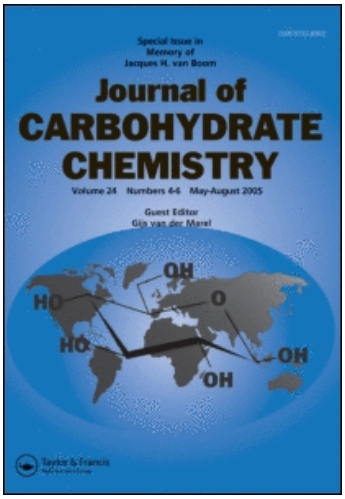

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The High-Resolution ^{1}H NMR Spectra and Conformations of N-Acetyl-α-D-Galactopyranosylamine Peracetate and 1,1-Bis(Acetamido)-1-Deoxy-D-Glucitol Peracetate in Aqueous Medium

María C. Matulewicz[a]; Carlos A. Stortz[a]; Ronald M. Jarret[b]; Alberto S. Cerezo[a]
[a] Departamento de Quimica Orgánica Facultad de Ciencias Exactas y Naturales Pabelldn 2, dudad Universitaria, Buenos Aires, Argentina [b] Department of Chemistry, College of the Holy Cross, Worcester, MA, USA

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THE HIGH-RESOLUTION ^{1}H NMR SPECTRA AND CONFORMATIONS OF N-ACETYL-α-D-GALACTOPYRANOSYLAMINE PERACETATE AND 1,1-BIS(ACETAMIDO)-1-DEOXY-D-GLUCITOL PERACETATE IN AQUEOUS MEDIUM

María C. Matulewicz,[a] Carlos A. Stortz,[a]

Ronald M. Jarret,[b] and Alberto S. Cerezo[a]*

[a]Departamento de Química Orgánica
Facultad de Ciencias Exactas y Naturales
Pabellón 2, Ciudad Universitaria
1428 Buenos Aires, Argentina

[b]College of the Holy Cross
Department of Chemistry
Worcester, MA 01610, USA

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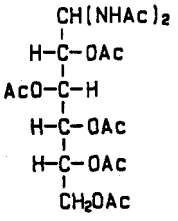
ABSTRACT

In contrast with the spectra previously measured with lower resolution equipment, the 500-MHz ^{1}H NMR spectra of 1,1-bis(acetamido)-1-deoxy-D-glucitol peracetate and N-acetyl-α-D-galactopyranosylamine peracetate in aqueous solution were amenable to full resolution. The former compound shows a "sickle" conformation produced by rotation of the C2-C3 bond out of the planar, zigzag arrangement, while the latter has a $^4C_1$ conformation.

INTRODUCTION

The ^{1}H NMR spectra and conformations acylated of 1,1-bis(acylamido)-1-deoxypentitols have been determined in organic solvents at 90 MHz.[1] Also, some N-arylglycosylamine acetates have been studied[2] by the same technique in chloroform solution at 270 or 500 MHz. Nevertheless, to the best of our knowledge, no data have been reported on the ^{1}H NMR spectra and conformations of these compounds nor on any other C-1-acylamido sugar derivatives in aqueous solution.

We herein report the 500-MHz ^1H NMR spectra of 1,1-bis(acetamido)-1-deoxy-D-glucitol peracetate (1) and N-acetyl-α-D-galactopyranosylamine peracetate (2) and their use in the determination of the conformations of these compounds. These are examples of the application of high-resolution ^1H NMR spectroscopy to the study of the conformation of acyclic and cyclic C-1-acylamido sugar derivatives in aqueous medium.



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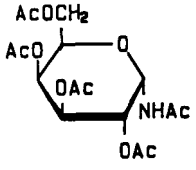

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RESULTS AND DISCUSSION

The ^1H NMR chemical shifts for 1 and 2 are listed in Table 1, and their coupling constants are listed in Table 2.

1,1-Bis(acetamido)-1-deoxy-D-glucitol peracetate (1). The 500-MHz ^1H NMR spectrum of this compound (FIG. 1) shows separate signals that were assigned for each proton. The signal at lower field is a doublet at δ5.82 ($J_{1,2}$ = 4.9 Hz) which was unambiguously assigned to H-1. The next signal, at δ 5.46, is a doublet of doublets (H-4) which yielded the values of $J_{3,4}$ and $J_{4,5}$. Protons H-2 and H-3 had close chemical shifts, and their signals could not be resolved by first-order analysis. They form part of an ABX-like system, which when solved gave $J_{2,3}$ and confirmed the previously determined $J_{1,2}$ and $J_{3,4}$. These values allowed the assignment of H-2 and H-3. The next signal was a seven-peak multiplet from which $J_{4,5}$ was confirmed and $J_{5,6}$ and $J_{5,6'}$ were calculated. The methylene protons of C-6 gave rise to an eight-peak signal with intensities characteristic of an ABX system. From these signals, the chemical shifts and the geminal coupling constant of H-6

TABLE 1. 500-MHz ^1H NMR Chemical Shifts of 1,1-Bis-(acetamido)-1-deoxy-D-glucitol Peracetate (1) and N-Acetyl-α-D-galactopyranosylamine Peracetate (2) in D_2O[a]

Compound	1	2
H-1	5.82	5.85
H-2	5.41	5.38
H-3	5.38	5.44
H-4	5.46	5.50
H-5	5.06	4.29
H-6	4.33	4.19
H-6'	4.24	4.14
Ac protons	2.19, 2.15, 2.13, 2.11, 2.09, 2.02, 1.92	2.21, 2.09, 2.08, 2.06, 2.04

[a] Chemical shifts are in δ-units (ppm) downfield from a reference of external tetramethylsilane (TMS).

TABLE 2. Spin-Spin Coupling Constants of 1,1-Bis-(acetamido)-1-deoxy-D-glucitol Peracetate (1) and N-Acetyl-α-D-galactopyranosylamine Peracetate (2) in D_2O (in Hz)[a]

Compound	1	2
$J_{1,2}$	4.9	5.5
$J_{2,3}$	6.0	10.8
$J_{3,4}$	3.3	3.2
$J_{4,5}$	7.4	[b]
$J_{5,6}$	2.9	5.2
$J_{5,6'}$	4.7	7.1
$J_{6,6'}$	12.8	11.6

[a] Determined at 500 MHz.

[b] Negligible (value between 0.2 and 1 Hz).

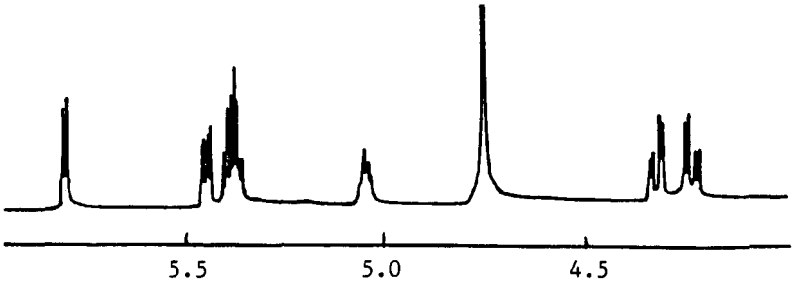

FIG. 1. Partial 500-MHz ^{1}H NMR spectrum of 1,1-bis(acetamido)-1-deoxy-D-glucitol peracetate (1)

and H-6' were calculated, and $J_{5,6}$ and $J_{5,6'}$ were confirmed. The methyl protons of the seven acetyl groups present in the molecule produced seven signals, indicating that the two acetamido groups were not equivalent, as previously suggested.[1,3]

It is noteworthy that in the ^{1}H NMR spectra of acylated 1,1-bis(acylamido)-1-deoxypentitols carried out in pyridine-d_5-hexafluorobenzene, the H-2 absorption appeared at lower field than that of H-1 and that this situation was reversed by addition of 30% of deuterium oxide.[1] The effect was attributed to the displacement of the hexafluorobenzene from a collision complex or hydrogen-bonding site that causes shielding of H-1 by virtue of a favored orientation of the hexafluorobenzene molecule.[1] Nevertheless, a similar solvent shift was found in the chemical shift of the anomeric proton in the ^{1}H NMR spectrum of N-acetyl-β-D-xylopyranosylamine when the pyridine-d_5 was replaced by mixtures of pyridine-d_5 and deuterium oxide with increasing amounts of the latter, and it was explained in terms of an amide-pyridine complex based upon electrostatic attraction between the amido group and the pyridine, in which the lone pair of electrons of the nitrogen atom of the pyridine might be partially bonded to the electron-deficient C1-N linkage.[4]

The spectra of the acetylated aldononitrile and 5-(polyacetoxyalkyl)-tetrazol with the D-gluco configuration in pyridine-d_5 show all

the protons at lower field[5] than the corresponding ones of 1,1-bis(acetamido)-1-deoxy-D-glucitol peracetate (1) in deuterium oxide, even if these compounds have the same conformation (see below). This is explained if we assume that the pyridine complex is also formed with ester groups, possibly with the electron-deficient C-O linkage. In agreement with this hypothesis, the methyl protons of the acetyl groups for the three compounds appear at the same fields in spite of the change of solvent.[4]

On the basis of the fact that vicinal coupling constants of 2-4 Hz correspond to protons with gauche orientation, and those of 8-9 Hz are due to protons with trans orientation,[6] the favored conformation of the 1,1-bis(acetamido)-1-deoxyglucitol peracetate (1) is determined to be the "sickle" conformation obtained by rotation of the C2-C3 bond out of the planar, zigzag arrangement to relieve parallel 1,3 interactions between substituents. The value of $J_{2,3}$ (6.0 Hz) indicates a disposition for H-2 and H-3 that is not entirely antiparallel.

From the coupling constant $J_{1,2}$ and the fact that the two acetamido groups are not equivalent, it is evident that some rotation of the H-1 and H-2 protons deviate them from the trans-relationship. The $J_{5,6}$ and $J_{5,6'}$ may indicate two possibilities, namely: a) a preferred conformation produced by a rotation around the C5-C6 bond producing a non-staggered projection, and b) there are two stabilized conformers in which H-6 is always gauche to H-5, but H-6' is gauche in one case and trans in the other.

The same conformation was found for per-O-acetylgluconononitrile and 5-(penta-O-acetyl-D-gluco-pentitol-1-yl)tetrazole in pyridine solution[5] in agreement with the previously known fact that the conformational populations of the 1,1-bis(acylamido)-1-deoxypentitols show little dependence of the solvent.[1]

N-Acetyl-α-D-galactopyranosylamine peracetate (2). The 500-MHz ^1H NMR spectrum of 2, which has been completely assigned, also showed (FIG. 2) separate signals for each proton. The signal at lower field was

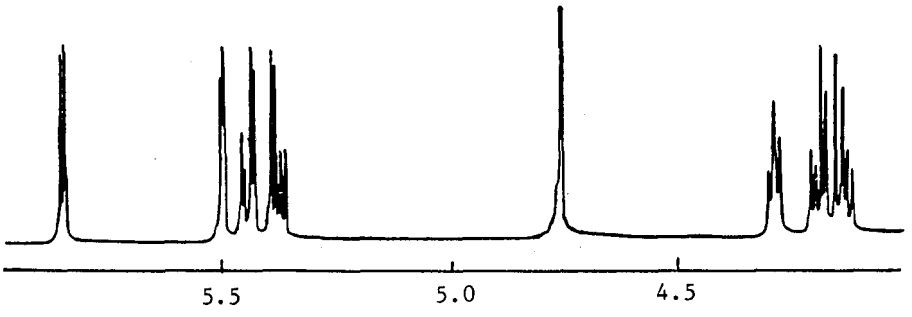

FIG. 2. Partial 500-MHz ^1H NMR spectrum of N-acetyl-α-D-galactopyranosylamine peracetate (2)

unambiguously assigned to H-1 ($J_{1,2}$ = 5.5 Hz). The resonance at next higher field was a distorted doublet with a coupling constant of 3.2 Hz which was assigned to H-4. The next eight-peak signal was the AB part of an ABX-like system from which the chemical shifts of H-2 and H-3, and $J_{2,3}$ were determined, and the $J_{1,2}$ and $J_{3,4}$ were confirmed. H-6 and H-6' gave rise to another AB system with very close chemical shifts and coupling constants. H-5 showed a distorted triplet, with J= 6.2 Hz, which is the average of the otherwise determined $J_{5,6}$ and $J_{5,6'}$ (Table 2); $J_{4,5}$ was negligibly small. The small $J_{3,4}$ and $J_{4,5}$ values and the large $J_{2,3}$ value agree with the $^4C_1$ conformation, which is also the most stable one. Nevertheless the value for $J_{1,2}$ (Table 2), which is higher than could be expected for an α-anomer, and the small $J_{4,5}$ might indicate some distortion of the ring to relieve the 1,3 interaction of the H-3 and H-5 with the acetamido group. The lower field signal for the acetyl groups was assigned to the axial one,[2] while the acetamido group appeared at higher field.[7]

In summary, the use of a 500-MHz instrument permits well resolved ^1H NMR spectra of acyclic and cyclic C-1-acylamido sugar derivatives in aqueous solution to be measured. The conformations thus determined for the 1,1-bis(acetamido)-1-deoxy-D-glucitol peracetate and N-acetyl-α-D-galactopyranosylamine peracetate with these spectra are in agreement

with those obtained for these types of compounds in organic solvents with lower field equipment.

EXPERIMENTAL

The 1,1-bis(acetamido)-1-deoxy-D-glucitol peracetate (1) and N-acetyl-α-D-galactopyranosylamine peracetate (2) were prepared as previously reported.[8,9] The spectra were recorded at 500 MHz, at room temperature, in D_2O solutions (12 mg/mL) with external TMS as reference. Specific parameters include a pulse width of 6 μsec, an acquisition time of 2.032 sec, no pulse delay, a spectral width of 8 kHz and 90-150 scans.

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