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## Note

# The $^{13}$C-n.m.r. spectra of peracetylated cello-oligosaccharides

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Gagnaire *et al.*[1] determined the $^{13}$C-n.m.r. spectrum of α-cellobiose octa-acetate and compared it with the spectrum of cellulose triacetate. They commented that the atoms directly involved in the glycoside bond (C-1′ and C-4) of the cellobiose octa-acetate have chemical shifts that coincide with those of C-1 and C-4 of cellulose triacetate, but that in order to obtain a precise correlation for the other atoms, it would be necessary to obtain the spectrum of at least the trimer. We have now determined the $^{13}$C-n.m.r. spectra of peracetylated α-cellotriose, α-cellotetraose, and α-cellopentaose, in addition to those for the compounds studied previously[1].

## EXPERIMENTAL

The samples of the peracetylated oligosaccharides and of *p*-nitrophenyl hepta-*O*-acetyl-β-cellobioside used were those previously described[2]. Pulsed Fourier-transform $^{13}$C-n.m.r. spectra with a digital resolution of 0.05 p.p.m./data point were recorded for $CDCl_3$ solutions at room temperature (~25°) on a Varian XL-100-12 spectrometer. Chemical shifts are expressed as p.p.m. downfield from internal $Me_4Si$.

## RESULTS AND DISCUSSION

The $^{13}$C-n.m.r. spectra for the ring carbon atoms of 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose (α-D-glucose penta-acetate), the per-*O*-acetylated cello-oligosaccharides with two to five D-glucose residues, and cellulose triacetate are shown as line diagrams in Fig. 1, and the chemical shifts are listed in Table I.

The chemical shifts for α-D-glucose penta-acetate and for α-cellobiose octa-acetate were assigned by comparison with the results of Gagnaire *et al.*[1]. These workers were unable to assign specifically the signals for C-6 and C-6′ of α-cellobiose octa-acetate. Therefore, the $^{13}$C spectrum of *p*-nitrophenyl hepta-*O*-acetyl-β-cellobioside was recorded, in order to find if the chemical shift of C-6 on the "reducing" unit would be altered. As can be seen (Table II), the C-6 chemical shifts are 61.66 and 61.85 p.p.m., as compared with 61.65 and 61.50 p.p.m. for α-cellobiose octa-acetate.

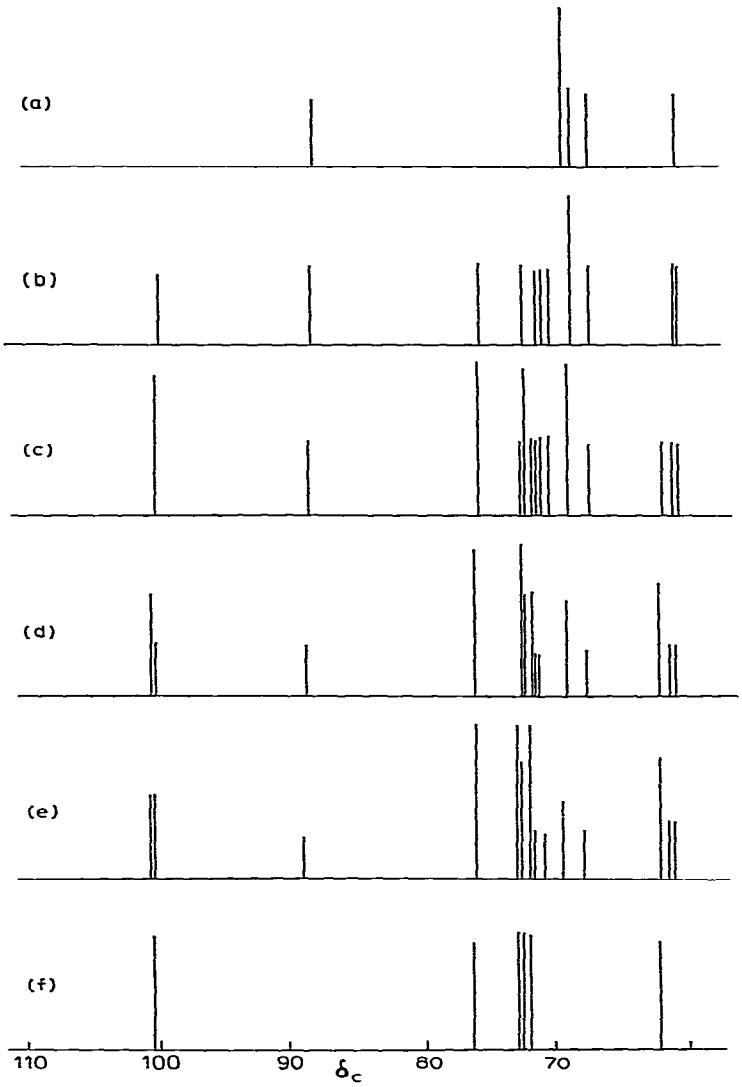


Fig. 1. The $^{13}C$-n.m.r. spectra of the ring carbon atoms of the peracetates of (*a*) α-D-glucopyranose; (*b*) α-cellobiose; (*c*) α-cellotriose; (*d*) α-cellotetraose; (*e*) α-cellopentaose; and (*f*) cellulose.

It is therefore concluded that the signals at 61.66 and 61.65 p.p.m. may be assigned to C-6 of the non-reducing units, and those at 61.85 and 61.50 p.p.m. to C-6 of the reducing units.

The spectrum of α-cellotriose peracetate was assigned by assuming that the carbon atoms of the terminal units have nearly the same chemical shifts as those in the corresponding units in α-cellobiose octa-acetate and that the new signals arise from the internal unit. The signals for C-1, C-4, and C-6 of each unit are assigned easily, as are the signals for C-2, C-3, and C-5 of the reducing unit and C-2 of the

TABLE I

$^{13}$C-N.M.R. CHEMICAL SHIFTS[a] FOR PERACETATES OF α-D-GLUCOSE AND α-CELLO-OLIGOSACCHARIDES

| *Parent sugar* | *Chemical shifts (p.p.m.)*[b] | | | | |
|---|---|---|---|---|---|
| | *Non-reducing and internal units* | | | | *Reducing unit* |
| α-D-Glucose | | | | | C-1 89.08 |
| | | | | | C-2 69.25 |
| | | | | | C-3 69.86 |
| | | | | | C-4 67.96 |
| | | | | | C-5 69.86 |
| | | | | | C-6 61.51 |
| α-Cellobiose | | | | C-1 100.89 | C-1 88.96 |
| | | | | C-2 71.69 | C-2 69.38 |
| | | | | C-3 72.99 | C-3 69.38 |
| | | | | C-4 67.88 | C-4 76.05 |
| | | | | C-5 71.99 | C-5 70.80 |
| | | | | C-6 61.65 | C-6 61.50 |
| α-Cellotriose | | | C-1 100.81 | C-1 100.81 | C-1 88.98 |
| | | | C-2 71.68 | C-2 72.09† | C-2 69.45 |
| | | | C-3 72.92** | C-3 72.80** | C-3 69.45 |
| | | | C-4 67.85 | C-4 76.17 | C-4 76.17 |
| | | | C-5 71.89† | C-5 72.80** | C-5 70.80 |
| | | | C-6 61.57* | C-6 62.26 | C-6 61.32* |
| α-Cellotetraose | | C-1 100.81 | C-1 100.54 | C-1 100.81 | C-1 88.98 |
| | | C-2 71.66 | C-2 72.05 | C-2 72.05 | C-2 69.42 |
| | | C-3 72.87 | C-3 72.71 | C-3 72.71 | C-3 69.42 |
| | | C-4 67.84 | C-4 76.15 | C-4 76.15 | C-4 76.15 |
| | | C-5 71.87 | C-5 72.87 | C-5 72.87 | C-5 70.79 |
| | | C-6 61.58* | C-6 62.15 | C-6 62.15 | C-6 61.33* |
| α-Cellopentaose | C-1 100.81 | C-1 100.53 | C-1 100.53 | C-1 100.81 | C-1 88.96 |
| | C-2 71.66 | C-2 71.95 | C-2 71.95 | C-2 71.95 | C-2 69.40 |
| | C-3 72.86 | C-3 72.66 | C-3 72.66 | C-3 72.66 | C-3 69.40 |
| | C-4 67.83 | C-4 76.13 | C-4 76.13 | C-4 76.13 | C-4 76.13 |
| | C-5 71.95 | C-5 72.86 | C-5 72.86 | C-5 72.86 | C-5 70.80 |
| | C-6 61.56* | C-6 62.12 | C-6 62.12 | C-6 62.12 | C-6 61.34* |

[a] *cf.* Cellulose triacetate: C-1 100.45; C-2 72.00; C-3 72.60; C-5 72.95; C-6 62.15. [b] Signals marked *, †, or ** may be interchanged with others similarly marked for the same compound.

TABLE II

$^{13}$C-N.M.R. CHEMICAL SHIFTS FOR THE RING CARBON ATOMS OF *p*-NITROPHENYL HEPTA-*O*-ACETYL-β-CELLOBIOSIDE

| *Carbon atom* | *Chemical shifts (p.p.m.)* | |
|---|---|---|
| | *Non-reducing unit* | *Reducing unit* |
| C-1 | 100.81 | 97.84 |
| C-2 | 71.62 | 72.29 |
| C-3 | 72.85 | 71.11 |
| C-4 | 67.83 | 76.20 |
| C-5 | 71.98 | 73.22 |
| C-6 | 61.66 | 61.85 |

non-reducing end-unit. The signals at 72.09 p.p.m., assigned to C-2 of the internal unit, and at 71.89 p.p.m., assigned to C-5 of the non-reducing end-unit, may be interchanged, as may the values at 72.92 p.p.m. for C-3 of the non-reducing end-unit and at 72.80 p.p.m. for C-3 and C-5 of the internal unit. It is also possible that the signals for C-6 of the two end-units may be interchanged.

The chemical shifts of the β-anomeric carbons of α-cellotriose peracetate are identical (100.81 p.p.m.). On addition of an acetylated D-glucosyl residue to form α-cellotetraose peracetate, a new signal for an anomeric carbon appears at 100.54. On addition of a further acetylated D-glucosyl residue to form α-cellopentaose peracetate, the relative intensity of this signal doubles. The signal lies close to that (100.45 p.p.m.) of the anomeric carbon of cellulose triacetate, and is therefore considered to be the signal of a normal internal unit. In the spectra of both α-cellotetraose peracetate and α-cellopentaose peracetate, however, the signal at 100.81 represents that for two anomeric carbon atoms. One of these is that of the non-reducing end-unit, and so the other must be that of a special internal unit. Since this resonance is also found in the spectrum of α-cellotriose peracetate, the special internal unit must be adjacent to one of the terminal units. The special unit appears to differ from other internal units only in the chemical shift of its anomeric carbon atom. It is therefore suggested that the special unit is the one next to the reducing end-unit, since the anomeric carbon would then be only five atoms away from the point at which the structural difference from a normal unit occurs, whereas if the special unit were adjacent to the non-reducing end-unit, the anomeric carbon would be eight atoms away.

On this basis, the chemical shifts were assigned to the ring carbon atoms of cellotetraose peracetate as shown in Table I. The assignments for C-1, C-4, and C-6 were readily made, and the signals for C-2, C-3, and C-5 of the reducing unit and for C-2 of the non-reducing end-unit are easily identified. Other assignments were made on the assumption that the terminal units have the same chemical shifts as in cellobiose octa-acetate and that the signals of the normal internal unit are similar to those of cellulose triacetate.

On addition of a further acetylated D-glucosyl residue to form cellopentaose peracetate, the $^{13}C$-n.m.r. spectrum does not become more complicated. On the assumption that the terminal units retain their chemical-shift identity, that the special internal unit is adjacent to the reducing terminus, and that the spectrum is tending towards that of cellulose triacetate, the assignments shown in Table I result.

If one takes an overall view of the $^{13}C$-n.m.r. spectra of acetylated cello-oligosaccharides, it can be seen that the spectra of cellobiose and cellotriose peracetates are not characteristic of the spectrum of cellulose peracetate. It is only when cellotetraose peracetate is reached that all of the signals shown by the polymer are found.

From the foregoing discussion, it is concluded that the signals of the ring carbon atoms of the residues that are underlined in Fig. 2 are probably those responsible for the spectrum of cellulose triacetate.

Glc—Glc—Glc—Glc—Glc—---- Glc—Glc—Glc—Glc—Glc—Glc

Fig. 2. The acetylated D-glucosyl residues (underlined) that are responsible for the $^{13}C$-n.m.r. spectrum of cellulose triacetate.

ACKNOWLEDGMENT

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