Phytochemistry, Vol. 21, No. 7, pp. 1705–1710, 1982.
Printed in Great Britain.

0031–9422/82/071705–06$03.00/0

FIVE 3β, 6α-DIHYDROXYSTEROLS IN ORGAN-PIPE CACTUS

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(*Received* 15 *September* 1981)

Key Word Index—*Stenocereus thurberi*; Cactaceae; organ-pipe cactus; 3β, 6α-dihydroxysterols; 5α-cholest-8(9)-en-3β, 6α-diol; 5α-cholesta-8, 14-dien-3β, 6α-diol; 14α-methyl-5α-cholest-8-en-3β, 6α-diol; 14α-methyl-5α-cholesta-8, 24-dien-3β, 6α-diol; 14α-methyl-9, 19-cyclo-5α-cholestan-3β, 6α-diol.

Abstract—The sterol diol fraction from the lipids of organ-pipe cactus, *Stenocereus thurberi*, was separated into five compounds: macdougallin, peniocerol, cyclostenol, stenocereol and thurberol. The last three compounds have not been described before. All compounds were characterized by physical and spectroscopic properties.

INTRODUCTION

The organ-pipe cactus, *Stenocereus thurberi* [1], is a large columnar succulent growing in southern Arizona and north-western Mexico whose decaying stems are one of the breeding sites for *Drosophila mojavensis* in the Sonoran Desert [2]. The cactus is rich in acidic triterpene glycosides and lipids [3–5]. The latter, which comprise 10–17% of the dry weight of large stems, consist of neutral oleanene and lupene mono-, di- and triols, a small amount (0.07%) of phytosterols (cholesterol, campesterol, sitosterol) and a large proportion of dihydroxysterols [5]. All of these are partially esterified with medium-chain fatty acids [6]. The ratio of non-saponifiables to fatty acids in the lipid fraction varies, but is usually about 2:1. The sterol diol fraction, 34% of the non-saponifiables and 2.6% of the cactus dry weight, elutes from Si gel columns with 1:1–2:1 ether–light petroleum (l.p.) after removal of di- and trihydroxytriterpenes with solvent mixtures of lower polarity [5].

RESULTS AND DISCUSSION

The five sterol diols in this fraction (R_f 0.03, 6:4, hexane–EtOAc, R_f 0.65, 90:10:1, $CHCl_3$–MeOH–HOAc) could not be adequately resolved by GC as free alcohols ($RR_{t_{\text{chol}}}$ 1.83–2.00), TMS-ethers ($RR_{t\text{TMS chol.}}$ 1.32–1.42) or diacetates ($RR_{t\text{chol. ac}}$ 1.80–2.09). Chromatography of the free diols or their acetates on $AgNO_3$-TLC plates first made us aware of the complexity of the mixture and was the best way of assessing purity during subsequent CC and crystallization of the five compounds (Table 1). Two of these, macdougallin (**5**) and peniocerol (**7**), had been previously isolated from underground tubers of night-blooming cereus cacti [7–10]. We named the other three, which have not yet been described, cyclostenol (**3**), stenocereol (**4**) and thurberol (**6**) (Fig. 1).

Peniocerol (**7**) and macdougallin (**5**) diacetates were readily separated from the remaining diol diacetates and each other with 2–5% ether–light petroleum or CH_2Cl_2 on 20% $AgNO_3$–Si gel columns and identified by their physical and spectroscopic properties [7–9].

Stenocereol (**4**) diacetate was purified by repeated chromatography on 10% $AgNO_3$–Si gel columns with CH_2Cl_2 and crystallized from MeOH: ^1H NMR and MS spectra suggested its structure to be 24-dehydromacdougallin diacetate and this was substantiated by reduction of the compound to macdougallin diacetate and ozonolysis to acetone.

Thurberol (**6**) diacetate, whose UV spectrum ($\lambda_{\max}$ 248) suggested an 8, 14-diene, was quite unstable to $AgNO_3$–Si gel CC and tended to elute with stenocereol diacetate. It was finally purified as the more stable dibenzoate which, when freed of most of its impurities by $AgNO_3$–Si gel chromatography with 1.5:1 l.p.–ether, was crystallized from EtOH–C_6H_6. The spectra (UV, NMR, MS, IR) of thurberol diacetate all supported its structure as 14-dehydropeniocerol. The dibenzoate was hydrogenated under non-isomerizing conditions to peniocerol dibenzoate and the diacetate to 3β,6α-diacetoxy-5α-cholest-8(14)-ene in the presence of HOAc.

Cyclostenol (**3**) was the last sterol diol to be recognized as a component of the mixture. It is present in smaller quantities than the other four diols in the cactus and could only be seen as a separate spot after careful $AgNO_3$–TLC chromatography of the diacetates with CH_2Cl_2. Slow CC of 3 g of a diacetate mixture of macdougallin, peniocerol and cyclostenol with 8:1–4:1 l.p.–CH_2Cl_2 followed by CH_2Cl_2 gave mixtures of various ratios of the three compounds plus a small amount (~25 mg) of oily cyclostenol diacetate that was relatively free of the other two compounds. This sample gave an MS fragmentation pattern similar to macdougallin diacetate and its ^1H NMR spectrum showed no vinyl protons but two doublets at δ0.20 and 0.45 suggestive of cyclopropyl protons. These data immediately suggested the structure to be a diacetoxy 4, 4′-desmethylcycloartane and led to the purification of larger amounts of the compound by epoxidation of contaminating macdougallin and peniocerol diacetates with *m*-chloroperbenzoic acid (*m*-PCBA) followed by CC. It was then easy to crystallize cyclostenol

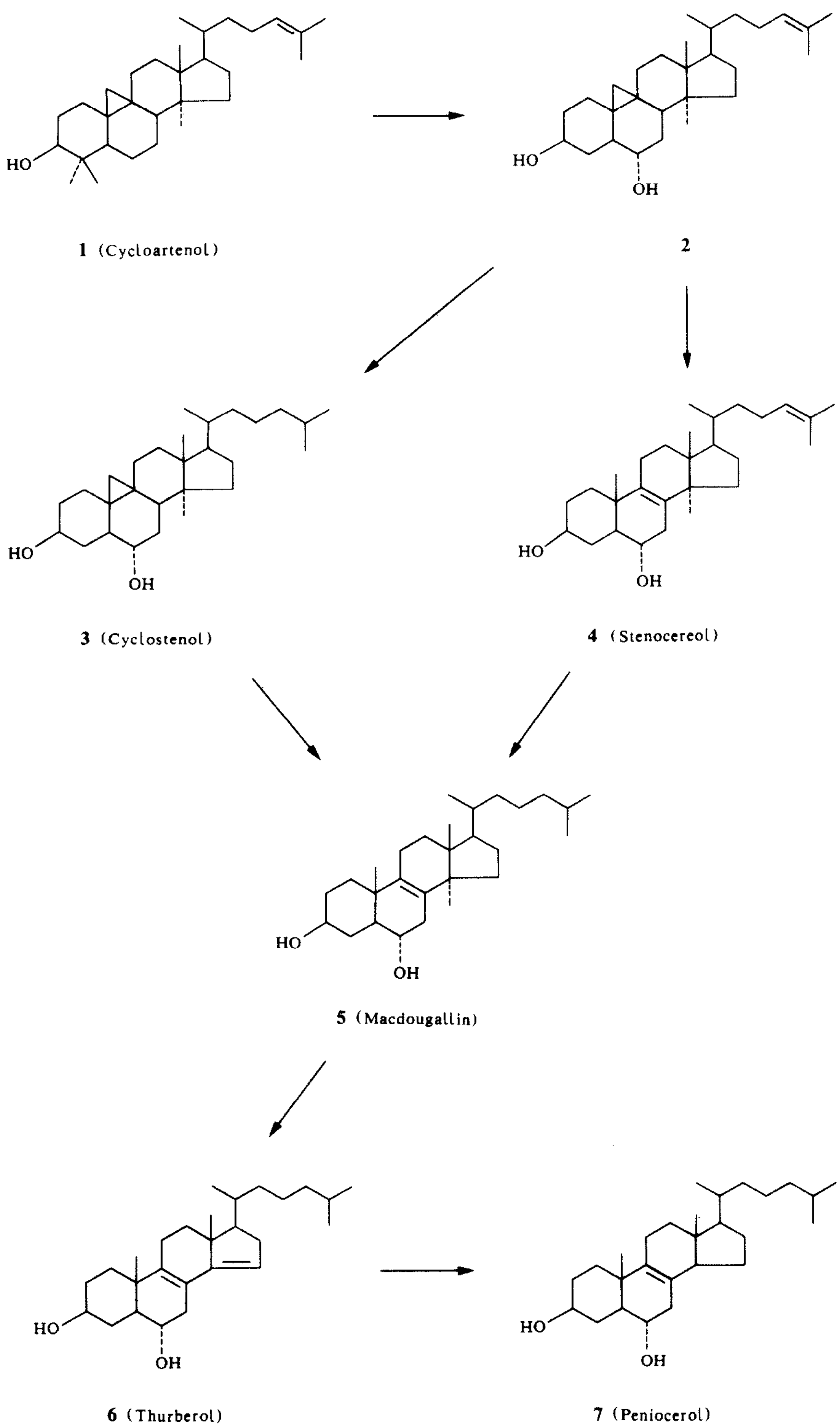

Fig. 1. Structures and possible biosynthetic pathways of the 3β, 6α-dihydroxysterols in organ-pipe cactus.

diacetate and convert it to the pure free diol and dibenzoate.

The mps, optical rotations and $AgNO_3$–Si gel TLC mobilities of the five sterol diols, their diacetates and dibenzoates are given in Table 1. The lower R_f of cyclostenol diacetate on $AgNO_3$-TLC plates than that observed for the unsaturated macdougallin and peniocerol diacetates is probably due to distortion of the orientation of the equatorial 3β and 6α acetoxy groups by the cyclopropane ring to make them more polar in cyclostenol diacetate than in the other two derivatives. This is supported by shifts of the 3α and 6β protons and of the 6-acetoxy methyl protons in the ^1H NMR spectrum of cyclostenol diacetate when

Table 1. Chromatographic mobilities, melting points and specific rotations of the sterol diols, diacetates and dibenzoates from organ-pipe cactus

Sterol	Derivative	$AgNO_3$–TLC $R_{\text{chol. deriv.}}$	Mp, vacuum, corrected	$[\alpha]_D^{24}$ (C3,.$CHCl_3$)
Cyclostenol (**3**)	Diol	0.63*	222–223°	+42°
	Diacetate	0.44†	96–98°	+58°
	Dibenzoate	0.58‡	196–198°, clears 199°	+83°
Stenocereol (**4**)	Diol	0.63	150.5–151.5°	+72°
	Diacetate	0.21	114.5–116°	+53°
	Dibenzoate	0.23	165–166°	+102°
Macdougallin (**5**)	Diol	0.62	174–175° lit. [9] 173–174.5°	+69° lit [7] +72°
	Diacetate	0.54	126–127.5° lit. [9] 124–126°	+56° lit. [7] +55°
	Dibenzoate	0.60	150.7–151°	+104°
Thurberol (**6**)	Diol	0.51	190–190.5° (sinters 174°)	+2°
	Diacetate	0.14	106.5–108°	+10°
	Dibenzoate	0.15	186–188°	+73°
Peniocerol (**7**)	Diol	0.55	183°, clears 203–205° lit. [7] 181–183°	+49° lit. [8] +53°
	Diacetate	0.51	51.5–52° lit. [7] 50–51°	+41° lit. [8] +42°
	Dibenzoate	0.58	210–211° lit. [8] 202–204°	+95°

*Diols, $R_{\text{cholesterol}}$, 95:5 EtOAc–HOAc 2×. †Diacetates, $R_{\text{chol. acetate}}$, CH_2Cl_2 3×. ‡Dibenzoates, $R_{\text{chol. benzoate}}$, CH_2Cl_2 1×.

compared to these absorptions in the other four compounds (Table 2).

The 600–1000 and 1100–1200 cm^{-1} regions of the IR spectra of the five sterol diol diacetates are shown in Fig. 2. The other regions of their spectra are all alike except for a very small cyclopropane peak at 1650 cm^{-1} in the spectrum of cyclostenol diacetate. Cyclopropyl absorption of this derivative at 900 cm^{-1} and the band at 803 cm^{-1} for the $\Delta^{8,14}$ system in thurberol diacetate are the principal distinguishing features in these spectra.

The ^1H NMR spectra of the diacetates are given in Table 2 and are as expected from the structures assigned to the five compounds. The downfield shift of the 18-CH_3 resonance is in accord with the cycloartane skeleton [11] of cyclostenol diacetate and the changes in its resonances at C_3 and C_6 have been noted above. This spectrum also lacks the 7α-H resonance at δ 2.5–2.6 caused by a combination of the 6α-acetoxy group and $\Delta^{8(9)}$ unsaturation in the four other compounds. The spectrum of stenocereol diacetate closely resembles that of macdougallin diacetate except for the two vinyl methyl groups ($C_{26,27}$) and the vinyl proton on C_{24}. The C_{18} methyl protons in thurberol diacetate are also shifted downfield because of the Δ^{14} bond [12] and its vinyl proton at C_{15} is barely split by the adjoining protons on C_{16}. The spectrum of peniocerol diacetate also resembles that of macdougallin diacetate except for the C_{32} resonance at δ 0.90 and the effect of this group on C_{18} (δ 0.69 in macdougallin and 0.59 in peniocerol diacetate).

The mass spectra of the sterol diol diacetates are given in Table 3. The base peaks are all M^+–2HOAc or M^+–(2HOAc + Me). The M^+-side-chain (SC) fragments are variable and is not accentuated in the Δ^{24} unsaturated stenocereol diacetate because of $\Delta^{8(9)}$ unsaturation in the nucleus [13].

The five sterol diols in organ-pipe cactus fall into a logical biosynthetic sequence (Fig. 1). Squalene is cyclized to cycloartenol (**1**) and a small portion of this is eventually converted to cholesterol, campesterol and sitosterol [5]. Most of the cycloartenol however is hydroxylated in the 6α position and the 4,4′-methyl groups are removed to form 6α-hydroxy-4, 4′-desmethylcycloartenol (**2**). This compound was not isolated but the appearance of a minor spot on $AgNO_3$–TLC just below stenocereol (**4**) diacetate in one of the many fractions obtained from various

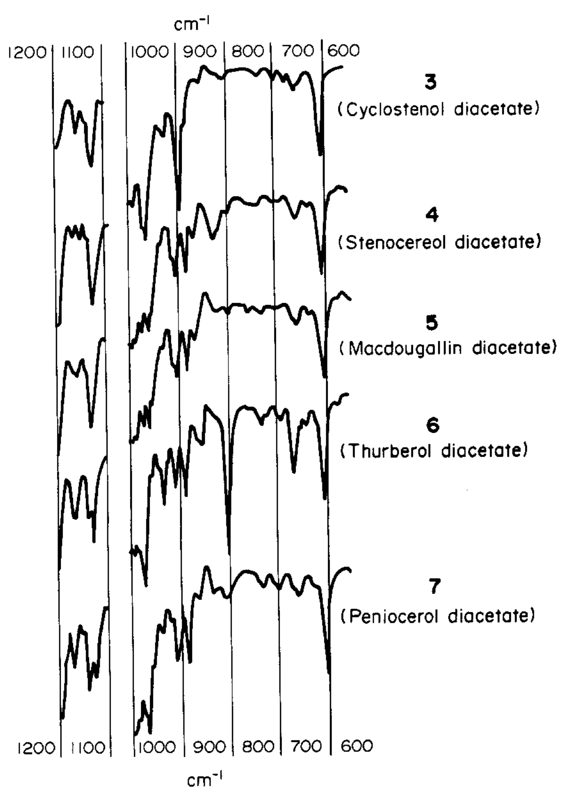

Fig. 2. IR spectra of the sterol diol diacetates in the ranges of 1200–1100 and 1000–600 cm^{-1}.

Table 2. ^{1}H NMR spectra of the sterol diol diacetates

Sterol diacetate	Chemical shifts of proton signals in the diacetates‡											
	C_{18} (s)	C_{19}	C_{21} (d)	$C_{26,27}$	C_{32} (s)	3β-OAc (s)	6α-OAc (s)	3α-H (m)	6β-H (m)	7α-H (q)	Vinyl proton	Others
Cyclostenol (**3**)	0.95	0.20(*d*) 0.45(*d*)	0.90	0.87(*d*)	0.88	2.03	2.03	4.36	4.78			
Stenocereol (**4**)	0.69	1.04(*s*)	0.92	1.61(*s*) 1.69(*s*)	0.90	2.06	2.04	4.66	4.92	2.52	5.08(*t*) (24–H)	
Macdougallin* (**5**)	0.69	1.04(*s*)	0.89	0.87(*d*)	0.90	2.06	2.04	4.66	4.93	2.53		
Thurberol (**6**)	0.80	1.08(*s*)	0.94	0.87(*d*)		2.07	2.04	4.66	4.92	2.65	5.35(*t*) (15–H)	2.19(*d*) (1H)
Peniocerol† (**7**)	0.59	1.05(*s*)	0.93	0.87(*d*)		2.05	2.04	4.66	4.88	2.50		

*Lit. [9] δ: 0.7, 0.84, 1.04, 2.02, 2.04.
†Lit. [9] δ: 0.6, 0.85, 0.90, 1.05, 2.06, 2.10.
‡Absorptions are in ppm (δ) from tetramethylsilane.

Table 3. Mass spectra of the sterol diol diacetates

Fragment	*m*/*z* (% base peak)				
	Cyclostenol (**3**) diacetate	Stenocereol (**4**) diacetate	Macdougallin (**5**) diacetate	Thurberol (**6**) diacetate	Peniocerol (**7**)* diacetate
M^+	500 (7)	498 (0.5)	500 (0)	484 (2)	486 (0)
$M^+ - HOAc$	440 (21)	438 (68)	440 (53)	424 (56)	426 (64)
$M^+ - 2HOAc$	380 (100)	378 (71)	380 (59)	364 (48)	366 (100)
$M^+ - (2HOAc + Me)$	365 (43)	363 (100)	365 (100)	349 (100)	351 (99)
$M^+ - (HOAc + SC)$	327 (5)	325 (0)	327 (0)	311 (3)	313 (12)
$M^+ - (2HOAc + SC)$	267 (62)	265 (5)	267 (2)	251 (15)	253 (23)
$M^+ - (2HOAc + SC + C_{15\text{-}17} + H)$	225 (13)	223 (5)	225 (4)	209 (10)	211 (19)
$(C_{5\text{-}19})^+ + H$	199 (26)	199 (13)	199 (8)	197 (12)	199 (23)
$(C_{5\text{-}19})^+ - H$	197 (9)	197 (13)	197 (5)	195 (13)	197 (14)

*Lit. [8] 426, 366, 351, 313, 253.

organ-pipe cacti worked-up during this study makes us believe in retrospect that it must have been diol **2**. At the time we thought it was an artefact of stenocereol, the structure of which had not yet been established.

Diol **2** is then reduced to cyclostenol (**3**) or its cyclopropane ring is opened [14] to form stenocereol (**4**) and either of these can be metabolized to macdougallin (**5**). The latter is then demethylated at C_{14} [15] to form the 8, 14-diene thurberol (**6**) which in turn is reduced to peniocerol (**7**). The isolation of thurberol together with macdougallin and peniocerol from the same plant strongly supports the hypothesis that 8, 14-dienes rather than 8(14)-monoenes [16] are the intermediates in the removal of 14α-methyl groups during sterol biosynthesis and that the next step in the sequence is reduction of the $\Delta^{14(15)}$ double bond [17].

The $\Delta^8 \rightarrow \Delta^7$ isomerization which follows in normal sterol biosynthesis is presumably inhibited by the 6α-OH group of peniocerol and the biosynthesis stops with this diol. The early 4, 4′-demethylations and 6α-hydroxylation in this sequence may also prevent attack of *S*-adenosylmethionine on C_{24} of the unsaturated diols **2** and **4** and thereby maintain the cholesterol side-chain in these compounds.

The literature on naturally occurring 6-hydroxysterols is sparse. Besides peniocerol and macdougallin [7–10] only 6β-hydroxycampest-4-en-3-one and the corresponding stigmastene isomer have been isolated from plants [18, 19] and the latter and stigmasta-4, 22-dien-3-on-6β-ol were among the products obtained by oxidation of sitosterol and stigmasterol by a soil pseudomonad [20]. A number of side-chain oxidized 3β, 6α-dihydroxy-$\Delta^{9(11)}$-sterols were present as saponins in the crown-of-thorns starfish [21] and ergosta-8, 24(28)-dien-3β, 6α-diol (24-methylenepeniocerol) has recently been identified in a $\Delta^8 \rightarrow \Delta^7$ blocked yeast mutant [22]. We have investigated the lipid fraction of agria cactus (*Stenocereus gummosis*), a plant related to organ pipe [1] and the principal host for *Drosophila mojavensis* in Baja California, and it also appeared to contain at least two of the sterol diols described here (H. W. Kircher and L. Chernetz, unpublished work).

EXPERIMENTAL

Mps, *in vacuo*, corr., were taken in capillary tubes with a Thomas–Hoover apparatus; $[\alpha]_D^{24}$ (C-3, $CHCl_3$) with a Rudolph DP-06-01 polarimeter; MS 70 eV, direct inlet with a Varian 311–A; IR, 2.5% in CS_2; ^1H NMR in $CDCl_3$; UV in EtOH.

$AgNO_3$–TLC plates were prepared by dipping Merck aluminium sheet Si gel coated plates in 10% $AgNO_3$–4:1 EtOH–H_2O followed by activation at 110° for 20 min; solvents are given as footnotes to Table 1.

Sterol diols were isolated from saponified organ-pipe cactus lipids by CC [5] and separated by crystallization from acetone into fractions containing various ratios of the five diols. The diols were acetylated and separated on $AgNO_3$–Si gel columns as follows.

Nomenclature. Cyclostenol (**3**), 14α-methyl-9,19-cyclo-5α-cholestan-3β,6α-diol; stenocereol (**4**), 14α-methyl-5α-cholesta-8,24-dien-3β,6α-diol; macdougallin (**5**), 14α-methyl-5α-cholest-8-en-3β,6α-diol; thurberol (**6**), 5α-cholesta-8,14-dien-3β,6α-diol; and peniocerol (**7**), 5α-cholest-8(9)-en-3β,6α-diol.

Macdougallin (**5**). The diacetate was eluted from a 20 g mixture placed on a 1 kg 20% $AgNO_3$–Si gel column with 2% ether–l.p. (light petroleum) and purified as the free diol on a Si gel column with 35% ether–l.p. followed by crystallization from MeOH. The diacetate was also crystallized from MeOH and the dibenzoate from EtOH.

Peniocerol (**7**). The diacetate eluted from $AgNO_3$–Si gel columns with 5% ether–l.p. after macdougallin diacetate and was purified by crystallization from MeOH. The free diol was crystallized from EtOH and the dibenzoate from EtOH–C_6H_6.

Stenocereol (**4**). The diacetate was purified on a 1 kg 20% $AgNO_3$–Si gel column with 3:7 C_6H_6–hexane and several crystallizations from MeOH and EtOH. The free diol was crystallized from MeOH–H_2O and the dibenzoate from EtOH.

Stenocereol diacetate, 0.75 g, was hydrogenated in 40 ml EtOH over 50 mg PtO_2 until H_2 absorption ceased. After removal of catalyst and solvent the residue was crystallized from MeOH, mp and mmp with macdougallin diacetate 125.5–127.5°. The mother liquors were hydrolysed with alkali to the diol, mp (MeOH) and mmp with macdougallin 174–175°, which was benzoylated, mp (EtOH) and mmp with macdougallin dibenzoate 149–150°.

Stenocereol diacetate, 0.5 g, was ozonized in 10 ml HOAc at 10° for 10 min [23]. The mixture was treated with Zn and H_2O on the steam-bath and distilled. The distillate was redistilled into a solution of 2, 4-dinitrophenylhydrazine and the precipitate crystallized from MeOH, mp and mmp with acetone 2, 4-dinitrophenylhydrazone 125–127° (air, corr.).

Thurberol (**6**). The diacetate was partially purified on 20% $AgNO_3$–Si gel columns with 20 and 30% benzene in hexane and crystallized from MeOH but could not be separated from stenocereol diacetate. The mixture was hydrolysed, the dibenzoate prepared and the latter chromatographed in 2-g quantities on 250 g 10% $AgNO_3$–Si gel columns with 2:1 and 1.5:1 l.p.–CH_2Cl_2 and crystallized from EtOH–$CHCl_3$. The diol was crystallized from $CHCl_3$ and the diacetate from MeOH, ϵ_{EtOH}^{249} 18 000 ($\Delta^{8,14}$).

Thurberol diacetate was hydrogenated overnight in EtOH and HOAc over 10% Pd–C to 5α-cholest-8(14)-en-3β, 6α-diol diacetate, mp 140–141° (MeOH), lit. [24] 141–142°. The IR spectrum no longer showed the 809 cm^{-1} band due to the $\Delta^{8,14}$ system and the MS (*m*/*z*: 426, 411, 366, 351, 313, 211) and NMR (δ 0.78, 0.82, 0.89, 0.95, 2.00) matched those of an authentic sample prepared in the same way from peniocerol diacetate [8].

Thurberol dibenzoate, 0.54 g, was hydrogenated in 50 ml EtOAc and 2 ml Et_3N over 150 mg 10% Pd–C for 20 hr. After removal of catalyst and solvent the residue was chromatographed on a 100 g 10% $AgNO_3$–Si gel column with 2:1 l.p.–CH_2Cl_2 and the product, peniocerol-dibenzoate crystallized from EtOAc, mp and mmp 209–211°. The residue in the mother liquors was hydrolysed, mp (EtOH, MeOH) and mmp with peniocerol, sinters 184°, melts 201–203°.

Cyclostenol (**3**). The diacetate was enriched by slow chromatography of mixtures containing macdougallin and peniocerol diacetates on 10% $AgNO_3$–Si gel columns with 8:1–4:1 l.p.–CH_2Cl_2 mixtures followed by CH_2Cl_2 only. A series of products was obtained ranging from 50 to 90% cyclostenol diacetate as judged by TLC spot intensities plus a small amount of non-crystalline material that was contaminated with lower R_f impurities. This was purified by Si gel CC with 5% ether–l.p. to yield ~25 mg of oily material that appeared fairly pure by TLC. Its ^1H NMR spectrum, δ 0.20, 0.45 (2H, *dd*) and no vinyl protons and its mass spectrum (M^+ 500) suggested the compound had a cyclopropane ring and was an isomer of macdougallin diacetate. Small scale experiments with the five diol diacetates showed that cyclostenol diacetate was the only one left unoxidized with *m*-CPBA, R_fs on 80:10:10 l.p.–ether–HOAc: cyclostenol diacetate 0.78, macdougallin diacetate epoxide 0.67, peniocerol diacetate epoxide 0.63, thurberol and stenocereol diacetate diepoxides 0.27.

The various impure fractions of cyclostenol diacetate were accordingly oxidized with an equal weight of *m*-CPBA in 25 vols CH_2Cl_2 for 18 hr at room temp. The reaction mixtures were evapd to dryness and partitioned between satd aq. $NaHCO_3$ and ether. The ether solutions were evaporated and the residues combined (17.5 g) and eluted from two 850 g Si gel columns with 5–15% ether–l.p. Residual *m*-chlorobenzoic acid was removed from the elute with $NaHCO_3$ solution and cyclostenol diacetate crystallized twice from methanol. The free diol was crystallized from MeOH and the dibenzoate from EtOH followed by EtOAc.

Acknowledgements—We thank Dr C. Djerassi for spectra and samples of macdougallin and peniocerol derivatives, Dr R. B. Bates for assistance with NMR, The National Science Foundation for a Science Faculty Fellowship (H.L.B.) and for Grants DEB 74–19148A07 and DEB 7912924 to W. B. Heed and H. W. Kircher for support of this work. Dr Fumiko Rosenstein and Kristin Leiser also contributed by assistance during a portion of this study.

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