after reflux during 3 h, and destruction of the excess of reagent, was a *ca.* 6:4 mixture of 5α-cholest-6-ene-3β,4β-diol (**9**) and cholest-6-ene-3β,5β-diol (**10**) (n.m.r. evidence). The mixture was separated by flash chromatography. Compound (**9**) (40 mg) had m.p. 145—146 °C (from hexane) $[\alpha]_D$ − 25° (*c* 0.1, $CHCl_3$) (Found: C, 80.3; H, 11.4. $C_{27}H_{44}O_2$ requires C, 80.6; H, 11.4%). Compound (**10**) (20 mg) had m.p. 135—137 °C (hexane–ethyl acetate) (lit.,[8] 137–140 °C) (Found: C, 80.4; H, 11.3. $C_{27}H_{44}O_2$ requires C, 80.6; H, 11.4%).

6α,7α-Epoxy-5α-cholestane-3β,5β-diol (**11**).—The epoxidation of compound (**9**) (38 mg) was effected with *m*-chloroperbenzoic acid as described for compound (**3**). The crude product (32 mg) was purified on a chromatoplate [ethyl acetate–toluene (1:2)], m.p. 219—221 °C (from methanol) $[\alpha]_D$ − 29° (*c* 0.05, $CHCl_3$) (Found: C, 77.3; H, 11.2. $C_{27}H_{46}O_3$ requires C, 77.5; H, 11.1%); *m/z* (c.i.) 419 (MH^+, 4.8%), 401 ($MH^+ - H_2O$, 79.7), and 383 ($MH^+ - 2H_2O$, (100).

Epoxidation of Cholest-6-ene-3β,5β-diol (**10**).—The epoxidation of compound (**10**) (62 mg) with *m*-chloroperbenzoic acid in benzene solution required 96 h at room temperature. The solution was washed with 5% aqueous ammonia and with water and the crude product (52 mg) was separated on a preparative chromatoplate [ethyl acetate–hexane (2:3)]. Extraction of the lower band gave 6β,7β-epoxycholestane-3β,5β-diol (**12**) (11 mg), m.p. 182—185 °C (from methanol) $[\alpha]_D$ + 18° (*c* 0.05, $CHCl_3$) (Found: C, 77.3; H, 11.2. $C_{27}H_{46}O_3$ requires C, 77.5; H, 11.1%); *m/z* (c.i.) 419 (MH^+, 0.16%); 401 ($MH^+ + H_2O$, 38%), and 383

($MH^+ - 2H_2O$, 100%). The upper band gave 6α,7α-epoxycholestane-3β,5β-diol (**13**) (19 mg), m.p. 162—165 °C (from methanol); $[\alpha]_D$ − 20° (*c* 0.1, $CHCl_3$) (Found: C, 77.4; H, 11.0. $C_{27}H_{46}O_3$ requires C, 77.5; H, 11.1%); *m/z* (c.i.) 419 (MH^+, 0.7%); 401 ($MH^+ - H_2O$, 29.3), and 383 ($MH^+ - 2H_2O$, 100).

Sodium Borohydride Reduction of 3β-*Acetoxy*-7α-*bromo*-5α-*hydroxycholestan*-6-*one* (**14**).—Compound (**14**) (200 mg) in methanol (50 ml) was reduced with $NaBH_4$ (160 mg) for 2 h at room temperature. After neutralization (dilute HCl) the volume was reduced to *ca.* 10 ml, water was added and the precipitate was filtered off and washed with water. The crude product (one spot on a chromatoplate) was characterized as 3β-acetoxy-6β,7β-epoxycholestan-5α-ol (**15**) (n.m.r. evidence), m.p. 139—142 °C (from methanol), $[\alpha]_D$ − 17° (*c* 0.1, ethanol) (Found: C, 75.4; H 10.6. $C_{29}H_{48}O_4$ requires C, 75.6; H, 10.5%); *m/z* (c.i.) 461 (MH^+), 419 ($MH^+ - COCH_2$, 37.6%); 401 (MH^+ − AcOH, 79), 383 (MH^+ − AcOH − H_2O, 100).

Preparation of 5α-*Hydroxy*-6α,7α-*epoxycholest*-2-*en*-1-*one* (**16**) (Scheme 2).—The benzene solution of crude 4α,5α-epoxycholest-6-ene-1α,3α-diol (**4**) prepared from the dienediol (**2**) (560 mg) was transferred with a syringe from the reaction vessel into a three necked flask containing a stirred suspension of $LiAlH_4$ (500 mg) in dry tetrahydrofuran (20 ml). The mixture was heated to reflux for 2 h prior to work-up. The n.m.r. spectrum of the crude product showed the presence of the two vinylic protons as doublets at δ 5.4 and 5.9. *m*-Chloroperbenzoic acid (250 mg) in dry benzene (6 ml) was added to the solution of the reduced product (350 mg) in benzene (10 ml). After 24 h at room temperature and work-up as indicated for compound (**7**), the crude epoxidized product (345 mg) which was obtained, showed no signals for vinylic protons. The epoxy alcohol obtained was acetylated with acetic anhydride and pyridine overnight at room temperature to yield a product (290 mg) which was oxidized with Jones reagent at 10 °C. After work-up, the oxidized product in benzene solution (5 ml) was introduced onto a column of neutral alumina (Woelm activity II, 20 g) made up with light petroleum; the product was kept for 24 h in contact with the adsorbent, and was then washed with chloroform and purified on two chromatoplates [ethyl acetate–toluene (1:9)]. The major band afforded the title compound (**16**) (95 mg) [17% from the dienediol (**2**)], m.p. 162—164 °C (from hexane), $\lambda_{max.}$(EtOH) 221 nm (ε 9 600); $\nu_{max.}$($CHCl_3$) 1 685 cm^{-1}; *m/z* (e.i.) 414 (M^+); 397 (M^+ − OH); 396 ($M^+ - H_2O$.

t-Butyl Hydroperoxide Oxidation of 1α,2α-*Epoxycholesta*-4,6-*dien*-3α-*ol* (**18**).—The reaction was done with compound (**18**) (100 mg) overnight at 40 °C. After filtration through Florisil, 1α,2α-epoxycholesta-4,6-dien-3-one (**17**) (82 mg) was obtained.

MnO_2 *Oxidation of Cholesta*-4,6-*diene*-1α,3α-*diol* (**2**).—To a solution of compound (**2**) (90 mg) in chloroform–ethyl acetate [(3:5); 16 ml] freshly prepared MnO_2 (590 mg) was added and the mixture was stirred overnight at room temperature. After filtration and evaporation of the solvent, almost pure 1α-hydroxycholesta-4,6-dien-3-one (**19**)[13] (81 mg) was obtained. The compound was characterized by its n.m.r. spectrum.

1α-*Hydroxy*-4α,5α-*epoxycholest*-6-*en*-3-*one* (**20**).—The epoxidation of the dienone (**19**) (60 mg) was carried out as described for compound (**1**). After filtration through Florisil, the epoxide (**20**) (42 mg) was obtained; it showed one major spot on a chromatoplate. The compound was not further purified and was characterized by its n.m.r. spectrum.

Acknowledgements

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