Carbohydrate Research, 105 (1982) 266–268
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

N.m.r. (^{1}H and ^{13}C) studies of some carbohydrate acetates

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(Received October 27th, 1981; accepted for publication, December 1st, 1981)

In recent ^{13}C-n.m.r. studies of D-gluco-[1] and L-rhamno-pyranose[2] acetates, signals were assigned by decoupling techniques and by reference to published data. The assignments were in some cases interchangeable. We now report on the assignment of the ^{13}C-n.m.r. spectra of benzyl[3] (**1**) and methyl[4] (**6**) tetra-*O*-acetyl-β-D-galactopyranosides, methyl tetra-*O*-acetyl-β-D-glucopyranoside[4] (**7**), penta-*O*-acetyl-[5] (**2**) and 1,2,3,6-tetra-*O*-acetyl-β-D-galactopyranose[6] (**5**), benzyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (**8**), and the 2,4,6- (**3**) and 2,3,6-tri-acetates (**4**) of benzyl β-D-galactopyranoside[3]. N.m.r. line-shifts (^{1}H and ^{13}C) induced by Eu(fod)$_3$ were used in some cases for complete assignment of signals. Chemical-shift displacements of the ^{13}C-lines of the ring-carbon atoms on acetylation of **3**, **4**, **5**, and **8**, and on change of configuration at C-4 of **1**, **2**, **3**, **5**, and **6**, are discussed.

^{13}C-N.m.r. chemical shifts for the acetates **1–8** are given in Table I, together with data for benzyl tetra-*O*-acetyl-β-D-glucopyranoside[7] (**9**), and penta-*O*-acetyl- (**10**) and 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose[1] (**11**). The ^{13}C-n.m.r. spectra of **1**, **2**, **4**, and **5** were assigned by selective ^{1}H-spin-decoupling and off-resonance experiments. ^{13}C-Europium-shift data and selective ^{1}H-decoupling allowed complete assignment of the resonances in the spectra of **3**, **6**, and **8**. On addition of Eu(fod)$_3$ to a CDCl$_3$ solution of **7**, the ^{1}H-n.m.r. spectrum was poorly resolved. The complete assignment of the ^{13}C spectrum was obtained by using Pr(fod)$_3$ and selective ^{1}H-decoupling.

For example, the signals for the carbon atoms of the pyranoid ring and the methylene-carbon atom of the benzyl group in the ^{13}C-n.m.r. spectrum of **3** occurred between 100 and 62 p.p.m. The signal for C-1 appeared at lowest field (99.6 p.p.m.), and the high-field signal (62 p.p.m.) for C-6 was assigned from the decoupled off-resonance spectrum and selective irradiation of the H-6 signals. However, the C-3, C-4, and C-5 signals were close together, and there was partial overlap of the H-3 and H-5 signals in the ^{1}H spectrum (60 MHz). Incremental additions of Eu(fod)$_3$ resolved the H-3 and H-5 signals and allowed the resonances due to C-3, C-4, and C-5 to be assigned by spin-decoupling experiments. Extrapolation to zero concentration of europium gave the ^{13}C chemical-shift values listed in Table I.

TABLE I

^{13}C-N.M.R. CHEMICAL-SHIFT DATA (P.P.M. DOWFIELD FROM Me_4Si)

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*$PhCH_2$*	*CH_3O*
1	99.8	68.9	70.8	67.1	70.8	61.3	70.8	—
2	92.2	67.9	70.9	66.9	71.7	61.1	—	—
3	99.6	72.9	71.6	69.8	71.1	62.0	70.8	—
4	99.7	69.2	73.2	67.2	72.1	62.2	70.5	—
5	92.2	68.2	73.0	66.9	73.0	62.1	—	—
6	102.1	68.9	71.0	67.1	70.7	61.3	—	57.0
7	101.6	71.2	72.9	68.5	71.7	61.9	—	56.9
8	99.3	74.2	73.8	71.1	71.9	62.2	70.6	—
9	99.3	71.4	72.9	68.6	71.9	62.1	70.8	—
10	91.8	70.5	72.9	68.0	72.9	61.6	—	—
11	91.9	70.5	75.2	68.5	75.0	62.7	—	—

It can be seen (Table I) that acetylation of the *galacto* acetates **3** and **4** to give **1**, and of **5** to give **2**, caused a 1.3 ($\Delta\delta$ for C-5 in **4** compared to **1**)→4 p.p.m. ($\Delta\delta$ for C-2 in **3** compared to **1**) upfield shift in the resonances for β-carbon atoms, and slight shielding [ranging from 0.0 ($\Delta\delta$ for C-4 in **5** compared to **2**) to 0.8 p.p.m. ($\Delta\delta$ for C-3 in **3** compared to **1**)] for the α-carbon atoms. A similar trend in chemical shifts was observed on peracetylation of the HO-3-free acetate **8**. There was an upfield shift (~7.6→10 p.p.m.) in the signal of the acetoxyl-bearing carbon (C-1) of **2** and **5** relative to the C-1 signals of **1**, **3**, **4**, **6**, **7**, and **8**, as expected[1]. Similar trends in the displacement of the ^{13}C lines of the ring-carbon atoms have been observed for some D-gluco-[1] and L-rhamno-pyranose[2] acetates. Comparison of the ^{13}C-n.m.r. data for **1** and **6** indicated that, apart from the expected[2] downfield shift for the C-1 signal, replacement of the C-1 benzyloxy group by a methoxyl group had little or no effect on the chemical shifts of the remaining ring-carbon atoms. The acetoxyl substituent at C-1 in the peracetate **2** had a significant effect upon the chemical shifts of C-2 (upfield by 1.0 p.p.m.) and C-5 (downfield by ~1.0 p.p.m.) compared to **1** or **6**. Replacement of the benzyl substituent at C-1 in the HO-4 free triacetate **4** by an acetoxyl group, to give the tetra-acetate **5**, had a similar effect on the C-2 and C-5 shifts both in direction and magnitude.

Changes in chemical shift values brought about by inversion of configuration at C-4 can be seen by comparison of the data for the epimeric pairs **1** and **9**, **2** and **10**, **3** and **8**, and **6** and **7**. For **1**, **2**, **3**, and **6**, the signal for the axial acetoxyl-bearing carbon (C-4) undergoes a notable upfield-shift (1.1→1.5 p.p.m.), together with similar shifts (0.8→2.6 p.p.m.) for the adjacent carbon atoms (C-3 and C-5) and for the γ-carbons (C-2), a small downfield-shift (0.3→0.5 p.p.m.) for C-1, and slight shielding (0.2→0.8 p.p.m.) of the exocyclic carbon (C-6). Comparison of the direction and magnitude of the shifts for the acetates **5** and **11**[1], in which HO-4 is unsubstituted, gave corresponding results.

TABLE II

OBSERVED, RELATIVE SHIFT-GRADIENTS[a,b] (^1H) FOR COMPOUNDS **1**, **3**, **4**, **8**, AND **9**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*Ph-CH$_2$*	*OH*	*O-Acetyl*			
1	3.3	7.6	7.3	10	4.8	7.0	7.0	1.8	—	3.9	3.2	3.8	2.3
3	2.1	5.7	5.2	10	2.2	4.4	3.5	1.0	17.8	5.0	0.7	0.0	—
4	2.7	10	5.9	6.1	4.6	6.2	6.2	1.7	16.1	3.2	2.4	2.4	—
8	3.8	10	5.8	8.3	3.6	4.7	4.7	1.1	17.7	2.1	2.1	1.6	—
9	4.6	9.8	10	9.8	4.6	9.6	9.6	2.3	—	8.0	4.5	3.2	3.7

[a] P.p.m. per mol of Eu(fod)$_3$ per mol of substrate. [b] All shifts for a given compound are normalised to the hydrogen(s) which exhibit the greatest induced shift.

Examination of Eu(fod)$_3$-induced shifts. — The relative shift gradients, derived from the experimental plots of induced shift *vs.* molar ratio of shift reagent to substrate, are given in Table II. Comparison of the induced-shift values for the benzyl β-D-galacto- and β-D-gluco-pyranoside tetra-acetates (**1** and **9**) with those reported[4] for the corresponding methyl glycosides indicates a degree of competitive binding with the shift reagent between the acetoxyl groups. Moreover, the expectedly large shift-values for the hydroxyl signals for the 2,3,6- and 2,4,6-triacetates (**4** and **8**) are accompanied by a significant range of shift values for the acetoxyl signals. Furthermore, the marked shift-value for one of the three acetoxyl signals relative to the other two signals for triacetate **3**, together with the large value for HO-3, may indicate that chelation of the shift reagent involves HO-3 and, most probably, AcO-4.

EXPERIMENTAL

^{1}H-N.m.r. spectra (100 MHz) were recorded with a Jeol MH-100 spectrometer, and ^{1}H- and ^{13}C-n.m.r. spectra (59.75 and 15.03 MHz, respectively) were recorded with a Jeol FX-60 spectrometer. Chemical shifts are in δ units (^{1}H) and p.p.m. downfield from Me_4Si (^{13}C).

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