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HIGHFIELD ^{1}H AND ^{13}C NMR OF 5-OXYGENATED CHOLESTANE-6-OXIME DERIVATIVES

Helmut Duddeck[a]*, Jadwiga Frelek[b], Wojciech J. Szczepek[b] and Wladislaw J. Rodewald[b].
[a]Ruhr University Bochum, Faculty of Chemistry, P.O.B. 102148, D-4630 Bochum 1, West Germany; [b]University of Warsaw, Department of Chemistry, Pasteura 1, PL-02-093 Warsaw, Poland.

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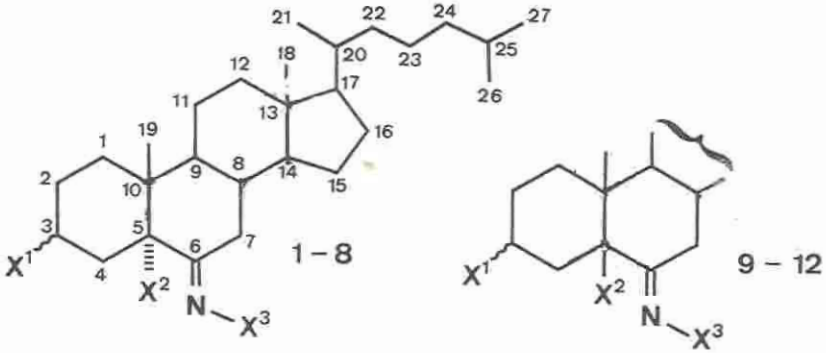
ABSTRACT: The oxime groups in twelve title compounds were found to be in the E-configuration by determination of the chemical shifts of the ring B carbons. For some compounds all ^{1}H and ^{13}C NMR signals were assigned by using two-dimensional correlated NMR methods.

INTRODUCTION

In continuation of CD investigations of simple hydrazones a



	X^1	X^2	X^3
1	H	OH	OH
2	α-OAc	OH	OH
3	α-OAc	OH	OAc
4	β-OAc	OH	OH
5	β-OAc	OH	OAc
6	β-OAc	OCH_3	OH
7	β-OAc	OCH_3	OAc
8	β-Cl	OH	OH
9	β-OAc	OH	OH
10	β-OAc	OH	OAc
11	β-OAc	OAc	OH
12	β-OAc	OAc	OAc

series of steroidal oximes and acetoximines substituted at rings A and B with different stereochemistry and substitution pattern have been synthesized from the corresponding ketones using conventional methods (1). For the CD interpretations, of course, a sound knowledge of the oxime configuration was mandatory.

RESULTS AND DISCUSSION

The easiest way to establish the stereochemistry of the 6-oxime groups in the cholestanes 1-12 is to compare the ^{13}C chemical shifts of C-7 in these compounds with those of corresponding ketones, since in the E-orientation of the hydroxyl group the C-7 signal should be shielded much more significantly compared to the keto derivative than in the Z-configuration (2,3). Moreover, in the E-configuration C-8 should suffer a 1-2 ppm shielding whereas its signal shift should be very similar to that of the ketone if the hydroxyl group is in Z-orientation.

A ^{13}C signal assignment of steroids can be achieved by comparing the spectral data with those of documented spectra with similar structure. The ^{13}C NMR data of a large number of cholestanes have been collected in reviews published by Blunt and stothers and by other authors (4). This method, however, is purely empirical and therefore we decided to confirm such assignments by a more rigorous method using two-dimensional homo- (^{1}H-^{1}H) and heteronuclear (^{1}H-^{13}C) correlated NMR techniques (COSY) which afford unambiguous atom connectivities (5). Such application has been described by us recently in a paper on the ^{1}H and ^{13}C NMR spectroscopy of corticosteroids (6).

In the past, proton signal assignments of steroids were restricted to high-frequency signals which are not overlapped by others or to sharp methyl peaks (7). ^{1}H assignments of signals in highly crowded spectral areas of steroids became possible only after the availability of highfield spectrometers and two-dimensional techniques (6,8). To the best of our knowledge, however, no such ^{1}H NMR investigation of cholestane derivatives has been described. In fact, such spectra are particularly difficult to interpret because signal overlap in the region of δ = 1-2 is extremely severe due to the many hydrogens in the aliphatic C_7 side chain. In four instances (**1,4,6** and **10**) we carried out the full ^{1}H signal assignments of the cholestane 6-oxime compounds and the chemical shifts are listed in Table 1. For all other compounds we can find overlapped signals which apparently correspond to those of the four but their identity has not been proven. In such cases only the chemical shifts of the prominent peaks are noted in the Experimental Part.

For the compounds **1,4,6** and **10** the application of Homo- and heteronuclear COSY spectroscopy enabled reliable ^{13}C signal assignments (Tables 2 and 3) except in a few cases where the carbon resonances were too close to be resolved in the two-dimensional experiment and the resonances of the attached protons could not be identified unambiguously because they were also very near to each other. In such cases we refrained from further painstaking experiments because this was not necessary for our main goal, namely

to establish the oxime configuration. The ^{13}C assignments of all other compounds were achieved using analogy arguments and contain also a few minor ambiguities.

Table 1: ^{1}H chemical shifts of some cholestane derivatives[a]

H[b]	1	4	6	10
1	1.37/1.43	1.67/1.50	1.66/1.45	1.90/1.43
2α	1.4 -1.55	1.78	1.80	1.67
2β	1.4 -1.55	1.60	1.53	1.67
3	1.4 -1.55	5.02	4.85	5.05
4α	1.89	2.20	2.21	1.90[c]
4β	1.50	1.74	1.58	2.16[c]
7α	1.82	1.74	1.43	1.52
7β	3.10	3.02	3.10	3.13
8	1.47	1.43	1.46	1.52
9	1.66	1.72	1.72	1.4 -1.45
11	1.15/1.28	1.35/ -[d]	1.25/1.36	1.42/2.02
12	1.17/1.98	1.19/1.96	1.19/1.96	1.16/2.01
14	1.18	1.22[c]	1.22[c]	1.13
15	1.10/1.62	1.10/1.65	1.10/1.62	1.12/1.62
16	1.22/1.88	1.25/1.83	1.25/1.84	1.28/1.85
17	1.07	1.13[c]	1.12[c]	1.12
18	0.62	0.62	0.62	0.63
19	0.81	0.80	0.83	0.83
20	1.31	1.32	1.32	1.37
21	0.88	0.88	0.87	0.88
22	0.97/1.33	0.97/1.32	0.97/1.32	0.98/1.33
23	1.11/1.60	1.11/ -[d]	1.10/1.32	1.12/1.58
24	ca 1.1	ca 1.1	ca 1.1	1.07/1.07
25	1.45	1.47	1.49	1.47
26[c]	0.84	0.84	0.84	0.84
27[c]	0.84	0.83	0.83	0.84
NOH	9.2	9.4	9.5	-
C^5-OH	-[d]	2.89		3.63
Ac		2.03	2.00	2.03
OCH_3			3.07	

[a]In ppm, relative to the solvent peak ($CDCl_3$: δ=7.24), at 400.1 MHz. For the other compounds see Experimental Part. [b]Stereochemical notation only if proven unequivocally. [c]May be interchanged. [d]Could not be identified accurately.

The C-7 chemical shifts are δ = 25-26 for the 6-oximes (X^3 = OH). A comparison of these values with corresponding chemical shifts in cholestan-6-ones (4a) reveals that downfield shifts of ca 18-19 ppm occur if the keto oxygen is substituted by NOH. This clearly proves that the oxime hydroxy group is E-oriented since in Z-configuration chemical shifts in the range of δ = 35-36 would be expected (2,3). Moreover, the C-8 atoms suffer a 2-3 ppm shielding upon the same molecular transformation again indicating E-

configuration (2,3) (see above). In the spectra of the acetoximines the C-7 chemical shifts are ca 2 ppm higher.

Table 2: ^{13}C chemical shifts of the 5α-cholestane oximes[a]

C-No.	1	2	3	4	5	6	7	8
1	30.7	25.8[b]	25.8	29.7	29.5	29.8	29.8	31.2
2	20.6[b]	24.8[b]	24.8	26.5	26.4	26.5	26.4	32.0
3	20.2[b]	70.3	70.2	72.0	70.5	70.3	69.8	56.7
4	29.0	31.7	31.7	33.5	34.2	27.8	27.8	39.9
5	75.7	75.8	76.4	76.7	77.4	81.8	82.3	77.4
6	162.7	161.3	168.4[b]	62.9	169.6	160.3	167.8	161.8
7	25.3	25.0[b]	27.1	24.9	27.3	25.6	27.8	25.1
8	34.7	34.8	35.3	34.8	35.3	35.2	35.6	34.6
9	45.2	44.9	44.8	44.4	44.4	44.3	44.1	44.7
10	41.6	42.1	42.5	41.1	41.5	42.2	42.6	40.9
11	21.0	21.0	20.9	21.3	21.3	21.3	21.2	21.3
12	39.8	39.8[b]	39.4[b]	39.7[b]	39.4[b]	39.5[b]	39.4[b]	39.7[b]
13	43.0	43.0	43.0	43.0	43.0	43.0	43.0	43.0
14	56.4	56.3[b]	56.1	56.1[b]	56.1[b]	56.2[b]	56.0	56.2[b]
15	24.0	24.0	23.9	24.0	24.0	24.0	24.0	24.0
16	28.2	28.2	28.1	28.2	28.1	28.2	28.0	28.2
17	56.1	56.2[b]	56.1	56.0[b]	56.0[b]	56.1[b]	56.0	56.1[b]
18	12.1	12.1	12.0	12.1	12.0	12.1	12.0	12.1
19	14.3	14.1	14.0	14.2	14.2	14.6	14.6	14.4
20	35.8	35.8	35.7	35.7	35.7	35.7	35.6	35.7
21	18.6	18.6	18.6	18.6	18.6	18.6	18.5	18.6
22	36.1	36.1	36.0	36.1	36.1	36.1	36.0	36.1
23	23.8	23.9	23.8	23.8	23.9	23.8	23.7	23.8
24	39.5	39.5[b]	39.6[b]	39.5[b]	39.6[b]	39.7[b]	39.5[b]	39.5[b]
25	28.0	28.0	27.9	28.0	27.7	28.0	27.9	28.0
26	22.5	22.5	22.5	22.6	22.5	22.5	22.5	22.5
27	22.8	22.8	22.7	22.8	22.8	22.8	22.7	22.8
Ac		21.4	21.4	21.6	21.4	21.4	21.3	
			19.9		17.5		19.8	
		169.1	169.6[b]	172.0	170.9	170.7	170.5	
			168.4[b]		169.3		169.2	
OCH_3						49.5	49.8	

[a]In ppm, relative to the central peak of the solvent ($CDCl_3$: δ=77.0), at 100.6 MHz. [b]may be interchanged.

For the interpretation of various substitutent effects on carbon signals and chemical shift alterations by A/B ring junction changes, the reader is referred to review articles elsewhere (4).

It is interesting to observe the signals of the equatorial H-7β appearing at δ = 2.9-3.25 in all compounds. In most cases it is a doublet of doublet due to the couplings $J_{7\alpha,7\beta}$ = 13-14 Hz and $J_{7\beta,8}$ = 4-5Hz (cf. Fig. 1, left). For **6** and **10**, however, they are different (cf. Fig. 1, right). Here the signals represent X-parts

Table 3: ^{13}C Chemical shifts of 5 β-cholestane acetoximes[a]

C-No.	9	10	11	12
1	25.3	25.1	26.1[b]	26.0
2	24.4	24.4	24.4	24.4
3	69.0	68.1	68.2	67.8
4	36.4	36.5	28.7	29.1
5	75.6	76.1	84.3	84.0
6	160.3	168.3[b]	155.0	170.0[b]
7	26.3	28.7	26.8[b]	28.0
8	34.6	35.0	35.2	35.9
9	42.7	42.5	42.9	43.0
10	42.1	43.2	42.5	43.6
11	21.4	21.3	21.4	21.4
12	39.4[b]	39.5	39.4[b]	39.4[b]
13	42.8	42.9	42.9	43.0
14	56.8	56.6	56.6	56.5
15	24.0	24.0	24.0	24.1
16	28.1	28.0	28.1	28.0
17	56.0	56.0	56.0	56.0
18	11.9	11.9	12.0	12.0
19	16.3	16.8	16.8	16.7
20	35.6	35.6	35.6	35.6
21	18.6	18.6	18.6	18.6
22	36.1	36.0	36.0	36.0
23	23.7	23.7	23.7	23.7
24	39.6[b]	39.5	39.6[b]	39.5[b]
25	28.0	27.9	27.9	28.0
26	22.5	22.5	22.5[b]	22.5[b]
27	22.8	22.7	22.7	22.8
Ac	21.6	21.5	21.3	20.2
		19.7	22.4[b]	21.3
				22.3[b]
	170.9	170.7	170.4	169.8[b]
		169.0[b]	170.1	171.1

[a]In ppm, relative to the central peak of the solvent ($CDCl_3$: δ =77.0), at 100.6 MHz. [b]May be interchanged.

of ABX spectra because the signals of the two coupling partners H-7α and H-8 are nearly coinciding. Each of the large center lines of these signals consist of two accidentally overlapping lines with a distance of ca 9 Hz. This is, indeed, the sum of the two coupling constants since the geminal coupling constant ($J_{7\alpha,7\beta}$) is negative and the vicinal ($J_{7\beta,8}$) positive. The small outer lines are due to the so called "virtual" coupling (combination lines) (9). The reason for the overlap of the singals of H-7α and H-8 is different for both molecules:

Fig. 1: H-7β signals of **9** (left) and **10** (right)

The H-7β atoms resonate uniformly at δ =2.9-3.1 in the 5α- and δ = 3.1-3.25 in the 5β-cholestanes. Likewise, the H-8 chemical shifts (δ = 1.4-1.5) are rather independent of the substitution pattern. The shielding of H-7α, however, reacts sensitively on the nature of nearby substituents. In the dihydroxy compound **4** it appears at δ = 1.74, remote enough from the H-8 signal to produce a first-order AMX spectrum. Acetylation of the oxime OH (**4**→**5**) further enhances the distance (δ[H-7α] = 2.04). Methylation of the hydroxyl group at C-5, however, (**4**→**6**) causes a 0.3 ppm shielding of H-7α so that this signal and that of H-8 are nearly isochronous. In contrast to the acetoximine **5** the chemical shifts of H-7α and H-8 in **10** are nearly indistinguishable even at 400 MHz again giving rise to an ABX spectrum. In **9**, however, this is different because the 0.3 ppm deshielding exerted by the acetyl group is missing.

EXPERIMENTAL

The melting points were determined on a Boetius micro-melting point apparatus and are uncorrected. Column chromatography was performed on silica gel (Kieselgel 60, 70-230 mesh, Merck). Optical rotations were measured on a Perkin-Elmer 241 polarimeter in chloroform solutions and concentrations are expressed in mg/cm^3. The infrared spectra were recorded on a UR-20 spectrophotometer in KBr. Mass spectra were taken on a LKB 2031 or a Varian MAT CH-4 spectrometer. ^{1}H NMR spectra were taken at 100 MHz on a Bruker WP-100SY or at 400.1 MHz on a Bruker AM-400 and ^{13}C NMR spectra on a Bruker AM-400 spectrometer in $CDCl_3$ solutions under normal conditions. For the two-dimensional spectra (^{1}H-^{1}H and ^{1}H-^{13}C correlated) standard Bruker software and parameter sets were used as described earlier (10).

Synthesis of the oximes 1, 2, 4, 6, 8, 9 and 11

To a solution of the corresponding hydroxyketone in pyridine an excess of hydroxylamine hydrochloride was added and the reaction mixture was left at room temperature for a definite time. Then the excess solvent was evaporated under reduced pressure and the residue was treated with dilute hydrochloric acid. The product was extracted with benzene and the organic layer was washed with water, aqueous $NaHCO_3$ solution and finally with water. The extract was dried over anhydrous Na_2SO_4, filtered and the solvent removed under reduced pressure giving a crude product which was purified by filtration through alumina and then by crystallization from the indicated solvent. The results of these reactions are summarized below.

Hydroxyketone [g]	Pyridine [cm^3]	$NH_2OH.HCl$ [g]	Reaction Time [days]	Product [g]	Yield [%]
2.0	50	2	3	1:1.95	97
3.0	30	3	1	2:2.80	90
2.0	20	2	3	4:1.50	73
3.0	30	4	9	6:2.90	94
5.0	50	5	2	8:4.00	77
8.0	80	8	3	9:5.00	61
4.0	80	4	4	11:3.50	83

The isolated products gave the following data:

6E-Hydroximino-5α-cholestan-5-ol (1) (11,12)
M.p. 192-195°C (Et_2O-hexane); $[\alpha]_D$ -49.6 (c, 10.8); IR, cm^{-1}: 3380, 1660, 1166, 940, 912, 879; MS, m/z (relative intensity): 417 (M^+, 18.6), 400 (M^+-OH, 100), 357 (M^+ H_2O-CH_2CO, 49.4), 112 ($C_7H_{12}O^+$, 51.4); Anal.: calcd. for $C_{27}H_{47}NO_2$: C, 77.64; H, 11.34; N, 3.35; found: C, 77.5; H, 11.22; N, 3.30.

6E-Hydroximino-5α -cholestan-3α ,5-diol 3-acetate (2)
M.p. 223-224.5°C (MeOH); $[\alpha]_D$ -58.6 (c, 14.6); IR, cm^{-1}: 3572, 3456, 1729, 1275, 1030, 942, 916; ^1H NMR, δ ($CDCl_3$): 9.7 (NOH), 5.25 (H-3β), 3.33 (C^5-OH), 3.09 (H-7β), 2.16 (H-4α), 2.03 (Ac), 0.88 (H-21), 0.84 (H-26/H-27), 0.78 (H-19), 0.63 (H-18); MS, m/z (relative intensity): 475 (M^+, 25.0), 458 (M^+-OH, 39.7); 415 (M^+-AcOH, 14.7), 398 (M^+-OH-AcOH, 33.8), 388 (M^+-CO-AcO, 17.6), 387 (M^+-CO-AcOH, 17.6), 110 ($C_7H_{10}O^+$, 40.2), 43 (100); Anal.: calcd. for $C_{29}H_{49}NO_4$: C, 73.22; H, 10.38; N, 2.94; found: C, 73.12; H, 10.19; N, 2.79.

6E-Hydroximino-5α -cholestan-3β , 5-diol 3-acetate (4) (12-14)
M.p. 135-136.5/167-168°C (EtOH); $[\alpha]_D$ -96 (c, 10.5); IR, cm^{-1}: 3466, 1724, 1652, 1274, 1050, 947, 918; MS, m/z (relative intensity) : 475 (M^+, 25.8), 458 (M^+-OH, 43.3), 398 (M^+-OH-AcOH, 24.2), 110 ($C_7H_{10}O^+$, 95), 68 (100); Anal. calcd. for $C_{29}H_{49}NO_4$: C, 73.22; H, 10.38; N, 2.94; found: C, 73.06; H, 10.21; N, 2.83.

6E-Hydroximino-5-methoxy-5α-cholestan-3β-ol 3-acetate (6) (15) M.p. 230-232°C (MeOH); $[\alpha]_D$ -68.6 (c, 10.5); IR, cm^{-1}: 3458, 1718, 1664, 1274, 1067, 946, 918; MS, m/z (relative intensity): 489 (M^+, 23.4), 472 (M^+-OH, 20.9), 412 (M^+-OH-AcOH, 37.5), 123 ($C_8H_{11}O^+$, 100); Anal.: calcd. for $C_{30}H_{51}NO_4$: C, 73.58; H, 10.50; N, 2.86; found: C, 73.32; H, 10.41; N, 2.76.

3β-Chloro-6E-hydroximino-5α-cholestan-5-ol (8) (13,16,17) M.p. 193-195°C (Et_2O-hexane); $[\alpha]_D$ -49.9 (c,9.1); IR, cm^{-1}: 3480, 1660, 943, 913, 764, 693; ^{1}H NMR, δ ($CDCl_3$): 9.75 (NOH), 4.28 (H-3α), 3.12 (H-7β), 0.88 (H-21), 0.85 (H-19), 0.84 (H-26/H-27), 0.62 (H-18); MS, m/z (relative intensity): 451 (M^+, 29.2), 434 (M^+-OH, 89.2), 388 (M^+-CO-Cl, 54.2), 146 ($C_7H_{11}ClO^+$, 44.2), 110 ($C_7H_{10}OH^+$, 78.3), 68 (85.9), 43 (100); Anal. calcd. for $C_{27}H_{46}ClNO_2$: C, 71.73; H, 10.18; N, 3.10; found: C, 71.59; H, 10.10; N, 2.95.

6E-Hydroximino-5β-cholestan-3β, 5-diol 3-acetate (9) (14) M.p. 182-184.5°C (EtOH); $[\alpha]_D$ +7.4 (c, 14.6); IR, cm^{-1}: 3420, 1733, 1715, 1670, 1243, 1170, 1052, 1020, 923; ^{1}H NMR, δ ($CDCl_3$): 9.5 (NOH, broad), 5.08 (H-3α), 3.7 (C^5-OH), 3.25 (H-7β), 2.19 (H-4β), 2.04 (Ac), 0.88 (H-21), 0.84/0.83 (H-26/H-27), 0.81 (H-19), 0.62 (H-18); MS, m/z (relative intensity): 388 (M^+-AcO-CO, 100), 387 (M^+-AcOH-CO, 68.7); 110 ($C_7H_{10}O^+$, 52.5); Anal.: calcd. for $C_{29}H_{49}NO_4$: C, 73.22; H, 10.38; N, 2.94; found: C, 72.98; H, 10.17; N, 2.86.

6E-Hydroximino-5β-cholestan-3β, 5-diol 3, 5-diacetate (11) M.p. 216-219°C (EtOH); $[\alpha]_D$ -34.3 (c, 11.4); IR, cm^{-1}: 3440, 1747, 1730, 1657, 1280, 1245, 1100, 1050, 1022, 948, 926, 903; ^{1}H NMR, δ ($CDCl_3$): 9.9 (NOH), 5.15 (H-3α), 3.3-3.2 (C^5-OH), 3.25 (H-7β), 2.20 (H-4β), 2.04/1.96 (2Ac), 0.87 (H-19/H-21), 0.83 (H-26/H-27), 0.62 (H-18); MS, m/z (relative intensity): 457 (M^+-AcOH, 29.6), 398 (M^+-AcO-AcOH, 100), 397 (M^+-2AcOH); Anal. calcd. for $C_{31}H_{51}NO_5$: C, 71.92; H, 9.93; N, 2.71; found: C, 71.81; H, 9.76; N, 2.68.

Synthesis of the oxime acetates 3, 5, 7, 10 and 12

A mixture of the oxime, pyridine and acetic anhydride was left at room temperature for a definite time. Then the excess solvent was removed under reduced pressure (using a water bath heated to 50°C). The residue was treated with water and then extracted with ether. The organic layer was washed successively with 5% HCl, aq. Na_2CO_3, water and then dried over anhydrous Na_2SO_4. After evaporation of the solvent the residue was chromatographed and fractions of the main product (less polar than the substrate) were collected and evaporated to dryness. The oxime acetate was crystallized by dissolution in ether, addition of hexane or pentane and slow evaporation of the ether at room temperature. The results of these reactions are summarized below:

Oxime [g]	Pyridine [cm^3]	Ac_2O [cm^3]	Reaction Time [hours]	Product [g]	Yield [%]
2: 0.55	5	1.5	1	**3**: 0.50	77
4: 1.53	30	2	1	**5**: 1.26	81
6: 0.60	5	2	24	**7**: 0.60	83
9: 2.50	50	3	72	**10**: 2.50	92
11:0.27	2	1	24	**12**: 0.28	97

6E-Acetoximino-5α-cholestan-3α,5-diol 3-acetate (3)
M.p. 135-136.5°C (Et_2O-hexane); $[\alpha]_D$ -54.7 (c, 9.0); IR, cm^{-1}: 3570, 1780, 1740, 1650, 1213, 1028, 940, 871; ^{1}H NMR, δ: 5.25 (H-3β), 3.55 (C^5-OH), 2.94 (H-7β), 2.34 (H-4α), 2.14 (NOAc), 2.03 (C^3-OAc), 0.87 (H-21), 0.83 (H-26/27), 0.80 (H-19), 0.62 (H-18); MS, m/z (relative intensity): 458 (M^+-AcO, 3.1), 397 (M^+-2AcOH, 17.2), 369 (M^+-2AcOH-CO, 15.3), 110 ($C_7H_{10}O^+$, 100); Anal.: calcd. for $C_{31}H_{51}NO_5$: C, 71.92; H, 9.93; N, 2.71; found: C, 71.89; H, 9.92; N, 2.61.

6E-Acetoximino-5α-cholestan-3β, 5-diol 3-acetate (**5**) (12,18)
M.p. 156-158°C (Et_2O-hexane); $[\alpha]_D$ -74.3 (c, 9.6); IR, cm^{-1}: 3430, 1777, 1743, 1715, 1648, 1250, 1044, 940, 920; ^{1}H NMR, δ : 5.02 (H-3α), 2.93 (H-7β), 2.7 (C^5-OH), 2.14 (NOAc), 1.98 (C^3-OAc), 0.88 (H-21), 0.84 (H-19), 0.84/0.83 (H-26/27), 0.62 (H-18); MS, m/z (relative intensity): 458 (M^+-OAc, 42.0), 397 (M^+-2AcOH, 42.1), 369 (M^+-2AcOH-CO, 63.9), 110 ($C_7H_{10}O^+$, 100); Anal. calcd. for $C_{31}H_{51}NO_5$: C, 71.92; H, 9.93; N, 2.71, found: C, 71.86; H, 9.81; N, 2.68.

6E-Acetoximino-5-methoxy-5α-cholestan-3β-ol 3-acetate (**7**)
M.p. 127-130°C (Et_2O-pentane); $[\alpha]_D$ -62.1 (c, 10.7); IR, cm^{-1}: 1783, 1734, 1647, 1245, 1068, 939, 871; ^{1}H NMR, δ : 4.82 (H-3α), 3.08 (OCH_3), 2.92 (H-7β), 2.13 (NOAc), 1.96 (C^3-OAc), 0.86 (H-21), 0.83 (H-19), 0.83/0.82 (H-26/27), 0.62 (H-18); MS, m/z (relative intensity): 531 (M^+, 0.6), 473 (M^+-OAc, 56.8), 413 (M^+-2AcO, 37.6), 412 (M^+-AcO-AcOH, 100), 123 ($C_8H_{11}O^+$, 50.7); Anal.: calcd. for $C_{32}H_{53}NO_5$: C, 72.28; H, 10.05; N, 2.63; found: C, 72.19; H, 9.98; N, 2.51.

6E-Acetoximino-5β-cholestan-3β, 5-diol 3-acetate (**10**)
M.p. 157-158.5°C (Et_2O-pentane); $[\alpha]_D$ -0.7 (c, 10.0); IR, cm^{-1}: 3475, 1765, 1735, 1716, 1643, 1217, 1175, 1053; MS, m/z (relative intensity): 457 (M^+-AcOH, 6.8), 397 (M^+-2AcOH, 30.4), 369 (M^+-2AcOH-CO, 60.6), 110 ($C_7H_{10}O^+$, 100); Anal.: calcd. for $C_{31}H_{51}NO_5$: C, 71.92, H, 9.93; N, 2.71; found: C, 71.84, H, 9.83; N, 2.65.

6E-Acetoximino-5β-cholestan-3β, 5-diol 3, 5-diacetate (**12**)
Amorphous; $[\alpha]_D$ -43.4 (c, 9.8); IR, cm^{-1}: 1775, 1750, 1647, 1260, 1223, 926; ^{1}H NMR, δ : 5.18 (H-3α), 3.18 (H-7β), 2.18 (NOAc), 2.07 (C^3-OAc), 1.98 (NOAc), 0.88 (H-21), 0.91 (H-19), 0.85 (H-26/27), 0.62 (H-18); MS, m/z (relative intensity): 440 (M^+-AcO-AcOH, 10.7); 398(48.1); 397(100); 110 ($C_7H_{10}O^+$,5.2); Anal. calcd. for $C_{33}H_{53}NO_6$: C, 70.81; H, 9.54; N, 2.50; found: C, 70.69; H, 9.36; N, 2.37.

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