

A Study of ^{13}C H Coupling Constants in Pentopyranoses and Some of their Derivatives

KLAUS BOCK and CHRISTIAN PEDERSEN

Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

Proton decoupled and undecoupled ^{13}C NMR spectra were measured on the D-pentopyranoses and a number of their derivatives. The direct coupling constants between the anomeric carbon atoms and protons $^1J(^{13}\text{C}\text{H}1)$ were found to be *ca.* 10 Hz lower when H1 was axial than when it was equatorial. The $^1J(^{13}\text{C}\text{H}1)$ values may therefore be used for the determination of conformational equilibria. Chemical shifts and $^1J(^{13}\text{C}\text{H}1)$ values of the other carbon atoms in the pyranose rings were also measured.

Directly bonded $^{13}\text{C}\text{H}$ coupling constants were reported previously for a number of hexopyranoses and it was found that the $^1J(^{13}\text{C}\text{H}1)$ value is consistently *ca.* 10 Hz lower when H1 is axial than when it is equatorial.^{1,2} These coupling constants may therefore be used for the assignment of anomeric structure.

It was of interest to see whether pentopyranoses and their derivatives have similar $^1J(^{13}\text{C}\text{H}1)$ values and, especially, whether these constants can be used as a supplement to proton-proton coupling constants for the determination of conformational equilibria. We have therefore measured proton decoupled and undecoupled ^{13}C NMR spectra of a number of pentopyranoses and of some of their derivatives; their chemical shifts and coupling constants are shown in Table 1.

Some of the chemical shifts shown in Table 1 differ slightly from those reported previously. This is probably due to the use of internal references in the present work whereas many previous workers used external references. The assignments shown in Table 1 were in some cases confirmed by selective proton decoupling.³ This method works well with compounds which have reasonable well resolved proton spectra,

such as acetylated sugars. In other cases assignments could be made from the proton undecoupled ^{13}C spectra since C2 in most cases gives a less complicated signal than C3. This is probably due to the fact that $^3J(\text{CH}1)$ values are considerably larger than $^2J(\text{CH})$ values⁴ and C2 has only one proton (H4) three bonds away, whereas C3 has three protons (H1 and H5) in this position.

The $^1J(^{13}\text{C}\text{H}1)$ values of the D-xylopyranoses (α - and β -1*a*) and of the methyl D-xylosides (α and β -1*b*) were found to be 158–160 Hz for the β -anomers and 170 Hz for the α -anomers. Slightly higher values were found for the acetylated methyl xylosides (α - and β -1*c*), in agreement with previous results.¹ All these xylopyranose derivatives are almost completely in the 4C_1 conformation⁵⁻⁷ and thus the β -anomers have an axial H1 and the α -anomers an equatorial H1. The $^{13}\text{C}\text{H}1$ coupling constants are therefore in agreement with those found in the hexose-series.¹

Spectra of the 2,4-phenylboronates derived from (α - and β -1*b*) were also measured. These two compounds must necessarily adopt the 1C_4 conformation and this is seen clearly from the $^1J(^{13}\text{C}\text{H}1)$ values (Table 1).

Tetra-*O*-acetyl- α - and β -D-xylopyranose (α - and β -1*d*) have $^1J(^{13}\text{C}\text{H}1)$ values of 177 and 166 Hz, respectively. These values are very close to those of the homomorphous α - and β -D-glucopyranose pentaacetates² indicating that α -1*d* and β -1*d* are almost completely in the 4C_1 conformation in chloroform solution. If β -1*d* adopted the 1C_4 conformation it would be similar to penta-*O*-acetyl- α -D-idopyranose which has $^1J(^{13}\text{C}\text{H}1)$ 175 Hz (Table 2). In acetone-*d*₆,

Table 1. Chemical shifts (ppm) and observed first-order coupling constants (± 1 Hz) of pentopyranoses and some derivatives in D₂O or in deuteriochloroform solution.

Compound	C1 ¹ J _{CH1}	C2 ¹ J _{CH2}	C3 ¹ J _{CH3}	C4 ¹ J _{CH4}	C5 ¹ J _{CH5}	OMe ¹ J _{CH}	Conforma- tional equi- librium % ± 10 % ⁴ C ₁ ¹ C ₄	Ref.																																																																																																																																																																																																
α -1a	93.08	72.38	73.75	70.28	61.81		100	10,11,12,13																																																																																																																																																																																																
	170	147.5	145	147	142.5 151				β -1a	97.51	74.96	76.74	70.12	66.01		>90	10,11,12,13	160.5	147.5	145	147	142.5 150.0		α -1b	100.29	72.29	74.20	70.31	61.90	56.01	100	10,11,12,14	170	146	145	146	145 148	143	α -1b phenyl- boronate ¹⁶ in DMSO-d ₆	98.50	70.34 ^a	65.17 ^a	68.21 ^a	64.65	56.17	100		159	154	148	151	145	143	β -1b	104.82	73.88	76.72	70.12	66.00	57.82	100	10,11,12,14	159	144	144	147	142 150	142	β -1b phenyl- boronate ¹⁶ in CDCl ₃	100.2	68.9 ^a	64.9	66.3 ^a	58.6	55.7	100		171	156	154	155	145	143	β -1b phenyl- boronate ¹⁶ in DMSO-d ₆	99.93	68.92	64.20	67.69	58.24	53.33	100		170	154	150	157	145	142	α -1c	96.40	70.46	69.10	68.77	57.66	54.73	100	15, ^c	171.0	153	155 ^b	155 ^b	147.5 ^b	142	β -1c	100.95	70.21	70.99	68.32	61.30	55.84	100	^c	161.0	153	152	153	143 151	144	α -1d	88.94	69.20	69.20	68.84	60.52		100		177	153	153	152	148 ^b		β -1d	91.72	69.33	70.75	68.10	62.53		100		166	155	156	153	146 151		α -2a	97.64	72.83	73.34	69.34	67.14		>90	10,11,12,13	160.0						β -2a	93.44	69.53	69.53	69.34	63.30		20 80	10,11,12,13	168.0				142.5 150		α -2b	104.75	71.61	73.29	69.15	66.95	57.82	>90	10,11,14	160	148	143
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α -2b	104.75	71.61	73.29	69.15	66.95	57.82	>90	10,11,14																																																																																																																																																																																																
	160	148	143	146	140 150	145																																																																																																																																																																																																		

Table 1. Continued.

β -2b	100.74	69.80	69.80	69.15	63.39	56.07	10	90	10,11,14
	169	145 ^b	145 ^b	145	142 149	143			
α -2c	101.91	69.28	70.38	67.92	63.24	56.61		100	^c
	159	153	148	152	140 150	143			
β -2c	97.62	68.43	69.28	67.20	60.25	55.44		100	^c
	171	153	152.5	152	144.5 151.5	143			
α -2d	92.16	68.24	69.86	67.26	63.82		20	80	
	168	156	149	150	147.5				
β -2d	90.40	67.27	68.70	66.94	62.85			100	
	176	154 ^b	153	154 ^b	145 152				
α -3a	94.92	70.96	71.41	68.40	63.88		75	25	12,13
	167	146	146	147.5	147.5				
α -3b	101.97	70.44	71.61	67.72	63.25	55.88	90	10	
	169	145	142	147	144 150	143			
α -3c	98.41	69.26	68.23	66.57	59.42	54.93	100		^c
	170.5	156	153	154	147 149	143.5			
α -3d	90.66	68.24	68.24	66.55	61.94		100		^c
	175	155	155	154	146 151				
β -3d	90.0						60	40	
	169.5								
β -4a	94.73	71.92	69.69	68.18	68.83		70	30	10,12,13,14
	164	146	175	146	147.5				
β -4a with 2N CaCl ₂	94.76	70.89	69.82	67.34	63.53		10	90	
	168	146	146 ^b	146 ^b	147				
α -4b	100.41	69.18	70.41	67.40	60.78	56.65	30	70	
	167.5	145	146	146.5	146	144			
β -4b	103.07	71.0	68.6	68.6	63.9	57.0	50	50	10,12,14
	166	146	146	146	147	143			
β -4b with 2 N CaCl ₂	101.87	70.15	68.50	66.76	63.56	56.58	10	90	
	170	148	147.5	148	146	144			
α -4c	97.49	67.52	67.39	66.09	57.91	56.22	50	50	^c
	166	146.5	146.5	148	147	143			

Table 1. Continued.

β -4c	99.37	68.31	65.97	66.88	61.09	55.70	30	70	c
	168	153	149	151	145 151	143			
α -4d	88.71	67.14	65.58	66.49	59.27		70	30	c
	173	154	148	147	149				
β -4d in CDCl ₃	90.68	67.13	66.03	66.03	62.45		10	90	
	174.5	152	152 ^b	152 ^b	~150 ^b				
β -4d in acetone-d ₆	91.14	67.48	66.38	66.38	62.61		10	90	
	174	152	152 ^b	152 ^b	150 ^b				

^a Assignment may be reversed. ^b Measured from center of broad multiplet. ^c Assignment confirmed by selective proton decoupling.

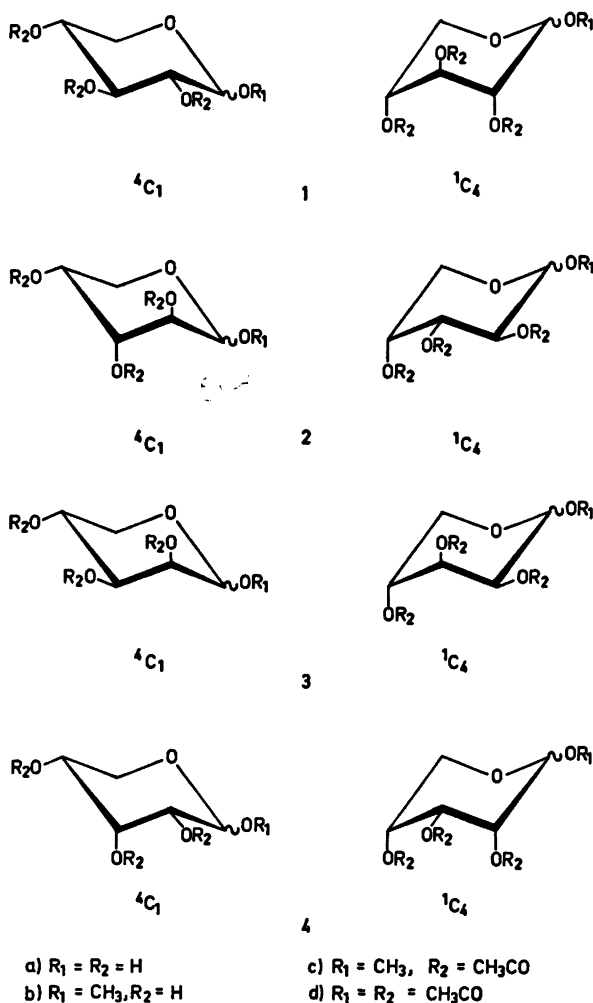
solution (α -1d) is reported to be more than 98 % in the ⁴C₁ conformation whereas (β -1d) is only 72 % in this conformation.⁸

The D-arabinopyranoses (α - and β -2a) and the methyl D-arabinosides (α - and β -2b) have ¹³C1H1 coupling constants of 160 Hz for the α -anomers and 168–169 Hz for the β -anomers in aqueous solution. Comparison of these values with those described above and previously¹ show that the four compounds are more than 90 % in the ¹C₄ form. This has also been shown for the α -series from proton spectra whereas the conformation of β -2a was uncertain.^{5,6} The acetylated methyl D-arabinopyranosides (α - and β -2c) adopt the same conformation in chloroform. The 168 Hz found for tetra-O-acetyl- α -D-arabinopyranose (α -2d) may be compared to the values found for acetylated hexoses such as penta-O-acetyl- β -D-galactopyranose with an axial H1 (*J* 167 Hz) and penta-O-acetyl- α -D-altropyranose with an equatorial H1 (*J* 175.5 Hz) (Table 2). This would indicate that ca. 20 % of α -2d is in the ⁴C₁ form, in agreement with results found from proton spectra in acetone.⁸ The β -anomer (β -2d) has ¹J(¹³CH1) 176 Hz, very close to that of acetylated α -D-hexopyranoses (Table 2).¹ It must therefore have an equatorial H1 and be almost exclusively in the ¹C₄ form.⁸

The ¹J(¹³CH1) value of 167 Hz for α -D-lyxopyranose (α -3a) is 2–3 Hz too low for a con-

formation with an equatorial H1; (α -3a) must therefore be a 3:1 mixture of ⁴C₁ and ¹C₄ form. Lemieux and Stevens⁵ found from proton spectra that equal amounts of the two conformers were present. Methyl α -D-lyxopyranoside (α -3b) and its triacetate (α -3c) have coupling constants corresponding to higher proportions of ⁴C₁ form. A solution of (α -3c) in acetone has been found to contain 83 % ⁴C₁ form.⁸ Tetra-O-acetyl- α -D-lyxopyranose (α -3d) has ¹J(¹³CH1) 175 Hz which, compared to 176 Hz for α -D-mannopyranose pentaacetate,² shows that it is completely in the ⁴C₁ conformation. The β -anomer (β -3d) with *J* 169.5 Hz must be a ca. 4:6 mixture of ¹C₄ and ⁴C₁ forms. Using acetone as solvent Durette and Horton⁸ found 60 % ¹C₄ for β -3d and 70 % ⁴C₁ for α -3d.

An aqueous solution of β -D-ribose (β -4a) has ¹J(¹³CH1) 164 Hz, i.e. 3 Hz higher than that of β -D-allopyranose (Table 2). It is therefore reasonable to assume that β -4a is a mixture of ca. 30 % ¹C₄ and 70 % ⁴C₁ form in agreement with the results obtained from ¹H NMR.^{5,7} Methyl β -D-ribose (β -4b) with *J* 166 Hz is approximately a 1:1 mixture of the two chair forms whereas the α -anomer (α -4b) contains ca. 70 % ¹C₄ form. The coupling constant of the acetylated methyl α -D-ribose (α -4c) in chloroform corresponds to a 1:1 mixture of the chair forms whereas the β -anomer (β -4c)



has 70 % 1C_4 form. These values agree fairly well with those found in acetone by proton spectroscopy.⁸

When calcium chloride was added to aqueous solutions of β -D-ribofuranose (β -4a), or methyl β -D-ribofuranoside (β -4b), the ${}^1J({}^{13}CH1)$ values increased by 4 Hz corresponding to a conformational change towards ca. 90 % 1C_4 form. This is in complete agreement with the results found by Angyal and Davies from proton spectra.⁹

Tetra-*O*-acetyl- β -D-ribofuranose (β -4d) has ${}^1J({}^{13}CH1)$ 174.5 Hz and must therefore largely adopt the 1C_4 conformation. Penta-*O*-acetyl

β -D-allofuranose, with an axial H1, has ${}^1J({}^{13}CH1)$ 10 Hz lower whereas penta-*O*-acetyl- α -D-talofuranose, with an equatorial H1, has J 177 Hz (Table 2).

Durette and Horton found that β -4d contains approximately equal amounts of the two chair forms in acetone solution.⁸ An undecoupled ${}^{13}C$ NMR spectrum of β -4d in acetone- d_6 gave ${}^1J({}^{13}CH1)$ 174 Hz, indicating that ca. 80 % of β -4d is in the 1C_4 form. The difference between the results obtained from proton spectra and from ${}^{13}C$ spectra could be explained by assuming that the chair form is distorted. This would probably not affect the ${}^{13}CH1$ coupling constant,

Table 2. Chemical shifts (ppm) and observed first-order coupling constants (± 1 Hz) of hexopyranoses in D_2O or in deuteriochloroform solution.

Compound	C1 $^1J_{\text{CH}_1}$	C2 $^1J_{\text{CH}_2}$	C3 $^1J_{\text{CH}_3}$	C4 $^1J_{\text{CH}_4}$	C5 $^1J_{\text{CH}_5}$	C6 $^1J_{\text{CH}_6}$	Ref.
Penta- <i>O</i> -acetyl- α -D-idopyranose	90.36 175	65.90 ^a 152 ^b	66.15 ^a 152 ^b	65.90 152 ^b	66.15 152 ^b	61.75 149	
Penta- <i>O</i> -acetyl- β -D-galactopyranose	91.79 167	67.84 156	70.56 147	66.80 153	71.46 143	60.98 150	
Penta- <i>O</i> -acetyl- α -D-altropyranose	90.23 175.5	68.16 ^a 155	66.41 ^a 155 ^b	66.41 155 ^b	64.41 148	62.14 149	
β -D-Allopyranose	94.28 161	72.15 142	72.02 148	67.69 145	74.41 150 ^b	62.10 145	12,13
Penta- <i>O</i> -acetyl- β -D-allopyranose	90.14 165	68.24 155 ^b	68.24 155 ^b	65.83 145	71.16 148	61.94 149	
Penta- <i>O</i> -acetyl- α -D-talopyranose	91.44 177	65.19 ^a 151 ^b	66.29 ^a 154	65.32 ^a 151 ^b	68.83 145	61.48 149	

but the proton-proton coupling constants would be different from those expected for an ideal chair and might therefore not give correct information about the conformational equilibrium.

The two protons at C5 in a pentopyranose are in a position similar to that of H1 with regard to the electrons at the ring-oxygen, and it might be expected that $^1J[^{13}\text{CH}(5\text{ax})]$ should be smaller than the corresponding value for H5eq. This was actually found in many cases as seen from Table 1. The couplings between C5 and H5ax were *ca.* 142 Hz whereas the corresponding values for H5eq were found to be *ca.* 150 Hz in free sugars and methyl glycosides. Acetylated pyranoses gave slightly higher values. In compounds which contain appreciable amounts of both chair forms only an average value for $^1J(^{13}\text{CH}_5)$ could be measured. It should, however, be remembered that because of the complexity of the undecoupled ^{13}C NMR spectra the C5H5 coupling constants cannot always be measured accurately on a first-order basis.

In hexopyranoses and derivatives thereof H5 is usually axially oriented and consequently a $^1J(^{13}\text{CH}_5)$ value of *ca.* 145 Hz would be expected. This was observed in many cases, but in some cases a higher value (*ca.* 150 Hz) was found,¹ possibly because a wrong signal was assigned to C5. Some of the previous assign-

ments in the hexose series were therefore reassigned using selective proton decoupling.³ This gave the following revised results (*cf.* Table 1 in Ref. 1): methyl tetra-*O*-acetyl- α -D-glucopyranoside; C2 70.4; C3 69.7; C4 68.2; C5 66.8 ppm. [$^1J(^{13}\text{CH}_5)$ 145 Hz]; methyl tetra-*O*-acetyl- α -D-galactopyranoside; C2 and C3 67.6; C4 67.0; C5 65.7 ppm [$^1J(^{13}\text{CH}_5)$ 143 Hz]; methyl tetra-*O*-acetyl- α -D-mannopyranoside; C2 69.1; C3 68.8; C4 65.8; C5 68.0 ppm. [$^1J(^{13}\text{CH}_5)$ 148 Hz]; methyl tetra-*O*-acetyl- β -D-glucopyranoside; C2 70.9; C3 72.5; C4 68.1; C5 71.4 ppm. [$^1J(^{13}\text{CH}_5)$ 140 Hz].

EXPERIMENTAL

Spectra were obtained as previously described.¹ Unacetylated compounds were measured in D_2O , acetylated compounds in deuteriochloroform unless otherwise stated. The solutions were *ca.* 20 %. Free sugars were measured as mutarotated solutions.

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