Oxidative Fragmentations of the 5α- and 5β-Hydroxy-*B*-norcholestan-3β-yl Acetates

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In memory of Professor *Oskar Jeger*, deceased on September 14, 2002

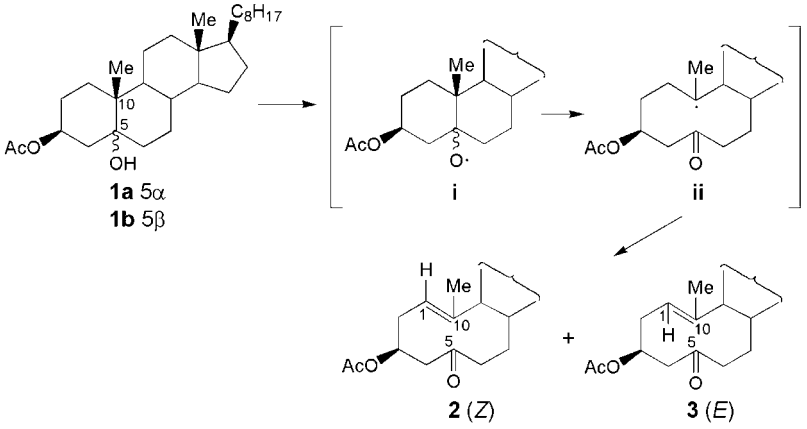
Oxidations of 5α-hydroxy-*B*-norcholestan-3β-yl acetate (**8**) with $Pb(OAc)_4$ under thermal or photolytic conditions or in the presence of iodine afforded only complex mixtures of compounds. However, the HgO/I_2 version of the hypoiodite reaction gave as the primary products the stereoisomeric (*Z*)- and (*E*)-1(10)-unsaturated 5,10-seco *B*-nor-derivatives **10** and **11**, and the stereoisomeric (5*R*,10*R*)- and (5*S*,10*S*)-acetals **14** and **15** (*Scheme 4*). Further reaction of these compounds under conditions of their formation afforded, in addition, the *A*-nor 1,5-cyclization products **13** and **16** (from **10**) and **12** (from **11**) (see also *Scheme 6*) and the 6-iodo-5,6-secolactones **17** and **19** (from **14** and **15**, resp.) and 4-iodo-4,5-secolactone **18** (from **15**) (see also *Scheme 7*). Oxidations of 5β-hydroxy-*B*-norcholestan-3β-yl acetate (**9**) with both hypoiodite-forming reagents ($Pb(OAc)_4/I_2$ and HgO/I_2) proceeded similarly to the HgO/I_2 reaction of the corresponding 5α-hydroxy analogue **8**. Photolytic $Pb(OAc)_4$ oxidation of **9** afforded, in addition to the (*Z*)- and (*E*)-5,10-seco 1(10)-unsaturated ketones **10** and **11**, their isomeric 5,10-seco 10(19)-unsaturated ketone **22**, the acetal 5-acetate **21**, and 5β,19-epoxy derivative **23** (*Scheme 9*). Exceptionally, in the thermal $Pb(OAc)_4$ oxidation of **9**, the 5,10-seco ketones **10**, **11**, and **22** were not formed, the only reaction being the stereoselective formation of the 5,10-ethers with the β-oriented epoxy bridge, *i.e.* the (10*R*)-enol ether **20** and (5*S*,10*R*)-acetal 5-acetate **21** (*Scheme 8*). Possible mechanistic interpretations of the above transformations are discussed.

1. Introduction. – Previous studies have shown that alkoxy radicals of type **i** (obtained by oxidation of the 5α- or 5β-hydroxysteroids **1a**,**b** with lead tetraacetate ($Pb(OAc)_4$) under thermal or photolytic conditions or with hypoiodite-forming reagents) readily undergo β-fragmentation of the C(5)–C(10) bond (*Scheme 1*) to give, *via* the C(10) radical intermediate **ii**, the diastereoisomeric (*Z*)- and (*E*)-1(10)-unsaturated 5-oxo-5,10-secosteroids **2** and **3** in high yield and, depending on the oxidant used, in different proportions [1].

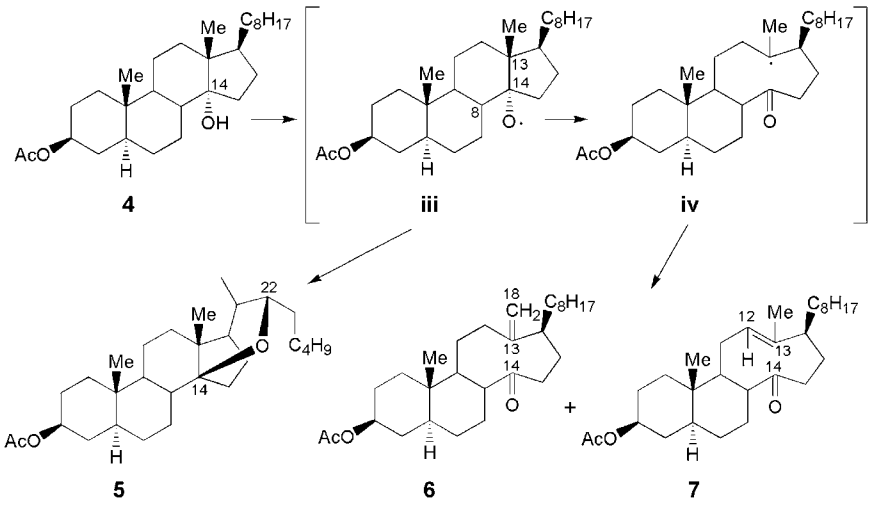
On the other hand, alkoxy radical **iii** generated by similar oxidations of the 14α-hydroxy-5α-cholestan-3β-yl acetate (**4**) reacted preferentially [2] by β-fragmentation of the C(13)–C(14) bond to afford, *via* the C(13) radical **iv**, the methylidene derivative **6** and the (*E*)-12-unsaturated 14-oxo-13,14-seco compound **7** (*Scheme 2*)[1]). Exception-

[1]) Further reactions of **6** and **7** under conditions of their formation either with oxidant or with some other species present in the reaction solution afforded products of allylic and α-acetoxylation from **6** and a *D*-homo-*C*-nor derivative and a (12*R*,13*R*)-epoxy derivative from **7**.

Scheme 1



Scheme 2

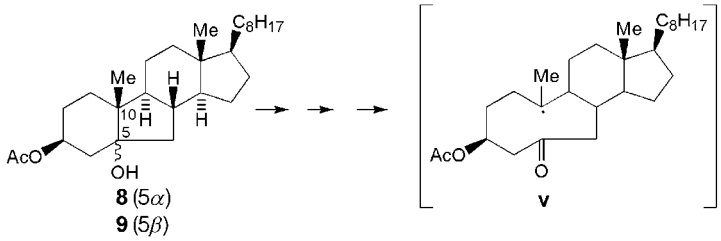


ally, the photolytic $Pb(OAc)_4$ oxidation of **4** resulted, in addition (to *ca.* 20%), in a reversible fragmentation of the alkoxy radical **iii**, involving splitting and recombination of the C(8)–C(14) bond with inversion of the configuration at C(14), followed by formation of the 14*β*,22-epoxy derivative **5**.

In connection with these results, we investigated in the present work oxidative fragmentations of the 5*α*- and 5*β*-hydroxy-*B*-norcholestan-3*β*-yl acetates **8** and **9** [3][4] which, by analogy with the above examples, could involve as an intermediate the C(10) radical **v** incorporated in a nine-membered ring (*Scheme 3*).

Oxidations of alcohols **8** and **9** were performed with $Pb(OAc)_4$ and hypoiodite-forming reagents (hypoiodite reaction [5]) under conditions similar to those previously applied to the compounds **1** and **4**.

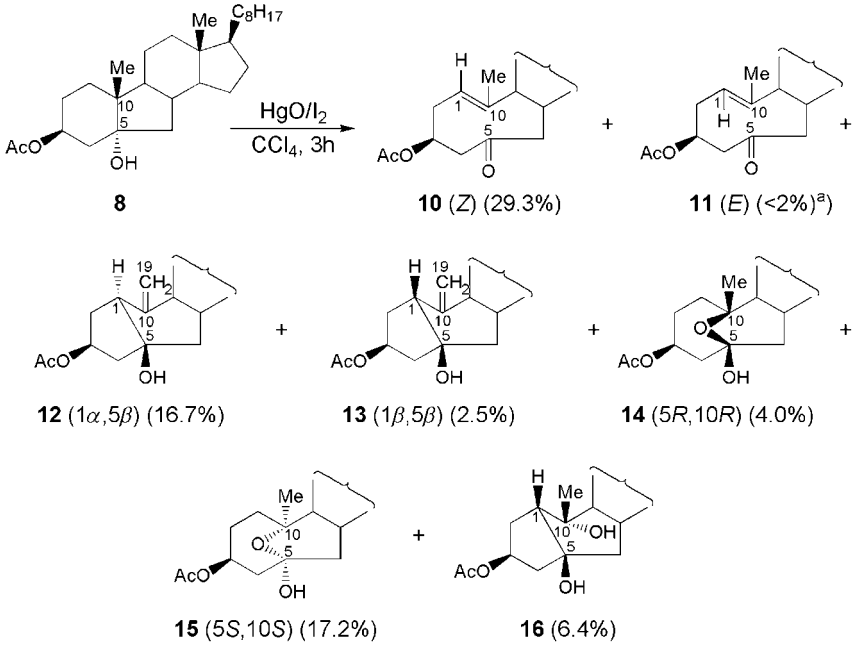
Scheme 3



2. Oxidations of 5*α*-Hydroxy-*B*-norcholestan-3*β*-yl Acetate (8). – 2.1. *Attempted Thermal and Photolytic $Pb(OAc)_4$ Oxidation and $Pb(OAc)_4$ Version of the Hypoiodite Reaction of* **8**. These reactions were performed under typical experimental conditions. However, in all cases they resulted only in complex mixtures of compounds, unresolvable by chromatographic methods.

2.2. *HgO/I_2 Version of the Hypoiodite Reaction*. The HgO/I_2 oxidation of **8** was carried out with an excess of oxidant in CCl_4 solution by irradiation with a 800-W lamp at 60 V at room temperature for 3 h. The mixture obtained after usual workup was separated by column chromatography (silica gel) to give (*Scheme 4*)[2]): the stereoisomeric (*Z*)- and (*E*)-1(10)-unsaturated *B*-nor-5,10-secosteroidal ketones **10** and **11**

Scheme 4



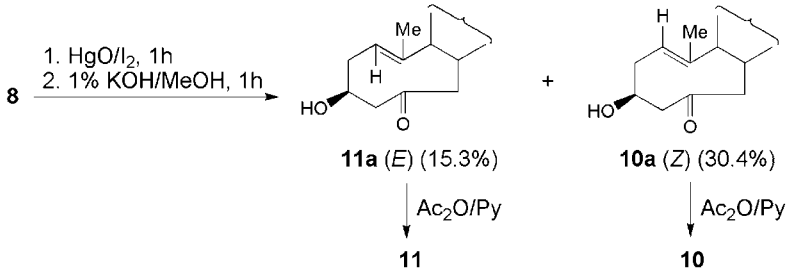
a) This sample was mixed with the (*Z*)-isomer **10**.

2) Yields given in the *Schemes* refer to the isolated pure (by TLC) compounds.

(29.3 and $<2\%$, resp.), the stereoisomeric (1α,5β)-*A*-nor and (1β,5β)-*A*-nor cyclization products **12** and **13** (16.7 and 2.5%, resp.), the stereoisomeric (5*R*,10*R*)- and (5*S*,10*S*)-acetals **14** and **15** (4.0 and 17.2%, resp.) and (1β,5β)10α-hydroxy cyclization product **16** (6.4%).

The low yield of the (*E*)-seco ketone **11** (as indicated by TLC) was due to its easy cyclization to product **12**. To avoid this transformation, in a similar experiment, the oxidation mixture was saponified with 1% KOH/MeOH at room temperature. This mixture, upon column chromatography (silica gel), afforded the (*Z*)- and (*E*)-3β-hydroxy derivatives **10a** and **11a** (30.4 and 15.3%, resp.), which were re-acetylated to the corresponding acetates **10** and **11** (Scheme 5)[2]).

Scheme 5



The structures of the oxidation products **10**–**16** were deduced from their analytical and spectral data (IR, ^{1}H- and ^{13}C-NMR, MS). The proposed configurations of the (*Z*)- and (*E*)-1(10)-unsaturated *B*-nor-seco ketones **10** and **11** were confirmed by X-ray crystallographic determination[3]).

In the IR spectra of seco ketones **10** and **11** ($C_{28}H_{46}O_3$), the absorption of the original 5α-hydroxy group is missing. Instead a new absorption is observed at 1704 and 1678 cm^{-1}, respectively, for the 5-oxo function. The ^{1}H-NMR spectra[4]) show the following characteristic signals: AcO at 1.68 and 1.80 ppm, respectively, 1 Me–C=C bond at 1.59 and 1.44 ppm, respectively, and 1 olefinic proton at 5.37 and 5.01 ppm, respectively. In the ^{13}C-NMR spectra, Me(19) of **10** resonates at 19.3 ppm and that of **11** at 13.6 ppm. The upfield shift of the C(19) resonance of **11**, due to the γ-*cis* effect (*cis*-C(2)–C(1)=C(10)–C(19)) [6], exists only in the (*E*)-isomer (conformation **C**, *Fig. 1*), as a result of the shielding interaction of the H_β–C(2) bond with the Me(19) group. This establishes the (*E*)-configuration of **11** and therefore the (*Z*)-configuration of **10**.

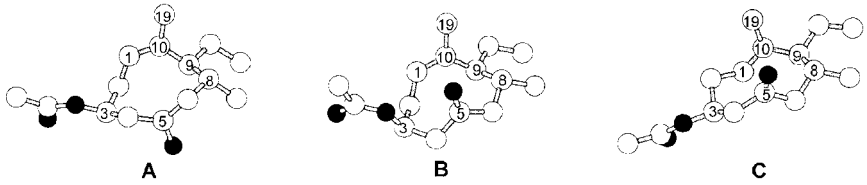


Fig. 1. *Conformations* **A** *and* **B** *of* **10** *and conformation* **C** *of* **11**

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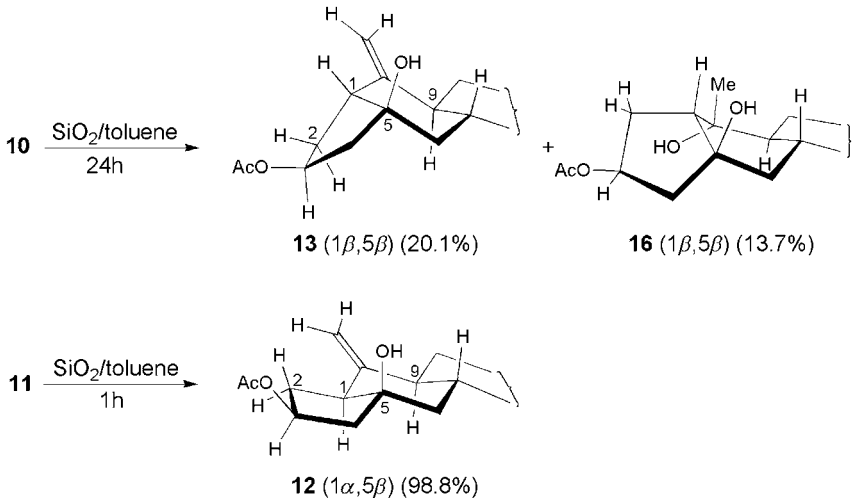
[3]) Results of the crystallographic and conformational analyses (in solution) of **10** and **11** will be presented and discussed in detail in a subsequent publication.

[4]) The ^{1}H- and ^{13}C-NMR spectra of **10** and **11** were recorded in C_6D_6 solution because of instability of the (*E*)-seco ketone **11** in $CDCl_3$.

In addition, conformations of the nine-membered ring of **10** and **11** in solution were deduced from the ^{1}H- and ^{13}C-NMR spectral analysis[3]). The results showed that the (*Z*)-stereoisomer **10** and its 3*β*-OH derivative **10a** exist in solution in two conformations (*Fig. 1*), the major conformer **A** and the minor conformer **B**, while (*E*)-isomer **11** and the corresponding 3*β*-alcohol **11a** are present in solution in only one conformation (**C**).

Compounds **12**, **13**, and **16** (for data, see *Exper. Part*) are the secondary products formed by intramolecular cyclization of the (*Z*)- and (*E*)-seco ketones **10** and **11**, respectively[5]). Thus, upon stirring in the presence of SiO_2 in toluene solution at room temperature, the (*Z*)-isomer **10** afforded, after 24 h, the cyclization products **13** and **16** in 20.1 and 13.7% yield (besides recovered starting material), while the (*E*)-isomer **11** was transformed, after 1 h, to the cyclization product **12** in almost quantitative yield (*Scheme 6*)[2]). The configurations of **12** and **13** were deduced from their ^{13}C-NMR data.

Scheme 6



The C(9) resonance of **13** (41.7 ppm) is shifted upfield with respect to the C(9) resonance of **12** (48.3 ppm) as the result of the *γ*-gauche effect due to the H_α–C(2) bond. This interaction exists only in the (1*β*,5*β*)-isomer, indicating the *cis*-(1*β*,5*β*)-configuration for **13**. On the other hand, the difference of the chemical shifts for C(2) of **12** and **13** (31.7 ppm for **12** and 37.0 ppm for **13**) can be attributed to the shielding effect by the HO–C(5) group, which is present only in the (1*α*,5*β*)-isomer. This establishes the *trans*-(1*α*,5*β*)-configuration for **12**.

Acetal structures for compounds **14** and **15** were determined on the basis of spectral characteristics (see *Exper. Part*). However, the (5*R*,10*R*)-configuration for **14** and the (5*S*,10*S*)-configuration for **15**[6]) were deduced from their ^{13}C-NMR data. Also, the

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[5]) Intramolecular cyclization of the (*Z*)- and (*E*)-1(10)-unsaturated 5,10-seco ketones **10** and **11** is initiated by protonation of the 5-oxo group and proceeds with participation by the *π*-electrons of the C(1)=C(10) bond. The mutual neighborhood of the reacting groups in the (*E*)-isomer **11** (*Fig. 1*, conformation **C**) favors this transannular process. For mechanistic and stereochemical aspects of the reaction, see [1][2].

[6]) The other two possible stereoisomers with the (5*R*,10*S*)- and the (5*S*,10*R*)-configuration, respectively, are too strained to exist as stable compounds.

proposed (5*S*,10*S*)-structure of **15** was unequivocally confirmed by X-ray analysis (see below).

The chemical shift of C(1) of acetal **15** appears at a much higher field (28.9 ppm) than the corresponding chemical shift of acetal **14** (40.9 ppm). In the (5*S*,10*S*)-isomer **15** (*Fig. 2*), the two γ-effects due to the H_β–C(8) and H_β–C(11) bonds [7] can cause an overall upfield shift of the C(1) signal of 12 ppm relative to the value found for the isomer **14**, where these effects are inexistent.

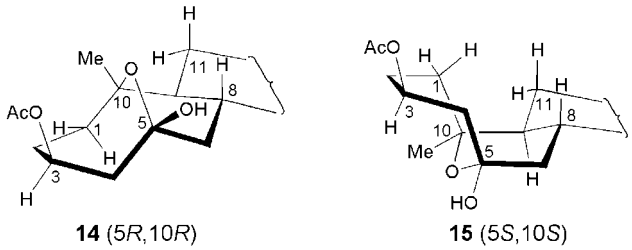
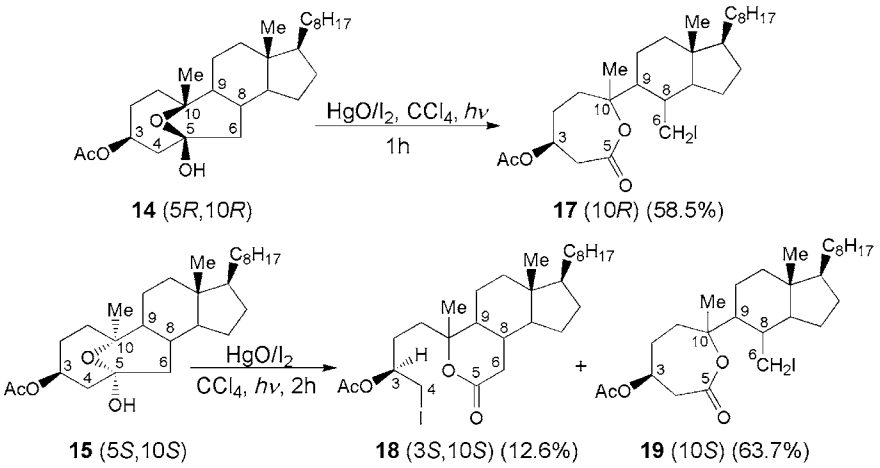


Fig. 2. *Structures of* **14** *and* **15**

In the course of the HgO/I_2 oxidation of **8**, it was observed (by TLC) that acetals **14** and **15** were also consumed by reacting with the oxidant. Since the thereby formed compounds could not be separated by chromatographic methods, in an attempt to obtain pure samples of these products for their identification, the acetals **14** and **15** were treated with the HgO/I_2 reagent under conditions similar to those applied to alcohol **8** (*Scheme 7*)[2]).

Scheme 7



Thus, HgO/I_2 reaction of acetals **14** and **15**, respectively, consisted in the oxidative fragmentation of their C(5)–C(6) bond to give the corresponding 6-iodo-5,6-secolactones **17** (from **14**, 58.5%) and **19** (from **15**, 63.7%), while oxidation of acetal **15** involved, in addition, the competing fragmentation of the C(4)–C(5) bond, affording as the minor component the 4-iodo-4,5-secolactone **18** (12.6%). Spectral data

obtained for compounds **17**–**19** were in complete agreement with the proposed structures. Also, since the oxidative fragmentations of the acetals **14** and **15** took place without change of configuration at the stereogenic centers, the obtained lactones have the (10*R*)-, (3*S*,10*S*)- and (10*S*)-configurations, respectively.

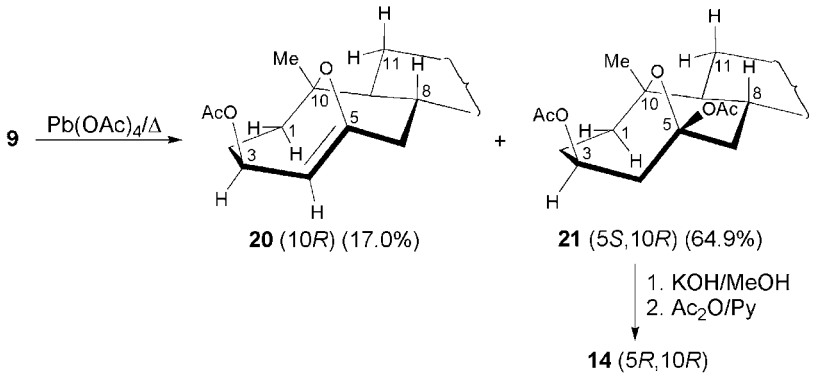
Differentiation between the 5,6-seco lactones **17** and **19** on one hand and the structurally different 4,5-seco lactone **18** on the other was possible from their ^{1}H-NMR spectral characteristics.

Appearance of two *dd* at 3.31 and 3.95 ppm for **17** and at 3.37 and 3.73 ppm for **19** indicates the presence of the iodomethylene (ICH_2(6)) group [8], while in **18**, a *m* at 3.30 ppm (2 H) suggests the presence of a CH_2 group situated between the I-atom and the AcO function.

3. Oxidations of 5β-Hydroxy-*B*-norcholestan-3β-yl Acetate (**9**). – 3.1. *Thermal $Pb(OAc)_4$ Oxidation*. The thermal $Pb(OAc)_4$ oxidation of **9** was carried out with an excess of oxidant (50%) in the presence of $CaCO_3$ in boiling benzene for 22 h, when practically all starting material was consumed. Column chromatography (SiO_2) of the resulting mixture afforded only two products (*Scheme 8*)[2]): the transannular (10*R*)-enol ether **20** (17.0%) and the (5*S*,10*R*)-acetal 5-acetate **21**[7]) (64.9%). Acetal 5-acetate **21** was identified by correlation with the (5*R*,10*R*)-acetal **14**. Saponification of **21** with 1% KOH/MeOH at room temperature and subsequent acetylation of the obtained 3β,5α-diol with Ac_2O/pyridine yielded **14** of the known structure[7]).

In the IR spectrum of **20**, the 5β-hydroxyl band is missing, instead, new absorptions for an ether bond at 1028 cm^{-1} and an olefinic C=C bond at 1669 cm^{-1} are observed. The ^{1}H-NMR spectrum shows a *s* for Me(19) at 1.25 ppm and a *fd* for 1 olefinic proton at 5.31 ppm. This indicates a transannular 5,10-enol ether structure for compound **20**. The (10*R*)-configuration was deduced from the ^{13}C-NMR spectrum: the chemical shift of C(1) at 38.0 ppm is very similar to the value (of *ca.* 40 ppm) observed for the (5*R*,10*R*)-acetal **14** and also the (5*S*,10*R*)-acetal 5-acetate **21**, which possess the β-oriented epoxy bridge[8]).

Scheme 8



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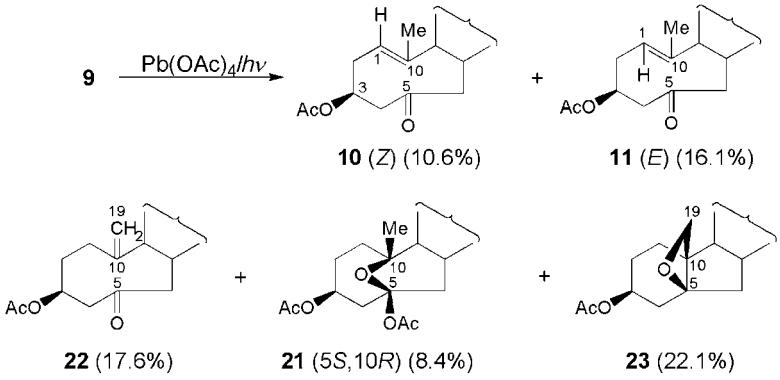
[7]) Different assignment of the configuration at C(5) of **21** (5*S*) with respect to the configuration of C(5) in acetal **14** (5*R*) is only formally arising from the differencies in *CIP* priority of the groups attached at C(5) in these two compounds.

[8]) The configurational dependence of chemical shifts of C(1) in ^{13}C-NMR spectra for stereoisomeric (5*R*,10*R*)- and (5*S*,10*S*)-acetals is discussed above (see **14** *vs.* **15**).

3.2. *Photolytic $Pb(OAc)_4$ Oxidation*. The photolytic $Pb(OAc)_4$ oxidation of **9** was carried out in benzene solution with 3 mol-equiv. of oxidant in the presence of $CaCO_3$ by irradiation with a high-pressure mercury lamp (*Q81*) at room temperature for 5 h. Analysis of products separated by column chromatography (SiO_2) revealed that, under photolytic conditions, the following compounds were formed (*Scheme 9*)[2]: the (*Z*)- and (*E*)-5,10-seco 1(10)-unsaturated ketones **10** and **11** (10.6 and 16.1%, resp.), their isomeric 5,10-seco 10(19)-unsaturated derivative **22** (17.6%), the (5*S*,10*R*)-acetal 5-acetate **21** (8.4%), and the 5β,19-epoxy derivative **23** (22.1%)[9].

Scheme 9



In the IR spectrum of **22**, the absorption of the 5β-hydroxy group is replaced by an absorption at 1707 cm^{-1} for the 5-oxo group, while the presence of an exocyclic methylidene group is evident from the absorptions at 3070 and 1639 cm^{-1}. In the ^{1}H-NMR spectrum, the *s* of Me(19) is replaced by a pair of *s* at 4.93 and 4.96 ppm, and in the ^{13}C-NMR spectrum, a *t* appears at 116.9 ppm. The ^{1}H-NMR spectrum of epoxy derivative **23** shows, instead of a *s* of Me(19), 2 *d* at 3.92 and 4.43 of the CH_2(19) group. The structure is confirmed by the IR absorptions at 1023 and 964 cm^{-1} for a four-membered ether and by the ^{13}C-NMR data (1 *s* at 93.8 ppm for C(5) and 1 *t* at 74.0 ppm for C(19)).

3.3. *$Pb(OAc)_4/I_2$ and HgO/I_2 Version of the Hypoiodite Reaction*. The $Pb(OAc)_4/I_2$ reaction [5] of **9** was carried out with a large excess of oxidant in cyclohexane solution by irradiation with a 800-W lamp at 60 V at room temperature for 1 h. Column chromatography (SiO_2) allowed the isolation of the known compounds **10**–**12**, **14**, and **15** in yields presented in *Scheme 10*[2]).

The HgO/I_2 version of the hypoiodite reaction of **9** was performed under experimental conditions similar to those applied to the 5α-hydroxy-*B*-nor derivative **8** (*Scheme 10*). Analysis of the reaction products **10**–**12**, **14**, and **15** separated by column chromatography (SiO_2) indicated that the HgO/I_2 oxidation of **9** took a similar course as that of the corresponding 5α-OH analogue **8** (see *Scheme 4*)[10]), and also as that of **9** with $Pb(OAc)_4/I_2$ (see *Scheme 10*).

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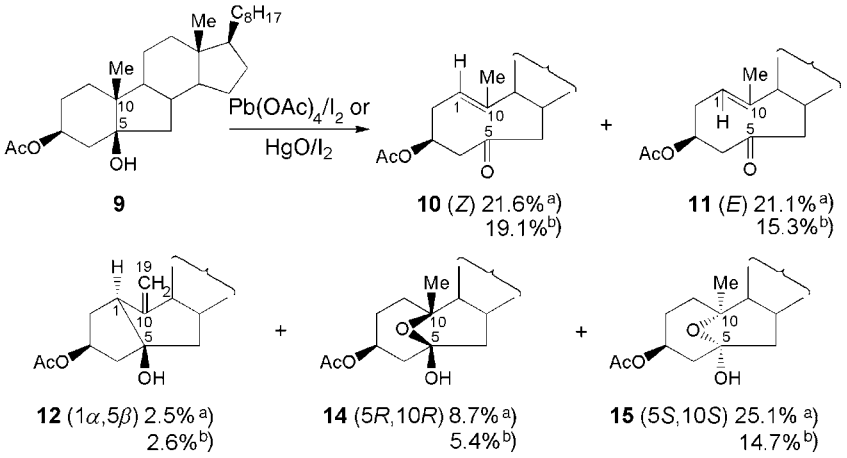
[9]) Preliminary experiments showed that epoxy derivative **23** is formed from **22** by transannular cycloaddition of the 5-oxo function to the methylene group induced by UV light.

[10]) In this reaction with **9**, the iodo derivatives **17**–**19** were also detected by TLC, but not isolated in pure form.

Scheme 10.



a) Oxidant $Pb(OAc)_4/I_2$. b) Oxidant HgO/I_2

4. X-Ray Crystal-Structure Analysis of Compound 15. – The structure deduced by spectroscopic means for compound **15** was confirmed by X-ray analysis (*Fig. 3*, *Table*). H-Atom positions were calculated with the assumption of normal geometry. Lists of fractional atomic coordinates, isotropic thermal parameters, and bond lengths and angles have been deposited at the *Cambridge Crystallographic Data Centre* as supplementary publication No. 188127.

5. Discussion. – The above results indicated that oxidations of the (5α)- and (5β)-*B*-nor alcohols **8** and **9** with the HgO/I_2 reagent and also oxidations of the (5β)-isomer **9**

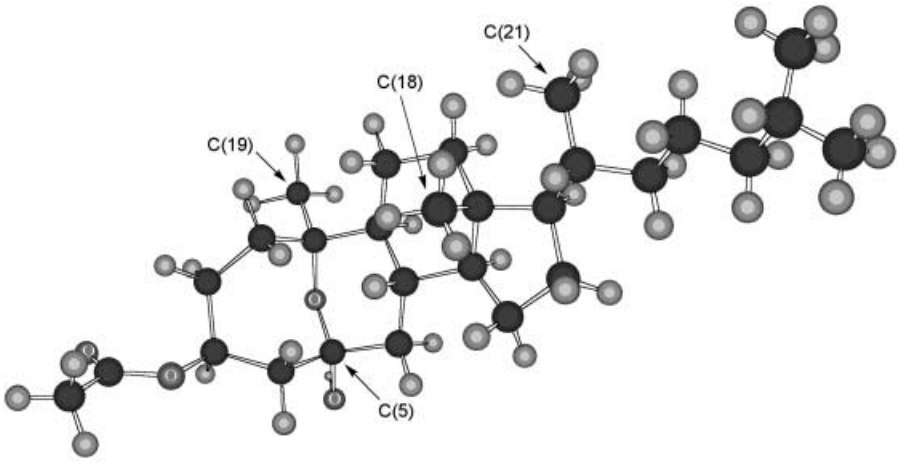


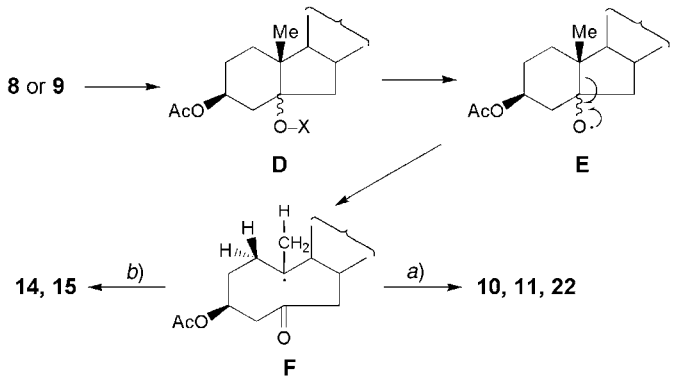
Fig. 3. *X-Ray crystal structure of* **15**

Table. *Crystal Data of Compound* **15**

Empirical formula	$C_{28}H_{48}O_4 \cdot ½\ CH_3OH$
M_r	464.68
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P21/c$
Unit cell dimensions	$a = 11.894(4)$ Å, $\alpha = 90°$
	$b = 11.414(4)$ Å, $\beta = 95.57°$
	$c = 21.059(7)$ Å, $\gamma = 90°$
Volume	2845.4(17) Å^3
Z	4
Density (calc.)	1.085 Mg/m^3
Absorption coefficient	0.071 mm^{-1}
F (000)	1028
Crystal size	$0.22 \times 0.16 \times 0.14$ mm
θ range for data collection	1.89–24.74°
Index ranges	$-13 \le h \le 13,\ -13 \le k \le 13,\ -24 \le l \le 24$
Reflections collected	20050
Independent reflections	8559 (R(int) = 0.067)
Refinement method	full-matrix least-squares on *Fsqd*
Data, restraints, parameters	8559, 47, 615
Goodness-of-fit on F^2	1.046
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0628$, $wR_2 = 0.1762$
R indices (all data)	$R_1 = 0.0769$, $wR_2 = 0.1900$
Absolute structure parameter	−0.3(12)
Extinction coefficient	0.049 (4)
Largest diff. peak and hole	0.348 and −0.223 e · Å^{-3}

by the $Pb(OAc)_4/h\nu$ and $Pb(OAc)_4/I_2$ methods proceed, as expected, *via* the C(10)-centered alkyl radical **F**. It is generated by homolysis of the O–X bond (X = I or $Pb(OAc)_3$) in the primarily formed species **D**, followed by β-fragmentation of the C(5)–C(10) bond in the alkoxy radical **E** thus obtained (*Scheme 11*). However, the fate of the nine-membered-ring C(10) radical **F** is considerably different from that of

Scheme 11



the corresponding ten-membered-ring analogue **ii** (results shown in *Scheme 1*) and also from the nine-membered-ring C(13) radical **iv** (see *Scheme 2*). In the present case, stabilization of the C(10) radical **F** proceeds by two independent reaction pathways: *a*) it takes place by elimination of $H_\alpha-$ or $H_\beta-C(1)$ to produce the stereoisomeric (*Z*)- and (*E*)-seco ketones **10** and **11**, or by elimination of a H-atom from the Me(19) group to give the 10(19)-unsaturated seco ketone **22**; or *b*) it involves a non-stereoselective attack of the O-atom of the 5-oxo group at C(10) to give finally the (5*R*,10*R*)-acetal **14** (the minor product with the β-oriented epoxy bridge) and the (5*S*,10*S*)-isomer **15** (the major product with the α-oriented epoxy bridge).

However, the thermal $Pb(OAc)_4$ oxidation of 5β-hydroxy-*B*-nor compound **9** (see *Scheme 8*) deviates from the above mechanistic scheme: *1*) in this reaction, the 5,10-seco ketones **10**, **11**, or **22** are not found among oxidation products, and *2*) the reaction results exclusively in the stereoselective formation of the 5,10-ethers with the β-oriented epoxy bridge[11]), *i.e.*, the (10*R*)-enol 5,10-ether **20** and the (5*S*,10*R*)-acetal 5-acetate **21**[12]). This indicates that the C(10) radical **F** does not participate in the thermal $Pb(OAc)_4$ oxidation of compound **9**[13]) and suggests that not only radicals but also various cationic species should be considered as possible intermediates in the above reaction[14]).

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Experimental Part

1. *General*. Column chromatography (CC): silica gel 0.04–0.063 mm; FC = flash chromatography. TLC: monitoring and separation of products with silica gel *G* (*Stahl*), detection with aq. 50% H_2SO_4 soln. M.p.: uncorrected. IR Spectra: *Perkin-Elmer 337* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian Gemini-200* (^1H at 200, ^{13}C at 50 MHz); $CDCl_3$ or C_6D_6 soln. at r.t.; $SiMe_4$ as internal standard; δ in ppm, *J* in Hz; *f:* 'fine structure' of signals. Mass spectra: *Finnigan MAT 8230*; ionization energy 70 eV; *m*/*z* (rel. intensity in %).

2. *Oxidation of* **8**: *Hypoiodite HgO Oxidation of (5α,3β)*-B-*Nor-5-cholestane-3,5-diol 3-Acetate* (**8**). A stirred suspension of **8** (500 mg, 1.157 mmol), yellow HgO (1.595 g, 7.36 mmol), and I_2 (2.13 g, 8.39 mmol) in anh. CCl_4 (50 ml) was irradiated with a 800-W *Osram-Halogen-Bellaphot* lamp (at 60 V) at r.t. for 3 h. The mixture was filtered, the filtrate was washed successively with aq. $Na_2S_2O_3$ soln., aq. $NaHCO_3$ soln., and H_2O, dried (Na_2SO_4), and evaporated, and the resulting mixture (605 mg) was separated by FC (SiO_2 (80 g), toluene/AcOEt 97:3 (→ **10**, **11**), 95:5 (→ **12**, **13**), 70:30 (→ **14**, **15**), 50:50 (→ **16**)): **10** (146 mg, 29.3%), **10**/**11** (10 mg, 2%), **12** (83 mg, 16.7%), **13** (12.4 mg, 2.5%), **14** (20.7 mg, 4.0%), **15** (89.2 mg, 17.2%), and **16** (33.2 mg, 6.4%).

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11) As mentioned above, oxidations of 5-hydroxy-*B*-nor compounds **8** and **9** with hypoiodite-forming reagents ($Pb(OAc)_4/I_2$ and/or HgO/I_2), which proceed by the intermediacy of the C(10) radical **F**, give the (5*R*,10*R*)-acetal **14** with the β-oriented epoxy bridge as the minor product.

12) *Rosenthal et al*. [9][10] obtained similar results upon oxidation of 6β-methyl-*B*-nor-5β-androstane-3β,5β,17β-triol 3,17-diacetate with $Pb(OAc)_4$ under thermal conditions. With this substrate, the corresponding enol 5,10-ether and the 5,10-acetal 5-acetate with β-epoxy bridge were also the only isolated reaction products.

13) *Rosenthal et al.* considered as possible mechanisms of the thermal $Pb(OAc)_4$ oxidation of the androstane *B*-nor-5β-hydroxysteroid a direct rearrangement of the alkoxy radical of type **E** to the corresponding epoxy derivatives by 1,2-migration of the 10-alkyl group [10].

14) This topic will be discussed in detail in a subsequent publication.

[1(10)Z,3β]-3-(Acetyloxy)-B-*nor-5,10-secocholest-1(10)-en-5-one* (**10**)[15]: M.p. 81–82° (from MeOH). $[\alpha]_D^{20} = +11.7$ ($c = 1.2$, $CHCl_3$). IR (KBr): 1740, 1704, 1236, 1029. ^{1}H-NMR (C_6D_6): 0.61 (*s*, Me(18)); 0.94 (*d*, Me(26), Me(27)); 0.96 (*d*, Me(21)); 1.59 (*s*, Me(19)); 1.68 (*s*, AcO); 2.20 (*dd*, $J = 4.7$, 13, H_β–C(4)); 2.57 (*t*, $J = 3.3$, H_β–C(2)); 5.37 (*fdd*, $J \approx 1$, 6, 11, H–C(1)); 5.65 (*m*, H–C(3)). ^{13}C-NMR (C_6D_6): 209.6 (*s*, C(5)); 169.3 (*s*, Me*C*OO); 143.3 (*s*, C(10)); 121.5 (*d*, C(1)); 72.7 (*d*, C(3)); 56.7 (*d*, C(17)); 53.2 (*d*, C(14)); 48.5 (*t*, C(4)); 44.2 (*t*, C(6)); 43.7 (*d*, C(9)); 43.0 (*s*, C(13)); 39.9 (*t*, C(24)); 39.5 (*t*, C(12)); 39.4 (*d*, C(8)); 36.5 (*t*, C(22)); 36.1 (*d*, C(20)); 30.3 (*t*, C(2)); 28.3 (*d*, C(25)); 28.1 (*t*, C(16)); 26.5 (*t*, C(11)); 25.2 (*t*, C(15)); 24.3 (*t*, C(23)); 23.0 (*q*, C(27)); 22.7 (*q*, C(26)); 20.7 (*q*, *Me*COO); 19.3 (*q*, C(19)); 18.9 (*q*, C(21)); 11.8 (*q*, C(18)). CI-MS: 431 (23, $[M+1]^+$), 413 (100, $[M-18+1]^+$), 371 (46, $[M-60+1]^+$), 353 (70, $[M-18-60+1]^+$). Anal. calc. for $C_{28}H_{46}O_3$ (430.34): C 78.09, H 10.77; found: C 77.80, H 10.51.

*Separation of (*Z*)- and (*E*)-Seco Ketones* **10** and **11**. A stirred suspension of **8** (300 mg, 0.694 mmol), yellow HgO (957 mg, 4.42 mmol), and I_2 (1.278 g, 5.03 mmol) in anh. CCl_4 (25 ml) was irradiated with two 800-W *Osram-Halogen-Bellaphot* lamps (at 60 V) at r.t. for 1 h. The resulting mixture (370 mg), isolated after the usual workup, was dissolved in MeOH (50 ml) and hydrolyzed with 1% KOH/MeOH (10 ml). The resulting mixture was left at r.t. for 1 h, evaporated at r.t. to *ca.* 10 ml, diluted with H_2O, and extracted with Et_2O. The org. layer was washed with H_2O until neutral, dried (Na_2SO_4), and evaporated. The residue (310 mg) was subjected to FC (SiO_2 (6 g), toluene/AcOEt 96:4): **11a** (41.3 mg, 15.3%) and **10a** (82 mg, 30.4%).

[1(10)Z,3β]-3-Hydroxy-B-*nor-5,10-secocholest-1(10)-en-5-one* (**10a**): ^{1}H-NMR (C_6D_6; two nine-membered-ring conformations I/II 74:26): 0.63 (I), 0.73 (II) (parts of 2*s*, Me(18)); 1.64 (I), 1.69 (II) (parts of 2*s*, Me(19)); 4.39 (I), 4.14 (II) (parts of 2*m*, H–C(3)); 5.57 (I), 5.05 (II) (*dd*, *J* (I) = 5.3, 10.9, *J*(II) = 6.1, 11.5, H–C(1)).

*[1(10)*E*,3β]-3-Hydroxy*-B-*nor-5,10-secocholest-1(10)-en-5-one* (**11a**): ^{1}H-NMR (C_6D_6): 0.63 (*s*, Me(18)); 0.94 (*d*, Me(26), Me(27)); 0.97 (*d*, Me(21)); 1.53 (*s*, Me(19)); 2.68 (*dd*, $J = 10.3$, 14.3, H_β–C(2)); 4.29 (*fq*, $J = 7$, H–C(3)); 5.20 (*m*, H–C(1), OH). ^{13}C-NMR (C_6D_6): 212.0 (*s*, C(5)); 144.8 (*s*, C(10); 127.5 (*d*, C(1)); 76.0 (*d*, C(3)); 56.9 (*d*, C(9)); 56.7 (*d*, C(17)); 54.6 (*d*, C(14)); 48.8 (*t*, C(4)); 45.2 (*t*, C(6)); 43.3 (*s*, C(13)); 42.5 (*d*, C(8)); 39.9 (*t*, C(24)); 39.6 (*t*, C(12)); 36.5 (*t*, C(22)); 36.0 (*d*, C(20)); 35.0 (*t*, C(2)); 28.3 (*t*, C(16)); 28.2 (*d*, C(25)); 25.7 (*t*, C(15)); 25.0 (*t*, C(11)); 24.2 (*t*, C(23)); 22.9 (*q*, C(27)); 22.7 (*q*, C(26)); 18.9 (*q*, C(21)); 12.9 (*q*, C(19)); 12.1 (*q*, C(18)).

The (*Z*)-ketone **10a** (82 mg) was acetylated with Ac_2O/pyridine 1:1 (3.5 ml) for 3 h. Purification by FC (SiO_2, 1 g) gave **10** (88.1 mg, 97.0%), which was recrystallized from MeOH (yield: 68.2 mg, 75.1%).

The (*E*)-ketone **11a** (41.3 mg) was acetylated with Ac_2O/pyridine 1:1 (2 ml) for 8 h: **11** (40 mg, 87.4%). The crude material was purified by FC (SiO_2 (0.5 g), toluene/AcOEt 95:5) and recrystallized from MeOH (yield: 16 mg, 35.0%).

*[1(10)-*E*,3β]-3-Acetoxy*-B-*nor-5,10-secocholest-1(10)-en-5-one* (**11**): M.p. 116–118° (from MeOH). $[\alpha]_D^{20} = +33.8$ ($c = 1$, $CHCl_3$). IR (KBr): 1725, 1678, 1638, 1248, 1033. ^{1}H-NMR (C_6D_6): 0.67 (*s*, Me(18)); 0.94 (*d*, Me(26), Me(27)); 0.97 (*d*, Me(21)); 1.44 (*s*, Me(19)); 1.80 (*s*, AcO); 2.18 (*td*, $J = 5.6$, 16.2, H_α–C(2)); 2.44 (*d*, $J = 4.8$, H_α–C(4)); 2.57 (*dd*, $J = 7.8$, 13.6, H_β–C(4)); 5.01 (*dd*, $J = 4.7$, 10.9, H–C(1)); 5.15 (*fquint.* $J = 5.7$, 1.1, H–C(3)). ^{13}C-NMR (C_6D_6): 202.9 (*s*, C(5)); 169.9 (*s*, Me*C*OO); 145.1 (*s*, C(10)); 123.5 (*d*, C(1)); 74.4 (*d*, C(3)); 57.4 (*d*, C(9)); 56.9 (*d*, C(17)); 54.7 (*d*, C(14)); 47.2 (*t*, C(4)); 46.8 (*t*, C(6)); 43.5 (*s*, C(13)); 41.9 (*d*, C(8)); 39.9 (*t*, C(24)); 39.7 (*t*, C(12)); 36.5 (*t*, C(22)); 36.1 (*d*, C(20)); 31.8 (*t*, C(2)); 28.3 (*t*, C(16)); 28.2 (*d*, C(25)); 25.7 (*t*, C(15)); 25.1 (*t*, C(11)); 24.3 (*t*, C(23)); 22.9 (*q*, C(27)); 22.7 (*q*, C(26)); 20.9 (*q*, *Me*COO); 18.9 (*q*, C(21)); 13.6 (*q*, C(19)); 12.2 (*q*, C(18)). CI-MS: 431 (12, $[M+1]^+$). Anal. calc. for $C_{28}H_{46}O_3$ (430.34): C 78.09, H 10.77; found: C 78.42, H 11.04.

(1α,3β,5β)-5(10→1)Abeo-B-*norcholest-10(19)-ene-3,5-diol 3-Acetate* (**12**): Oil. $[\alpha]_D^{20} = +11.5$ ($c = 2.2$, $CHCl_3$). IR ($CHCl_3$): 3493, 3090, 3072, 1738, 1650, 1246, 892. ^{1}H-NMR ($CDCl_3$): 0.70 (*s*, Me(18)); 0.86 (*d*, Me(26), Me(27)); 0.92 (*d*, Me(21)); 2.06 (*s*, AcO); 4.71, 4.92 (2*s*, CH_2(19)); 5.24 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 171.0 (*s*, Me*C*OO); 149.4 (*s*, C(10)); 105.8 (*t*, C(19)); 79.0 (*s*, C(5)); 73.4 (*d*, C(3)); 56.1 (*d*, C(17)); 56.0 (*d*, C(14)); 53.2 (*d*, C(1)); 48.3 (*d*, C(9)); 45.3 (*t*, C(4)); 43.1 (*s*, C(13)); 41.0 (*t*, C(6)); 39.4 (*t*, C(24)); 39.4 (*t*, C(12)); 39.4 (*d*, C(8)); 36.0 (*t*, C(22)); 35.6 (*d*, (20)); 31.7 (*t*, C(2)); 28.1 (*t*, C(16)); 27.9 (*d*, C(25)); 24.4 (*t*, C(15)); 23.8 (*t*, C(23)); 23.7 (*t*, C(11)); 22.7 (*q*, C(27)); 22.4 (*q*, C(26)); 21.2 (*q*, *Me*COO); 18.5 (*q*, C(21); 12.1 (*q*, C(18)). CI-MS: 431 (6, $[M+1]^+$), 353 (100, $[M-18-60+1]^+$).

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[15]) (*Z*)-Seco ketone **10** exists in solution in two conformations **A** and **B** (see *Fig. 1*); **A**/**B** *ca.* 85:15. The given ^{1}H- and ^{13}C-NMR data refer to the main conformation.

(1β,3β,5β)-5(10 → 1)Abeo-B-*norcholest-10(19)-ene-3,5-diol 3-Acetate* (**13**): Oil. $[\alpha]_D^{20} = -1.2$ ($c = 2.0$, $CHCl_3$). IR ($CHCl_3$): 3452, 3083, 1738, 1641, 1247, 893. ^{1}H-NMR ($CDCl_3$): 0.68 (*s*, Me(18)); 0.86 (*d*, Me(26), Me(27)); 0.92 (*d*, Me(21)); 2.04 (*s*, AcO); 2.84 (*dd*, $J = 9, 12$, H−C(1)); 4.80, 4.88 (2*s*, CH_2(19)); 5.07 (*fq*, $J \approx 7$, H−C(3)). ^{13}C-NMR ($CDCl_3$): 170.8 (*s*, Me*C*OO); 149.1 (*s*, C(10)); 109.3 (*t*, C(19)); 79.6 (*s*, C(5)); 72.7 (*d*, C(3)); 56.1 (*d*, C(17)); 55.9 (*d*, C(14)); 54.0 (*d*, C(1)); 47.5 (*s*, C(13)); 43.0 (*t*, C(4)); 41.7 (*d*, C(9)); 40.2 (*t*, C(6)); 39.4 (*t*, C(12)); 39.3 (*t*, C(24)); 38.2 (*d*, C(8)); 37.0 (*t*, C(2)); 36.1 (*t*, C(22)); 35.7 (*d*, C(20)); 28.2 (*t*, C(16)); 27.9 (*d*, C(25)); 24.4 (*t*, C(15)); 23.9 (*t*, C(11)); 23.8 (*t*, C(23)); 22.8 (*q*, C(27)); 22.5 (*q*, C(26)); 21.2 (*q*, *Me*COO); 18.6 (*q*, C(21)); 12.0 (*q*, C(18)). CI-MS: 431 (2, $[M+1]^+$), 353 (100, $[M-18-60+1]^+$).

*(3β,5*R*,10*R*)-5,10-Epoxy*-B-*nor-5,10-secocholestane-3,5-diol 3-Acetate* (**14**): Oil. $[\alpha]_D^{20} = +1.1$ ($c = 1.7$, $CHCl_3$). IR ($CHCl_3$): 3425, 1735, 1367, 1246, 757. ^{1}H-NMR ($CDCl_3$): 0.70 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.90 (*d*, Me(21)); 1.15 (*s*, Me(19)); 2.07 (*s*, AcO); 5.01 (*m*, H−C(3)). ^{13}C-NMR ($CDCl_3$): 170.3 (*s*, Me*C*OO); 97.0 (*s*, C(5)); 76.0 (*s*, C(10)); 72.3 (*d*, C(3)); 56.3 (*d*, C(17)); 56.0 (*d*, C(14)); 48.7 (*d*, C(9)); 47.4 (*t*, C(4)); 42.7 (*s*, C(13)); 40.9 (*t*, C(1)); 39.7 (*t*, C(12)); 39.4 (*t*, C(24)); 39.3 (*t*, C(6)); 36.1 (*t*, C(22)); 35.7 (*d*, C(20)); 31.6 (*d*, C(8)); 28.8 (*t*, C(2)); 28.1 (*t*, C(16)); 27.9 (*d*, C(25)); 25.8 (*q*, C(19)); 23.8 (3*t*, C(11), C(15), C(23)); 22.8 (*q*, C(27)); 22.5 (*q*, C(26)); 21.4 (*q*, *Me*COO), 18.6 (*q*, C(21)); 12.1 (*q*, C(18)). MS: 448 (7, M^+), 388 (40, $[M-60]^+$), 135 (100%).

*(3β,5*S*,10*S*)-5,10-Epoxy*-B-*nor-5,10-secocholestane-3,5-diol 3-Acetate* (**15**): M.p. 112–113° (from acetone/MeOH). $[\alpha]_D^{20} = +29.5$ ($c = 1.5$, $CHCl_3$). IR (KBr): 3422, 1734, 1367, 1250, 757. ^{1}H-NMR ($CDCl_3$): 0.72 (*s*, Me(18)); 0.86 (*d*, Me(26), Me(27)); 0.90 (*d*, Me(21)); 1.15 (*s*, Me(19)); 2.01 (*s*, AcO); 2.39 (*m*, CH_2(6)); 3.26 (br. *s*, OH); 5.29 (*m*, H−C(3)). ^{13}C-NMR ($CDCl_3$): 170.4 (*s*, Me*C*OO), 95.8 (*s*, C(5)); 77.1 (*s*, C(10)); 69.1 (*d*, C(3)); 56.2 (*d*, C(17)); 54.9 (*d*, C(14)); 51.3 (*d*, C(9)); 42.8 (*t*, C(4)); 42.3 (*s*, C(13)); 39.6 (*t*, C(12)); 39.4 (*t*, C(24)); 39.4 (*t*, C(6)); 36.0 (*t*, C(22)); 35.6 (*d*, C(20)); 32.8 (*d*, C(8)); 28.9 (*t*, C(1)); 28.1 (*t*, C(16)); 27.9 (*d*, C(25)); 27.9 (*t*, C(2)); 26.9 (*q*, C(19)); 23.7 (*t*, C(23)); 23.6 (*t*, C(15)); 22.7 (*q*, C(27)); 22.6 (*t*, C(11)); 22.5 (*q*, C(26)); 21.3 (*q*, *Me*COO), 18.6 (*q*, C(21)); 12.1 (*q*, C(18)). MS: 448 (4, M^+), 388 (59, $[M-60]^+$), 371 (10, $[M-60-17]^+$). Anal. calc. for $C_{28}H_{48}O_4$ (448.36): C 74.95, H 10.78; found: C 75.01, H 11.01.

*(1β,3β,5β,10*R*)-5(10 → 1)Abeo*-B-*norcholestane-3,5,10-triol 3-Acetate* (**16**): Oil. $[\alpha]_D^{20} = +23.7$ ($c = 1.2$, $CHCl_3$). IR ($CHCl_3$): 3441, 1718, 1260. ^{1}H-NMR ($CDCl_3$): 0.69 (*s*, Me(18)); 0.86 (*d*, Me(26), Me(27)); 0.91 (*d*, Me(21)); 1.38 (*s*, Me(19)); 2.02 (*s*, AcO); 5.0 (*dq*, $J = 2, 7$, H−C(3)). ^{13}C-NMR ($CDCl_3$): 170.8 (*s*, Me*C*OO); 78.8 (*s*, C(5)); 73.1 (*s*, C(10)); 71.3 (*d*, C(3)); 56.0 (*d*, C(17)); 55.8 (*d*, C(14)); 55.1 (*d*, C(1)); 49.6 (*t*, C(4)); 46.4 (*d*, C(9)); 42.6 (*s*, C(13)); 40.3 (*t*, C(6)); 39.4 (*t*, C(24)); 39.4 (*t*, C(12)); 36.0 (*t*, C(22)); 35.7 (*d*, C(20)); 33.8 (*d*, C(8)); 32.9 (*t*, C(2)); 28.1 (*t*, C(16)); 27.9 (*d*, C(25)); 24.9 (*q*, C(19)); 24.1 (*t*, C(15)); 23.8 (*t*, C(23)); 22.7 (*q*, C(27)); 22.5 (*q*, C(26)); 21.2 (*q*, *Me*COO); 20.5 (*t*, C(11)); 18.6 (*q*, C(21)); 12.0 (*q*, C(18)). CI-MS: 431 ($[M-18+1]^+$), 371 (100, $[M-60-18+1]^+$).

Treatment of **10** *with SiO_2 in Toluene.* A mixture of **10** (100 mg) and SiO_2 (3 g) in toluene (10 ml) was stirred for 24 h at r.t. Workup gave a mixture (95 mg), which was separated by CC (SiO_2 (10 g), toluene/AcOEt 97:3 → 70:30): starting material **10** (52 mg, 52.0%), **13** (20.1 mg, 20.1%), and **16** (14.3 mg, 13.7%).

Treatment of **11** *with SiO_2 in Toluene.* A mixture of **11** (10 mg) and SiO_2 (300 mg) in toluene (1 ml) was stirred for 30 min at r.t. Silica gel was removed by filtration and washed several times with toluene. The filtrates were combined and evaporated. The residue was chromatographed (SiO_2 (1 g), toluene/AcOEt 95:5): **12** (9.9 mg, 98.8%).

*Hypoiodite HgO Oxidation of (5*R*,10*R*)-Acetal* **14**. A stirred suspension of **14** (100 mg, 0.22 mmol), yellow HgO (319 mg, 1.47 mmol), and I_2 (425 mg, 1.67 mmol) in CCl_4 (60 ml) was irradiated with a 800-W *Osram-Halogen-Bellaphot* lamp (at 60 V) at r.t. for 1 h. The resulting mixture (115 mg), isolated after the usual workup, was separated by FC (SiO_2 (20 g), toluene/AcOEt 85:15): **17** (75 mg, 58.5%), and starting material **14** (10 mg, 10%).

*(4*S*,7*R*)-4-(Acetyloxy)-7-[(1*R*,3a*S*,4*S*,5*S*,7a*R*)-1-[(1*R*)-1,5-dimethylhexyl]octahydro-4-(iodomethyl)-7a-methyl-1*H*-inden-5-yl]-7-methyloxepan-2-one* (**17**): Oil. $[\alpha]_D^{20} = +11.9$ ($c = 0.7$, $CHCl_3$). IR (neat): 1737, 1235, 1147, 1033. ^{1}H-NMR ($CDCl_3$)[16]: 0.75 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.93 (*d*, Me(21)); 1.39 (*s*, Me(19)); 2.07 (*s*, AcO); 3.24 (*m*, H_α−C(4)); 3.31 (*dd*, $J = 2.4$, 9.6, H−C(6)); 3.95 (*dd*, $J = 2.0$, 9.8, H−C(6)); 5.18 (*m*, H−C(3)). ^{13}C-NMR ($CDCl_3$)[16]: 170.2 (*s*, C(5)); 169.9 (*s*, Me*C*OO); 86.8 (*s*, C(10)); 66.3 (*d*, C(3)); 56.0 (*d*, C(17)); 54.3 (*d*, C(14)); 43.2 (*d*, C(9)); 43.0 (*t*, C(4)); 41.8 (*s*, C(13)); 39.4 (*t*, C(24)); 39.1 (*t*, C(12)); 36.7 (*d*, C(8)); 35.9 (*t*, C(22)); 35.6 (*d*, C(20)); 33.8 (*t*, C(1)); 28.0 (*t*, C(16)); 28.0 (*d*, C(25)); 27.5 (*t*, C(2)); 24.8 (*q*, C(19)); 24.7 (*t*, C(15)); 23.7 (*t*, C(23)); 23.4 (*t*, C(11)); 22.8 (*q*, C(27)); 22.5 (*q*, C(26)); 21.1 (*q*, *Me*COO);

[16]) Steroid numbering.

20.1 (*t*, C(6)); 18.5 (*q*, C(21)); 12.8 (*q*, C(18)). CI-MS: 575 (100, $[M+1]^+$), 515 (68, $[M-60+1]^+$), 447 ($[M-128+1]^+$), 387 ($[M-60-128+1]^+$).

*Hypoiodite HgO Oxidation of (5*S*,10*S*)-Acetal* **15**. As described for **17**, with **15** (180 mg, 0.40 mmol), HgO (574 mg, 2.65 mmol), I_2 (765 mg, 3.01 mmol), and CCl_4 (60 ml) (for 2 h). The residue (206 mg) was separated by FC (SiO_2 (30 g), toluene/AcOEt 90:10): **18** (29 mg, 12.6%) and **19** (147 mg, 63.7%).

*(4*S*,4a*S*,6a*R*,7*R*,9a*S*,9b*S*)-4-[(3*S*)-3-(Acetyloxy)-4-iodobutyl]-7-[(1*R*)-1,5-dimethylhexyl]-4,4a,5,6,6a,7,8,9,-9a,9b-decahydro-4,6a-dimethylcyclopenta[f][2]benzopyran-2(1*H*)-one* (**18**): Oil. $[\alpha]_D^{20} = -9.6$ ($c = 1.0$, $CHCl_3$). IR (neat): 1737, 1239, 1024. ^{1}H-NMR ($CDCl_3$)[16]): 0.70 (*s*, Me(18)); 0.89 (*d*, Me(26), Me(27)); 0.95 (*d*, Me(21)); 1.39 (*s*, Me(19)); 2.10 (*s*, AcO); 2.60 (*dd*, $J = 4.9$, 17.3, H_β–C(6)); 3.30 (*m*, CH_2(4)); 4.72 (*quint.*, $J = 5.4$, H–C(3)). ^{13}C-NMR ($CDCl_3$)[16]): 170.8 (*s*, C(5)); 170.4 (*s*, Me*C*OO); 86.3 (*s*, C(10)); 72.5 (*d*, C(3)); 55.9 (*d*, C(17)); 55.8 (d, C(14)); 49.3 (*d*, C(9)); 42.5 (*s*, C(13)); 39.4 (*t*, C(24)); 39.1 (*t*, C(12)); 36.0 (*t*, C(22)); 35.6 (*t*, C(6)); 35.6 (*d*, C(20)); 31.6 (*t*, C(1)); 30.8 (*d*, C(8)); 28.1 (*t*, C(2)); 27.9 (*t*, C(16)); 27.9 (*d*, C(25)); 26.2 (*q*, C(19)); 23.7 (*t*, C(23)); 23.4 (*t*, C(15)); 22.8 (*t*, C(11)); 22.7 (*q*, C(27)); 22.5 (*q*, C(26)); 21.0 (*q*, *Me*COO); 18.6 (*q*, C(21)); 12.5 (*q*, C(18)); 7.5 (*t*, C(4)). CI-MS: 575 (100, $[M+1]^+$).

*(4*S*,7*S*)-4-(Acetyloxy)-7-[(1*R*,3a*S*,4*S*,5*S*,7a*R*)-1-[(1*R*)-1,5-dimethylhexyl]octahydro-4-(iodomethyl)-7a-methyl- 1*H*-inden-5-yl]-7-methyloxepan-2-one* (**19**): Oil. $[\alpha]_D^{20} = +20.5$ ($c = 1.6$, $CHCl_3$). IR (neat): 1750, 1720, 1246, 1153, 1022. ^{1}H-NMR ($CDCl_3$)[16]): 0.72 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.90 (*d*, Me(21)); 1.46 (*s*, Me(19)); 2.07 (*s*, AcO); 2.88 (*dd*, $J = 2.1$, 15.3, H_β–C(4)); 3.13 (*fdd*, $J = 5.3$, 15.3, H_α–C(4)); 3.37 (*dd*, $J = 2.4$, 9.8, H–C(6)); 3.73 (*dd*, $J = 2.2$, 9.8, H–C(6)); 5.17 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$)[16]): 169.9 (*s*, C(5)); 169.3 (*s*, Me*C*OO); 86.1 (*s*, C(10)); 66.4 (*d*, C(3)); 55.9 (*d*, C(17)); 54.3 (*d*, C(14)); 49.6 (*d*, C(9)); 42.0 (*t*, C(4)); 41.7 (*s*, C(13)); 39.4 (*t*, C(24)); 39.0 (*t*, C(12)); 36.3 (*d*, C(8)); 35.9 (*t*, C(22)); 35.6 (*d*, C(20)); 27.9 (*d*, C(25)); 27.9 (*t*, C(16)); 27.6 (2*t*, C(1), C(2)); 24.0 (*q*, C(19)); 23.7 (2*t*, C(15), C(23)); 23.7 (*t*, C(11)); 22.8 (*q*, C(27)); 22.5 (*q*, C(26)); 21.1 (*q*, *Me*COO); 18.5 (*q*, C(21)); 17.9 (*t*, C(6)); 12.7 (*q*, C(18)). CI-MS: 575 (67, $[M+1]^+$), 515 (100, $[M-60+1]^+$), 447 ($[M-128+1]^+$), 387 ($[M-60-128+1]^+$).

3. *Oxidations of* **9**. 3.1. *Thermal Pb(OAc)$_4$ Oxidation of (3β,5β)*-B-*Norcholestane-3,5-diol 3-Acetate* (**9**). A suspension of **9** (200 mg, 0.463 mmol), $Pb(OAc)_4$ (307.8 mg, 0.694 mmol), and $CaCO_3$ (69.5 mg, 0.694 mmol) in dry benzene (25 ml) was heated under reflux with stirring for 22 h (monitoring by the starch/KI test). The mixture was diluted with Et_2O and filtered through a *Celite* pad, and the insoluble precipitate was thoroughly washed with Et_2O. The combined filtrate was washed with H_2O, sat. aq. $NaHCO_3$ soln. and H_2O, dried (Na_2SO_4), and evaporated and the residue (240 mg) separated by FC (SiO_2 (25 g), toluene/AcOEt 95:5): **20** (34 mg, 17.0%) and **21** (148 mg, 64.9%).

*(3β,10*R*)-5,10-Epoxy*-B-*nor-5,10-secocholest-4-en-3-ol Acetate* (**20**): Oil. $[\alpha]_D^{20} + 32.8$ ($c = 1.4$, $CHCl_3$). IR (neat): 1737, 1669, 1242, 1028. ^{1}H-NMR ($CDCl_3$): 0.72 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.91 (*d*, Me(21)); 1.25 (*s*, Me(19)); 2.06 (*s*, AcO); 2.61 (*dd*, $J = 6.9$, 13.5, H_α–C(6)); 4.86 (*fq*, $J = 6$, H–C(3)); 5.31 (*fd*, $J = 2.5$, H–C(4)). ^{13}C-NMR ($CDCl_3$): 170.7 (*s*, Me*C*OO); 151.2 (*s*, C(5)); 118.2 (*d*, C(4)); 81.0 (*s*, C(10)); 73.4 (*d*, C(3)); 56.1 (*d*, C(17)); 55.9 (*d*, C(14)); 53.4 (*d*, C(9)); 42.7 (*s*, C(13)); 39.8 (*t*, C(6)); 39.6 (*t*, C(12)); 39.4 (*t*, C(24)); 38.0 (*t*, C(1)); 36.1 (*t*, C(22)); 36.0 (*d*, C(8)); 35.7 (*d*, C(20)); 28.1 (*t*, C(16)); 28.0 (*d*, C(25)); 27.6 (*t*, C(2)); 24.2 (*t*, C(15)); 24.1 (*t*, C(11)); 23.8 (*t*, C(23)); 23.6 (*q*, C(19)); 22.8 (*q*, C(27)); 22.5 (*q*, C(26)); 21.3 (*q*, *Me*COO); 18.7 (*q*, C(21)); 11.8 (*q*, C(18)). CI-MS: 431 (73, $[M+1]^+$), 371 (100, $[M-60+1]^+$).

*(3β,5*S*,10*R*)-5,10-Epoxy*-B-*nor-5,10-secocholestane-3,5-diol Diacetate* (**21**): Oil. $[\alpha]_D^{20} = -28.9$ ($c = 1.7$, $CHCl_3$). IR (neat): 1737, 1240, 1053, 1015. ^{1}H-NMR ($CDCl_3$): 0.69 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.90 (*d*, Me(21)); 1.22 (*s*, Me(19)); 2.02 (*s*, AcO); 2.05 (*s*, AcO); 2.39 (*dd*, $J = 2.8$, 14.8, H_β–C(6)); 2.63 (*dd*, $J = 8.2$, 14.8, H_α–C(6)); 4.98 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 170.5 (*s*, Me*C*OO–C(3)); 168.9 (*s*, Me*C*OO–C(5)); 105.4 (*s*, C(5)); 78.0 (*s*, C(10)); 70.8 (*d*, C(3)); 56.2 (*d*, C(17)); 55.8 (*d*, C(14)); 46.8 (*d*, C(9)); 44.9 (*t*, C(4)); 42.6 (*s*, C(13)); 39.9 (*t*, C(1)); 39.4 (2*t*, C(12), C(24)); 37.8 (*t*, C(6)); 36.0 (*t*, C(22)); 35.6 (*d*, C(20)); 31.1 (*d*, C(8)); 29.3 (*t*, C(2)); 28.0 (*t*, C(16)); 27.9 (*d*, C(25)); 25.8 (*q*, C(19)); 23.7 (2*t*, C(15), C(23)); 23.5 (*t*, C(11)); 22.7 (*q*, C(27)); 22.4 (*q*, C(26)); 22.4 (*q*, *Me*COO–C(5)); 21.3 (*q*, *Me*COO–C(3)); 18.5 (*q*, C(21)); 11.9 (*q*, C(18)). CI-MS: 491 (3, $[M+1]^+$), 431 (14, $[M-60+1]^+$), 371 (100, $[M-2\times60+1]^+$).

3.2. *Photolytic Pb(OAc)$_4$ Oxidation of* **9**. To a soln. of **9** (400 mg, 0.926 mmol) in anh. benzene (80 ml), $Pb(OAc)_4$ (1.23 g, 2.775 mmol) and $CaCO_3$ (0.278 g) were added. The vigorously stirred mixture was irradiated with a high-pressure Hg lamp *Q81 Hanau* at r.t. for 5 h (monitoring by the starch/KI test). The mixture was worked up as above, leaving a mixture (495 mg), which was separated by FC (SiO_2 (90 g), toluene/AcOEt 95:5): **10** (42 mg, 10.6%), **11** (64 mg, 16.1%), **22** (70 mg, 17.6%), **21** (38 mg, 8.4%), and **23** (88 mg, 22.1%).

(3β)-3-(Acetyloxy)-B-*nor-5,10-secocholest-10(19)-en-5-one* (**22**): Oil. $[\alpha]_D^{20} = +34.8$ ($c = 1.1$, $CHCl_3$). IR (neat): 3070, 1739, 1707, 1639, 1241, 1025. ^{1}H-NMR ($CDCl_3$): 0.79 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.91 (*d*, Me(21)); 2.03 (*s*, AcO); 2.99 (*dd*, $J = 10.3$, 13.5, H_β–C(4)); 4.93, 4.96 (2*s*, CH_2(19)); 5.20 (*m*, H–C(3)).

^{13}C-NMR ($CDCl_3$): 210.3 (*s*, C(5)); 170.0 (*s*, Me*C*OO); 148.8 (*s*, C(10)); 116.9 (*t*, C(19)); 71.9 (*d*, C(3)); 56.3 (*d*, C(17)); 54.7 (*d*, C(14)); 53.8 (*d*, C(9)); 48.9 (*t*, C(4)); 47.0 (*t*, C(6)); 42.9 (*s*, C(13)); 39.5 (*t*, C(12)); 39.4 (*t*, C(24)); 36.5 (*d*, C(8)); 36.0 (*t*, C(22)); 35.7 (*d*, C(20)); 33.3 (*t*, C(2)); 29.0 (*t*, C(1)); 28.6 (*t*, C(16)); 27.9 (*d*, C(25)); 27.7 (*t*, C(11)); 24.8 (*t*, C(15)); 23.7 (*t*, C(23)); 22.7 (*q*, C(27)); 22.5 (*q*, C(26)); 21.3 (*q*, *Me*COO); 18.6 (*q*, C(21)); 12.1 (*q*, C(18)). CI-MS: 431 (100, $[M+1]^+$), 371 (50, $[M-60+1]^+$).

(3β,5β)-5,19-Epoxy-B-*norcholestan-3-ol Acetate* (**23**): Oil. $[\alpha]_D^{20} = +11.9$ ($c = 1.7$, $CHCl_3$). IR (neat): 1739, 1242, 1023, 964. ^{1}H-NMR ($CDCl_3$): 0.65 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.94 (*d*, Me(21)); 2.01 (*s*, AcO); 3.92, 4.43 (2*d*, $J = 6$, CH_2(19)); 5.23 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 170.1 (*s*, Me*C*OO); 93.8 (*s*, C(5)); 74.0 (*t*, C(19)); 68.3 (*d*, C(3)); 56.9 (*d*, C(17)); 55.6 (*d*, C(14)); 55.4 (*d*, C(9)); 46.9 (*s*, C(10)); 46.7 (*t*, C(4)); 43.5 (*s*, C(13)); 42.3 (*d*, C(8)); 39.5 (*t*, C(12)); 39.4 (*t*, C(24)); 39.3 (*t*, C(6)); 36.1 (*t*, C(22)); 35.6 (*d*, C(20)); 28.4 (*t*, C(16)); 27.9 (*d*, C(25)); 25.2 (*t*, C(1)); 24.8 (*t*, C(15)); 23.7 (*t*, C(23)); 22.7 (*q*, C(27)); 22.5 (*q*, C(26)); 21.2 (*t*, C(11)); 21.1 (*q*, *Me*COO); 20.1 (*t*, C(2)); 18.7 (*q*, C(21)); 12.0 (*q*, C(18)). CI-MS: 431 (14, $[M+1]^+$), 371 (100, $[M-60+1]^+$).

Saponification of Diacetate **21**. Diacetate **21** (50 mg) was dissolved in MeOH (5 ml) and hydrolyzed with 1% KOH/MeOH (0.5 ml) at r.t. for 1 h. The mixture was evaporated, the residue diluted with H_2O and extracted with Et_2O, and the org. layer was washed with H_2O, dried (Na_2SO_4) and evaporated; 42 mg of diol. The crude diol was acetylated with Ac_2O (0.2 ml) in anh. pyridine (0.2 ml) overnight at r.t. Usual workup gave a residue, which was subjected to FC (SiO_2 (2 g), toluene/AcOEt 95:5): **14** (41 mg, 82%). Spectral data: identical to those of **14** (see above).

3.3. *Hypoiodite Pb(OAc)$_4$ Oxidation of* **9**. A mixture of **9** (200 mg, 0.46 mmol), $Pb(OAc)_4$ (841 mg, 1.897 mmol), and I_2 (670 mg, 2.640 mmol) in cyclohexane (80 ml) was stirred and irradiated with a 800-W *Osram-Halogen-Bellaphot* lamp (at 60 V) at r.t. for 1 h. The mixture was filtered off, and the filtrate was washed successively with aq. $NaHCO_3$ soln. and H_2O, dried (Na_2SO_4), and evaporated. The residue (250 mg) was separated by FC (SiO_2 (40 g), toluene/AcOEt 96:4 (→ **10**–**12**), 80:20 (→ **14**, **15**)): **10** (43 mg, 21.6%), **11** (42 mg, 21.1%), **12** (5 mg, 2.5%), **14** (18 mg, 8.7%), and **15** (52 mg, 25.1%).

3.4. *Hypoiodite HgO Oxidation of* **9**. A stirred suspension of **9** (360 mg, 1.83 mmol), yellow HgO (1.148 g, 5.30 mmol), and I_2 (1.530 g, 6.03 mmol) in anh. CCl_4 (30 ml) was irradiated with a 800-W *Osram-Halogen-Bellaphot* lamp (at 60 V) at r.t. for 1 h. The mixture was filtered, the filtrate was washed successively with aq. $Na_2S_2O_3$ soln., aq. $NaHCO_3$ soln., and H_2O, dried (Na_2SO_4), and evaporated, and the resulting mixture (410 mg), separated by FC (SiO_2 (60 g), toluene/AcOEt 97:3 (→ **10**–**12**), 80:20 (→ **14**, **15**)): **10** (68 mg, 19.1%), **11** (54.7 mg, 15.3%), **12** (9.3 mg, 2.6%), **14** (20 mg, 5.4%), and **15** (54.8 mg, 14.7%).

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