

## Note

### Assignment of the *O*-acetyl carbonyl carbon atoms of cellulose triacetate via 2D, long-range, proton–carbon chemical-shift-correlation data

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Nuclear magnetic resonance spectroscopy has been used extensively for the structural characterization of cellulose derivatives<sup>1–16</sup>; in particular, for determining degrees of substitution and distributions of substituents on the D-glucosyl residues. Applied to cellulose acetates, the number and distribution of the *O*-acetyl groups have been determined by using both the <sup>1</sup>H-n.m.r. resonances of the methyl protons<sup>10,11</sup> and the <sup>13</sup>C-n.m.r. signals of the carbonyl and ring-carbon atoms<sup>12,14</sup>.

Although both methods appear to give reliable results for the determination of these two quantitative parameters, integration of the carbonyl resonances is the more advantageous, for two reasons. First, the carbonyl signals in the <sup>13</sup>C-n.m.r. spectrum are better resolved than those of the ring carbon atoms<sup>14,15</sup>, and second, quantitative analysis of the methyl protons requires an additional esterification of the free hydroxyl groups of the D-glucosyl units, *e.g.*, with acetyl-*d*<sub>3</sub> chloride<sup>10</sup>. Nevertheless, the assignments of the *O*-acetyl carbonyl carbon atoms have yet to be established in an unambiguous manner<sup>12,14</sup>.

Herein, advantage is taken of the 2D, long-range, heteronuclear-shift-correlation technique<sup>17</sup> to confirm the location of acetylation sites on cellulose by using a sample of cellulose triacetate (CTA). This 2D-n.m.r. experiment, the so-called COLOC<sup>17</sup> experiment, which is based on the pulse sequence 90° (<sup>1</sup>H), *t*<sub>1</sub>/2, 180° (<sup>1</sup>H, <sup>13</sup>C), [Δ<sub>1</sub> – (*t*<sub>1</sub>/2)], 90° (<sup>1</sup>H, <sup>13</sup>C), Δ<sub>2</sub>, acq (<sup>13</sup>C, BB<sup>1</sup>H), is used here in attempting to identify long-range couplings between the carbonyl carbon atoms and sugar-ring protons, or between the carbonyl carbon atoms and methyl protons, or both. Because these long-range couplings are unknown for CTA, the delays, Δ<sub>1</sub> and Δ<sub>2</sub>, in the COLOC experiment were optimized by using a range of <sup>3</sup>J<sub>CH</sub> couplings from 3 to 15 Hz, which covers the range of couplings observed<sup>18</sup> for *O*-acetylated sugar compounds. None of these values afforded a correlation between the carbonyl carbon atoms and ring protons, even at temperatures as high as 120°. This fact can

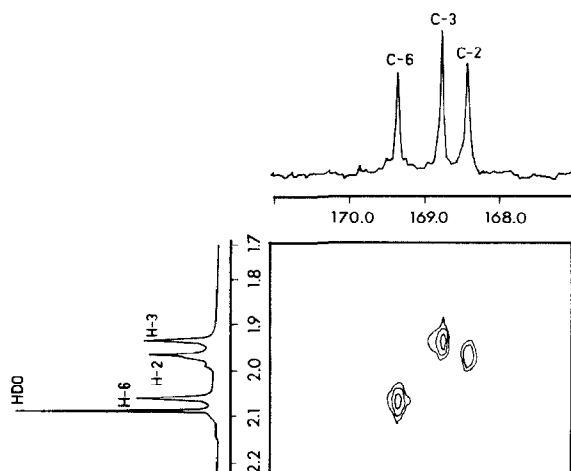


Fig. 1. Long-range, 2D, heteronuclear chemical-shift correlation-spectrum of the 2-, 3-, and 6-(acetoxymethyl) protons (H-2, -3, and -6), and 2-, 3-, and 6-carbonyl carbon atoms (C-2, -3, and -6), obtained for a solution of CTA (5% w/v) in 1,1,2,2-tetrachloroethane- $d_2$  at 80°, with a Bruker-400 spectrometer, using the COLOC pulse sequence, with delays of  $\Delta_1 = \Delta_2 = 39.8$  ms. Transients (128) were accumulated for each of 128  $t_1$  increments, using spectral widths of 400 Hz in  $f_2$ , and 900 Hz in  $f_1$ .

be explained by the very short spin-spin relaxation times ( $T_2$ ) of the ring protons, at least for the present high-molecular-weight CTA sample, which do not permit detection of the  $^{13}\text{C}$  signal in the last period of the experiment. By contrast, a good correlation was obtained between the carbonyl carbon atoms and methyl protons, as shown in Fig. 1. The spectrum in Fig. 1 was obtained by using delays  $\Delta_1 = \Delta_2 = 39.8$  ms, chosen to give strongest signals for couplings of  $\sim 12.5$  Hz. The three proton peaks, at  $\delta$  2.07, 1.97, and 1.94, have been assigned<sup>10,11</sup> to the acetoxyl groups attached to C-6, C-2, and C-3, respectively. Although the assignments of the three carbonyl carbon atoms shown in Fig. 1 are in agreement with those of Miyamoto *et al.*<sup>14</sup>, they differ from those obtained by Kamide and Okajima<sup>12</sup>. Clearly, in offering these carbonyl-carbon assignments, we have assumed that the assignments of the methyl-proton resonances are correct. Where feasible, however, correlation with ring-proton resonances should be the more reliable<sup>19,20</sup>, as the latter are the more easily designated.

It is noteworthy that the  $^{13}\text{C}$  spin-lattice relaxation times ( $T_1$ ), measured at 300 MHz, for the carbonyl carbon atoms of CTA (10% w/v) in 1,1,2,2-tetrachloroethane- $d_2$  solution at 80°, constitute an efficient basis for distinguishing the acetoxyl group on C-6 relative to those on C-2 and C-3. That is, the higher  $T_1$  value of  $2.53 \pm 0.08$  s for the former, as compared to those of  $1.90 \pm 0.04$  and  $1.98 \pm 0.07$  s for the latter two, respectively, can be attributed to differences in the local environment of the acetyl groups<sup>6</sup> and to the additional degree of freedom about the exocyclic, C-5–C-6 bond for the substituent group on C-6.

## EXPERIMENTAL

$^{13}\text{C}$   $T_1$  measurements were carried out at  $80^\circ$  with a VARIAN XL-300 spectrometer. Solutions of CTA (10% w/v) in 1,1,2,2-tetrachloroethane- $d_2$  were used. Two hundred transients were accumulated over a spectral window of 800 Hz for each partially relaxed spectrum, using the IRFT method. The repetition time was longer than  $^5T_1$  to ensure return of the magnetization vector to thermal equilibrium before application of the succeeding sequence. The  $90^\circ$  pulse-width was  $21\ \mu\text{s}$ . The COLOC experiments were performed at  $80^\circ$ , using the sequence already noted and the microprogram COLOC.AV, with a Bruker 400-MHz spectrometer. The delays  $\Delta_1$  and  $\Delta_2$  were both 39.8 ms. One hundred and twenty-eight transients were measured for each 128  $t_1$  increment, using spectral widths of 400 Hz in  $f_2$  and 900 Hz in  $f_1$ .

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