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Note

^{13}C-N.m.r. studies of mono- and di-*O*-methyl derivatives of methyl 2-acetamido-2-deoxy-D-glucopyranosides

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^{13}C-N.m.r. spectroscopy is now used extensively in structural studies of carbohydrates. Partially methylated methyl glycosides are the most simple models for the monosaccharide units in oligo- and poly-saccharides, and assignments of ^{13}C-n.m.r. signals for such derivatives have been reported[1–5]. However, the corresponding derivatives of amino sugars have not been systematically studied. We now report ^{13}C-n.m.r. data for mono- and di-*O*-methyl derivatives of methyl 2-acetamido-2-deoxy-α- (**1**) and -β-D-glucopyranosides (**2**).

The data for these derivatives (Tables I and II) were interpreted by comparison with those[6,7] for **1** and **2**, taking into consideration the known effects of *O*-methylation[8].

Although the absolute values of the C-1 signals for 2-acetamido-2-deoxy-D-glucopyranosyl residues in polysaccharide chains may not be identical with those obtained for the model compounds, the characteristic difference (3.5–4.0 p.p.m., Table I) between the signals for C-1α and C-1β may be expected for oligo- and polysaccharides.

The characteristic signals of C-2 (52–56 p.p.m.) and the NHAc carbon atoms (22.3–22.7 and 173–175 p.p.m.) are diagnostic for 2-acetamido-2-deoxy-D-glucopyranosyl residues in a polysaccharide chain and also indicate the anomeric configuration. Thus, a signal at 56 ±0.5 p.p.m. is typical for 4-*O*- and 6-*O*-substituted 2-acetamido-2-deoxy-β-D-glucopyranosyl residues, whereas one at 52 ±0.5 p.p.m. indicates a 3-*O*-substituted α-unit. Also, the signal at 54.5 ±0.5 p.p.m. may be assigned to C-2 of 4-*O*- and 6-*O*-substituted units (**1**) as well as to C-2 of 3-*O*-substituted units (**2**). It is possible to distinguish between these possibilities by using the C-1 resonances.

The data in Table II show that the α-, β-, and γ-effects for amino-sugar methylation are of the same direction as those obtained for non-nitrogenous sugars[1].

The observed characteristic differences in ^{13}C chemical shifts for the 2-acetamido-2-deoxy-D-glucopyranose derivatives should be useful in the structural analysis of carbohydrate chains that contain these residues.

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS (p.p.m.) FOR METHYLATED DERIVATIVES OF METHYL 2-ACETAMIDO-2-DEOXY-D-GLUCOPYRANOSIDE[a]

	Anomer	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*MeO-1*	*MeO-3*	*MeO-4*	*MeO-6*
Methyl 2-acetamido-2-deoxy-D-glucopyranoside	α (1)	98.6	54.25	71.9	70.4	72.2	61.4	55.6	—	—	—
	β (2)	102.3	56.1	74.6	70.9	76.3	61.5	57.2	—	—	—
–, 3-*O*-methyl	α	98.7	52.6	81.1	69.6	72.2	61.2	55.6	59.15	—	—
	β	102.2	54.4	83.6	69.4	76.2	61.4	57.2	59.1	—	—
–, 4-*O*-methyl	α	98.4	54.2	71.25	80.2	71.25	61.1	55.5	—	60.1	—
	β	102.3	56.1	74.05	80.25	75.5	61.25	57.2	—	60.2	—
–, 6-*O*-methyl	α	98.5	54.0	71.7	70.8	71.7	70.8	55.65	—	—	58.9
	β	102.3	55.9	74.4	70.8	75.0	71.7	57.2	—	—	59.1
–, 3,4-di-*O*-methyl	α	98.6	52.9	81.0	79.4	71.4	60.9	55.5	59.2	59.9	—
	β	102.2	54.9	83.5	79.3	75.4	61.1	57.2	59.4	59.9	—
–, 4,6-di-*O*-methyl	α	98.4	54.2	71.4	80.4	71.25	69.9	55.65	—	60.1	58.8
	β	102.2	56.0	74.0	80.4	74.2	71.5	57.1	—	60.2	58.9
–, 3,6-di-*O*-methyl	α	98.6	54.2	81.0	69.7	71.4	70.8	55.5	58.9	—	58.9
	β	102.2	54.5	83.5	69.55	75.0	71.7	57.2	59.05	—	59.0

[a] D_2O, 80°, internal Me_2SO.

TABLE II

DISPLACEMENTS[a] OF ^{13}C SIGNALS IN METHYLATED DERIVATIVES OF METHYL 2-ACETAMIDO-2-DEOXY-D-GLUCOPYRANOSIDES

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
α-Series						
3-*O*-Methyl	+0.1	−1.65	+9.2	− 0.8	0	− 0.2
4-*O*-Methyl	−0.2	−0.05	−0.65	+ 9.8	−0.95	− 0.3
6-*O*-Methyl	−0.1	−0.25	−0.2	+ 0.4	−0.5	+ 9.4
3,4-Di-*O*-methyl	0	−1.35	+9.1	+ 8.9	−0.8	− 0.5
4,6-Di-*O*-methyl	−0.2	−0.05	−0.5	+10.0	−0.95	+ 8.5
3,6-Di-*O*-methyl	0	−1.85	+9.1	− 0.7	−0.6	+ 9.4
β-Series						
3-*O*-Methyl	−0.1	−1.7	+9.0	− 1.5	−0.1	− 0.1
4-*O*-Methyl	0	0	−0.55	+ 9.35	−0.8	− 0.25
6-*O*-Methyl	0	−0.2	−0.2	− 0.1	−1.3	+10.2
3,4-Di-*O*-methyl	−0.1	−1.2	+8.9	+ 8.4	−0.9	− 0.4
4,6-Di-*O*-methyl	−0.1	−0.1	−0.6	+ 9.5	−2.1	+10.0
3,6-Di-*O*-methyl	−0.1	−1.6	+8.9	− 1.35	−1.3	+10.2

[a] Relative to those of the corresponding carbon atoms in the parent glycoside.

EXPERIMENTAL

^{13}C-N.m.r. spectra were obtained at 80° with a Bruker WP-60 instrument (deuterium lock) for solutions in D_2O (internal Me_2SO). The chemical shift for Me_2SO compared to that of Me_4Si was 39.5 p.p.m. Proton-decoupled FT-spectra were measured by using a scan time of 1.1 sec, pulse width of 5.5 μsec (—45°), 4K real data points, and a sweep width of 3750 Hz.

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