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^{13}C-NMR SPECTRA OF 6-AMINOHEXYL GLYCOSIDES OF O-β-D-GALACTOPYRANOSYL-2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSE

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ABSTRACT: *^{13}C-NMR spectral data on 6-aminohexyl glycosides of O-β-D-galactopyranosyl-2-acetamido-2-deoxy-β-D-glucopyranose are presented and discussed.*

We have recently prepared[1] a series of 6-aminohexyl glycosides of all positional isomers of O-β-D-galactopyranosyl-2-acetamido-2-deoxy-β-D-glucopyranose. While these glycosides provide useful carbohydrate prosthetic groups in our studies[2,3] of biological interactions involving carbohydrates, they are also valuable reference compounds for determining the structure of important, more complex oligosaccharides of natural origin. We now report the ^{13}C-NMR spectra of a series of disaccharide glycosides which differ only in the position of linkage between the monosaccharide units.

All samples were dissolved in 99.8% D_2O (~150 mg/mL). ^{13}C-NMR were recorded at room temperature using a Varian CFT-20 NMR spectrometer, operating at 20.0 MHz, with Fourier transform, and tubes of outside diameter 8 mm. The sweep width used was 4500 Hz, the acquisition time 0.9 s, and the pulse width 10 μs. Chemical shifts were measured relative to that of the internal standard p-dioxane which was set as 67.4 ppm downfield from that of tetramethylsilane.

The results are summarized in Tables I-II. It is clear that the chemical shifts of all of the carbons of the β-galactopyranosyl residue remain nearly constant regardless of the position of attachment of the two monosaccharide rings. Likewise, chemical shifts of both carbonyl and methyl carbons of the acetyl groups are nearly indifferent to the position of glycosyl substitution even when the galactopyranosyl residue is located at C-3 (structure 2). However, as expected[4,5], the signals of the carbons where glycosylation occurred are signigicantly deshielded. Thus, C-3 of the 1,3-linked compound 2 showed a downfield shift (Tables I and II) of 8.6 ppm relative to the parent glycoside (1). Similarly, the 1,6-linked (3) and 1,4-coupled (4) isomers showed downfield shifts of 7.5 and 8.6 ppm for the signals from C-6 and C-4, respectively. Lemieux and co-workers reported[4] similar changes in chemical shifts as shown in Table 2. The deshielding effect of 8.4 to 9 ppm reported in Table 1 is

TABLE I - ^{13}C-NMR DATA OF GLYCOSYL RESIDUES (CHEMICAL SHIFTS IN D_2O RELATIVE TO p-DIOXANE)[a]

Compounds	β-D-GlcNAc Residue								β-D-Gal Residue					
	C-1	C-2	C-3	C-4	C-5	C-6	CO	CH_3	C-1´	C-2´	C-3´	C-4´	C-5´	C-6´
1	102.0	56.5	74.7	70.8	76.7	61.6	175.2	23.0						
2	101.8	55.5	83.3	69.6	76.2	61.7	175.3	23.3	104.4	71.6	73.4	69.4	76.2	61.5
				(69.4)[b]		(61.5)						(69.6)		(61.7)
3	102.1	56.4	74.6	70.6	75.7	69.1	175.3	23.0	104.2	71.6	73.6	69.5	76.0	61.8
4	101.9	56.0	74.3	79.4	75.6	61.0	175.1	23.1	103.7	71.9	73.4	69.4	76.2	61.9
						(61.9)								(61.0)
5[c]	101.4	55.1	83.1	69.1	75.8	61.5	174.9	22.9	104.0	71.2	73.0	69.1	75.8	61.5

[a]Used as internal standard.

[b]Brackets indicate alternate assignments.

[c]From ref. 4.

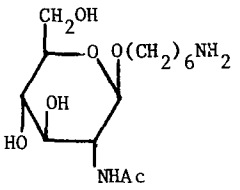
TABLE II - CHEMICAL SHIFT EFFECTS OF GLYCOSYLATION

Glycosyl Residue	Position on β-D-GlcNAc Residue	Shielding Effects at Position of Substitution	Shielding Effects at Carbons Adjacent to Position of Substitution
β-D-Gal[a]	3	C-3 (+8.6 ppm)	C-2 (-1 ppm) C-4 (-1.2 ppm)
β-D-Gal[b]	3	C-3 (+9.0 ppm)	C-2 (-0.8 ppm) C-4 (-1.2 ppm)
α-L-Fuc[b]	4	C-4 (+7.8 ppm)	C-3 (-0.9 ppm) C-5 (-0.4 ppm)
β-D-Gal[a]	4	C-4 (+8.6 ppm)	C-3 (-0.4 ppm) C-5 (-1.1 ppm)
β-D-Gal[a]	6	C-6 (+7.6 ppm)	C-5 (-1 ppm)

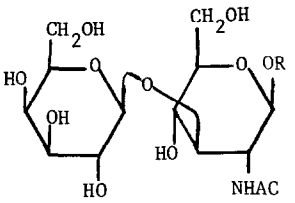
[a]From Table 1.

[b]From Ref. 4.

FIGURE I

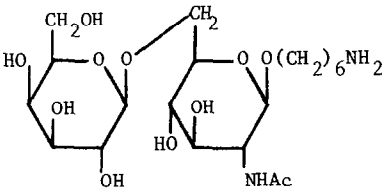


1



2 R=$(CH_2)_6NH_2$

5 R=$(CH_2)_8CO_2H$



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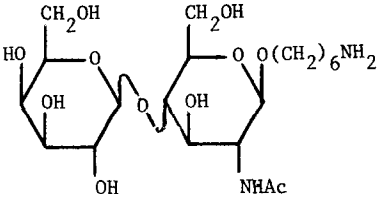

4

known as the β shift[5] and is within the range normally observed for etherification of glycosylation.

Furthermore, it is noteworthy that the upfield shifts (-0.4 to -1.2 ppm) were observed for the carbons adjacent to the carbon of the β-galactopyranose attachment to the N-acetylglucosamine residue. These shifts can be predicted by the empirical model provided by Levy and Nelson[6] and may be used as a diagnostic and confirming means for the determination of the site of etherification or "glycosidic" linkage.

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