Carbohydrate Research, 117 (1983) 285–290
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

N.m.r. spectra (^1H, ^{13}C) of the methyl mono-, di-, and tri-*O*-acetyl-β-D-xylopyranosides, and additivity effects

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(Received November 1st, 1982; accepted for publication, December 8th, 1982)

In a recent communication on ^1H- and ^{13}-C-n.m.r. chemical shifts for acetylated methyl α- and β-D-xylopyranosides in solution in $(CD_3)_2SO$, McEwan *et al.*[1] reported good additivity of acetylation effects and, from the nearly constant $J_{H,H}$ values, concluded that the conformation of the pyranoid ring was altered very little, if at all, by the introduction of an acyl group at any position. For benzoylated methyl β-D-xylopyranosides in solution in $CDCl_3$, we have found[2] that (*a*) ^{13}C benzoylation effects are not additive, (*b*) coupling constants depend on the number and position of benzoyl groups, and (*c*) benzoylation affects conformer populations.

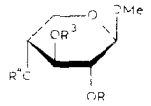
Therefore, we have undertaken a limited study of ^{13}C- and ^1H-n.m.r. spectra of all possible mono-, di-, and tri-*O*-acetyl derivatives of methyl β-D-xylopyranoside as solutions in $CDCl_3$, in order to identify the factor (substituent or solvent) responsible for the reported difference in behaviour.

Syntheses of the acetylated methyl β-D-xylopyranosides have been described[4–7], and n.m.r. measurements were carried out as described previously[2]. With the exception of three pairs of lines noted in Table I, all ^{13}C chemical shifts were assigned unambiguously by ^{13}C–^1H heteronuclear-decoupling experiments. Ambiguity in the assignment of the signals of C-2 and C-3 for methyl 4-*O*-acetyl-β-D-xylopyranoside (**4**) is not important, since the chemical shifts differ only by 0.01 p.p.m. For methyl 2,3-di-*O*-acetyl-β-D-xylopyranoside (**5**), the chemical shifts of these signals differ by 5 p.p.m. and they can be assigned according to the additivity rule. The signals for C-2 and C-4 of methyl 2,4-di-*O*-acetyl-β-D-xylopyranoside (**6**) were also assigned according to the additivity rule, although less convincingly.

The ^{13}C chemical shifts of *O*-acetyl derivatives of methyl β-D-xylopyranoside in $CDCl_3$ (Table I) differ appreciably (up to ±2.5 p.p.m.) from those determined[1] in $(CD_3)_2SO$. Therefore, it is not surprising that significantly different acetylation-shifts (^{13}C-DCS values of Table II) were found. Most remarkable was the small,

0008-6215/83/$ 03 00

TABLE I



^{13}C-NMR CHEMICAL SHIFTS FOR METHYL *O*-ACETYL-β-D-XYLOPYRANOSIDES[a]

Compound	R^2	R^3	R^4	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	OCH_3	CH_3	*C=O*
1[b]	H	H	H	103.25	71.89	75.23	68.38	64.36	55.10	—	—
2	Ac	H	H	100.76	72.02	72.66	69.68	63.14	56.43	20.98	[d]
3	H	Ac	H	103.88	71.17	77.46	68.77	65.15	56.99	21.07	172.50
4	H	H	Ac	103.24	72.13[c]	72.15[c]	71.33	61.29	56.75	20.96	[d]
5	Ac	Ac	H	101.58	70.45[c]	75.30[c]	68.52	64.73	56.63	20.79,20.72	171.39,169.56
6	Ac	H	Ac	100.37	71.21[c]	69.65	70.84[c]	60.16	56.28	20.92,20.92	170.41,170.20
7	H	Ac	Ac	104.05	71.77	73.50	69.05	62.41	57.11	20.85,20.73	170.63,169.91
8	Ac	Ac	Ac	101.58	70.74	71.46	68.94	61.98	56.62	20.71,20.71,20.71	[d]

[a]Chemical shifts on the δ scale (error ±0.02 p.p.m.) for solutions in $CDCl_3$. [b]Measured with added $(CD_3)_2SO$. [c]Assignment of the two lines within the labelled pair could not be made by selective decoupling. [d]Not recorded.

TABLE II

^{13}C-DCS VALUES FOR *O*-ACETYLATION OF METHYL β-D-XYLOPYRANOSIDES, AND THE CALCULATED CHEMICAL-SHIFTS

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*
2[a]	−2.49	0.13	−2.57	1.30	−1.22
3[a]	0.63	−0.72	2.23	0.39	0.79
4[a]	−0.01	0.24	−3.08	2.95	−3.07
5[b]	101.39	71.30	74.89	70.07	63.93
	(0.19)	(−0.85)	(0.41)	(−1.55)	(0.80)
6[b]	100 75	72.26	69.58	72.63	60.07
	(−0.38)	(−1.05)	(0.07)	(−1.79)	(0.09)
7[b]	103.87	71.41	74.38	71.72	62.08
	(0.18)	(0.36)	(−0.88)	(−2.67)	(0.33)
8[b]	101.38	71.54	71.81	73.02	60.86
	(0.20)	(−0.80)	(−0.35)	(−4.08)	(1.12)

[a]Calculated by subtracting the chemical shift for the parent compound **1** from the corresponding shift for the monobenzoate. [b]Calculated as the sum of the corresponding chemical-shift for **1** and of the appropriate DCS values. Values in brackets are the differences between the experimental and calculated chemical-shifts.

positive DCS value for C-4 on 3-*O*-acetylation; β-acetylation shifts are usually[1,8,9] in the range of −1 to −4 p.p.m.

The deviations from the additivity (*i.e.*, the differences between the calculated and experimental chemical-shifts for di- and tri-acetates) are smaller for acetylation than for benzoylation[2] of methyl β-D-xylopyranosides with $CDCl_3$ as solvent, but are much larger than found[1], with $(CD_3)_2SO$ as solvent, for acetylation

TABLE III

^{13}C-DCS VALUES FOR DEACETYLATION OF METHYL 2,3,4-TRI-*O*-ACETYL-β-D-XYLOPYRANOSIDE, AND THE CALCULATED CHEMICAL-SHIFTS FOR METHYL *O*-ACETYL-β-D-XYLOPYRANOSIDES

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*
7[a]	2.47	1.03	2.04	0.11	0.43
6[a]	−1.11	0.47	−1.81	0.90	−1.82
5[a]	0.00	0.01	4.03	−0.42	2.75
4[b]	102.84	72.24	71.69	70.95	60.59
	(0.40)	(0.11)	(0.46)	(0.38)	(0.70)
3[b]	104.05	71.48	77.34	68.63	65.16
	(−0.17)	(−0.31)	(0.12)	(0.14)	(− 0.01)
2[b]	100.37	70.92	73.49	70.42	62.91
	(0.39)	(1.10)	(−0.83)	(0.74)	(0.24)

[a]DCS values calculated by subtracting the corresponding chemical-shift for the reference compound **8** from that for the dibenzoate. [b]The chemical shifts calculated as the sum of the corresponding shift for **8** and the appropriate DCS values. Values in brackets are the differences between the experimental and calculated chemical-shifts.

TABLE IV

^{1}H-NMR DATA ($CDCl_3$) FOR METHYL *O*-ACETYL β-D-XYLOPYRANOSIDES (**1–8**)

Compound[a]	*Chemical shifts*[b] (δ)								*Coupling constants*[c] (*Hz*)					
	H-1	*H-2*	*H-3*	*H-4*	*H-5*[d]	*H-5'*[d]	*OMe*	*OAc*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$
1[e]	4.13	3.21	3.36	3.52	3.88	3.19	3.47	—	7.14	8.3	8.5	5.0	10.0	−11.3
2	4.46	4.75	3.65[f]	3.70[f]	4.08	3.42	3.48		5.13	7.1	8.8[g]	3.6	7.0	−11.9
3	4.25	3.50	4.82	3.77	4.05	3.33	3.54	2.17	6.84	8.5	8.5	5.4	9.3	−11.7
4	4.33	3.50	3.73	4.84	4.10	3.37	3.52	2.12	5.86	7.4[g]	7.4	4.3	7.5	−12.1
5	4.38	4.91[f]	4.89[f]	3.80	4.08	3.37	3.47	2.10	6.8[h]	8.8[g]	8.7	4.9	8.9	−11.7
								2.07						
6	4.48	4.80	3.78	4.82	4.12	3.45	3.47	2.13	5.25	7.0	7.0	4.2	6.6	−12.2
								2.12						
7	4.25	3.51[f]	5.10	4.94	4.09	3.34	3.54	2.10	7.08	8.8[g]	8.8[g]	5.3	9.3	−11.6
								2.04						
8	4.40	4.91[f]	5.17	4.95[f]	4.13	3.37	3.47	2.06	6.71	8.5[g]	8.5[g]	5.0	8.7	−11.8
								2.05						
								2.03						

[a]For numbering of compounds, see Table I. [b]Error ±0.01 p.p.m. [c]Error ±0.1 Hz, except for $J_{5,5'}$ where the error is ±0.04 Hz. [d]The signal for H-5'*a* is at a higher field than that for H-5*e*. [e]Measured in a mixed solvent [$CDCl_3$ + $(CD_3)_2SO$]. [f]Strongly coupled protons (error ±0.04 p.p.m.). [g]Error ±0.5 Hz. [h]Virtually coupled system, error ±0.1 Hz. [i]Signal overlap possible, error ±0.03 p.p.m.

TABLE V

ESTIMATES OF $^4C_1$ CONFORMER POPULATIONS (P) FOR METHYL O-ACETYL-β-D-XYLOPYRANOSIDES (**1–8**)[a]

Compound[b]	P_I[c]	P_{II}[d]	*Average*
1	0.86	0.89	0.87 ±0.02
2	0.58	0.57	0.58 ±0.01
3	0.88	0.81	0.82 ±0.01
4	0.68	0.62	0.65 ±0.03
5	0.82	0.77	0.79 ±0.03
6	0.60	0 53	0.56 ±0 04
7	0.86	0.81	0.83 ±0.03
8	0.80	0.75	0.78 ±0.03

[a]In mol fractions. [b]For numbering of the compounds, see Table I. [c]Estimated from the equation $J_{1,2} = 8.1\,P_I + 1.0\,(1 - P_I)$. [d]Estimated from the equation $J_{4,5'} = 11.1\,P_{II} + 1.5\,(1 - P_{II})$.

of the same compounds. For example, application of the additivity rule gives a wrong prediction of shielding order of skeletal carbons for **8** [predicted: δ(C-4) > δ(C-3) > δ(C-2); observed: δ(C-3) > δ(C-2)> δ(C-4)], which invalidates the rule for assignment purposes.

Acetylation DCS-values and the calculated shifts in Table II are based on the chemical shifts for **1**, which served as a reference compound. Since the chemical shifts were shown above to be solvent-dependent and since the data for **1** had to be obtained using a mixed solvent, the additivity rule should be better satisfied if deacetylation DCS-values[2,8,9] are considered. These values are based on the chemical shifts for the triacetate **8**, the data for which were obtained using the same solvent as for the other compounds. The data in Table III indicate that this is the case; the additivity rule is satisfied with a standard deviation of ±0.52 p.p.m. [for $(CD_3)_2SO$, the standard deviation was ±0.40 p.p.m. for the same series of compounds[1]] which, for many purposes, is acceptable.

The non-validity of the additivity rule for the series of benzoylated methyl β-D-xylopyranosides was explained[2] in terms of conformational heterogeneity in which the populations of the $^4C_1$ conformers varied between 28 and 88%. Using the $J_{1,2}$ and $J_{4,5}$ values (Table IV), conformer populations for solutions in $CDCl_3$ were derived for **2–8**. The conformer populations given in Table V seem to be realistic, since they exhibit good, linear correlation with ^{13}C chemical shifts of MeO-1 signals which are dependent on conformer populations[10] (notable deviations occur only for **5** and **8**). In qualitative agreement with the extent to which the additivity rule is satisfied in the series considered, the conformer populations of acetates vary for solutions in $CDCl_3$ more than for those in $(CD_3)_2SO$ and less than those for benzoates in $CDCl_3$.

The conclusion of Yoshimoto *et al.*[11], accepted by McEwan *et al.*[1], that the conformation of the pyranoid ring is altered very little, if at all, by the introduction of an acyl group at any position is not substantiated by our results, which indicate

that the conformer populations of the pyranoid ring depend on the nature and position of the acyl group, and on the solvent.

REFERENCES

1 T McEwan, A. G McInnes, and D. G Smith, *Carbohydr. Res*, 104 (1982) 161–168.
2 E. Petrakova and J. Schraml, *Collect. Czech. Chem. Commun.*, 48 (1983) 877–888.
3 P. L Durfitf and D Horton, *Carbohydr. Res.*, 18 (1971) 403–418.
4 P. Kovač and R. Palovčik, *Chem Zvesti*, 31 (1977) 98–105.
5 P Kovač and J Alfoldi, *Chem Zvesti*, 32 (1978) 519–523
6 P Kovač and J Alfoldi, *Chem. Zvesti*, 33 (1979) 785–791.
7 E Petrakova and P Kovac, *Carbohydr Res*, 101 (1982) 141–147
8 H. Komura, A Matsuno, Y Ishido, K Kushida and K Aoki, *Carbohydr Res*, 65 (1978) 271–277.
9 J -P. Utille and P. J A. Vottero, *Carbohydr Res*, 85 (1980) 289–297
10 E. Breitmaier and W Voelter, ^{13}C *NMR Spectroscopy*, Verlag Chemie, Weinheim, 1974, pp 223–233.
11 K Yoshimoto, Y Itatani, K Shibata, and Y Tsuda, *Chem Pharm Bull*, 28 (1980) 208–219.