96. Some Observations Concerning ^{1}H-NMR. Spectra of 5-Hydroxy- and 5-Acetoxy-steroid Compounds

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Summary

It was found that analysis of the ^{1}H-NMR. signals (at 360 (preferably) and/or 100 MHz) of the protons at C(4) and of the equatorial α-proton at C(6), particularly when these are located in the 2–3 ppm region and therefore convenient for detection and identification, may be of valuable aid in the structural and configurational characterization of 5-hydroxy- and 5-acetoxy-steroids (unsubstituted or containing a hydroxy or acyloxy substituent at C(3)).

Introduction. – Although ^{1}H-NMR. spectroscopy has been extensively applied to steroid compounds [1–3], little attention has been paid, so far, to the relationship between substitution at C(5) (and C(3)) and the position of the resonance signals of protons at adjacent C-atoms, *i.e.* at C(4) and C(6). For that reason, we wish to present in this paper some observations on the ^{1}H-NMR. chemical shifts (at 360 (preferably) and/or 100 MHz) of the equatorial α-proton at C(6) and of both protons at C(4) of 5α- and 5β-steroids containing a hydroxy- or acetoxy-substituent at C(5), and without or with a substituent (hydroxy, acetoxy, *p*-nitrobenzoyloxy group) at C(3). The structural types used in this study are shown in the *Scheme* and the relevant ^{1}H-NMR. data are given in the *Table*[1]).

Discussion. – 1. *Equatorial α-proton at C(6).* In 5α- and 5β-unsubstituted steroids **1** and **2** (**A** or **B**, Z = H), respectively, even in those containing a 3α- or 3β-*p*-nitrobenzoyloxy group (Y = PNBO) [2], the signal of the equatorial H_α–C(6) (not shown in the *Table*) is located at or upfield of 2.0 ppm, and is not easily identifiable, particularly in 60- and 100-MHz-^{1}H-NMR. spectra.

The same is true for 5α- and 5β-hydroxy-steroids **1** and **2** (Z = HO), respectively, in which the resonance of the equatorial H_α–C(6) appears at 1.97–2.03 ppm,

[1]) Chemical shifts are given in ppm relative to tetramethylsilane (= 0 ppm) as internal standard.

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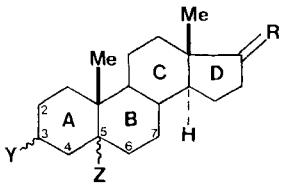
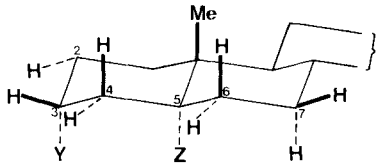
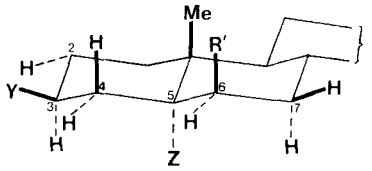
Scheme



1 5α-Z; **2** 5β-Z
A 3α-Y; **B** 3β-Y

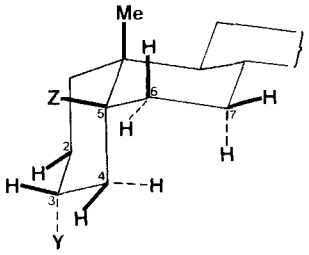


1A 3α-Y_{ax}, 5α-Z_{ax} (3β – H_{eq})

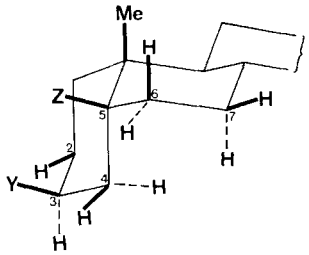


1B (R′ = H), **1BB** (R′ = AcO)
3β – Y_{eq}, 5α-Z_{ax} (3α – H_{ax})

A/B = *trans*
5α-steroids **1**



2A 3α – Y_{eq}, 5β – $Z_{ax,eq}$ (3β – H_{ax})



2B 3β – Y_{ax}, 5β – $Z_{ax,eq}$ (3α – H_{eq})

A/B = *cis*
5β-steroids **2**

aa Z = HO; Y = H; **dd** Z = AcO, Y = H;
a Z = Y = HO; **b** Z = HO, Y = AcO; **c** Z = HO, Y = PNBO; **d** Z = AcO, Y = HO; **e** Z = Y = AcO;
f Z = AcO, Y = PNBO; **g** Z = $CCl_3CONHCOO$, Y = AcO
(PNBO = *p*-$NO_2C_6H_4COO$)

regardless of substitution at C(3) (Y = H, α- or β-HO, -AcO, -PNBO). (The value of 2.03 ppm is observed for 3β,5β-cholestanediol 3-*p*-nitrobenzoate (**2Bc**)).

However, when the substituent at C(5) is an acetoxy group (Z = AcO) or *N*-trichloroacetyl-carbamoyloxy group (Z = $CCl_3CONHCOO$), its ester carbonyl moiety assumes such a conformation as to cause deshielding of the equatorial H_α–C(6), both in the 5α- and 5β-series. The signal of this H_α–C(6) (irrespective of substitution at C(3), *i.e.* Y = H, α- or β-HO, -AcO, -PNBO) is now readily detectable around 2.5 ppm, *i.e.* at 2.44–2.55 ppm for the 5α-acetoxy compounds (**1dd**; **1Ad**, **1Ae**, **1Af**; **1Bd**, **1Be**, **1Bf**), and at 2.48–2.62 ppm for the 5β-acyloxy steroids (**2dd**; **2Ad**, **2Ae**, **2Af**; **2Be**, **2Bf**, **2Bg**″)[2]).

2. *Protons at C(4).* In 5α- and 5β-unsubstituted steroids **1** and **2** (Z = H), respectively, without or with substituents at C(3) (Y = H, α- or β-HO, -AcO, -PNBO) [2], the two protons at C(4) resonate upfield of 2.0 ppm. An exception is 5β-cholestan-3β-ol *p*-nitrobenzoate (**2B**, Z = H, Y = PNBO) [2], which shows a

Table. *Chemical shifts of protons at C(4) and C(6) in various 5-hydroxy- and 3,5-dihydroxy-steroids and their acetate and* p*-nitrobenzoate esters* **1** *and* **2** (see *Scheme*)[a])

5α-Steroid[b])	MHz	^{1}H-NMR. signals (ppm)[c])		
		H_α–C(4)[d]) equatorial	H_β–C(4)[e]) axial	H_α–C(6)[f]) equatorial
5α-Z_{ax} (**1**)				
1aa Z = HO, Y = H	360	g)	g)	1.98 *d*×*t* (J_{gem} = 12, J_{vic} = 4)
1dd Z = AcO, Y = H	100	2.45[h]) *m* ($J_{gem} \approx$ 12–14)	g)	2.45[h]) *m* ($J_{gem} \approx$ 12–14)
3α-Y_{ax}, 5α-Z_{ax} (**1A**)[i])				
1Aa Z = HO, Y = HO	360	1.61 *d*×*d*×*d* (J_{gem} = 16, J_{vic} = 2.5, $J_{2eq,4eq}$ = 2)	1.79 *d*×*d* (J_{gem} = 16, J_{vic} = 4)	1.98 *d*×*t* (J_{gem} = 12, J_{vic} = 4)
1Aa irrad. at 4.07 ppm (*m*, $w_{1/2} \approx$ 7, = eq. H_β–C(3))		1.61 *d*×*d* (J_{gem} = 16, $J_{2eq,4eq}$ = 2)	1.79 *d* (J_{gem} = 16)	1.98 *d*×*t* (J_{gem} = 12, J_{vic} = 4)
1Ab Z = HO, Y = AcO	360	1.64 *d*×*t* (J_{gem} = 16, J_{vic} = $J_{2eq,4eq}$ = 2)	1.89 *d*×*d* (J_{gem} = 16, J_{vic} = 4)	1.99 *d*×*t* (J_{gem} = 12, J_{vic} = 4)
1Ab irrad. at 5.20 ppm (*m*, $w_{1/2} \approx$ 8, = eq. H_β–C(3))		1.64 *d*×*d* (J_{gem} = 16, $J_{2eq,4eq}$ = 2)	1.89 *d* (J_{gem} = 16)	1.99 *d*×*t* (J_{gem} = 12, J_{vic} = 4)
1Ad Z = AcO, Y = HO	100	2.82 *d*×*t* (J_{gem} = 16, J_{vic} = $J_{2eq,4eq}$ = 2)	g)	2.49 *d*×*t* (J_{gem} = 14, J_{vic} = 3)

[2]) For the reason already discussed previously [3] [4], the signal of the equatorial H_α–C(6) in the steroidal 3β,5α,6β-triol 3,6-diacetates **1BBb** and **1BBb′**, which is situated at 4.75–4.76 ppm, is shifted downfield by about 1.2 ppm when the 5α-hydroxy group is acetylated, appearing at 5.92–5.93 ppm in the triacetates **1BBe** and **1BBe′** (see *Table*).

Table (continued)

5α-Steroid[b])	MHz	^{1}H-NMR. signals (ppm)[c])		
		H_a–C(4)[d]) equatorial	H_β–C(4)[e]) axial	H_a–C(6)[f]) equatorial
1Ae Z = AcO, Y = AcO	360	2.84 $d \times t$ (J_{gem} = 16, $J_{vic} = J_{2eq,4eq}$ = 2)	g)	2.44 $d \times t$ (J_{gem} = 14, J_{vic} = 3.5)
1Af Z = AcO, Y = PNBO[j])	100	3.21 $d \times d \times d$ (J_{gem} = 16, J_{vic} = 2.5, $J_{2eq,4eq}$ = 2)	g)	2.44 $d \times t$ (J_{gem} = 14, J_{vic} = 3)
3β-Y_{eq}, 5α-Z_{ax} (**1B**)[k])				
1Ba Z = HO, Y = HO	360	g)	g)	1.99 $d \times t$ (J_{gem} = 12, J_{vic} = 4)
1Bb Z = HO, Y = AcO	360	g)	g)	1.98 $d \times t$ (J_{gem} = 12, J_{vic} = 4)
1Bb irrad. at 5.16 ppm (m, $w_{1/2} \approx 23$, = ax. H_a–C(3))		g)	g)	1.98 $d \times t$ (J_{gem} = 12, J_{vic} = 4)
1Bc Z = HO, Y = PNBO[j])	360	g)	g)	2.00 $d \times t + m$ (1H) (J_{gem} = 12, J_{vic} = 3)
1Bc irrad. at 5.47 ppm (*sept*, l.s. ≈ 5, = ax. H_a–C(3))		g)	g)	*dito*
1Bd Z = AcO, Y = HO	100	2.83 $d \times d \times d$ (J_{gem} = 14, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	g)	2.52 $d \times t$ (J_{gem} = 14, J_{vic} = 3)
1Be Z = AcO, Y = AcO	100	2.80 $d \times d \times d$ (J_{gem} = 14, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	g)	2.54 $d \times t$ (J_{gem} = 14, J_{vic} = 3)
1Bf Z = AcO, Y = PNBO[j])	360	2.96 $d \times d \times d$ (J_{gem} = 16, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	g)	2.55 $d \times t$ (J_{gem} = 14, J_{vic} = 3)
1Bf irrad. at 5.07 ppm (*sept*, l.s. ≈ 5, = ax. H_a–C(3))		2.96 $d \times d$ (J_{gem} = 16, $J_{2eq,4eq}$ = 2)	g)	2.55 $d \times t$ (J_{gem} = 14, J_{vic} = 3)
1BBb[l]) Z = HO, Y = AcO	60	g)	g)	4.75 m ($w_{1/2} \approx 5$)
1BBb′[l]) Z = HO, Y = AcO, R = H_2	60	g)	g)	4.76 m ($w_{1/2} \approx 5$)
1BBe[l]) Z = AcO, Y = AcO	60	2.85 $d \times d \times d$ (J_{gem} = 14, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	g)	5.92 m ($w_{1/2} \approx 5.5$)
1BBe′[l]) Z = AcO, Y = AcO, R = H_2	60	2.87 $d \times d \times d$ (J_{gem} = 14, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	g)	5.93 m ($w_{1/2} \approx 5$)

Table (continued)

5β-Steroid[b])	MHz	^{1}H-NMR. signals (ppm)[c])		
		H_α–C(4)[m]) axial	H_β–C(4)[n]) equatorial	H_α–C(6)[f]) equatorial
5β-$Z_{ax,eq}$ (**2**)[o])				
2aa Z = HO Y = H	360	2.13 *d*×*d*×*d* (J_{gem} = 14, J_{vic} = 12, J_{vic} = 6)	g)	1.98 *d*×*t* (J_{gem} = 13, J_{vic} = 3)
2dd Z = AcO Y = H		g)	2.51[h]) *m* (J_{gem} ≈ 14)	2.51[h]) *m* (J_{gem} ≈ 14)
3α-Y_{eq}, 5β-$Z_{ax,eq}$ (**2A**)[k])[o])				
2Aa Z = HO Y = HO	360	2.03[h]) *m* (J_{gem} ≈ 14)	g)	1.98[h]) *m* (J_{gem} ≈ 14)
2Ab Z = HO Y = AcO	100	2.15 *d*×*d* (J_{gem} = 14, J_{vic} = 12)	g)	g)
2Ad Z = AcO Y = HO	360	g)	2.81 *d*×*d*×*d* (J_{gem} = 14, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	2.54 *d*×*d*×*d* (J_{gem} = 13, J_{vic} = 4, J_{vic} = 3)
2Ad irrad. at 3.73 ppm (*sept*, l.s. ≈ 5, = ax. H_β–C(3))		g)	2.81 *d*×*d* (J_{gem} = 14, $J_{2eq,4eq}$ = 2)	2.54 *d*×*d*×*d* (J_{gem} = 13, J_{vic} = 4, J_{vic} = 3)
2Ae Z = AcO Y = AcO	360	g)	2.78 *d*×*d*×*d* (J_{gem} = 14, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	2.58 *d*×*d*×*d* (J_{gem} = 14, J_{vic} = 5, J_{vic} = 3)
2Af Z = AcO Y = PNBO[j])	360	2.22 *d*×*d* (J_{gem} = 14, J_{vic} = 12)	2.98 *d*×*d*×*d* (J_{gem} = 14, J_{vic} = 5, $J_{2eq,4eq}$ = 2)	2.62 *d*×*t* (J_{gem} = 14, J_{vic} = 4)
3β-Y_{ax}, 5β-$Z_{ax,eq}$ (**2B**)[i])[o])				
2Ba Z = HO Y = HO	100	2.23 *d*×*d* (J_{gem} = 15, J_{vic} = 3.5)	g)	g)
2Ba′ Z = HO Y = HO R = H_2	100	2.22 *d*×*d* (J_{gem} = 15, J_{vic} = 3.5)	g)	g)
2Ba″ Z = HO Y = HO R = β-HO, α-H	100	2.22 *d*×*d* (J_{gem} = 15, J_{vic} = 4)	g)	g)
2Ba‴ Z = HO Y = HO R = O	360	2.18[p]) *d*×*d* (J_{gem} = 15, J_{vic} = 3.5)	g)	g)
2Ba‴ irrad. at 4.17 ppm (*m*, $w_{1/2}$ ≈ 7, = eq. H_α–C(3))	100	2.18 *d* (J_{gem} = 15)	g)	g)
2Bb Z = HO Y = AcO	100	2.32 *d*×*d* (J_{gem} = 16, J_{vic} = 4)	g)	g)
2Bb′ Z = HO Y = AcO R = H_2	100	2.34 *d*×*d* (J_{gem} = 16, J_{vic} = 4)	g)	g)

Table (continued)

5β-Steroid[b])	MHz	^{1}H-NMR. signals (ppm)[c])		
		H_α–C(4)[m]) axial	H_β–C(4)[n]) equatorial	H_α–C(6)[f]) equatorial
2Bb″ Z = HO Y = AcO R = β-AcO, α-H	100	2.28 *d*×*d* (J_{gem} = 16, J_{vic} = 4)	g)	g)
2Bb″ + TAI[q]) (= **2Bg″**) Z = $CCl_3CONHCOO$ Y = AcO R = β-AcO, α-H	100	2.20 *d*×*d* (J_{gem} = 16, J_{vic} = 4)	2.92 *d*×*t* (J_{gem} = 16, J_{vic} ≈ 2)	2.52 *d*×*t* (J_{gem} = 14, J_{vic} = 3)
2Bc Z = HO Y = PNBO[j])	360	2.43 *d*×*d* (J_{gem} = 16, J_{vic} = 4)	g)	2.03 *d*×*t* (J_{gem} = 13, J_{vic} = 3)
2Bc irrad. at 5.49 ppm (*m*, $w_{1/2}$ ≈ 7, = eq. H_α–C(3))		2.43 *d* (J_{gem} = 16)	g)	2.03 *d*×*t* (J_{gem} = 13, J_{vic} = 3)
2Be Z = AcO Y = AcO	100	g)	2.92 *d*×*t* (J_{gem} = 16, J_{vic} ≈ 2)	2.50 *d*×*t* (J_{gem} = 13, J_{vic} = 4)
2Bf Z = AcO Y = PNBO[j])	360	2.21 *d*×*d* (J_{gem} = 16.5, J_{vic} = 4)	3.18 *d*×*t* (J_{gem} = 16.5, J_{vic} ≈ 2)	2.48 *d*×*d*×*d* (J_{gem} = 13, J_{vic} = 5, J_{vic} = 3)[r])

[a]) ^{1}H-NMR. signals of other protons in these compounds were given and discussed previously [2] [3].

[b]) If not stated otherwise, compounds **1** and **2** (of the A and B series) listed in this *Table* are cholestane derivatives (R = β-CHMe$(CH_2)_3CHMe_2$, α-H).

[c]) Coupling constants *J* in Hz. Internal standard: tetramethylsilane (= 0 ppm). Abbreviations: *d* doublet, *t* triplet, *qa* quadruplet, *qi* quintuplet, *sept.* septuplet, *m* multiplet, l.s. line spacing (splitting) in Hz, $w_{1/2}$ half-band width in Hz; gem geminal, vic vicinal, eq equatorial, ax axial.

[d]) J_{vic} for eq. H_α–C(4) corresponds in compounds **1** to $J_{3ax,4eq}$ and $J_{3eq,4eq}$, in **1A** to $J_{3eq,4eq}$, and in **1B** to $J_{3ax,4eq}$; $J_{2eq,4eq}$ refers to 'W'-type-4σ-bond-long-range coupling.

[e]) J_{vic} for ax. H_β–C(4) corresponds in compounds **1** to $J_{3ax,4ax}$ and $J_{3eq,4ax}$, in **1A** to $J_{3eq,4ax}$, and in **1B** to $J_{3ax,4ax}$.

[f]) J_{vic} for eq. H_α–C(6) in all compounds **1** and **2** corresponds to $J_{6eq,7ax}$ and $J_{6eq,7eq}$.

[g]) Not easily observable since within the methylene envelope, in the region upfield of 2.0 ppm.

[h]) Signals of H–C(4) and eq. H_α–C(6) overlapping.

[i]) The signal of the eq. H–C(3) in compounds **1A** (*i.e.* eq. H_β–C(3)) and **2B** (*i.e.* eq. H_α–C(3)) appears as a *m* (ill-resolved *qi*) with $w_{1/2}$ ≈ 5–8 Hz.

[j]) PNBO = *p*-nitrobenzoyloxy group.

[k]) The signal of the ax. H–C(3) in compounds **1B** (*i.e.* ax. H_α–C(3)) and **2A** (*i.e.* ax. H_β–C(3)) appears usually in the 360 MHz spectra as a *sept.* with l.s. of about 4.5–5.5 Hz, and in 100 MHz spectra as a broad *m* with $w_{1/2}$ ≈ 22–24 Hz.

[l]) ^{1}H-NMR. spectra of these compounds were discussed previously [3] [4].

[m]) J_{vic} for ax. H_α–C(4) corresponds in compounds **2** to $J_{3ax,4ax}$ and $J_{3eq,4ax}$, in **2A** to $J_{3ax,4ax}$, and in **2B** to $J_{3eq,4ax}$.

[n]) J_{vic} for eq. H_β–C(4) corresponds in compounds **2** to $J_{3ax,4eq}$ and $J_{3eq,4eq}$, in **2A** to $J_{3ax,4eq}$, and in **2B** to $J_{3eq,4eq}$; $J_{2eq,4eq}$ refers to 'W'-type-4σ-bond-long-range coupling.

[o]) $Z_{ax,eq}$ means axial on ring A and equatorial on ring B.

[p]) The two four line signals at 2.07 and 2.46 ppm (at 360 MHz) belong to $H_2C(16)$.

[q]) TAI = trichloroacetyl-isocyanate (CCl_3CO–N=C=O).

[r]) J_{vic} = 5 refers to $J_{6eq,7ax}$, and J_{vic} = 3 refers to $J_{6eq,7eq}$.

signal at 2.10 ppm (not given in the *Table*), attributed to the axial H_α–C(4), because, upon irradiation of the equatorial H_α–C(3) at 5.38 ppm, the triplet of doublets centered at 2.10 ppm ($J_{gem} \approx J_{4ax,5ax} \approx 14$ Hz, $J_{3eq,4ax} \approx 3$ Hz) is reduced to a triplet ($J \approx 14$ Hz).

2.1. *Equatorial H–C(4).* The equatorial proton at C(4) is α in 5α-steroids **1** and β in 5β-compounds **2**. Regardless of substitution at C(3) (Y = H, α- or β-HO, -AcO, -PNBO), the signal of the equatorial H–C(4) is located upfield of 2.0 ppm in 5α- and 5β-hydroxy-steroids **1** and **2** (Z = HO), respectively (*e.g.* **1Aa** (Y = HO) and **1Ab** (Y = AcO) in the *Table*).

However, when the 5-hydroxy group is acylated, as in the 5α- and 5β-acetoxy-steroids **1** and **2** (**A** and **B**, Z = AcO), respectively, and also in the 5β-*N*-trichloro-acetyl-carbamoyloxy-steroid **2Bg''**, then the equatorial H–C(4) is deshielded by the 5α- or 5β-ester carbonyl group (cf. section 1). It now resonates at 2.5–3.2 ppm, the downfield shift increasing somewhat with the deshielding influence (and polarity) of the substituent at C(3) (in order of compound type: **dd** < **d** ≈ **e** (≈ **g**) < **f**, in both the 5α-series **1A** and **1B**, and 5β-series **2A** and **2B**). Thus, for Y = H the equatorial H–C(4) appears at 2.45–2.5 ppm, for Y = HO or AcO at 2.8–2.9 ppm, and for Y = PNBO at 2.95–3.2 ppm.

It should be noted that when the resonances of both the equatorial H_α–C(6) and the equatorial H–C(4) are situated around 2–3 ppm, the signal of H–C(4) is always at lower field, the difference being in general 0.2–0.4 ppm (but 0.77 and 0.70 ppm for the 5α- and 5β-acetoxy compounds containing an axial 3-*p*-nitro-benzoyloxy group, *i.e.* **1Af** and **2Bf**, respectively).

2.2. *Axial H–C(4).* The axial proton at C(4) is β in 5α-steroids **1** and α in 5β-compounds **2**. In the 5α-series **1**, irrespective of substitution at C(5) (Z = H, HO or AcO) and at C(3) (Y = H, α- or β-HO, -AcO, -PNBO), the signal of this axial H_β–C(4) is located upfield of 2.0 ppm (*e.g.* **1Aa** and **1Ab** in the *Table*), and thus not easily identifiable.

In the 5β-series **2**, the 5β-hydroxy-steroids without or with substituents at C(3) (Z = HO; Y = H, α- or β-HO, -AcO, -PNBO) show a signal for the axial H_α–C(4) around 2.0–2.4 ppm, the downfield shift being more pronounced (by about 0.2 ppm) in 5β-hydroxy compounds with an axial 3β-substituent (compare **2Aa** and **2Ab** with **2Ba** and **2Bb**).

In 5β-acetoxy-steroids **2** (Z = AcO; Y = H, α- or β-HO, and α- or β-AcO) the signal of the axial H_α–C(4) is situated upfield of 2.0 ppm, except when the 5β-acetoxy compound contains an equatorial 3α- or axial 3β-*p*-nitrobenzoyloxy group (**2Af** and **2Bf**, respectively), in which case the signal of the axial H_α–C(4) is located at about 2.2 ppm. When the 5β-acetoxy group is replaced by the 5β-(*N*-trichloroacetyl-carbamoyloxy) group, as in **2Bg''**, the axial H_α–C(4) resonates at 2.20 ppm too.

In conclusion it can be said that the appearance of ^{1}H-NMR. signals in the 2–3 ppm region and their assignment to the proton(s) at C(4) and/or the equatorial α-proton at C(6) may be of diagnostic value (in combination with other ^{1}H-NMR. data) for an easier structural and configurational identification and/or characterization of 5-hydroxy- and 5-acetoxy-steroid compounds (unsubstituted or containing a

hydroxy, acetoxy or *p*-nitrobenzoyloxy group at C(3)), particularly when 360-MHz-^{1}H-NMR. spectra are available.

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Experimental Part

^{1}H-NMR. spectra were measured in $CDCl_3$ at 360 MHz on a *Bruker* HX-360 spectrometer and/or at 100 MHz on a *Varian* XL-100-15 spectrometer, both equipped with a *Fourier* transform accessory. Noise decoupled ^{13}C-NMR. spectra were recorded (in $CDCl_3$) at 25.2 MHz on the same *Varian* apparatus. Deuterium atoms of the solvent ($CDCl_3$) were used for the 15.4 MHz ^{2}H-lock during ^{1}H-NMR. and ^{13}C-NMR. work. All the spectra were taken at room temperature.

The steroids used in this study were all known compounds, the preparation and properties of which were described previously [2] [3].

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