

Note

A ^{13}C -n.m.r. study of the 6-deoxy-D-altropyranose-containing pentasaccharide chain present in a polysialoglycoprotein isolated from the eggs of *Salvelinus leucomaenis pluvius* (Japanese common char; *Iwana*)

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A new deoxyhexose residue in the polysialoglycoprotein (PSGP) isolated¹ from the eggs of *Salvelinus leucomaenis pluvius* has been identified² as 6-deoxy-D-altrose (D-dAlt). The occurrence of D-dAlt has not been recognised hitherto in glycoproteins. The anomeric configuration of the D-dAlt moiety in the pentasaccharide¹, D-dAlt-(1→3)- β -D-GalNAc-(1→3)- β -D-Gal-(1→4)- β -D-Gal-(1→3)-D-GalNAcol (**1**), isolated¹ from PSGP has been assigned² tentatively as β on the basis of its ^1H -n.m.r. data. Recent technical developments have greatly facilitated the ^{13}C -n.m.r. spectroscopy of small samples (1 mg), and we now report on the ^{13}C -n.m.r. spectra of the dAlt-pentasaccharide **1** and the related di- and oligosaccharides α -L-Fuc-(1→3)- β -D-GalNAc-(1→3)- β -D-Gal-(1→4)- β -D-Gal-(1→3)-D-GalNAcol (**2**), β -D-Gal-(1→4)- β -D-Gal-(1→3)-D-GalNAcol (**3**), and β -D-Gal-(1→3)-D-GalNAcol (**4**).

The ^{13}C -n.m.r. data for solutions of **1–4** in D_2O are shown in Table I. The resonances of **1** were assigned on the basis of comparison with data for the constituent di- (**4**) and tri-saccharide (**3**), the homologous α -L-Fuc-containing pentasaccharide **2**, and related mono- and oligo-saccharide derivatives^{3–7}. The data in Table I confirm the sequence of monosaccharide residues in **1** and the positions of the linkages (the resonances of the carbons involved in the linkages can be assigned on the basis that *O*-glycosylation results^{8,9} in a downfield displacement of ~ 10 p.p.m.) already established^{2,10}. Except for the signals of the D-dAlt and α -L-Fuc residues, the other ^{13}C resonances of **1** and **2** show virtually the same chemical shifts. The resonances for the β -D-dAlt and α -L-Fuc residues were assigned by comparison with data^{3,5} for methyl α -D-dAltp, α - and β -D-Fuc, phenyl α -L-Fuc, methyl α - and β -L-dAltp, α -L-Fuc-(1→2)- β -D-Gal-(1→3)-D-GalNAcol, α -L-Fuc-(1→2)- β -D-Gal-(1→4)-D-GlcNAc, and α -L-Fuc-(1→4)-D-GlcNAcol.

The β configuration of the D-dAltp moiety is assigned on the basis of the data in Table II. The important signals are those for C-1 and C-5. Comparison of the

TABLE I

¹³C-N.M.R. CHEMICAL SHIFT DATA AND ASSIGNMENTS FOR 1-4

	4	3	2	1
<i>→3)-GalNAcol</i>				
C-1	61.5	61.5	61.5	61.5
C-2	52.4 ₅	52.4	52.4	52.4
C-3	77.2	77.7 ^a	77.7 ^b	77.7 ^c
C-4	70.3	70.2	70.2	70.2
C-5	70.0	70.0	70.0	70.0
C-6	63.9	63.8	63.8	63.8
-COCH ₃	23.0	23.0	23.0	23.0
-COCH ₃	175.1	175.0	175.0	175.0
<i>→4)-Gal-(1→</i>				
C-1	104.7	104.7	104.8	104.7
C-2	72.0	72.3	72.3	72.3
C-3	73.4	73.8	73.9	73.9
C-4	69.4	78.0 ₅ ^a	77.9 ^b	77.9 ^c
C-5	75.9 ₃	75.3	75.3	75.3
C-6	62.0	61.9	61.9	61.9
<i>→3)-Gal-(1→</i>				
C-1		105.1	105.0	105.0
C-2		72.3	71.4 ₅	71.4
C-3		73.7	82.8	82.8
C-4		69.6	69.4	69.3 ₅
C-5		76.1	75.6	75.6
C-6		61.9	61.9	61.9
<i>→3)-GalNAc-(1→</i>				
C-1			103.5	103.3
C-2			52.7	52.9
C-3			79.3	79.8
C-4			68.9 ₅	68.9
C-5			75.8	75.6
C-6			61.9	61.9
-COCH ₃			23.4	23.4
-COCH ₃			175.7	175.3
<i>Fuc- in 2 and dAlt in 1</i>				
C-1			102.0	100.4
C-2			69.1	72.0
C-3			70.3	71.1 ^d
C-4			72.6	70.3
C-5			68.1	70.8 ^d
C-6			16.5	18.3

^{a-d}Assignments are interchangeable.

TABLE II

¹³C-N.M.R. CHEMICAL SHIFT DATA FOR 6-DEOXYALTROPYRANOSIDES

	<i>Me α-D-dAlt</i> ^p	1	<i>Me α-L-dAlt</i> ^p	<i>Me β-L-dAlt</i> ^p
C-1	101.3	100.4	101.2	100.3
C-2	71.0	72.0	70.7	71.1
C-3	70.8	71.1 ^a	70.7	70.7
C-4	70.7	70.3	70.7	70.4
C-5	67.1	70.8^a	66.7	70.7
C-6	17.5	18.3	17.0	17.8
OCH ₃	56.4		56.1	57.3

^aAssignments are interchangeable.

chemical shifts of the C-1 resonances⁷ of the methyl α - (101.2 p.p.m.) and β -glycosides (100.3 p.p.m.) of L-dAlt shows that C-1 α resonates at \sim 1 p.p.m. downfield of the C-1 β resonance. In contrast, the C-5 α resonance is \sim 4 p.p.m. to higher field than the C-5 β resonance. Comparison of the data for Me α -D-dAlt and the D-dAlt residue in **1** indicates the latter to be β .

Empirical rules such as the one discussed above should be used with caution and their applicability to the 6-deoxyaltrosyl system (*cf.* ref. 11) may reflect the conformational properties of altrohexopyranosides^{2,12}.

EXPERIMENTAL

Materials. — Methyl 6-deoxy- α -D-altropyranoside was prepared² from methyl 4,6-*O*-benzylidene- α -D-altropyranoside. Oligosaccharides **1–4** were obtained as previously described^{1,2}.

¹³C-N.m.r. spectroscopy. — Natural-abundance proton-decoupled ¹³C-n.m.r. spectra were recorded at 27° with a JEOL-JNM-GX400 spectrometer operating at 100 MHz in the pulsed F.t. mode on solutions in D₂O [internal MeOH, 51.3 p.p.m. downfield from the resonance of sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS), 49.9 p.p.m. from the signal for Me₄Si]. The chemical shift data in Tables I and II are reported relative to Me₄Si. A solution of **1** (1 mg) in 99.75% D₂O (0.5 mL) in a 4-mm tube required 91,000 accumulations (68 h).

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