MAGNETIC RESONANCE IN CHEMISTRY, VOL. 29, 794–800 (1991)

NMR Spectra and Stereochemistry of *N*-Acetyl and *N*-Benzoyl Derivatives of Solasodine

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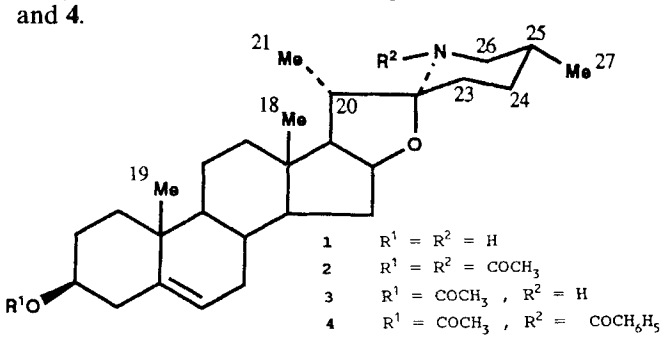
***N*-Acetylation of solasodine gives only one rotameric *N*-acetyl derivative compared with *N*-acetyl-3-methylpiperidine, which exists in solution as two equally populated rotamers. The ^{1}H and ^{13}C NMR spectra ($CDCl_3$) of *O,N*-diacetyl- and *O*-acetyl-*N*-benzoylsolasodine indicate significant deviations from F-ring chair geometry. Opening of the F ring of these derivatives in $CDCl_3$ solution at 25 °C, to give the corresponding furosta-5,20(22)-diene derivatives, was ascertained by NMR spectroscopy.**

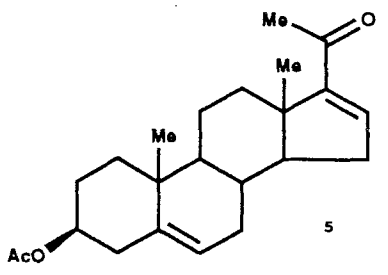
KEY WORDS Solasodine [(25*R*)-solasod-5-en-3β-ol] *O,N*-Diacetylsolasodine *O*-Acetyl-*N*-benzoylsolasodine 3β-Acetoxy-26-acetamidofurosta-5,20(22)-diene 3β-Acetoxy-26-benzamidofurosta-5,20(22)-diene

INTRODUCTION

Solasodine [(25*R*)-solasod-5-en-3β-ol] (**1**) can be converted to 3β-acetoxypregna-5,16-dien-20-one (**5**) via its *O,N*-diacetyl derivative (**2**), and this provides a route to medicinally-important steroids.[1] *N*-Formylsolasodine has been shown to exist as two distinct rotamers[2] whilst only one rotamer of the *N*-acetyl derivative has been detected by both ^{1}H NMR[3] and ^{13}C NMR[4] spectroscopy. An NMR study of *O,N*-diactyl-(**2**) and *O*-acetyl-*N*-benzoyl-solasodine (**4**) was undertaken in order to provide information on the stereochemistry of the F ring. *N*-Acetyl- and *N*-benzoyl-3-methylpiperidine were selected for a corresponding NMR study since these compounds resemble the F-ring of the derivatives **2** and **4**.



1 $R^1 = R^2 = H$
2 $R^1 = R^2 = COCH_3$
3 $R^1 = COCH_3$, $R^2 = H$
4 $R^1 = COCH_3$, $R^2 = COCH_6H_5$



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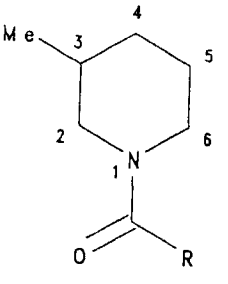
0749–1581/91/080794–07 $05.00

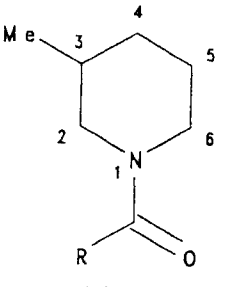
RESULTS AND DISCUSSION

NMR spectroscopy and stereochemistry of *N*-acetyl- and *N*-benzoyl-3-methylpiperidine

The ^{1}H NMR spectrum of *N*-acetyl-3-methylpiperidine in $CDCl_3$ at 25 °C showed two sets of signals corresponding to the two rotameric forms, (*Z*)-**6** and (*E*)-**6**. Assignment of the chemical shifts of the respective rotamers (Table 1) was assisted by the use of spin-decoupling difference methods and two-dimensional NMR spectroscopy.



6(Z) R = CH_3
7(Z) R = C_6H_5



6(E) R = CH_3
7(E) R = C_6H_5

The low-field signals at δ4.35 and 4.29 were assigned to the equatorial N-C*H* protons (in the two rotamers) *cis* to the amide carbonyl group, since this is known to exert a deshielding influence.[5] Distinction between these was made on the basis of the relative complexity of the signals, since the N–C-2–H-eq multiplet at δ4.35 is simpler than that of N–C-6–H-eq at δ4.29. The signals of the corresponding N-C*H* axial protons were located by spin decoupling and further confirmed from the 2D ^{1}H homonuclear connectivity spectrum. One of these protons absorbed as a doublet of doublets at δ2.15 (J = 10.6, −12.0 Hz) and was therefore assigned to the 2-axial proton [J(2ax, 2eq) = −12.0 Hz, J(2ax, 3ax) = 10.6 Hz] in rotamer (*Z*)-**6**. The shielding of this axial

Received 9 February 1991
Accepted (revised) 18 April 1991

proton (δ2.15) relative to that of the 6-axial proton (δ2.56) in (*E*)-**6** arises in part from the equatorial methyl group.[6] The remaining downfield ^{1}H NMR signals corresponding to H-2ax and H-2eq of (*E*)-**6** and H-6ax and H-6eq of (*Z*)-**6** were then unambiguously assigned from their multiplicities and from decoupling experiments. The ^{1}H NMR assignments are summarized in Table 1.

The assignment of the ^{13}C NMR signals of the two rotamers of **6** was assisted by a 2D heteronuclear (^{1}H–^{13}C) connectivity spectrum. The C-2 and C-6 signals of (*E*)-**6** and (*Z*)-**6** were identified by the correlation with the corresponding proton signals assigned above. These show that *N*-acetylation of 3-methylpiperidine results in upfield shifts relative to the free base, 5.8 and 4.7 ppm, of carbon nuclei *cis* to the amide carbonyl group in (*Z*)-**6** and (*E*)-**6**, respectively, whereas those *trans* to the amide function are relatively unaffected.

The spectra of *N*-benzoyl-3-methylpiperidine (**7**) showed very broad signals, indicating a near coalescence temperature for interconversion between the two rotamers. The ^{1}H NMR spectrum at −20 °C showed sharp signals for both rotamers. The signal assignments were made by spin-decoupling and comparison with the spectra of **6**, and these are provided in Table 1. The ^{13}C NMR spectrum at −30 °C also resolved into sharp signals, and the assignment of the signals of the two rotamers was facilitated by 2D heteronuclear (^{1}H–^{13}C) correlation spectroscopy (Table 2).

NMR spectroscopy and stereochemistry of *O*,*N*-diacetylsolasodine

The NMR spectra of *O*,*N*-diacetylsolasodine showed the presence of only one rotamer. This can be assigned the *E*/*Z* stereochemistry (**8**) by comparison of the chemical shift of H-26eq with that of H-2eq in the two rotamers of **6**. A marked deshielding (Δδ + 1.33) of this proton is observed when in a *cis* relationship to the amide carbonyl group (*Z*-isomer). The substituent effect (Δδ + 1.33) on H-26eq in **2** with reference to solasodine is very similar, indicating structure **8**.

In the ^{1}H NMR spectrum ($CDCl_3$) of solasodine (**1**), the 26-methylene protons absorb at δ2.57 [triplet, *J*(26ax, 26eq) = −10.8 Hz, *J*(26ax, 25ax) = 10.8 Hz, H-26ax] and at δ2.65 [broad doublet of doublets, *J*(26eq, 26ax) = −10.8 Hz, *J*(26eq, 25ax) = 6.5 Hz, H-26eq] consonant with a chair conformation and an equatorial C-25–Me group (compare δ2.17, *J* = 10.6, −12.0 Hz for H-2ax in 3-methylpiperidine), whereas in the spectrum of the *O*,*N*-diacetyl derivative (**2**) the one rotamer showed ^{1}H NMR signals for the C-26-methylene protons at δ2.83 [*J*(26ax, 26eq) = −13.5 Hz, *J*(26ax, 25) = 6.1 Hz] and δ3.98 [*J*(26eq, 26ax = −13.5 Hz, *J*(26eq, 25) = 2.6 Hz]. The observed vicinal couplings involving the C-26-methylene protons are different from those in solasodine and are not in accord with an F-ring chair conformation and an equatorial C-25-Me group.

The two possible rotamers (**8** and **9**) of *O*,*N*-diacetylsolasodine with a chair F-ring are shown in Fig. 1. Dreiding models of these show severe non-bonded interactions between 21-Me and the F-ring *N*-acetyl group. These may be relieved by chair inversion of the F-ring giving the two rotamers **10** and **11**. However, other severe non-bonded interactions arise in these conformations between the C-26-methylene group and the C-21-methyl group, and also between the axial C-25-methyl group and H-23ax. The stability of both rotamers **10** and **11** will also be affected by interactions between the acetyl group and the oxygen function of the E-ring, which are difficult to evaluate. The non-bonded interactions in conformations **10** and **11** may be reduced by bending away of the C-26-methylene groups; alternatively, considered as rotation about the C-26—N and C-26—C-25 bonds, resulting in twist-chair conformations **12** and **13**. The measured dihedral angles between the C-26-methylene protons and H-25 are then *ca.* 30° and 150°, which are in some agreement with the observed couplings (6.1 and 2.6 Hz). Such an argument for conformation based on coupling constants in the system must be qualitative, since effects such as that of the adjacent amide bond on the vicinal couplings cannot be determined.[7]

The ^{13}C NMR signals of **2** ($CDCl_3$) were assigned by direct comparison with those of **1** and 3-acetylsolasodine (**3**, Table 2) and also the use of the DEPT technique. The shifts are close to those reported,[4] but comparison of these with shifts for the rotamers of **6** shows very different trends.

The absorbances of C-23, C-24 and C-25 of *O*,*N*-diacetylsolasodine all show relatively large upfield shifts with respect to the chemical shifts of solasodine. Whilst the C-26 signal absorbs downfield by 1.4 ppm, the equivalent position carbons of the *Z*- and *E*-isomers of *N*-acetyl-3-methylpiperidine absorb upfield by 5.8 and 0.8 ppm, respectively, relative to 3-methylpiperidine. This lack of correlation between substituent effects in the two systems is consonant with the proposed conformational change (Fig. 1) consequent upon *N*-acetylation of solasodine.

NMR spectroscopy and stereochemistry of *O*-acetyl-*N*-benzoylsolasodine

Benzoylation of *O*-acetylsolasodine (**3**) gave *O*-acetyl-*N*-benzoylsolasodine (**4**). Examination of the ^{1}H NMR spectrum ($CDCl_3$) of **4** showed the presence of a single rotamer, and comparison of the parameters with those of the spectra of (*Z*)-**7** and (*E*)-**7** showed distortion of the F-ring as in **2**. Comparison of *N*-benzoylation on the H-2eq signals of (*E*)-**7** and (*Z*)-**7** (Δδ +0.61 and +1.57, respectively, relative to 3-methylpiperidine) with the corresponding effect (Δδ +1.34) on the H-26 eq signal of **4** indicates that the preferred rotamer possesses the (*Z*)-**7** stereochemistry, analogous to **12**.

The ^{13}C NMR shifts of the F-ring nuclei of **4** were strikingly similar to those of **2** (Table 2), indicating the same type of conformation. Dreiding models indicate the phenyl ring to be below the plane of the steroidal skeleton, directly under C-16, to minimize interactions with 21-Me.

Conversion of *O*,*N*-diacetylsolasodine and *O*-acetyl-*N*-benzoylsolasodine into furosta-5,20(22)-diene derivatives

During the ^{1}H NMR spectral analysis of *O*,*N*-diacetylsolasodine (**2**), the spectrum was observed to undergo

Table 1. ^{1}H NMR spectral parameters ($CDCl_3$) of 3-methylpiperidine, solasodine and derivatives

	Proton resonances (δ) Chemical shifts (δ, ppm) (J, Hz, in parentheses)													
Compound	18-Me	19-Me	21-Me	27-Me	H-3ax	H-6	H-8	H-15'eq'	H-15'ax'	H-16	H-17	H-26eq	H-26ax	Others
(25*R*)-Solasod-5-en-3β-ol (solasodine) (**1**)	0.81	1.02	0.94	0.84	3.50 m	5.31 br.d	—	1.98 m	—	4.25 q (6.4, 6.4, 6.4)	—	2.65 br.dd (6.5, −10.8)	2.57 t (−10.8, 10.8)	
(25*R*)-3β,*N*-Diacetoxy-solasod-5-ene (**2**)	0.91	1.03	1.07	0.93	4.57 m	5.34 br.d	—	—	—	4.17 q (6.4, 6.4, 6.4)	—	3.98 dd (2.6, −13.5)	2.83 dd (−13.5, 6.1)	2.19, 2.02 {s; $COCH_3$} 3.09 {H-20}
(25*R*)-3β-Acetoxy-solasod--5-ene (**3**)	0.81	1.03	0.95	0.85	4.58 m	5.35 br.d	—	—	—	4.28 q (6.4, 6.4, 6.4)	—	2.67	2.59 t	2.01 {s; $OCOCH_3$}
(25*R*)-3β-Acetoxy-*N*-benzoylsolasod-5-ene (**4**)	0.95	1.04	1.04	0.89	4.85 m	5.40 br.d	—	—	—	4.19 q (6.4, 6.4, 6.4)	—	3.99 dd (2.6, −13.5)	2.84 dd (−13.5, 6.1)	2.03, 2.21 {s; $COCH_3$} 5.37 {brs; N-*H*} 7.40 {t,(7.6, 7.6); aromatic 7.53 {t, 7.6, 7.6); aromatic-*H*} 8.03 {d, (7.6); aromatic-2*H*}
3β,26-Diacetoxy-5α-furost-20(22)-ene (pseudotigogenin) (**16**)	0.65	0.91	1.57 s	0.93	4.66 m	—	—	—	—	4.66 m	2.44 d (5.1)	3.87 t (−7.0, 7.0)	3.87 t (−7.0, 7.0)	
3β-Acetoxy-26-acetamidofurosta-5,20(22)-diene (**14**)	0.67	1.03	1.57 s	0.91	4.57 m	5.34 br.d	—	2.15	1.41	4.70 m	2.47 d (5.1)	3.11 br.t	3.11 br.t	1.97, 2.02 {s; $COCH_3$} 5.58 {brs; N-*H*}

3β-Acetoxy-26-benzamidofurosta-5,20(22)-diene (**15**)	0.69	1.08	1.56 s	0.93	4.86 m	5.38 br.d	—	—	—	4.86 m	—	3.14 m	3.14 m	7.39 {t, (7.6, 7.6); aromatic-2*H*} 7.52 {t, (7.6, 7.6); aromatic-*H*} 8.01 {d, (7.6); aromatic-2*H*}
	3-Me	H-2eq	H-2ax	H-6eq	H-6ax										
3-Methylpiperidine	0.81 d (7.6)	2.96 m	2.17 q (10.6, −12.0)	2.96 m	2.48 dt (3.3, 12.2, −12.2)										
	3-Me	H-2eq	H-2ax	H-6eq	H-6ax										
N-Acetyl-3-methyl piperidine (**6**):															
Z-Isomer	0.84 d (7.6)	4.35 br.d	2.15 t (10.6, −12.0)	3.65 br.d	2.90 dt (3.3, 12.2, −12.2)										
E-Isomer	0.87 d (7.6)	3.57 br.d	2.63 dd (10.6, −12.0)	4.29 br.d	2.56 br.dt										
N-Benzoyl-3-methyl piperidine (**7**):															
Z-Isomer	0.78 d (7.6)	4.55 br.s	2.42 br.t (5.6, −5.6)	3.64 br.d	2.90 br.t										
E-Isomer	0.97 d (7.6)	3.57 br.d	2.61 br.t (5.6, −5.6)	4.51 br.s	2.79 br.t										

Table 2. ^{13}C NMR chemical shifts (δ) of 3-methylpiperidine, solasodine and their derivatives in $CDCL_3$

Compound	^{13}C chemical shifts (δ), ppm																										
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
(25*R*)-Solasod-5-en-3β-ol (solasodine((**1**)	37.3	31.6	71.6	42.3	140.9	121.3	32.1[i]	31.4	50.1	36.7	20.9	40.0	40.5	56.5	32.2[i]	78.7	62.8	16.4	19.4	41.3	15.3	98.2	34.1	30.3	31.4	47.7	19.3
(25*R*)-3β,*N*-Diacetoxy solasod-5-ene[a] (**2**)	37.0	27.7	73.8	38.1	139.8	122.2	32.1[j]	31.1	50.0	36.7	20.9	40.1	40.9	55.8	32.1[j]	78.8	62.1	16.4	19.3	38.2	16.2	101.2	24.3[k]	24.0[k]	28.0	49.1	18.5
(25*R*)-3β-Acetoxy solasod-5-ene[b] (**3**)	37.0	27.7	73.8	38.1	139.7	122.3	32.1[l]	31.4	50.0	36.7	20.8	39.9	40.5	56.5	32.2[l]	78.7	62.8	16.4	19.3[m]	41.2	15.3	98.2	34.1	30.3	31.4	47.7	19.3[m]
(25*R*)-3β-Acetoxy-*N*-benzoyl solasod-5-ene[c] (**4**)	36.9	27.9	74.5	38.2	139.8	122.5	32.2[n]	31.2	50.1	36.8	20.9	40.2	41.0	55.9	32.2[n]	78.9	62.2	16.4	19.4	38.2	16.3	101.2	24.4	24.0	28.0	49.1	18.5
3β-Acetoxy-26-acetamido furosta-5, 20(22)-diene[d] (**14**)	36.9	27.7	73.8	38.0	139.7	122.3	32.1	31.2	49.9	36.7	20.9	39.3	42.2	54.9	31.7	84.3	64.1	11.6	19.3	103.9	17.6	151.3	34.1	23.2	32.7	45.2	13.9

	6	5	4	3	2	Me
3-methyl piperidine	46.8	26.9	33.7	32.4	54.8	19.8
N-Acetyl-3-methyl piperidine (**6**):						
Z-Isomer[e]	47.0	25.8	32.9	30.9	49.0	18.8
E-Isomer[f]	42.1	24.6	32.9	31.7	54.0	19.0
N-Benzoyl-3-methyl piperidine (**7**):						
Z-Isomer[g]	48.1	25.9	32.8	30.9	49.1	18.8
E-Isomer[h]	42.4	24.7	32.8	30.8	54.9	19.2

Chemical shifts of acetate groups and others:
[a] 170.4, 170.9, 21.4, 25.2.
[b] 170.5, 21.4.
[c] 170.9, 25.3, 130.8, 129.7, 128.3, 132.7, 128.3, 129.7, 166.0.
[d] 170.3, 170.5, 21.4, 23.2.
[e] 169.0, 21.0.
[f] 173.7, 21.4.
[g] 129.3, 128.3, 126.6, 136.1, 126.6, 128.3, 170.0.
[h] 129.3, 128.3, 126.5, 136.0, 126.5, 128.3, 170.1.
[i–n] Values with the same superscript letters may be interchanged.

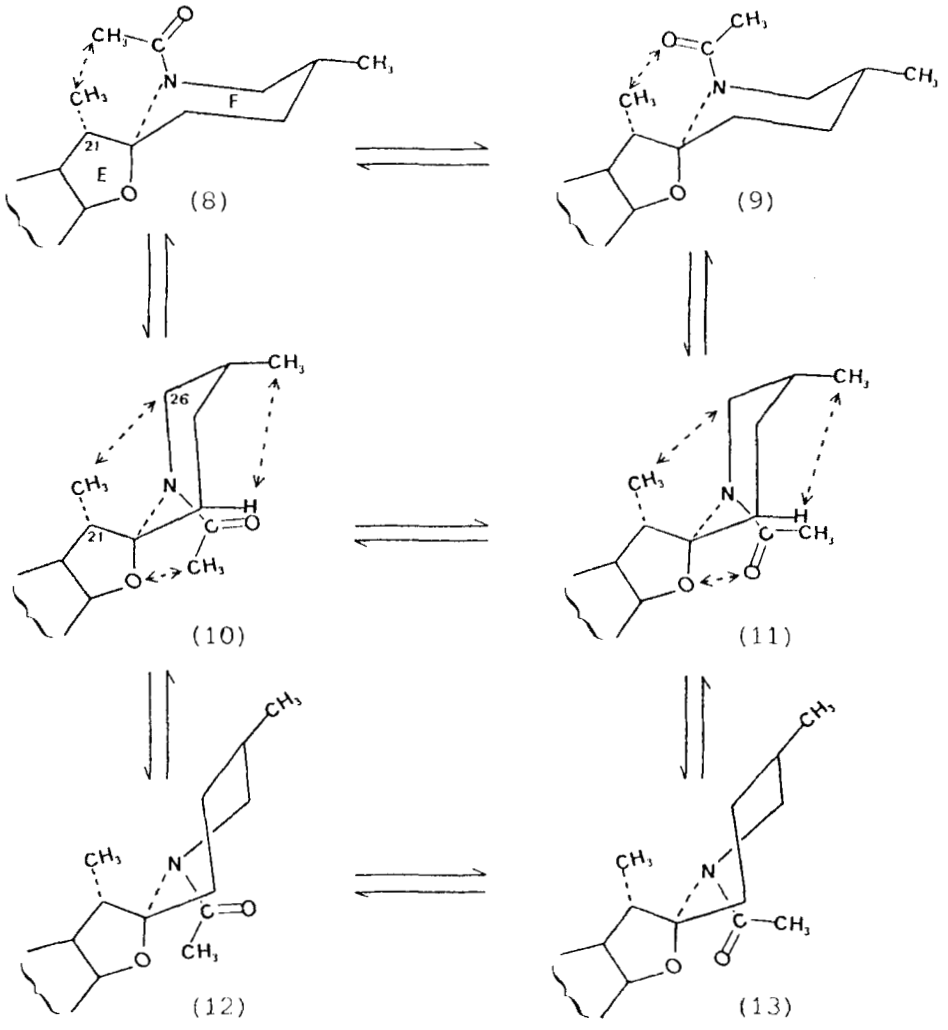
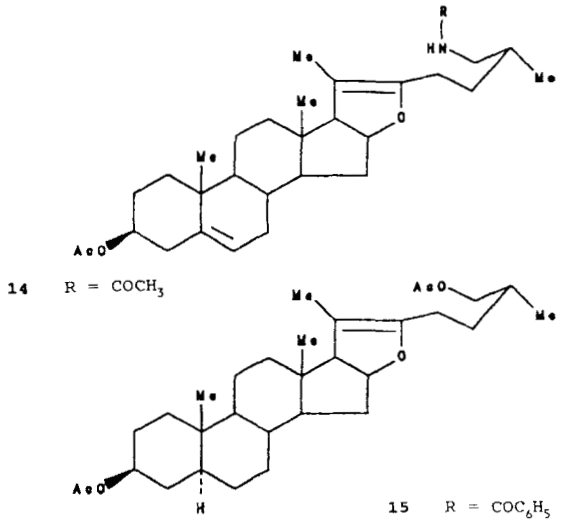


Figure 1. Possible conformations of the E–F ring system of the rotamers of *O,N*-diacetylsolasodine.

changes after a period of 3 h. The sample ($CDCl_3$ solution) was allowed to stand at room temperature for 27 h and re-examined, when several differences were noted with respect to the spectrum of **2**. The H-16 signals had shifted downfield from δ4.17 to δ4.70 ($\Delta\delta$ +0.53) and a very broad singlet appeared at δ5.58, downfield of the olefinic proton signal (δ5.34) in the spectrum of **2**. The signals previously assigned to the C-26-methylene protons had been replaced by a two-proton broad triplet at δ3.11. The multiplet arising from H-20 at δ3.09 no longer absorbed downfield of the methylene envelope.

A doublet absorbing at δ2.47 (J = 5.1 Hz) was shown to be coupled to H-16 by irradiation of the latter. The H-15′eq′ and H-15′ax′ signals were identified at *ca.* δ2.15 and *ca* δ1.41 from the changes in multiplicity. The doublet at δ2.47 was then assigned to H-17, and confirmation of this was obtained by decoupling. The 18-Me protons absorbed upfield at δ0.67 ($\Delta\delta$ −0.24). Similarly, the N-COCH_3 signal had shifted upfield to δ1.97 ($\Delta\delta$ −0.22). Of the usual four methyl signals, only three were observed, showing one of the doublets to have been affected by the changes. The latter was located at δ1.57 as a singlet and has the same shift as that of 21-Me in the spectrum of (25*R*)-3β,26-diacetoxy-5α-furost-20(22)-ene (**16**) (Table 1), which was prepared by acetylation of tigogenin [(25*R*)-5α-spirostan-3β-ol].

The rate of the above change was accelerated by the addition of a very small amount of DCl to a freshly prepared solution of **2** in $CDCl_3$. After consideration of the spectral data, the structure of the compound formed



14 R = $COCH_3$

15 R = COC_6H_5

was assigned as 3β-acetoxy-26-acetamidofurosta-5, 20(22)-diene (**14**).

The ^{13}C NMR spectrum of a $CDCl_3$ solution of *O,N*-diacetylsolasodine, which had been allowed to stand for 7 days, was consistent with the above conclusion. The absorbances of carbons of rings A to D were similar to those of **3** (Table 2). In addition to the carbon signals of the Δ^5-double bond at δ139.7 and 122.3, two other low-field signals at δ151.3 and 103.9 were as expected for the carbon shifts of the $\Delta^{20(21)}$-double bond.

The formation of **14** from *O,N*-diacetylsolasodine in an anhydrous medium in the presence of an acid is consistent with previous work.[8] The opening of the F-ring of the *N*-benzoyl derivative **4** in $CDCl_3$ had to be induced by the addition of a small amount of DCl to the sample. The changes in the ^1H NMR spectral features parallel those in the conversion of **2** to **14** and the relevant data are presented in Table 1.

EXPERIMENTAL

^1H (Table 1) and ^{13}C NMR spectra (Table 2) were recorded at 20 °C in $CDCl_3$ solution in 5-mm tubes on a JEOL GSX-270 (^1H, ^{13}C) Fourier transform spectrometer at 270.16 (^1H) and 67.97 MHz (^{13}C), using the deuterium signal of the solvent as the lock and TMS as internal standard. The most important measuring parameters were as follows: sweep width 3 (^1H) and 18 kHz (^{13}C), pulse width 3 (^1H) and 4.2 μs (^{13}C) (*ca.* 40° and 45° flip angle), acquisition time 5.459 or 0.901 s, number of scans 16–320 (^1H) and 1–20K (^{13}C), computer memory 32K.

Melting points are uncorrected. Mass spectra were obtained from PCMU, Harwell, on a VG Analytical ZAB-IF instrument.

(25*R*)-3β,*N*-Diacetoxysolasod-5-ene (2)

Acetylation of **1** (2 g) by refluxing for 30 min with acetic anhydride in pyridine gave a light-brown crude product. Repeated recrystallization of this from methanol gave **2** as a white solid (300 mg 12.5%), m.p. 162–164 °C (lit.[4] m.p. 164–165 °C). ν_{max} (Nujol) 1735, 1645, 1240, 1000, 970, 925 cm^{-1}. Electron impact mass spectrum (EI-MS), *m/z* 497.3490 (M^+) (calculated for $C_{31}H_{47}NO_4$, 497.3789).

(25*R*)-3β-Acetoxy-*N*-benzoylsolasod-5-ene (4)

Acetylation of **1** (5 g) (acetic anhydride, 1.15 ml) in pyridine at room temperature overnight gave **3** as a white powdery material (1 g, diethyl ether–acetone). Benzoylation of **3** (0.95 g) at room temperature by treatment with benzoyl chloride in pyridine afforded **4** (120 mg, diethyl ether), m.p. 224–226 °C. EI-MS, *m/z* 559.3676 (M^+) (calculated for $C_{36}H_{49}NO_4$, 559.3732).

N-Acetyl-3-methylpiperidine (6)

Acetylation of 3-methylpiperidine (2 g) overnight at room temperature by treatment with acetic anhydride in pyridine gave **6** (1.83 g) as a clear, slightly viscous liquid, b.p. 80–89 °C (7 mmHg) EI-MS, *m/z* 141.1150 (M^+) (calculated for $C_8H_{15}NO$, 141.1256).

N-Benzoyl-3-methylpiperidine (7)

3-Methylpiperidine (2 g) in sodium hydroxide (57%, 40 ml) was benzoylated by the addition of aliquots of benzoyl chloride (2.34 ml) with vigorous shaking after each addition. A thick oil separated and this was washed with water until neutral, before dissolving in dichloromethane (20 ml) and drying over anhydrous sodium sulphate. Removal of the dichloromethane and distillation of the residue gave **7** as a colourless liquid, b.p. 159–160 °C (5.5 mmHg). EI-MS, *m/z* 203.1323 (M^+) (calculated for $C_{13}H_{17}NO$, 203.1491).

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