

ASSIGNMENT OF ANOMERIC STRUCTURE TO CARBOHYDRATES
THROUGH GEMINAL ^{13}C -H COUPLING CONSTANTS

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Lately an increasing number of papers describing ^{13}C nmr spectra of carbohydrates have appeared. It has been shown that the chemical shift of the anomeric carbon atom is strongly dependent on the anomeric configuration. ¹⁻⁴ $J_{^{13}\text{C}-\text{H}}$ values have been measured in a few cases only. Perlin and Casu, ⁵ through ^{13}C and ^1H nmr spectra of ^{13}C enriched glucose, found that $J_{^{13}\text{C}_1-\text{H}_1}$ was 169 Hz for the α -anomer whereas the corresponding value for the β -anomer was 160 Hz.

By the use of gated decoupling⁶ with pulsed Fourier spectrometers it is possible, within a reasonable time, to measure C-H coupling constants on unenriched compounds. Using this technique we have measured C-H coupling constants of a number of carbohydrate derivatives. We found that $J_{^{13}\text{C}_1-\text{H}_1}$ was larger than the other geminal C-H coupling constants, involving C-2 to C-6. The latter had values of 143-148 Hz in free sugars and in methyl glycosides and did not appear to be very dependent on stereochemistry. This is, however, being further investigated.

The $J_{^{13}\text{C}_1-\text{H}_1}$ values, on the other hand, showed a clear dependence on the orientation of the substituent at C-1 and may therefore provide information about the anomeric structures and/or conformations.

In Table 1 are presented chemical shifts and $^{13}\text{C}_1-\text{H}_1$ coupling constants of a number of carbohydrates. Most of the chemical shifts were determined previously by other authors. The methyl glycosides in which H-1 is axially oriented have a $J_{^{13}\text{C}_1-\text{H}_1}$ value of 158-162 Hz, whereas the glycosides with an equatorial H-1 have higher J-values (169-171 Hz). This difference was found both in unsubstituted and in acetylated glycosides. In free sugars the same difference between $J_{^{13}\text{C}_1-\text{H}_1}$ of anomers was found from spectra measured on equilibrated mixtures in aqueous solution.

Table 1^a

Compound	anomer	axial H-1 ^b		equatorial H-1 ^b		
		C-1 p. p. m. ^c	J ₁₃ C1-H1 Hz ^d	C-1 p. p. m. ^c	J ₁₃ C1-H1 Hz ^d	
methyl D-glucopyranoside	β	105.8 ⁴	159	α	101.8 ⁴	170
tetra-O-acetate	β	101.1 ²	162	α	96.3 ²	173
methyl D-galactopyranoside	β	104.1 ²	160	α	99.8 ²	170
tetra-O-acetate	β	101.6	161	α	96.7 ²	172
methyl D-mannopyranoside				α	103.2 ²	170
tetra-O-acetate				α	97.8 ²	171
3-O-methyl-2, 4, 6-tri-O-acetyl	β	99.1	158.5			
methyl D-xylopyranoside	β	106.6 ²	158			
methyl D-arabinopyranoside				β	104.3 ⁴	170
methyl D-lyxopyranoside				α	105.6 ⁴	169
penta-O-acetyl-D-glucopyranose	β	91.0 ³	165	α	90.1 ³	177
tetra-O-acetyl-2-O-methyl-D-glucopyranose	β	91.9	165	α	87.1	175
penta-O-acetyl-D-mannopyranose				α	90.4 ³	175
tetra-O-acetyl-2-O-methyl-D-mannopyranose	β	90.1	163			
tetra-O-acetyl-D-glucopyranosyl fluoride	β	105.7	177.5	α	103.5	186
tetra-O-acetyl-D-glucopyranosyl chloride	β	87.1	172	α	89.8	184.5
D-glucopyranose ^e	β	96.3 ²	160	α	92.4 ²	169.5
D-galactopyranose ^e	β	97.0 ²	159.5	α	92.8 ²	169.5
β-mannopyranose ^e	β	94.6 ²	160	α	95.2 ²	170
D-xylopyranose ^e	β	97.3 ²	160	α	92.8 ²	170

Table 1 continued

Compound	ano- mer	axial H-1 ^b		equatorial H-1 ^b		
		C-1 p. p. m. ^c	J_{13}^{C1-H1} Hz ^d	C-1 p. p. m. ^c	J_{13}^{C1-H1} Hz ^d	
sucrose				^a gluc	92.9 ⁷	168.5
raffinose				^a gluc	92.2 ⁸	170
raffinose				^a galac	98.2 ⁸	169
maltose ^e C-1(OH)	β	95.6 ⁹	160	α	91.7 ⁹	172
maltose C-1(glycosidic)				α	99.4 ⁹	172
octa-O-acetyl- α -D-cellobiose C-1-(OAc)				α	88.6 ⁷	175
octa-O-acetyl- α -D-cellobiose C-1(glycosidic)	β	100.5 ⁷	160			

- a) The spectra were measured at 22.63 MHz on a Bruker WH-90 instrument equipped with a multipulse generator.
- b) In the preferred conformation.
- c) Recalculated to TMS as internal reference. Acetates were measured from internal $CDCl_3 = 76.9$ p. p. m. Glycosides and free sugars were measured from internal dioxane = 67.4 p. p. m.
- d) ± 0.7 Hz measured at 30°C.
- e) After equilibration in 50 % D_2O for 24 h at room temperature.

When a more electronegative substituent was introduced at C-1 the J_{13}^{C1-H1} increased, however, the difference of ca. 10 Hz between the two anomers was still observed. J_{13}^{C1-H1} may also be used for assignment of the anomeric structure of di- and oligosaccharides. Thus, J_{13}^{C1-H1} of the glucose moiety of sucrose was 170 Hz, in agreement with its α -glycosidic structure. The same value was found for both glucose and galactose in raffinose. Cellobiose octaacetate and maltose, the latter after mutarotation in water, also gave J_{13}^{C1-H1} values in accordance with their anomeric structures (Table 1).

Complete spectral data of the compounds shown in Table 1 will be published elsewhere

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