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Note

Acetylation of (4-*O*-methyl-D-glucurono)-D-xylan under homogeneous conditions using trifluoroacetic acid–acetic anhydride

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Although cellulose acetate is widely used in industry[1] and much work has been done on the acetylation of cellulose under homogeneous conditions[2–4], non-cellulosic plant polysaccharides have been largely ignored as substrates for acylation[5].

In previous work[6], organic solvents (CH_2Cl_2, $CHCl_3$) were used in combination with catalytic amounts of inorganic acids (H_2SO_4, $HClO_4$) and acetic anhydride for the acetylation of (4-*O*-methyl-D-glucurono)-D-xylan (**1**). The reactions were heterogeneous initially, but dissolution occurred as the reaction proceeded and the product obtained when all of the substrate had dissolved was fully acetylated **1** (**2**). In seeking conditions under which partially acetylated **1** could be prepared, the use of trifluoroacetic acid, a solvent for cellulose[7], was studied.

Dissolution of **1** in trifluoroacetic acid occurred within 5 min at room temperature with stirring at 1500 r.p.m. When the solution was diluted, dialysed, and lyophilised, and the residue was analysed by ^{13}C-n.m.r. spectroscopy, the resulting spectrum was similar to that of **1** (Table I, assigned according to known data[8]) except that the signals for C-2 and C-3 of the uronic acid residue had shifted to 71.8 and that for C-6 to 171.5 p.p.m. These differences could reflect a change in the supramolecular structure and the recycling of the uronate of **1** to the uronic acid form.

Addition of acetic anhydride (5–100 mmol) to 5 mmol of **1** in trifluoroacetic acid resulted in progressive acetylation up to a maximum of 30% (*cf.* the theoretical value of 40%), which indicates that some hydroxyl groups were not accessible to the reagent.

The ^{13}C-n.m.r. spectrum (Table I) of the sample (**2**) with an acetyl content of 30% contained signals for CH_3CO at 21.0, 20.8, 20.6, and 20.4 p.p.m. and for CH_3CO at 171.5, 170.9, 169.4, and 169.0 p.p.m. (two each on the D-xylose and two on 4-*O*-methyl-D-glucuronic residues). The intensities of the signals at 173.3 and 171.5 p.p.m. were much lower than those at 169.5 and 169.2 p.p.m. Hence, the former are attributed to acetyl groups attached to the uronic acid residues. The two signals of **1** still present in the spectrum of **2** were those at 72.6 and 74.0 p.p.m. (C-2 and C-3 of the unsubstituted

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TABLE I

^{13}C-N.m.r. data for solutions of (4-*O*-methyl-D-glucurono)-D-xylan (**1**) and its acetylated derivative (**2**) in $(CD_3)_2SO$

Compound		*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C*[a]
1	β-D-Xyl	101.7	72.6	74.0	75.4	63.2		
subst.	β-D-Xyl	101.0	76.2	74.0	75.4	63.2		
	β-D-GlcA	97.6	72.6	72.6	82.1	69.6	173.3	58.9
2[b]	β-D-Xyl	99.9	70.9	72.1	75.2	62.5		
subst.	β-D-Xyl	99.5	76.4	72.1	75.2	62.5		
	β-D-GlcA	97.9	69.9	69.9	78.7	69.1	169.8	59.8

[a] Signals of CH_3O of 4-*O*-Me-D-GlcA residue. [b] Other signals: 20.4–21.0 (CH_3CO) and 169.1–169.4 p.p.m. (CH_3CO).

the unsubstituted xylopyranosyl residues that are resistant to acetylation. The signals for C-1 to C-5 of the unsubstituted xylopyranosyl residues of **2** (Table I) were similar to those[9] of per-*O*-acetylated β-linked xylopentaose measured in $CDCl_3$.

From the d.p. values, it was concluded that the degradation of the substrate during the procedure was not influenced greatly by the quantity of trifluoroacetic acid used. The yields of the products indicated that, with 100 and 150 mmol of acid, there was little degradation.

EXPERIMENTAL

Materials. — (4-*O*-Methyl-D-glucurono)-D-xylan (**1**), isolated[10] from beech sawdust, contained uronic acids (19.3%), methoxyl (2.9%), and ash (3.4%). The neutral portion of the saccharides formed on hydrolysis contained 98% of D-xylose. The $\overline{M}_n$ and $\overline{M}_w$ values of 18 610 and 29 780, respectively, were determined by gel-permeation chromatography.

Acetylation. — (4-*O*-Methyl-D-glucurono)-D-xylan (**1**, 5 mmol) was solubilised in 50–200 mmol of trifluoroacetic acid within 5 min at 20° on stirring at 1500 r.p.m. To the homogeneous solution were added 5–100 mmol of acetic anhydride, and the mixture was stirred for 15 min at 20° and 1500 r.p.m., then diluted with water, dialysed, and freeze-dried. The ash content of each product was ~0%.

Methods. — ^{13}C-N.m.r. spectra (75.46 MHz) were measured at 25° (70–100 mg.mL^{-1}) for solutions in $(CD_3)_2SO$, using a Bruker AM-300 spectrometer. The acetyl content was determined potentiometrically as follows: 0.01M NaOH (100 mL) was added to the sample (100–200 mg), and the mixture was stored at room temperature for 48–75 h under nitrogen, then titrated with 0.01M HCl. The acetyl content was calculated as described[11]. The uronic acid content was determined as follows. The sample (100–200 mg) was mixed with aqueous 5% KIO_3 (5 mL), KI (~1 g), and 0.01M $Na_2S_2O_3$ (25 mL). The mixture was left overnight in the dark under nitrogen, then titrated with 0.01M iodine. The uronic acid was neglected when the acetyl content was calculated from the consumption of 0.01M NaOH because it represented only ~0.1 mmol of HCl.

The d.p. of the samples was determined, using a Ubbelohde viscosimeter having a capillary cross-section of 0.636 mm^2, in Schweizer's reagent (cuprammonium solution) at 23° and calculated with the help of data for cellulose. The d.p. of **1** (H^+ form) was 180. The values of acetylated samples were determined after deacetylation.

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