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THE PREPARATION AND PROPERTIES OF PERACETYLATED D-XYLO-OLIGOSACCHARIDES WITH ALL RESIDUES IN THE ALDEHYDROL FORM

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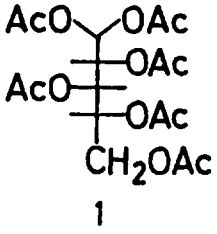
Abstract - Acetolysis of xylan with acetic anhydride, acetic acid and sulphuric acid yields hexa-*O*-acetyl-*aldehydo*-D-xylose aldehydrol and a series of related peracetylated oligosaccharides with the xylose residues in the acyclic form. These were characterised by their ^{1}H and ^{13}C-n.m.r. spectra, their mass spectra and by Zemplen deacetylation when they yielded D-xylose.

As far as we are aware the only previous investigation of the acetolysis of xylan or its acetate is that of Whistler, Heyne, and Bacharach[1] who obtained hexa-*O*-acetyl-D-xylose aldehydrol (1) from D-xylan acetate. We now report that this compound and an acetylated series of oligosaccharides (2) - (4) with all the xylose residues in the aldehydrol form may be obtained from the acetolysis of D-xylan, and describe the spectroscopic properties of this novel series.



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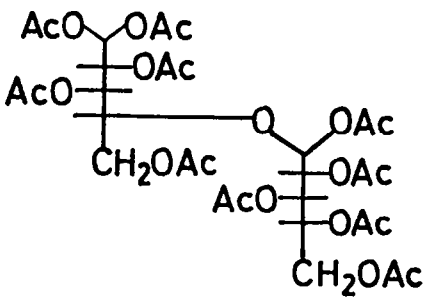

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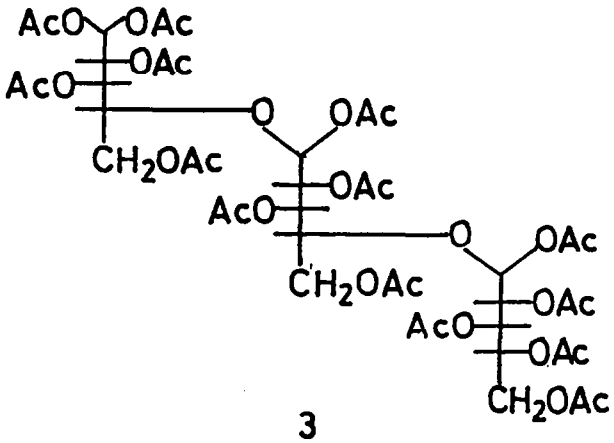

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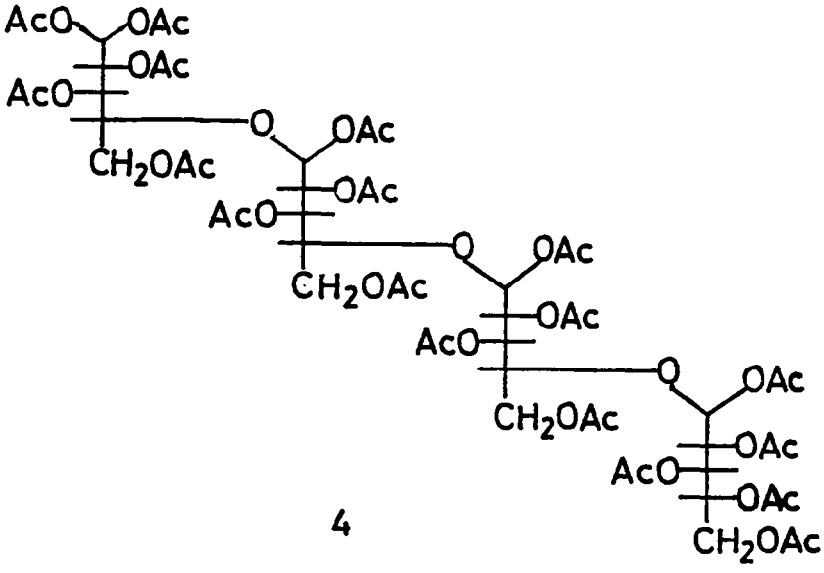

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EXPERIMENTAL

Mass spectra were recorded on a single-focussing G.E.C.-A.E.I. MS12 mass spectrometer with a direct insertion probe and operating at 70 ev. Infrared spectra were recorded in a Perkin-Elmer 580 infra-red spectrometer. 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. 90 MHz ^{1}H-n.m.r. spectra were

recorded in a Perkin-Elmer R-32 n.m.r. spectrometer. 360 MHz ^{1}H-n.m.r. spectra were recorded in a Bruker WH-360 n.m.r. spectrometer by the S.E.R.C. High Field n.m.r. Service at the University of Edinburgh. Optical rotations were measured in a Perkin-Elmer 141 polarimeter.

Preparation and properties of peracetylated D-xylo-oligosaccharides with all residues in the aldehydrol form. - Xylan from larchwood (Sigma) (20 g) was added slowly to a stirred, cooled mixture of acetic anhydride (75 ml), acetic acid (75 ml), and sulphuric acid (10 ml) at 15° to 20°. The mixture was maintained at 25-30° for 82 hours after which time t.l.c. showed the presence of appreciable quantities of acetylated oligosaccharides. Unreacted xylan was filtered off and the filtrate was poured into vigorously stirred ice-water (2 l). The oily layer which separated was extracted with chloroform (4 x 250 ml) and the extract was washed with water and sodium hydrogen carbonate solution and dried. The chloroform was removed on a rotatory evaporator and the resulting oil (25 g) chromatographed in 5 g portions on a 40 x 3 cm column of Kieselgel HF 254 for t.l.c. (Fluka) (180 g) using vacuum liquid chromatography.[2] The eluting solvent was chloroform-light petroleum (60-80) (75 v : 25 v) changing to chloroform-ethyl acetate (95 v : 5 v). The first compound to be eluted was tetra-*O*-acetyl-α-D-xylose (2 g) with a ^{1}H-n.m.r. spectrum identical to that of an authentic sample, followed by the following oily derivatives of aldehydo-D-xylose: hexa-*O*-acetyl-*aldehydo*-D-xylose aldehydrol, 1, (0.1 g), $[\alpha]_D^{20}$ = + 4.2° ($CHCl_3$, *c* = 1.1) (Lit.[3] + 4°); deca-*O*-acetyl-*aldehydo*-D-xylosyl-(1 → 4)-*aldehydo*-D-xylose aldehydrol, 2, (0.9 g), $[\alpha]_D^{20}$ = - 1.6 ($CHCl_3$, *c* = 44); tetradecyl-*O*-acetyl-*aldehydo*-D-xylosyl-(1 → 4)-aldehydo-D-xylosyl-(1 → 4)-*aldehydo*-D-xylose aldehydrol, 3, (0.5 g), $[\alpha]_D^{20}$ = + 1.35 ($CHCl_3$, *c* = 5.14); octadecyl-*O*-acetyl-*aldehydo*-D-xylosyl-(1 → 4)-*aldehydo*-D-xylosyl-(1 → 4)-*aldehydo*-D-xylosyl-(1 → 4)-*aldehydo*-D-xylose aldehydrol, 4, (0.5 g), $[\alpha]_D^{20}$ = - 1.3 ($CHCl_3$, *c* = 5.6). The i.r. spectra ($CHCl_3$) all showed absorptions at γ = 1750 (s), 1375 (s), 1230 (s), 1205 (m), 1050 (w), and 1015 cm^{-1} (w). The ^{1}H-n.m.r. spectra all had a doublet (J = 5.13-5.37 Hz) at δ = 6.84-6.89 characteristic of the $CH(OAc)_2$ group and those of the acetylated oligosaccharides had in addition one or more doublets at δ = *ca.* 5.9. The remaining 1 g of material from the column was mainly higher oligomers of the series which were only partially separated from one another. Three fractions were obtained all of whose ^{1}H-n.m.r. spectra showed signals at δ = *ca.* 6.5 and 5.9 but t.l.c. showed that more than one compound was present.

The 360 MHz ^{1}H-n.m.r. spectra of 1 and 2 were assigned completely on the basis of decoupling experiments (Table I) but those of 3 and 4 had too many unresolved peaks to make a complete assignment. The signals of the CH_3 groups of the acetoxy residues (Table II) showed that the required

TABLE I

^{1}H-N.M.R. CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE CHAIN PROTONS OF 1 AND 2[a]

			Reducing Unit	
1			H-1	6.84, d, J = 5.13
			H-2	5.34, dd, J = 5.13, 4.88
			H-3	5.48, dd, J = 5.86, 4.88
			H-4	5.23, dt, J = 5.86, 4.15
			H-5'	4.33, dd, J = 12.0, 4.15
			H-5^2	3.98, dd, J = 12.0, 5.86
2	H-1	5.96, d, J = 4.88	H-1	6.89, d, J = 5.37
	H-2	5.24, dd, J = 4,88, 4.39	H-2	5.40, dd, J = 5,37, 4.15
	H-3	5.45, dd, J = 6.10, 4.39	H-3	5.23, m
	H-4	5.23, m	H-4	4.00, m
	H-5'	4.34, dd, J = 12.2, 3.91	H-5	4.29, dd, J = 11.1, 2.32
	H-6'	4.00, m	H-6	4.00, m

[a] Measured at 360 MHz in $CDCl_3$ solution; chemical shifts are in p.p.m. downfield from internal TMS and coupling constants are in Hz.

TABLE II

^{1}H-N.M.R. CHEMICAL SHIFTS FOR THE ACETOXY GROUPS OF 1 - 4[a]

1	2.090, 2.067, 2.056, 2.050, 2.048, 2.033
2	2.115, 2.089(3), 2.082, 2.053(2), 2.038, 2.036, 2.033
3	2.116, 2.106, 2.103, 2.086, 2.081(2), 2.071, 2.059, 2.052(2), 2.044, 2.035(2), 2.029
4	2.138, 2.116, 2.106, 2.095(3), 2.082, 2.076(3), 2.066, 2.052, 2.047(2), 2.040, 2.031(2), 2.026

[a] Measured at 360 MHz in $CDCl_3$; each signal corresponds to one acetoxy group except where indicated.

number of these were present in each compound. The ^{13}C-n.m.r. spectrum of 1 (Table III) was assigned on the basis of the "off-resonance" spectrum and selective proton decoupling. The spectra of 2 to 4 were assigned on the basis of the "off-resonance"spectra and the assumption that the carbon atoms of the terminal residues of the higher oligomers had similar chemical shifts to the corresponding atoms in the lower oligomers. This means that there are some uncertainties in the assignments as indicated.

Compounds 2, 3, and 4 were deacetylated by Zemplen's method[4] using 10 vols of anhydrous methanol and 3 vols of sodium methoxide solution (0.5 g in 100 ml). Oils were obtained which on trituration with methanol and seeding yielded crystalline D-xylose, m.p. 144-146° (Lit.[5] 145°), equilibrium $[\alpha]_D^{20}$ = 19.1° (*c*, 1.4; H_2O) (Lit.[5] + 18.8°). The yields were 94, 88, and 90% respectively.

TABLE III

^{13}C-N.M.R. CHEMICAL SHIFTS FOR 1 TO 4

	Chemical shifts (p.p.m.)[a]			
	Non-reducing and internal units			Reducing unit
1				C-1 86.09
				C-2 69.61
				C-3 67.92
				C-4 69.32
				C-5 61.75
2			C-1 93.26	C-1 85.98
			C-2 68.06†	C-2 69.55*
			C-3 68.54†	C-3 69.74*
			C-4 69.25*	C-4 74.72
			C-5 61.85	C-5 63.34
3		C-1 93.11	C-1 93.54	C-1 85.95
		C-2 68.08†	C-2 68.08†	C-2 69.60*
		C-3 68.48†	C-3 69.37*	C-3 69.60*
		C-4 69.37*	C-4 75.95	C-4 74.46
		C-5 61.84	C-5 63.11	C-5 63.38
4	C-1 93.07	C-1 93.41	C-1 93.52	C-1 85.99
	C-2 68.12†	C-2 68.12†	C-2 68.12†	C-2 69.55*
	C-3 68.49†	C-3 69.55*	C-3 69.55*	C-3 69.55*
	C-4 69.55*	C-4 75.71	C-4 75.71	C-4 74.46
	C-5 61.83	C-5 62.89	C-4 63.19	C-5 63.42

[a] Signals marked* or † may be interchanged with others similarly marked for the same compound.

RESULTS AND DISCUSSION

Xylan was acetolysed under conditions similar to those used previously in the preparation of acetylated cello-oligosaccharides from cellulose.[6] The time and temperature were chosen to give what appeared from t.l.c. to be the maximum yield of acetylated xylo-oligosaccharides. These were then separated by vacuum liquid chromatography.[2] The first material to be eluted was tetra-*O*-acetyl-α-D-xylopyranose, identical with an authentic sample. This was followed by a compound identified from its ^{1}H-n.m.r. spectrum and optical rotation to be hexa-*O*-acetyl-*aldehydo*-D-xylose aldehydrol (1). The anomeric proton showed a chemical shift of δ = 6.84 (Lit.[3] 6.8) and the 90 MHz spectrum showed the presence of six acetyl groups. The signals of these were resolved from one another in the 360 MHz spectrum and had δ = 2.09, 2.07, 2.06, 2.05, 2.04, and 2.03. In the ^{13}C spectrum the signal of C-1 appeared at δ = 86.09. Three higher oligomers whose ^{1}H-n.m.r. spectra also showed signals at δ = 6.8-6.9 and whose ^{13}C-n.m.r. spectra showed signals at δ = *ca.* 86 were subsequently eluted from the column. These were assigned structures **2**, **3**, and **4** on the basis of their ^{1}H- (Tables I and II) and ^{13}C-n.m.r. (Table III) spectra and the chemical evidence outlined below.

In addition to the signals at δ = 6.84-6.89 in the ^{1}H-n.m.r. spectra of **2**, **3**, and **4** showed signals at δ = *ca.* 5.9 corresponding to one, two, and three protons. This value is very similar to that reported[3] for ^{1}H of the 1-*O*-methyl-1,2,3,4,5-penta-*O*-acetyl-*aldehydo*-D-xylose aldehydrols (5), δ = 5.8, and suggests that the non-reducing residues are in the acyclic form as shown. If they were in the pyranose form the signals of the anomeric protons would be expected to be close to that reported[7] for the anomeric proton of the non-reducing ring of hexa-*O*-acetyl-β-xylobiose, δ = 4.6. The ^{13}C-n.m.r. spectra of **2**, **3** and **4** also support the assigned structures. They all have signals at δ = *ca.* 86 similar to that of **1** which indicates that the reducing residue is in the acyclic form with two acetoxy groups attached to C-1. In addition they have respectively one, two, and three signals at δ = 93 to 93.5. This value is *ca.* 6 p.p.m. lower than would be expected for C-1 of non-reducing residues in the pyranose form, for which a good model would be C-1 of the non-reducing ring of hexa-*O*-acetyl-β-xylobiose, δ = 99.74.[8]

Chemical evidence which supports structure **2**, **3**, and **4** comes from deacetylation with sodium methoxide in methanol. If these structures were correct then the product should be D-xylose (after cleavage of the hemiacetal linkages), but if the ring structures were intact xylo-oligosaccharides should be obtained. All three compounds in fact yielded only D-xylose characterised by t.l.c., optical rotation, and melting point and

no oligosaccharides were detected. The anomeric carbon atoms of the non-reducing residues of 2, 3, and 4 are asymmetric therefore there is the possibility of the formation of diastereoisomers. Although the compounds we have obtained appear to be mainly one diastereoisomer there appear to be small amounts of some of the others present. Thus the ^{13}C-n.m.r. spectrum of 2 shows in addition to the signal at δ = 93.26 for the anomeric carbon of the non-reducing residue a signal at δ = 94.1 and several other small signals. The 360 MHz ^{1}H-n.m.r. spectrum also shows a small signal at δ = 5.95 in addition to the main signal at δ = 5.96 for the anomeric proton of the non-reducing residue. The ^{13}C- and ^{1}H-n.m.r. spectra of 3 and 4 show similar small additional signals. The presence of these small amounts of the other diastereoisomers is presumably the reason that they were only obtained as oils.

The mass spectra of 1 to 4 were also consistent with the assigned structures. As is frequently found with acetylated sugars the ions of highest mass of 1, 2 and 3 were those of M-59 (AcO^{-}).[10]

On the basis of this evidence it is concluded that the acid-catalysed acetolysis of xylan is unlike that of cellulose in that it yields this novel series peracetylated oligosaccharides with all the residues in the acyclic rather than the pyranose form.

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