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Non-Sensitized Photooxygenation of Some Steroidal Isoxazolidines

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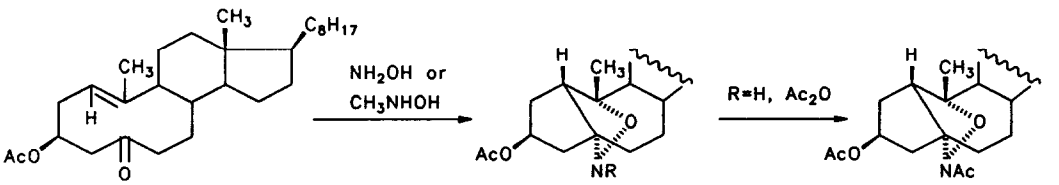
Abstract: *UV irradiation of the steroidal isoxazolidines* ***2a, 2b,*** *and* ***2c*** *in various solvents in the presence of molecular oxygen, results in oxidative cleavage of the epoxyimino bridge to give several products; the N--unsubstituted isoxazolidine* ***2a*** *afforded the nitro products* ***3, 4,*** *and* ***5*** *and the azoxy compounds* ***6*** *and* ***7,*** *while the N-methyl and N-acetyl derivatives* ***2b*** *and* ***2c*** *produced only the nitro compounds* ***3*** *and* ***5*** *as sole identifiable material. An explanation of the observed photooxygenation processes involving exciplex formation followed by proton transfer from isoxazolidine to molecular oxygen is presented.*

Photochemically induced oxygenation (sensitized[1] or non-sensitized[2]) of saturated organic molecules containing heteroatoms (O, N, S) has been widely investigated; mostly it involves homolytic abstraction of α-hydrogen atoms (when present). In a preliminary communication[3] we described briefly a non-sensitized photooxygenation of some steroidal isoxazolidines devoid of α-hydrogen atoms with respect to both heteroatoms, *i.e.*, 5,10α-epoxyimino-5(10→1)*abeo*-1ß(H)-5α-cholestan-3ß-ol acetate (**2a**), N-methyl-5,10α--epoxyimino-5(10→1)*abeo*-1ß(H)-5α-cholestan-3ß-ol acetate (**2b**), and N-acetyl-5,10α-epoxyimino-5(10→1)*abeo*--1ß(H)-5α-cholestan-3ß-ol acetate (**2c**) (Scheme 1). Now we wish to report more extensively on the behavior of these substrates when subjected to UV light in the presence of molecular oxygen.



1 2a R=H 2b R=CH_3 2c

Scheme 1

The steroidal isoxazolidines **2a** and **2b** were obtained by heating (*E*)-3ß-acetoxy--5,10-secocholest-1(10)-en-5-one (**1**)[4] with hydroxylamine or N-methylhydroxylamine in the presence of a proton donor catalyst (as the result of an intramolecular 1,3-dipolar cycloaddition of the intermediately formed

oxime or nitrone to the olefinic (*E*)-double bond in the cyclodecene moiety of the 5,10-secosteroidal system),[5] while compound **2c** was prepared by acylation of the N-unsubstituted isoxazolidine **2a** with acetic anhydride[5] (Scheme 1).

RESULTS AND DISCUSSION

UV irradiation of isoxazolidines **2a**, **2b**, and **2c** was carried out in various solvents, from which air was not expelled, with a medium pressure or low pressure Hg lamp contained in a water-cooled jacket of quartz, at room temperature and with stirring (for 1-6 h) (see Table 1). It was found that under these irradiation conditions all three isoxazolidines (**2a**, **2b**, and **2c**) underwent oxidative cleavage of the epoxyimino bridge to give several products. Thus, the N-unsubstituted isoxazolidine **2a** afforded the nitro products **3**, **4**, and **5**,[6] and the azoxy compounds **6** and **7**,while the N-methyl and N-acetyl derivatives **2b** and **2c** produced only the nitro compounds **3** and **5** as sole identifiable material (Scheme 2, Table 1)

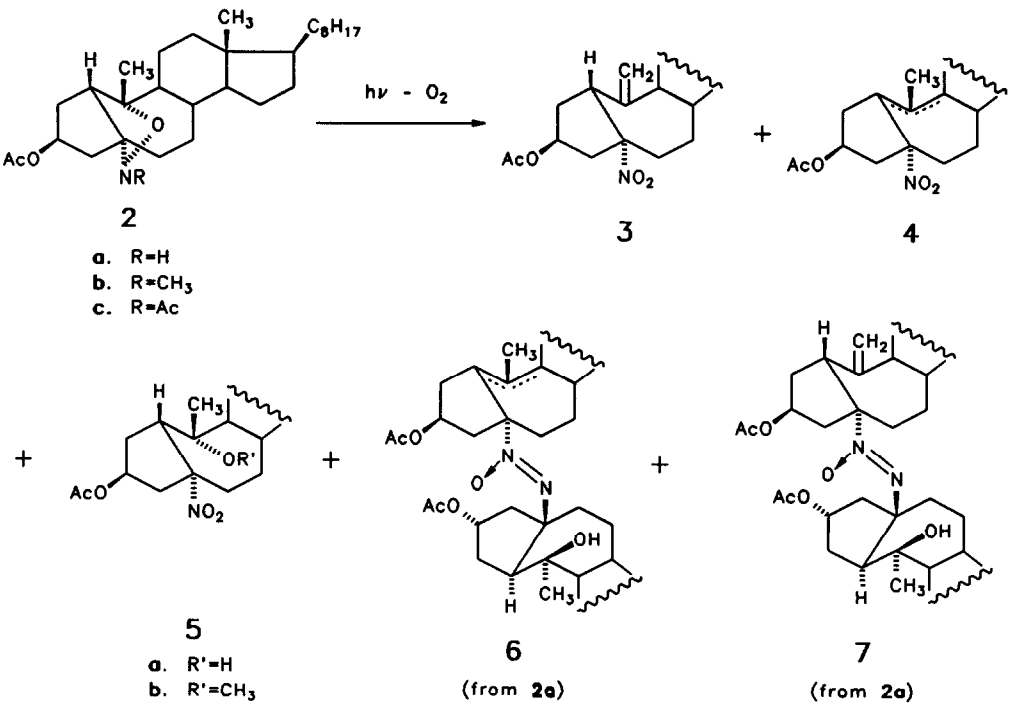
Table 1. Products Obtained by Irradiation[a,b] of the Isoxazolidines **2a**, **2b**, and **2c**, in the Presence of Molecular Oxygen

			Yields/% of reaction products[c]						
Substrate	Solvent	Time/h	**3**	**4**	**5a**	**5b**	**6**	**7**	S.M.[d]
2a	Acetone[a]	2	9	1	18		8	10	-
"	Acetone[b]	1	6	1	11	16	9	17	-
"	Dioxane[a]	2	8	1	10		12	9	-
"	Dioxane[b]	1	10	1	7		12	11	-
"	Et_2O[a]	1	11	1	14		27	6	-
"	Benzene[a]	3	8	1	5		30	16	-
"	Methanol[a]	4	18	5	8		traces		-
2b	Acetone[a]	2	6		16		-	-	44
2c	Acetone[a]	6	5		7		-	-	22
"	Dioxane[a]	2	9		9		-	-	-

a) Irradiations carried out with a medium pressure Hg 250 W lamp. b) Irradations carried out with a low pressure Hg lamp. c) All yields refer to crude products, separated and isolated by column chromatography on silica gel (yields after recrystallization were lower by 10-30%). d) Recovered starting material.

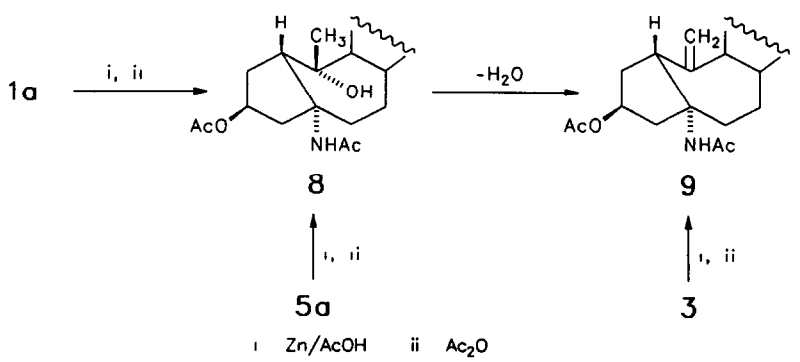
However, when similar UV irradiation of **2a**, **2b**, and **2c** was performed in the absence of oxygen (*i.e.* under nitrogen), the corresponding starting materials were recovered in high yield (*ca.* 90%), and none of the products **3** - **7** could be detected. This indicated that molecular oxygen is necessary for the above photoprocess to occur.

The structures of the photoproducts **3** - **7** were deduced on the basis of elemental microanalysis and spectral data. Thus, the presence of the nitro group in **3**, **4**, **5a**, and **5b** was detected by absorptions appearing between 1530-1545 cm^{-1} in the IR spectra of these compounds (for additional characteristic IR bands see Experimental). ^1H- and ^{13}C-NMR spectral data supporting the proposed structures are given in Tables 2 and



Scheme 2

3.[7] Besides, the structures of the nitro derivatives **3** and **5a** were confirmed by chemical transformations (*i.e.*, Zn/AcOH reduction of the NO_2 group and subsequent acetylation of the amino function formed), whereby they were correlated to the products of known structures and stereochemistry[5] (Scheme 3).



Scheme 3

Table 2. ^{1}H-NMR of Selected Protons of **3**, **5**, **6**, and **7** [a]

Proton	Chemical shifts and coupling patterns [b]				
	3	**5a**	**5b**	**6**	**7**
H-C(3)	5.48(*m*)	5.32(*m*)	5.23(*m*)	~4.90(*m*)	5.27(*m*)
H-C(3')				,4.90(*m*)	5.80(*w*)
AcO(3)	2.06(*s*)	2.08(*s*)	2.01(*s*)	2.12(*s*)	1.97(*s*)
AcO(3')				1.98(*s*)	1.92(*s*)
$H_2C(19)=$	4.97(*s*)				5.04(*s*)
	4.92(*s*)	1.22(*s*)	1.03(*s*)	1.64(*s*)	4.92(*s*)
$CH_3(19)$				1.07(*s*)	
$CH_3(19')$			3.25(*s*)		1.08(*s*)
CH_3O-C(10)					

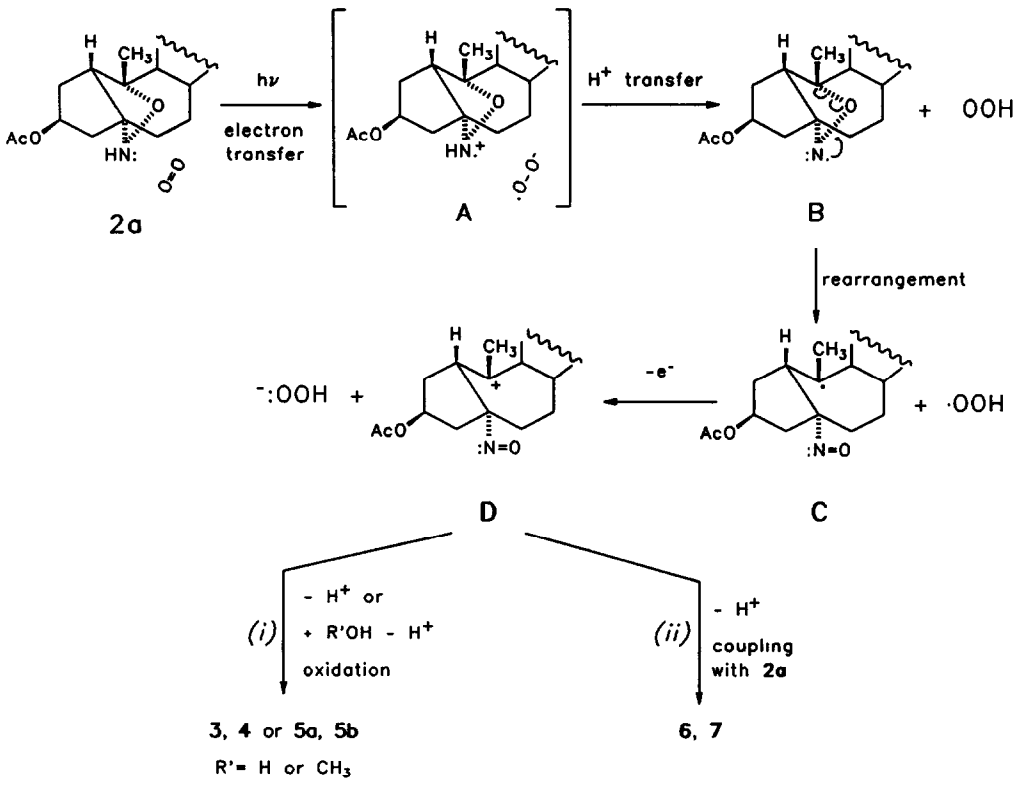
a) ^{1}H-NMR spectra were recorded at 100 MHz in $CDCl_3$ at room temp. b) δ in ppm ref. to TMS.

Table 3. ^{13}C-NMR Shifts of Selected Carbon Atoms in Compounds **3**, **5a**, **6**, and **7** [a]

Carbon	**3**	**5a**	**6**	**7**
C(1)	48.4	54.4	(128.6)	48.2
C(1')			54.4	54.6
C(2)	36.2	27.8		
C(3)	74.5	71.9	70.2	75.2
C(3')			72.9	72.6
C(4)	48.8	49.2		
C(5)	100.6	99.3	91.0	90.3
C(5')			74.6	74.6
C(6)	40.4	32.3		
C(7)	33.8	32.2		
C(8)	39.7	35.8		
C(9)	53.1	49.8	(128.6)	
C(10)	147.5	74.1	138.2	147.1
C(10')			72.3	73.0
C(18)	12.4	11.9	11.9	12.3
C(18')			11.9	12.0
C(19)	113.6	24.0	16.0	114.0
C(19')			24.7	24.6

a) Spectra were measured at 25.15 MHz in $CDCl_3$. Chemical shifts are given in δ ppm ref.to TMS.

On the other hand, absorptions at 1500 and 1490 cm^{-1}, respectively, in IR spectra of **6** and **7**, and their UV absorption at 208 and 223 nm, respectively, strongly suggested that these compounds contain an azoxy function in their molecules. In addition, their molar masses (determined by cryoscopic technique) were approximately twice as high as that of the starting isoxazolidine **2a** (*i.e.* 904 and 901 measured for **6** and **7**,

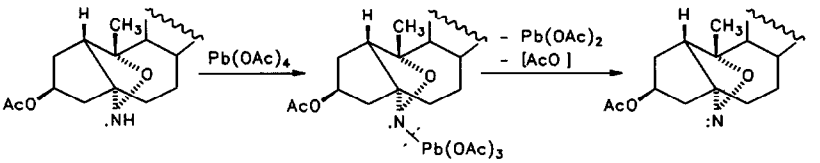


Scheme 4

respectively, in comparison with 459 computed for **2a**), indicating that both compounds arise from dimerization of **2a**. Particularly instructive data were obtained from ^{1}H- and ^{13}C-NMR spectra of **6** and **7**, in which some of the characteristic signals appeared as double peaks, this suggesting that **6** and **7** consist of two unequal parts of the modified steroid moiety; one containing, in both cases, the 10α-hydroxy group and the other an unsaturated center at C(10), namely the $\Delta^{9(10)}$- and/or $\Delta^{1(10)}$-double bond in **6**, and the exocyclic $\Delta^{10(19)}$-double bond in **7**. The ^{1}H- and ^{13}C-NMR spectral data relevant for structural determination are presented in Tables 2 and 3.

In order to get more information concerning the mechanistic pathway of the observed photooxygenations, compound **2a** was irradiated under oxygen with a medium pressure mercury lamp immersed in a Pyrex water cooling jacket and in the presence of Methylene blue or Crystal violet (dyes which are known to be sensitizers for singlet oxygen). However, under these conditions isoxazolidine **2a** remained unchanged (over 90%), indicating that the reaction does not proceed by the intermediacy of singlet oxygen.

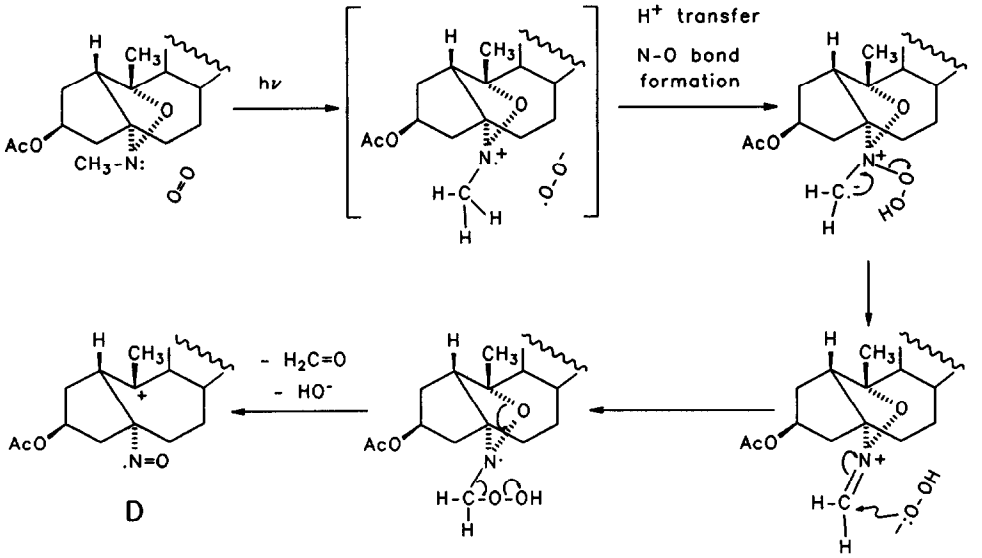
All the results obtained are consistent with a mechanism (Scheme 4) which involves as the primary photoprocess electron transfer from the substrate **2a** to molecular oxygen. The exciplex **A** so formed undergoes internal proton transfer to give the isoxazolidine radical **B** and a hydroperoxy radical. Rearrangement of **B** to the more stable 5-nitroso C(10)-radical **C** followed by one-electron oxidation at C(10) (by the hydroperoxy radical)[8] results in the formation of the C(10)-carbenium ion intermediate **D**, from which all the products isolated can be derived. Thus, upon stabilization of the cationic site in **D**, by removal of the



Scheme 5

adjacent proton, *i.e.* by double bond formation or by addition of water or methanol followed by proton elimination (reactions which are all characteristic only of carbocations, but not of other conceivable intermediates, such as carbon-centered radicals, alkyl hydroperoxides, alkoxy radicals, etc.), the 5-nitroso group can undergo (i) either further oxidation to give the nitro products **3-5**, or (ii) coupling with the starting isoxazolidine **2a** to give **6** and **7**.

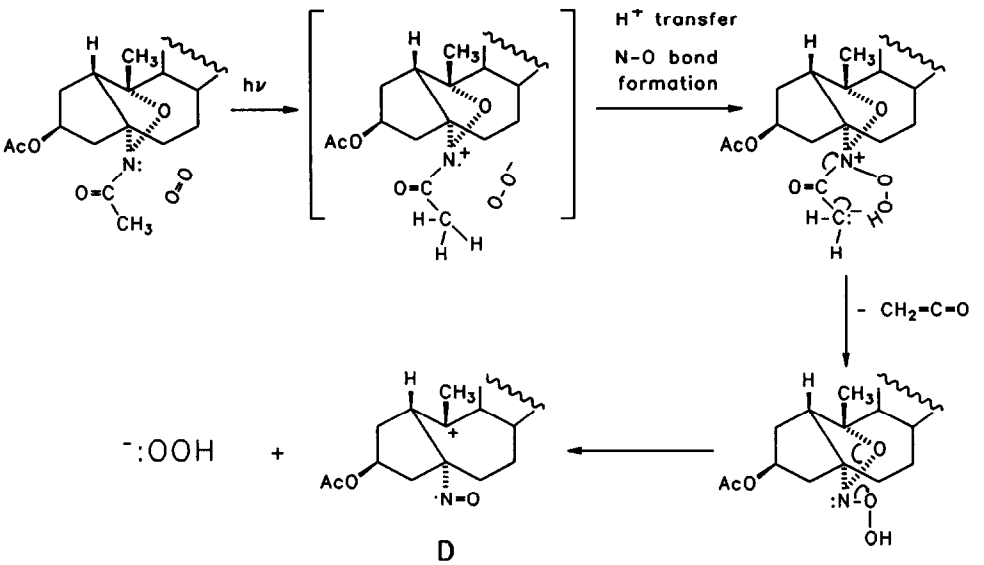
Following the above mechanistic scheme we anticipated that the isoxazolidine radical **B** could be also produced from **2a** with one-electron oxidants, such as lead tetraacetate (by homolysis of the N-Pb bond in the primarily formed N-lead triacetate species **E**[9] (Scheme 5), implying that the lead tetraacetate oxidation of **2a** could take an analogous reaction course and give products similar to those obtained in the photooxygenation process. This was found to be actually the case; when isoxazolidine **2a** was treated with lead tetraacetate in benzene solution it gave the unsaturated nitro derivatives **3** and **4**, and the azoxy compounds **6** and **7** (in various proportions which were dependent upon the experimental conditions used),[10] thus supporting the proposed mechanistic pathway.



Scheme 6

Photooxygenation of the N-substituted isoxazolidines **2b** and **2c**, which took place with elimination of the N-methyl and N-acetyl group, respectively, can be also explained by initial electron-transfer interaction

between molecular oxygen and substituted nitrogen. Possible mechanistic courses, proceeding with participation of these groups[11,12] to give the C(10)-carbenium ion intermediate **D** are shown in Schemas 6 and 7.



Scheme 7

As expected, in these cases stabilization of the nitroso group can be only achieved by oxidation to the nitro group, the coupling reaction being prevented due to substitution.

EXPERIMENTAL[13]

General. Removal of solvents was carried out under reduced pressure. Prep. column chromatography: silica gel 0.063-0.200 mm. TLC: control of reactions and separation of products on silica gel G (Stahl) with benzene-EtOAc 9:1 or 7:3, detection with 50% H_2SO_4 soln. M. ps: uncorrected. UV spectra: *Perkin Elmer 137 UV* spectrophotometer: λ_{max} nm (ϵ). IR spectra: *Perkin Elmer 337* spectrophotometer: $\bar{\nu}$ in cm^{-1}. ^{1}H-NMR spectra: at 100 MHz: *Varian AH-100* spectrometer; noise decoupled ^{13}C-NMR spectra at 25.15 MHz: *Varian XL-100* spectrometer equipped with Fourier transform accessory - $CDCl_3$ soln. at r.t., TMS as internal standard; chemical shifts in ppm as δ values. Mass spectra were obtained on a *Varian CH7* instrument. Light petroleum refers to the fraction boiling at 40-60°C.

Isoxazolidines **2a**, **2b**, and **2c** were obtained from (*E*)-3ß-acetoxy-5,10-secocholest-1(10)-en-5-one[4] by reaction with hydroxylamine (for the preparation of **2c** followed by N-acetylation) and N-methylhydroxylamine, respectively, as described in Ref. 5.

Photooxygenation of isoxazolidines **2a-c**. *General procedure.* - Compounds **2a-c** were irradiated in a cylindric flask with a medium pressure Hg 250 W lamp or a low pressure Hg lamp contained in a water-cooled

jacket of quartz at room temp. and with stirring (for 1-6 h, *i.e.* until starting material had been consumed). Solutions (not deaerated) were 2 x 10^{-3} M. Solvents (acetone, dioxane, diethyl ether, benzene, methanol) were not dried. After irradiation, the solvent was evaporated and the resulting mixtures were separated by column chromatography using benzene and benzene/Et_2O (in various proportions) as eluents. Benzene eluted unsaturated nitro derivatives **3** and **4**. Elution with benzene/Et_2O (99:1) afforded the azoxy compound **6**. Benzene/Et_2O (98:2) fractions contained the C(10)-methoxy-5-nitro derivative **5b** (when irradiation was performed in methanol). Elution with benzene/Et_2O (97:3) gave the C(10)-hydroxy-5-nitro derivative **5a**. Benzene/Et_2O (96:4) eluted the azoxy product **7**. More polar fractions contained unresolvable complex mixtures which were not further investigated. All yields (Table 1) refer to crude products (yields after recrystallization were lower by 10-30%).

*5-Nitro-5(10→1)*abeo-*1β(H)-5α-cholest-10(19)-en-3β-ol acetate* **3**. M.p. 143°C (from MeOH). $[\alpha]_D^{20}$ = -8.70 (c=1.15, $CHCl_3$). IR (CCl_4): 3095, 1738, 1640, 1540, 1240, 1200, 1023, 902. ^{1}H-NMR: 0.72 (*s*, CH_3(18)), 0.84 (*d*, CH_3(26), CH_3(27)), 0.89 (*d*, CH_3(21)), 2.06 (*s*, AcO), 4.92, 4.97 (two *s*, CH_2=(19)), 5.48 (*m*, H-C(3)). ^{13}C-NMR: 170.6 (*s*, CH_3COO), 147.5 (*s*, C(10)), 113.7 (*t*, C(19)), 100.6 (*s*, C(5)), 74.5 (*d*, C(3)), 56.5 (*d*, C(17)), 55.1 (*d*, C(14)), 53.1 (*d*, C(9)), 48.8 (*t*, C(4)), 48.4 (*d*,C(1)), 42.8 (*s*, C(13)), 40.4 (*t*, C(6)), 39.7 (*d*, C(8)), 39.6 (*t*, C(24)), 38.8 (*t*, C(12)), 36.2 (*t*, C(2)), 36.1 (*t*, C(22)), 35.8 (*d*, C(20)), 33.8 (*t*, C(7)), 28.9 (*t*, C(11)), 28.0 (*d*, C(25)), 27.9 (*t*, C(16)), 24.7 (*t*, C(15)), 23.9 (*t*, C(23)), 22.8 (*q*, C(27)), 22.6 (*q*,C(26)), 21.3 (*q*, CH_3COO), 18.6 (*q*, C(21)), 12.4 (*q*, C(18)). *m/z*: 473 (M^+). Anal. calc. for $C_{29}H_{47}NO_4$ (473.70): C, 73.53; H, 10.00; N, 2.96. Found: C, 73.26; H, 9.96; N, 2.71.

*5-Nitro-5(10→1)*abeo-*5α-cholest-9(and/or 1(10))-en-3β-ol acetate* **4**. - Oil. IR (CCl_4): 1745, 1545, 1243, 1020. *m/z*: 473 (M^+).

*5-Nitro-5(10→1)*abeo-*1β(H)-5α-cholestane-3β,10α-diol 3-acetate* **5a**. - M.p. 151°C (from MeOH). $[\alpha]_D^{20}$= +9.16 (c=1.55, $CHCl_3$). IR (CCl_4): 3590, 1745, 1545, 1240, 1200. ^{1}H-NMR: 0.73 (*s*, CH_3(18)), 0.87 (*d*, CH_3(26), CH_3(27)), 0.92 (*d*, CH_3(21)) 1.22 (*s*, CH_3(19)), 2.08 (*s*, AcO), 5.32 (H-C(3)). ^{13}C-NMR: 170.5 (*s*, CH_3COO), 99.3 (*s*, C(5)), 74.1 (*s*, C(10)), 71.9 (*d*, C(3)), 56.2 (*d*, C(17)), 55.1 (*d*, C(14)), 54.4 (*d*, C(1)), 49.2 (*t*, C(4)), 49.0 (*d*, C(9)), 42.7 (*s*, C(13)), 39.6 (*t*, C(24)), 39.2 (*t*, C(12)), 36.0 (*t*, C(22)), 35.8 (*d*, C(8), C(20)), 32.3 (*t*, C(7)), 32.1 (*t*, C(6)), 28.0 (*d*, C(25)), 27.6 (*t*, C(16)), 27.2 (*t*, C(2)), 25.7 (*t*, C(11)), 24.0 (*q*, C(19)), 23.8 (*t*, C(15)), 22.8 (*q*, C(27)), 22.6 (*t*, C(23)), 22.6 (*q*, C(26)), 21.2 (*q*, CH_3COO), 18.7 (*q*, C(21)), 11.9 (*q*, C(18)). *m/z*: 473 (M^+-18). Anal. calc. for $C_{29}H_{49}NO_5$ (491.72): C, 70.84; H, 10.04; N, 2.85. Found: C, 71.07; H, 9.98; N, 3.05.

*5-Nitro-10α-methoxy-5(10→1)*abeo-*1β(H)-5α-cholestan-3β-ol acetate* **5b**. - M.p. 114°C (from MeOH). $[\alpha]_D^{20}$= +0.40 (c=1.10, $CHCl_3$). IR (CCl_4): 1738, 1530, 1237, 1202, 1073, 1022, 852. ^{1}H-NMR: 0.68 (*s*, CH_3(18)), 0.84 (*d*, CH_3(26), CH_3(27)), 0.88 (*d*, CH_3(21)), 1.03 (*s*, CH_3(19)), 2.01 (*s*, AcO), 3.25 (*s*, CH_3O-C(10)), 5.23 (*m*, H-C(3)). *m/z*: 474 (M^+-31). Anal. calc. for $C_{30}H_{50}NO_5$ (505.75): C,71.25; H, 10.16; N,2.77. Found: C, 71.52; H, 9.94; N, 3.10.

*5[3β-Acetoxy-5(10→1)*abeo-*1β(H)-5α-cholest-9(and/or 1(10))-en-5-ONN-azoxy]5(10→1)*-abeo-*1β(H)-cholestane-3β,10α-diol 3-acetate* **6**. - M.p. 173°C (from acetone). $[\alpha]_D^{20}$= -92.80 (C=1.9, $CHCl_3$. UV (EtOH): 208 (12.850). IR (CCl_4): 3490, 1745, 1500, 1245, 1050. ^{1}H-NMR: 0.62, 0.64 (two *s*, CH_3(18), CH_3(18')), 0.84 (*d*, CH_3(26), CH_3(26'), CH_3(27), CH_3(27')), 0.88 (*d*, CH_3(21), CH_3(21')), 1.07 (*s*, CH_3(19')), 1.64 (*s*, CH_3(19)), 1.98, 2.12 (two *s*, AcO(3), AcO(3')), ~4.90 (two *m*, H-C(3), H-C(3')). *m/z*: 444 (M^+-RN_2O -H), 426 (M^+-R'ON_2 -H). Anal. calc. for $C_{58}H_{96}N_2O_6$ (917.42): C, 75.94; H, 10.55; N, 3.05. Found: C, 76.03; H, 10.45; N, 3.28.

*5[3β-Acetoxy-5(10→1)*abeo-*1β(H)-5α-cholest-10(19)-en-5-ONN-azoxy]5(10→1)*abeo-*1β(H)-cholestane-3β,10α-diol 3-acetate* **7**. - M.p. 114°C (from MeOH). $[\alpha]_D^{20}$= -12.06 (C=2.04, $CHCl_3$. UV (EtOH): 223 (5350). IR (CCl_4): 3530, 1738, 1630, 1490, 1200, 1020, 900. ^{1}H-NMR: 0.68, 0,72 (two *s*, CH_3(18), CH_3(18')), 0.86 (*d*, CH_3(26), CH_3(26'), CH_3(27), CH_3(27')), 0.89 (*d*, CH_3(21), CH_3(21')), 1.08 (*s*, CH_3(19')), 1.92, 1.97 (two *s*, AcO(3), AcO(3')), 4.92, 5.04 (two *s*, CH_2=(19)), 4.80, 5.27 (two *m*, H-C(3), H-C(3')). *m/z*: 444 (M^+-RN_2O -H), 426 (M^+-R'ON_2 -H). Anal. calc for: $C_{58}H_{96}N_2O_6$ (917.42): C, 75.94; H, 10.55; N, 3.05. Found: C, 75.92; H, 10.52; N, 3.29.

*N-Acetyl-5-amino-5(10→1)*abeo-*1β(H)-5α-cholestane-3β,10α-diol 3-acetate* **8** from **5a**. - To a stirred solution of **5a** (100 mg) in 90:10 AcOH/H_2O (5 ml) Zn dust (500 mg) was added. The mixture was heated at 70°C for 4 h, cooled at room temperature and excess of Zn filtered off and washed with 5% aq. HCl. The filtrate was made basic by addition of 10% aq. NaOH and extracted with diethyl ether. The residue (94 mg) obtained after evaporation of the solvent was dissolved in Ac_2O (1.5 ml) and left for 12 h at room temperature. The reaction mixture was diluted with water, extracted with diethylether - CH_2Cl_2, and the organic layer washed with sat. aq. $NaHCO_3$ soln. and water, dried over Na_2SO_4 and evaporated to dryness. The resulting oily product (100 mg, 97.6%) was recrystallized from acetone - light petroleum to give N-acetyl-5-amino-5(10→1)*abeo*-1ß(H)-5α-cholestane-3ß,10α-diol 3-acetate **8**, m.p. 117-118°C, $[\alpha]_D^{20}$= +26.0 (c=1.25, $CHCl_3$) (lit.[5] m.p. 117-119°C; $[\alpha]_D^{20}$= +28 ± 2). IR and NMR spectra were identical with those of an authentic sample.

*N-Acetyl-5-amino-5(10→1)*abeo-*1β(H)-5α-cholest-10(19)-en-3β-ol acetate* **9** from **3**. - To a stirred solution of **3** (100 mg) in 90:10 AcOH/H_2O (5 ml) Zn dust (500 mg) was added. The mixture was treated as above to give an oil (86 mg) which was acetylated with Ac_2O (1.5 ml) for 12 h at room temp. The residue obtained after the usual work up was chromatographed on SiO_2 (5 g). Elution with benzene-diethyl ether (85:15) afforded N-acetyl-5α-amino-5(10→1)*abeo*-1ß(H)-5α-cholest-10(19)-en-3ß-ol acetate **9** (70 mg, 68.3%). Oil. $[\alpha]_D^{20}$= +46.0° (c=0.53, $CHCl_3$). IR (CCl_4): 3410,1742, 1690, 1505, 1245, 1200, 1025, 865. ^{1}H-NMR: 0.66 (*s*, CH_3(18)), 0.84 (*d*, CH_3(26), CH_3(27)), 0.87 (*d*, CH_3(21)), 1.83 (*s*, Ac-N), 2.01 (*s*, AcO), 3.06 (*d*, H-C(1)), 5.00, 5.12 (two *s*, CH_2=(19)), ~5.10 (*m*, H-C(3)). All spectral data were identical with those of a previously prepared compound.[14] Anal. calc. for $C_{31}H_{51}NO_3$ (485.76): C, 76.65; H, 10.58; N, 2.89. Found: C, 76.42; H, 10.76; N, 2.71.

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