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Note

Solvent effects on one-bond, ^{13}C—^{1}H coupling constants of carbohydrates

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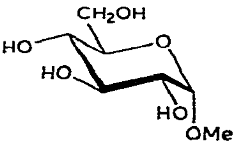
The use of one-bond, ^{13}C–^{1}H coupling constants for assignment of anomeric structure to hexopyranose derivatives[1,2] and for determination of conformational equilibria of pentopyranose derivatives[3] has been described recently. From these studies, it appears that the absolute value of the coupling constant between C-1 and H-1 is dependent on the electronegativity of the substituent at C-1, the orientation of the carbon–hydrogen bond relative to the lone pairs of the ring oxygen, and the nature and total number of electronegative substituents attached to the rest of the molecule. The last point is illustrated by comparison of the ^{13}C-1–H-1 coupling constant (172 Hz) of methyl tetra-*O*-acetyl-α-D-glucopyranoside (3) with the corresponding value (169 Hz) of the 3,4-dideoxy derivative (5) (see Table I). Similar results have been reported elsewhere[2b].

We have now investigated a number of simple sugar molecules in different solvents and found that, for compounds having unprotected hydroxyl groups, one-bond, carbon–hydrogen coupling constants vary with the solvent. This effect is probably caused by variation in the solvation and hence the electronegative character of the hydroxyl groups, rather than by conformational changes, because the chemical shifts are not drastically changed from one solvent to another.



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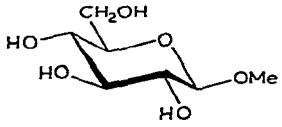

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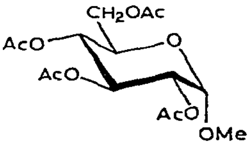

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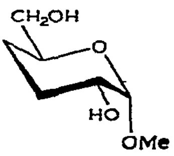

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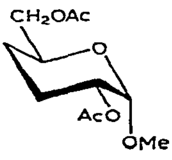

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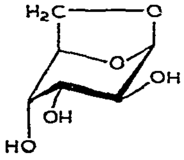

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TABLE I

ONE-BOND, $^{13}C-^{1}H$ COUPLING CONSTANTS[a] AND CHEMICAL SHIFTS[b] FOR HEXOPYRANOSE DERIVATIVES IN DIFFERENT SOLVENTS

Compound	Coupling constants (^1J, Hz)							Chemical shifts (δ)							Solvent
	C-1,H-1	C-2,H-2	C-3,H-3	C-4,H-4	C-5,H-5	C-6,H-6	C-OMe,H	C-1	C-2	C-3	C-4	C-5	C-6	C-OMe	
1	167	145	144	143	142	141	142	99.8	72.7	73.6	70.5	72.2	61.3	54.6	$(CD_3)_2SO$
	170	147	148	146	145	145	144	99.9	72.2	73.9	70.4	71.9	61.5	55.6	D_2O
2	156	142	[c]	[c]	[c]	140	142	104.0	73.6	76.9	70.3	76.9	61.4	56.4	$(CD_3)_2SO$
	160	145	145	143	141	145	144	103.7	73.7	75.5	70.3	75.5	61.7	57.8	D_2O
3	172	151	151	151	144	148	143	96.0	70.0	69.4	68.2	66.8	61.7	54.8	$(CD_3)_2SO$
	172	151	151	151	145	148	143	96.3	70.4	69.7	68.2	66.8	61.6	55.6	$CDCl_3$
4	165	140	[c]	[c]	140	140	141	99.7	68.7	26.5	26.9	68.0	64.3	54.3	$(CD_3)_2SO$
(Ref. 6)	168.5	143	[c]	[c]	143	143	143	100.0	69.8	26.0	26.3	68.5	64.8	55.6	D_2O
	167.5	143	[c]	[c]	143	143	142.5	99.4	68.8	26.0	26.8	68.2	65.1	54.9	$CDCl_3$
5	169	148	132.5	129	144	148	143	96.3	70.0	22.7	26.0	65.7	65.7	54.9	$(CD_3)_2SO$
(Ref 6)	169	148	132.5	128.5	143	148	142.5	97.0	70.2	22.9	26.5	66.2	66.1	54.9	$CDCl_3$
6	173	[c]	[c]	[c]	155	150		101.9	72.9	69.7	69.9	76.9	65.2		$(CD_3)_2SO$
(Refs 7 and 8)	175	[c]	[c]	[c]	157	153		101.9	73.0	70.4	70.1	77.7	66.1		D_2O

[a] Measured by using the gated decoupling technique[5] on a Bruker WH-90 instrument at 22.63 MHz, with a sampling time twice as large as the pulse repetition time, $\alpha = 90°$ (18 μsec), and digital resolution of ±0.7 Hz [b] Chemical shifts in $(CD_3)_2SO$ relative to $\delta[(CD_3)_2SO] = 39.6$ p.p.m., in $CDCl_3$ relative to Me_4Si, and in D_2O relative to δ(1,4-dioxane) = 67.4 p.p.m. Concentrations, 25% [c] Overlapping resonance

In Table I are shown the coupling constants for solutions of methyl α- and β-D-glucopyranoside (**1** and **2**) in D_2O (data from Ref 1) and in methyl sulfoxide-d_6 In both cases, the coupling constants are 2–4 Hz smaller in $(CD_3)_2SO$ than in D_2O, not only for the ^{13}C-1–H-1 values but also for the other $^{1}J_{^{13}\mathrm{C}\ \mathrm{H}}$ values The same change in coupling constants with solvent was found for methyl 3,4-dideoxy-α-D-*erythro*-hexopyranoside (**4**) In this case, it was possible to determine the coupling constants in D_2O, $CDCl_3$, and $(CD_3)_2SO$, the values decrease from D_2O to $(CD_3)_2SO$

The one-bond, ^{13}C–^{1}H coupling constant of methanol shows the same dependence on solvent in D_2O, 142 2 ±0 3 Hz, in $CDCl_3$, 141 0 ±0 3 Hz, and in $(CD_3)_2SO$, 138 5 ±0 3 Hz A similar solvent effect has been described by Evans[4] for the ^{13}C–^{1}H coupling constant of $CHCl_3$

The fully acetylated derivatives (**3** and **5**), however, do not exhibit any difference, all coupling constants being identical in $CDCl_3$ and $(CD_3)_2SO$ within experimental error The one-bond, C–H coupling constant of the H_3CO-group of methyl acetate was also found to be virtually independent of the solvent in D_2O, 147 7 ±0 3 Hz; in $CDCl_3$, 146 5 ±0 3 Hz, and in $(CD_3)_2SO$, 146 6 ±0 3 Hz

To eliminate the possibility of conformational changes induced by the solvent, we measured the $^{1}J_{^{13}\mathrm{C}\ \mathrm{H}}$ values of the more-rigid 1,6-anhydro-β-D-altropyranose (**6**) in D_2O and $(CD_3)_2SO$ and observed a difference of 1–3 Hz (Table I), with the smaller values being obtained in $(CD_3)_2SO$

Changes in one-bond, carbon–hydrogen coupling constants with change in solvent for molecules having unprotected hydroxyl groups (and possibly other polar substituents) can thus be relatively large Hence, comparison of one-bond, ^{13}C–^{1}H coupling constants should be made in the same solvent

ACKNOWLEDGMENT

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