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Note

Proton-n.m.r. studies of some *N*-acetylglycofuranosylamines and of their acylated derivatives

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Proton-n.m.r. studies of *N*-acylglycofuranosylamines and *N*-acylglycopyranosylamines have been published[1-6]. We now report ^{1}H-n.m.r.-spectral studies of *N*-acetyl-D-xylofuranosylamine (**1**), *N*-acetyl-D-glucofuranosylamine (**2**), *N*-acetyl-tetra-*O*-acetyl-D-glucofuranosylamine (**3**), *N*-acetyl-tetra-*O*-benzoyl-D-glucofuranosylamine (**4**), and *N*-benzoyl-tetra-*O*-benzoyl-D-glucofuranosylamine (**5**): the spectral data are summarized in Table I.

For obtaining the ^{1}H-n.m.r. spectra of **1** and **2** in pyridine-d_5, the protons in samples of these compounds were exchanged by several treatments with deuterium oxide, and precautions were then taken to eliminate the residual deuterium oxide. After recording these spectra for solutions in pyridine-d_5, the addition of a small amount of deuterium oxide ($\simeq$0.04 mL) was shown to modify the chemical shifts of all resonances, resulting in a weaker or stronger coupling of some proton-signals. The most important, relative differences (Hz) between coupled proton-signals of compounds **1** and **2** are listed in Table II.

These changes, as well as others produced among noncoupled protons, were helpful for making the assignments of several proton-signals. The relative displacements shown in Table II could be attributed to a competitive, solvation effect, which allows a partial replacement of pyridine-d_5 by deuterium oxide around the molecule of the *N*-acylglycofuranosylamine: this change modifies the environment around a given proton[7].

Most of the assignments were straightforward, but one point in Table I deserves comment. The proton signal of H-1 in **5** appears as a doublet, indicating that, in this case, $J_{\text{N-H,H-1}} = 0$.

TABLE I

CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (Hz, IN PARENTHESES) OF COMPOUNDS **1**–**5**

Compound	*Solvent*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*H-6*	*H-6'*	*N-H*	*N-Ac*	*O-Ac*
1	C_5D_5N	6.85dd $J_{1,2}$ (4.0)	4.73dd $J_{2,3}$ (1.6)	4.90dd $J_{3,4}$ (3.5)	4.98[a] $J_{4,5}$ (5.2)	4.52[b] $J_{4,5'}$ (5.5)	4.48[b] $J_{5,5'}$ (11.2)			8.8d $J_{N-H,1}$ (9.0)	2.14	
2	C_5D_5N[c]	6.90dd (3.5)	4.71dd (1.2)	5.08dd (2.8)	5.01dd (8.2)	4.89[a] $J_{5,6}$ (3.2)		4.48[b] $J_{6,6'}$ (11.0)	4.32[b] $J_{6',5}$ (6.1)	8.60d (10.0)	2.11	
3	$CDCl_3$	6.14dd (3.0)	5.06dd (1.0)	5.46dd (3.5)	4.35dd (10.0)	5.12m (2.5)		4.56dd (12.2)	4.10dd (5.0)	6.08d (10.8)	1.96	2.04 2.06 2.07 2.20
4	$CDCl_3$	6.39dd (3.7)	5.59dd (1.1)	5.84dd (3.5)	4.89dd (9.2)	5.75m (2.7)		4.89dd (12.0)	4.66dd (5.5)	6.20d (10.0)	2.00	
5	$CDCl_3$	6.97d (4.5)	5.83t (4.3)	6.22dd (5.8)	5.12dd (8.7)	5.84m (2.5)		4.99dd (12.5)	4.67dd (5.2)			

[a] Analyzed as the X part of a CXAB subsystem. [b] Analyzed as the AB part of a CXAB subsystem. [c] Spectral data for **2** in C_5D_5N–D_2O (220 MHz; undetermined amount of water) were reported in ref. 1; there are some differences from the chemical shifts reported herein.

TABLE II

DIFFERENCES (Hz) OF CHEMICAL SHIFTS BETWEEN SOME PROTON-SIGNALS OF **1** AND **2**

Compound	*Protons*	$\Delta\delta$		$\Delta(\Delta\delta)$
		C_5D_5N	C_5D_5N–D_2O	
1	H-5 and H-5′	33.6	32.4	+1.2
	H-3 and H-4	21.0	13.5	+7.5
2	H-6 and H-6′	44.0	47.0	−3.0
	H-4 and H-3	20.0	43.0	−23.0

A possible explanation for the observed splitting of the H-1 signal, as well as for the apparent lack of a signal for the N-H resonance of **5** (see Table I), could be that broadening of the N-H proton-resonance line takes place by ^{14}N quadrupole-induced relaxation. This effect in **5** would be related to the presence of the *N*-benzoyl group, as it does not operate in compounds **1–4**, and it would cause the proton signal of H-1 to appear as a doublet.

It should be pointed out that this result is in disagreement with all of the known values of $J_{N\text{-}H,H\text{-}1}$ (7.5–11.0 Hz) for *N*-acetylglycofuranosylamines, *N*-acylglycopyranosylamines, and 1,1-bis(acylamido)-1-deoxyalditols[1–3], although these results refer to spectra recorded for solutions in different solvents [C_5D_5N and $(CD_3)_2SO$].

Nevertheless, there are several facts that support the aforementioned assignment for compound **5**: (*a*) the value of $J_{1,2}$ (4.5 Hz) is in good agreement with the appearance of H-2, which is a triplet with a coupling-constant value of 4.3 Hz, (*b*) the signal at δ 6.97 is not removed after "exchanging" the sample with deuterium oxide, and (*c*) the value of the coupling constant of H-1 is in agreement with reported values of $J_{1,2}$ for *N*-acylglycofuranosylamines[1,2], and it does not support the assignment of the signal at δ 6.97 as being due to the amidic proton.

EXPERIMENTAL

Compounds **1–5** had values of m.p. and specific rotations in agreement with reported values. Proton-n.m.r. spectra were recorded and integrated at 270 MHz, with a 270-MHz spectrometer built at the University of British Columbia with Nicolet parts. Sample concentrations were 5–7%, and tetramethylsilane was used as the internal, reference standard. Samples of compounds **1** and **2** were separately dissolved in deuterium oxide, the solution freeze-dried, and the resulting product dried at 0.1 mm Hg for 6–8 h at 60°; this procedure was repeated twice more, before dissolution in pyridine-d_5. Coupling constants were measured, or calculated, from 250- or 500-Hz sweep-width spectra.

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