3. The Thermal Reactivity of 5,8α-Epidioxy-5α-cholestan-3β-yl Acetate in Acetic Acid

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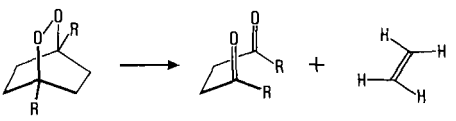
The thermolysis of the steroidal 5α,8α-peroxide **1**, under acidic conditions afforded in addition to the expected 5,10 : 8,9-diseco derivative **2**, the rearranged 5α,8α-epoxide **3**, the structure of which was determined by NMR spectroscopy and X-ray analysis.

Introduction. – In [1], we reported that the known [2] thermal cycloreversion-type reaction of saturated [2.2.2]endoperoxides *(Scheme 1)* was successfully applied to ste-

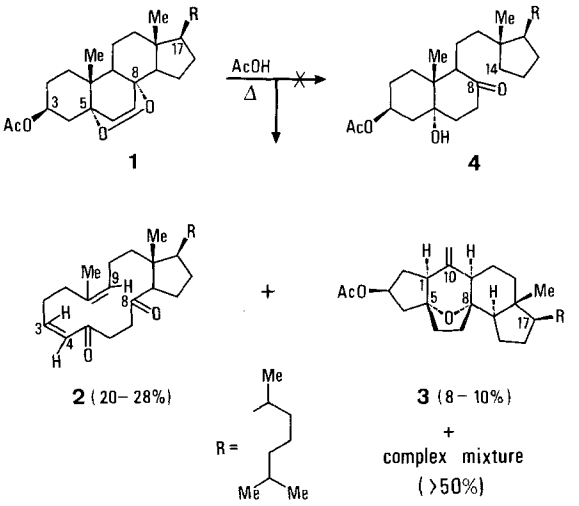
Scheme 1



roidal 5α,8α-peroxides to induce simultaneous fragmentation of the C(5)–C(10) and C(8)–C(9) bonds. Actually, when 5,8α-epidioxy-5α-androstane-3β,17β-diol diacetate was thermolyzed in boiling AcOH, it underwent the above bisfragmentation to produce a modified 5,10 : 8,9-diseco-steroid containing, instead of the rings A, B, and C, a 14-membered carbocyclic ring fused to ring D [1]. However, a more careful analysis of the thermolysis products revealed that under these conditions, as a competing process, a reductive 8,14-monofragmentation took also place [3].

In connection with this finding, we investigated, in more detail, the thermal behaviour of a structurally similar substrate, *i.e.* the 5,8α-epidioxy-5α-cholestan-3β-yl acetate (**1**; *Scheme 2*).

Scheme 2



Results and Discussion. – Peroxide **1** (prepared by photooxygenation of 5,7-cholestadien-3β-yl acetate [4] and subsequent diimide reduction [2] of the double bond in the resulting 6-ene 5α,8α-peroxide) was thermolyzed in boiling AcOH to give the expected (*E,E*)-5,10 : 8,9-diseco-3,9-cholestadiene-5,8-dione (**2**, 20–28% yield) and, in addition, a rearranged (formal dehydration) product **3** (8–10% yield). The structure of **3** was deduced from its ^{1}H- and ^{13}C-NMR and mass spectra and confirmed by X-ray analysis. Interestingly (and in contrast to the previously described behaviour of the 5α,8α-peroxide in the androstane series [3]; see above), in this case, the product **4** of the reductive 8,14-monofragmentation was not observed among the compounds present in the complex thermolysis mixture.

NMR and Mass Spectra of **3**. In the ^{1}H-NMR spectrum, the signal of the original angular tertiary CH_3(19) group is missing. Instead, a pair of small *d* is present at 4.60 and 4.72 ppm, which can be assigned to the protons of a CH_2=C group. Besides the signals for H_α–C(3) (5.22 ppm), the β-oriented AcO–C(3), and the 4 CH_3 groups of the (modified) cholestane system (*i.e.* CH_3(18), CH_3(21), CH_3(26), and CH_3(27)), no other characteristic proton resonances could be detected.

From the analysis of the ^{13}C-NMR spectrum of **3** (^{1}H-decoupled and in combination with an INEPT spectrum, allowing the differentiation between primary, secondary, tertiary, and H-free C-atoms), the presence of the following types of C-atoms could be deduced: *i*) 5 CH_3 groups, 3 of them being secondary (CH_3–CH as in **1**) and 2 tertiary (CH_3–C, including CH_3 of AcO; **1** has 3 tertiary CH_3 groups), *ii*) 12 CH_2 groups (as in **1**), one of them being, however, of the olefinic type, *iii*) 7 CH groups (1 more than in **1**), and *iv*) 5 H-free C-atoms (including C=O of AcO; as in **1**). Thus, a total of 29 C- and 46 H-atoms have to be accomodated in structure **3**.

Since the MS of **3** (parent peak at *m/z* 446) revealed the presence of 3 O-atoms (2 of them from AcO), the molecular formula of **3** was deduced to be $C_{29}H_{46}O_3$.

Whereas the ^{13}C-NMR spectrum of the starting peroxide **1** shows the presence of 4 H-free, saturated C-atoms in the cholestane skeleton (*i.e.* at 35.6 for C(10), 44.0 for C(13), 79.1 for C(8)–O, and 80.5 ppm for C(5)–O), the one of **3** has only 3, resonating at 44.5 for C(13), 85.9 for C(8)–O, and 87.6 ppm for C(5)–O (the last 2 C-atoms must be bound to O), besides an unsaturated H-free C-atom of the olefinic type ($(C)_2C$=), resonating at 148.4 ppm, which should be C(10). This, together with the signals of a CH_2=C group in the ^{1}H-NMR spectrum of **3** (see above) indicates a change from an sp^3 C-atom in **1** to a fully substituted sp^2 C-atom in the skeleton of product **3**. Thus, it was concluded that the new ether product should have the structure **3** *(Scheme 2)*.

X-Ray Analysis and Structure Determination of **3**. According to X-ray analysis, the molecular structure of **3** was confirmed to be 5,8α-epoxy-5(10→1)*abeo*-1α(H),5α-cholest-10(19)-en-3β-yl acetate.

The data obtained indicate that rings A, D, and E in **3** adopt an envelope conformation, while rings B and C assume the chair form *(Fig.)*.

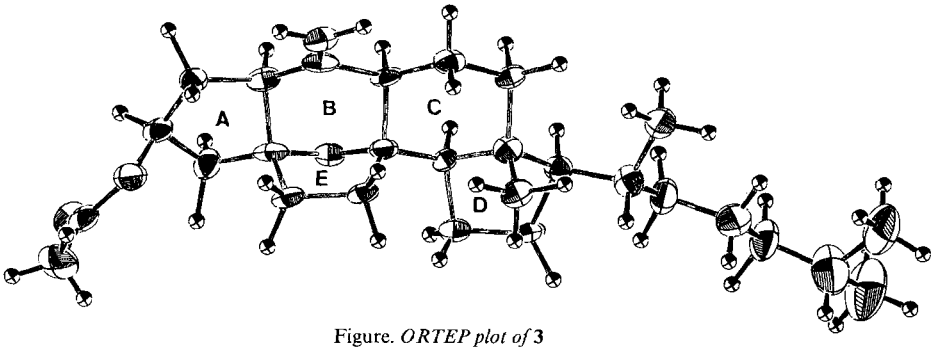


Figure. *ORTEP plot of* **3**

Crystal data for compound **3** are given in *Table 1*. Intensity measurements were made on a *Philips PW 1100* diffractometer, using graphite monochromatized Cu*K*α radiation (λ = 1.54178 Å). The structure was solved by direct methods using the computer program MULTAN 78 [5]. Blockdiagonal least-squares refinement (BDLS) with anisotropic temperature factors for 32 non-H-atoms converge to $R = 0.110$. The positions of the H-atoms were calculated. Inclusions of their coordinates and fixed thermal parameters refines the *R* factor to 0.099. Further refinement was not successful because of the poor quality of the intensities. Atomic coordinates and bond distances of **3** are given in *Tables 2* and *3*, respectively.

Table 1. *Crystal Data of* **3**

Crystal system	Orthorhombic
Space group	*P*212121 (No. 19)
a [Å]	53.891
b [Å]	8.376
c [Å]	5.949
Z	4
No. of reflections	2576
No. of parameters	473
Final *R* factor	0.099

The following tentative multistep mechanism can be proposed to explain the formation of compound **3** *(Scheme 3)*.

A homolytic rupture of the peroxide bridge in **1**(→**A**), followed by a carbonyl-forming fragmentation (of the C(5)–C(10) bond), can generate the diradical species **B** which would be stabilized by abstraction of H_α–C(1) by the ideally positioned oxy radical at C(8). The hemiacetal form **C** of the thus formed hydroxy ketone may finally undergo an acid-catalyzed or thermal transannular dehydration with concomitant formation of the olefinic methylidene group and a C(1)–C(5) bond (→**D**).

The authors from Yugoslavia are grateful to the *Serbian Academy of Sciences and Arts* and to the *Serbian Research Fund* for financial support.

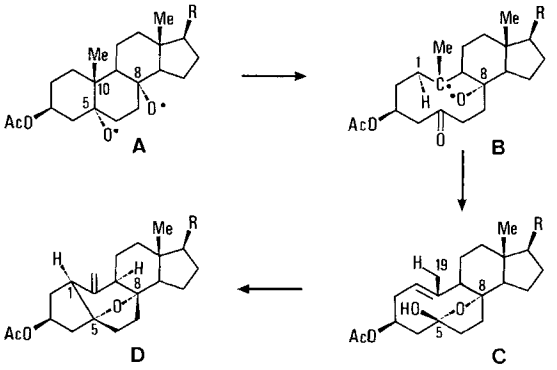
Table 2. *Atomic Coordinates of* **3**

Atom	*X/A*	*Y/B*	*Z/C*	Atom	*X/A*	*Y/B*	*Z/C*
C(1)	0.4277(2)	0.936(1)	0.183(2)	H(40)	0.459(1)	0.59(1)	0.00(1)
C(2)	0.4500(2)	1.035(1)	0.088(2)	H(41)	0.421(1)	0.47(1)	− 0.04(1)
C(3)	0.4728(2)	0.960(1)	0.204(2)	H(42)	0.406(1)	0.63(1)	− 0.17(1)
C(4)	0.4647(2)	0.809(1)	0.335(2)	H(43)	0.384(1)	0.83(1)	0.32(1)
C(5)	0.4403(2)	0.767(1)	0.207(2)	H(44)	0.352(1)	0.86(1)	0.02(1)
C(6)	0.4421(2)	0.675(1)	− 0.015(2)	H(45)	0.365(1)	0.71(1)	− 0.14(1)
C(7)	0.4166(2)	0.589(1)	− 0.031(2)	H(46)	0.343(1)	0.68(1)	0.34(1)
C(8)	0.4027(2)	0.631(1)	0.193(2)	H(47)	0.327(1)	0.61(1)	0.04(1)
C(9)	0.3868(2)	0.787(1)	0.148(2)	H(48)	0.379(1)	0.56(1)	0.46(1)
C(10)	0.4047(2)	0.915(1)	0.047(2)	H(49)	0.407(1)	0.35(1)	0.50(1)
C(11)	0.3624(2)	0.754(1)	0.030(2)	H(50)	0.407(1)	0.32(1)	0.23(1)
C(12)	0.3464(2)	0.628(1)	0.150(2)	H(51)	0.375(1)	0.12(1)	0.31(1)
C(13)	0.3622(2)	0.473(1)	0.169(2)	H(52)	0.373(1)	0.21(1)	0.59(1)
C(14)	0.3860(2)	0.516(1)	0.302(2)	H(53)	0.345(1)	0.41(1)	0.48(1)
C(15)	0.3974(2)	0.346(1)	0.364(2)	H(54)	0.409(1)	1.06(1)	− 0.21(1)
C(16)	0.3742(2)	0.241(1)	0.407(2)	H(55)	0.381(1)	0.97(1)	− 0.23(1)
C(17)	0.3510(2)	0.348(1)	0.341(2)	H(56)	0.377(1)	0.29(1)	− 0.03(1)
C(18)	0.3983(2)	0.987(1)	− 0.148(2)	H(57)	0.377(1)	0.48(1)	− 0.17(1)
C(19)	0.3661(2)	0.394(1)	− 0.057(2)	H(58)	0.348(1)	0.36(1)	− 0.14(1)
C(20)	0.3299(2)	0.240(1)	0.258(2)	H(59)	0.338(1)	0.18(1)	0.10(1)
C(21)	0.3071(2)	0.333(2)	0.184(3)	H(60)	0.314(1)	0.42(1)	0.03(1)
C(22)	0.3232(2)	0.138(2)	0.469(3)	H(61)	0.300(1)	0.39(1)	0.34(1)
C(23)	0.3048(2)	0.004(2)	0.410(3)	H(62)	0.293(1)	0.26(1)	0.13(1)
C(24)	0.3003(2)	− 0.102(2)	0.610(3)	H(63)	0.318(1)	0.22(1)	0.59(1)
C(25)	0.2845(3)	− 0.245(2)	0.560(3)	H(64)	0.340(1)	0.07(1)	0.53(1)
C(26)	0.2588(3)	− 0.213(2)	0.469(3)	H(65)	0.314(1)	− 0.07(1)	0.31(1)
C(27)	0.2783(3)	− 0.356(2)	0.754(3)	H(66)	0.288(1)	0.06(1)	0.36(1)
O(28)	0.4896(1)	0.919(1)	0.014(1)	H(67)	0.293(1)	− 0.04(1)	0.77(1)
C(29)	0.5136(2)	0.882(1)	0.069(2)	H(68)	0.321(1)	− 0.16(1)	0.68(1)
O(30)	0.5196(1)	0.879(1)	0.269(1)	H(69)	0.294(1)	− 0.32(1)	0.43(1)
C(31)	0.5288(2)	0.846(2)	− 0.132(2)	H(70)	0.250(1)	− 0.14(1)	0.60(1)
O(32)	0.4229(1)	0.671(1)	0.346(1)	H(71)	0.262(1)	− 0.14(1)	0.34(1)
H(33)	0.422(1)	0.97(1)	0.35(1)	H(72)	0.250(1)	− 0.32(1)	0.44(1)
H(34)	0.448(1)	1.17(1)	0.13(1)	H(73)	0.296(1)	− 0.40(1)	0.83(1)
H(35)	0.452(1)	1.03(1)	− 0.09(1)	H(74)	0.270(1)	− 0.28(1)	0.88(1)
H(36)	0.483(1)	1.03(1)	0.33(1)	H(75)	0.267(1)	− 0.44(1)	0.68(1)
H(37)	0.480(1)	0.70(1)	0.33(1)	H(76)	0.528(1)	0.74(1)	− 0.16(1)
H(38)	0.462(1)	0.84(1)	0.51(1)	H(77)	0.547(1)	0.87(1)	− 0.11(1)
H(39)	0.445(1)	0.75(1)	− 0.17(1)	H(78)	0.520(1)	0.91(1)	− 0.28(1)
H(40)	0.459(1)	0.59(1)	0.00(1)				
H(41)	0.421(1)	0.47(1)	− 0.04(1)				
H(42)	0.406(1)	0.63(1)	− 0.17(1)				
H(43)	0.384(1)	0.83(1)	0.32(1)				
H(44)	0.352(1)	0.86(1)	0.02(1)				
H(45)	0.365(1)	0.71(1)	− 0.14(1)				
H(46)	0.343(1)	0.68(1)	0.34(1)				
H(47)	0.327(1)	0.61(1)	0.04(1)				
H(48)	0.379(1)	0.56(1)	0.46(1)				
H(49)	0.407(1)	0.35(1)	0.50(1)				
H(50)	0.407(1)	0.32(1)	0.23(1)				
H(51)	0.375(1)	0.12(1)	0.31(1)				
H(52)	0.373(1)	0.21(1)	0.59(1)				
H(53)	0.345(1)	0.41(1)	0.48(1)				
H(54)	0.409(1)	1.06(1)	− 0.21(1)				
H(55)	0.381(1)	0.97(1)	− 0.23(1)				

Table 3. *Bond Distances of* **3**

C(1)–C(2)	1.571	C(11)–C(12)	1.537	C(21)–H(61)	1.105
C(1)–C(5)	1.570	C(11)–H(44)	1.051	C(21)–H(62)	1.045
C(1)–C(10)	1.490	C(11)–H(45)	1.049	C(22)–C(23)	1.539
C(1)–H(33)	1.096	C(12)–C(13)	1.555	C(22)–H(63)	1.055
C(2)–C(3)	1.543	C(12)–H(46)	1.228	C(22)–H(64)	1.148
C(2)–H(34)	1.152	C(12)–H(47)	1.250	C(23)–C(24)	1.502
C(2)–H(35)	1.049	C(13)–C(14)	1.551	C(23)–H(65)	0.974
C(3)–C(4)	1.548	C(13)–C(17)	1.582	C(23)–H(66)	1.052
C(3)–O(28)	1.492	C(13)–C(19)	1.512	C(24)–C(25)	1.501
C(3)–H(36)	1.097	C(14)–C(15)	1.592	C(24)–H(67)	1.170
C(4)–C(5)	1.563	C(14)–H(48)	1.058	C(24)–H(68)	1.279
C(4)–H(37)	1.208	C(15)–C(16)	1.553	C(25)–C(26)	1.509
C(4)–H(38)	1.082	C(15)–H(49)	0.988	C(25)–C(27)	1.516
C(5)–C(6)	1.533	C(15)–H(50)	0.986	C(25)–H(69)	1.083
C(5)–O(32)	1.489	C(16)–C(17)	1.589	C(26)–H(70)	1.117
C(6)–C(7)	1.550	C(16)–H(51)	1.166	C(26)–H(71)	0.986
C(6)–H(39)	1.122	C(16)–H(52)	1.114	C(26)–H(72)	0.997
C(6)–H(40)	1.140	C(17)–C(20)	1.537	C(27)–H(73)	1.133
C(7)–C(8)	1.570	C(17)–H(53)	1.059	C(27)–H(74)	1.082
C(7)–H(41)	1.025	C(18)–H(54)	0.958	C(27)–H(75)	1.055
C(7)–H(42)	1.075	C(18)–H(55)	1.067	O(28)–C(29)	1.373
C(8)–C(9)	1.588	C(19)–H(56)	1.031	C(29)–O(30)	1.235
C(8)–C(14)	1.467	C(19)–H(57)	1.121	C(29)–C(31)	1.481
C(8)–O(32)	1.457	C(19)–H(58)	1.132	C(31)–H(76)	0.924
C(9)–C(10)	1.564	C(20)–C(21)	1.524	C(31)–H(77)	1.017
C(9)–C(11)	1.515	C(20)–C(22)	1.561	C(31)–H(78)	1.140
C(9)–H(43)	1.101	C(20)–H(59)	1.154		
C(10)–C(18)	1.349	C(21)–H(60)	1.194		

Scheme 3



Experimental Part[1])

General. Prep. column chromatography: Silica gel 0.063–0.200 mm. TLC: control of reactions and separations of products on silica gel *G (Stahl)* with benzene/AcOEt 9:1, detection with 50% aq. H_2SO_4 soln. M.p.: uncorrec-

[1]) IR and UV spectral measurements, as well as elemental microanalysis, were carried out in the Laboratories for Instrumental Analysis of the Institute of Chemistry, Belgrade. NMR and mass spectra, and X-ray analysis were performed by *Ciba-Geigy Ltd.*, Basle.

ted. UV spectra: *Varian UV Super Scan 3* spectrophotometer: λ_{max} [nm] (ε). IR spectra: *Perkin-Elmer-337* spectrophotometer; in cm^{-1}. NMR spectra: *Bruker AM-360* (^1H (360 MHz), ^{13}C (90.55 MHz)), $CDCl_3$ soln. at r.t., TMS as internal standard; chemical shifts in ppm as δ values. MS: *Varian CH7* instrument; in *m/z*.

5,8α-Epidioxy-5α-cholestan-3β-yl Acetate (**1**). To a stirred mixture of 5,8α-epidioxy-5α-cholest-6-en-3β-yl acetate [4] (7.7 g) in CH_2Cl_2 (70 ml) and dipotassium azodicarboxylate (10 g) in 180 ml of abs. MeOH (30 ml), cooled in an ice bath, a soln. of AcOH (6.5 ml) in abs. MeOH (30 ml) was added dropwise within *ca.* 1 h. Stirring was continued at r.t. for additional 6 h, when the yellow colour disappeared. Most of the solvents were evaporated, and the residue was taken up in 300 ml of H_2O and extracted twice with CH_2Cl_2. The combined org. extracts were washed with sat. aq. $NaHCO_3$ soln. and H_2O, dried (Na_2SO_4), and evaporated. Recrystallization of the solid residue (7.5 g, 97%), m.p. 180°, from acetone/MeOH afforded 6.7 g (86.6%) of **1**, m.p. 183°; $[\alpha]_D^{20} = -40.2°$ ($c = 1.00$, $CHCl_3$). IR (CH_2Cl_2): 2950*s*, 2863*s*, 1738*s*, 1245*s*, 1040*m*, 1030*m*, 970*w*. ^1H-NMR: 0.69 (*s*, CH_3(18)); 0.86 (*d*, CH_3(26), CH_3(27)); 0.89 (*d*, CH_2(21)); 1.00 (*s*, CH_3(19)); 2.00 (*s*, AcO); 4.81 (*m*, H–C(3)). ^{13}C-NMR: 170.0 (*s*, CH_3COO); 80.5 (*s*, C(5)); 79.1 (*s*, C(8)); 69.9 (*d*, C(3)); 56.7 (*d*, C(17)); 54.3 (*d*, C(9)); 52.0 (*d*, C(14)); 44.0 (*s*, C(13)); 39.4 (*t*, C(12)); 36.5 (*t*, C(4)); 35.9 (*t*, C(22)); 35.9 (*d*, C(20)); 35.6 (*s*, C(10)); 35.4 (*t*, C(7)); 28.4 (*t*, C(6)); 28.0 (*d*, C(25)); 28.0 (*t*, C(16)); 26.2 (*t*, C(1)); 23.8 (*t*, C(23)); 22.8 (*q*, C(27)); 22.5 (*q*, C(26)); 21.5 (*t*, C(15)); 21.3 (*t*, C(11)); 21.2 (*t*, C(2)); 19.8 (*q*, CH_3COO); 18.5 (*q*, C(21)); 17.8 (*q*, C(19)); 12.6 (*q*, C(18)). MS (70 eV): 460 ($M^{+\cdot}$), 443 ($M^{+\cdot} - 17$), 426 ($M^{+\cdot} - 2 \times 17$), 400 ($M^{+\cdot} - 60$), 383 (400 – 17), 366 (400 – 2 × 17), 351 (366 – 15). Anal. calc. for $C_{29}H_{48}O_4$ (460.70): C 75.61, H 10.50; found: C 75.72, H 10.50.

Thermolysis of **1**. A soln. of **1** (4.2 g) in AcOH (200 ml) and H_2O (2 ml) was refluxed with stirring under N_2 for 24 h, when practically all starting material was consumed. The solvent was evaporated, leaving an oily residue (*ca.* 4.3 g) which was chromatographed on silica gel (120 g). Benzene eluted 253 mg of a complex mixture which was not investigated. Benzene/Et_2O 99:1 eluted *5,8α-epoxy-5(10→1)*abeo-*5α-cholest-10(19)-en-3β-yl acetate* (**3**) (431 mg, 10.7%), which was recrystallized from acetone (338 mg, 8.4%), m.p. 120–123°; $[\alpha]_D^{20} = +22.6°$ ($c = 1.00$, $CHCl_3$). IR (KBr): 2940–2850*s* (br.), 1728*s*, 1640*w*, 1264*s*, 1030*m*, 880*m*. ^1H-NMR: 0.64 (*s*, CH_3(18)); 0.87 (*d*, CH_3(26), CH_3(27)); 0.90 (*d*, CH_3(21)); 2.01 (*s*, AcO); 4.60, 4.72 (2 small *d*, CH_2=(19)); 5.22 (*m*, H–C(3)). ^{13}C-NMR: 170.7 (*s*, CH_3COO); 148.4 (*s*, C(10)); 103.9 (*t*, C(19)); 87.6 (*s*, C(5)); 85.9 (*s*, C(8)); 71.7 (*d*, C(3)); 56.9 (*d*, C(17)); 55.4 (*d*, C(9)); 52.1 (*d*, C(1)); 51.8 (*d*, C(14)); 44.5 (*s*, C(13)); 41.5 (*t*, C(4)); 39.5 (*t*, C(24)); 39.3 (*t*, C(12)); 36.0 (*t*, C(22)); 35.6 (*d*, C(20)); 33.6 (*t*, C(6)); 31.5 (*t*, C(7)); 28.1 (*t*, C(16)); 28.0 (*d*, C(25)); 26.4 (*t*, C(2)); 23.9 (*t*, C(23)); 22.8 (*t*, C(15)); 22.8 (*q*, C(27)); 22.5 (*q*, C(26)); 21.2 (*q*, CH_3COO); 20.2 (*t*, C(11)); 18.5 (*q*, C(21)); 12.6 (*q*, C(18)). MS (70 eV): 442 ($M^{+\cdot}$), 382 ($M^{+\cdot} - 60$), 367 (382 – 15), 364 (382 – 18), 329 ($M^{+\cdot} - 113$), 269 (329 – 60), 251 (269 – 18). Anal. calc. for $C_{29}H_{46}O_3$ (442.69): C 78.68, H 10.48; found: 78.66, H 10.50.

Elution with benzene/Et_2O 98:2 gave (E,E)-*5,10 : 8,9-diseco-3,9-cholestadiene-5,8-dione* (**2**; 1.056 g, 28.9%) as an oil, which was rechromatographed on a silica-gel column to afford a chromatographically (TLC) pure sample (781 mg, 21.4%); $[\alpha]_D^{20} = -47.4°$ ($c = 0.51$, $CHCl_3$). UV (MeOH): 214 (12160). IR (film): 2980–2890*s* (br.), 1725*s*, 1685*s*, 1640*m*. ^1H-NMR: 0.78 (*s*, CH_3(18)); 0.87 (*d*, CH_3(26), CH_3(27)); 0.94 (*d*, CH_3(21)); 1.56 (*s*, CH_3(19)); 5.19 (*q*, H–C(9)); 5.91 (*d*, $J = 16$, H–C(4)); 6.54 (*dt*, $J = 16$, 7.2, H–C(3)). ^{13}C-NMR: 209.8 (*s*, C(8)); 201.3 (*s*, C(5)); 147.6 (*d*, C(3)); 132.8 (*s*, C(10)); 130.2 (*d*, C(4)); 128.4 (*d*, C(9)); 57.9 (*d*, C(14)); 50.4 (*d*, C(17)); 48.4 (*s*, C(13)); 41.8 (*t*, C(7)); 39.5 (*t*, C(24)); 38:8 (*t*, C(6)); 37.9 (*t*, C(1)); 35.8 (*t*, C(12)); 34.7 (*t*, C(22)); 34.0 (*d*, C(20)); 29.4 (*t*, C(2)); 28.0 (*d*, C(25)); 26.7 (*t*, C(16)); 24.4 (*t*, C(11)); 23.9 (*t*, C(23)); 22.8 (*q*, C(27)); 22.6 (*q*, C(26)); 21.6 (*t*, C(15)); 18.8 (*q*, C(21)); 17.5 (*q*, C(19)); 15.8 (*q*, C(18)). MS (70 eV): 400 ($M^{+\cdot}$), 385 ($M^{+\cdot} - 15$), 382 ($M^{+\cdot} - 18$), 357 ($M^{+\cdot} - 43$). Anal. calc. for $C_{27}H_{44}O_2$ (400.65): C 80.94, H 11.07; found: C 80.65, H 11.06.

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