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^{1}H- AND ^{13}C-NUCLEAR MAGNETIC RESONANCE STUDY OF REDUCING DISACCHARIDES OF D-XYLOPYRANOSE

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ABSTRACT

^{1}H- and ^{13}C-n.m.r. data for the six hexa-*O*-acetyl, reducing disaccharides composed of D-xylopyranose units are reported. The chemical shifts were compared with those of some of the penta-*O*-acetyl or penta-*O*-acetyl-mono-*O*-chloroacetyl derivatives. The effects observed on the chemical shifts due to the absence of one *O*-acetyl group from the hexa-*O*-acetyl D-xylobioses are discussed, as well as the effects of the substitution of one *O*-acetyl by one *O*-chloroacetyl group on the protons of carbon atoms in a close vicinity to the substituted sites.

INTRODUCTION

Ten D-xylopyranose, reducing disaccharides have been synthesized[1], according to the Helferich and Zirner method[2], by condensation of 2,3,4-tri-*O*-acetyl-[3], 2,4-di-*O*-acetyl-3-*O*-chloroacetyl-[1], and 2,3-di-*O*-acetyl-4-*O*-chloroacetyl-α-D-xylopyranosyl bromide[4] with tri-*O*-acetyl-β-D-xylopyranose derivatives[5], in the same manner as previously reported[6] for the preparation of the per-*O*-acetyl derivatives of 4-*O*-α- and -β-D-xylopyranosyl-β-D-xylopyranose. Mixtures of the two possible glycoside anomers were separated by silica gel column chromatography; compounds **7** and **12** have been prepared[1] from **6** and **11**, respectively. This report describes the ^{1}H-n.m.r. data of **1**–**7**, **9**, **11**, and **12** for spectra recorded at 250 MHz, and the ^{13}C-n.m.r. data of **1**–**12** for spectra recorded at 62.86 MHz.

RESULTS AND DISCUSSION

^{1}H-N.m.r. — The ^{1}H-n.m.r. spectra of **1**–**7**, **9**, **11**, and **12** (Tables I and II) could be interpreted, in general, by a first-order analysis. The signals for H-4, -5a, and -5b on one hand, and for H-4′, -5′a, and -5′b on the other hand formed ABX spin systems. In order to refine the results of the analysis, experimental spectra were simulated. Successive homo-indor or double irradiation experiments, starting from H-1 or -1′ allowed an unequivocal assignment for all of the remaining ring-protons.

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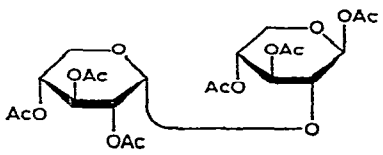

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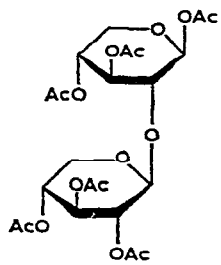

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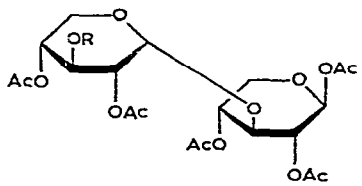

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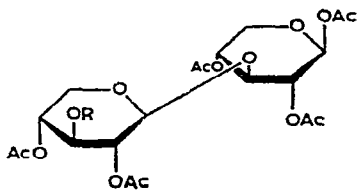
4 R = $ClCH_2CO$



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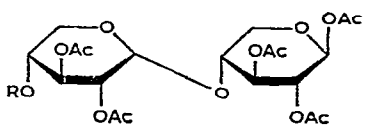

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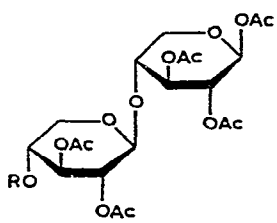

10 R = Ac
11 R = $ClCH_2CO$
12 R = H

The spectra of the per-*O*-acetylated compounds were compared with those of derivatives bearing, in the nonreducing unit, a chloroacetyl or a free hydroxyl group at the same position as that of the glycoside linkage in the reducing unit.

In ^{13}C-n.m.r. spectroscopy, substitution of an acetyl by a chloroacetyl group results in a downfield shift of the signal of the corresponding, substituted ring carbon-atom and in a slight upfield shift of the signals of the two neighboring carbon atoms (see section on ^{13}C-n.m.r. results). In ^{1}H-n.m.r. spectroscopy, substitution by a chloroacetyl group did not bring any important and characteristic modification of the ^{1}H chemical-shifts, and only slight downfield shifts ($\Delta\delta$ <0.8) were displayed by the signals of the protons in close proximity to the substituent group. However, the removal of one acetyl group in **5** and **10** to give **7** and **12**, respectively, resulted in a great upfield shift of the signal for the free hydroxyl geminal proton (α effect: δ −1.11 and −1.37) without significant changes in the other region of the spectrum (β effect: δ −0.10 to −0.20).

TABLE I

^{1}H-CHEMICAL SHIFTS[a] (δ) OF D-XYLOBIOSES **1–7**, **9**, **11**, AND **12**[b]

Compound		*H-1* (*d*)[c]	*H-2* (*dd*)	*H-3* (*t*)	*H-4* (*m*)	*H-5a*[d] (*dd*)	*H-5b*[d] (*dd*)	*H-1'* (*d*)	*H-2'* (*dd*)	*H-3'* (*t*)	*H-4'* (*m*)	*H-5'a*[d] (*dd*)	*H-5'b*[d] (*t or dd*)	CH_3 (*s*)	CH_2Cl (*s*)
1	[α-D-(1→2)]	5.52	3.67	5.13	4.81	3.93	3.38	5.20	4.58	5.21	4.83	3.64	3.48(t)	1.87–2.03	
2	[β-D-(1→2)]	5.73	3.76	5.20	4.92	4.08	3.52	4.69	4.85	5.10	4.91	4.14	3.42(dd)	2.00–2.10	
3	[α-D-(1→3)]	5.79	5.02	3.97	4.87	4.18	3.53	5.30	4.78	5.40	4.98	3.81	3.69(t)	2.00–2.16	
4[e]		5.79	5.01	3.96	4.87	4.18	3.53	5.29	4.82	5.46	5.01	3.82	3.70(t)	2.00–2.16	3.97
5	[β-D-(1→3)]	5.70	4.96	3.89	4.97	4.13	3.53	4.65	4.86	5.10	4.92	4.13	3.41(dd)	2.04–2.17	
6[e]		5.72	4.96	3.90	4.98	4.13	3.53	4.69	4.90	5.16	4.96	4.15	3.43(dd)	2.04–2.16	4.02
7[e]		5.72	4.96	3.89	4.96	4.14	3.53	4.65	4.74	3.73	4.81	4.11	3.39(dd)	2.05–2.11	
9	[α-D-(1→4)]	5.68	4.93	5.21	3.90	4.07	3.62	5.22	4.72	5.42	5.01	3.85	3.63(t)	2.04–2.08	4.01
11[e]	[β-D-(1→4)]	5.66	4.98	5.17	3.90	4.04	3.49	4.62	4.82	5.11	4.97	4.14	3.48(dd)	2.07–2.11	4.08
12[e]		5.66	4.98	5.17	3.88	4.03	3.48	4.56	4.80	4.90	3.79	4.02	3.39(dd)	2.04–2.12	

[a]From the signal of an internal standard of Me_4Si for solutions in chloroform-*d*. [b]^{1}H-n.m.r. data for **8** and **10** are given in ref. 6. [c]Multiplicity in parentheses. [d]The signals for H-5b and H-5'b are comparatively and respectively at a higher field than those for H-5a and H-5'a. [e]^{1}H-n.m.r. spectra are given in ref. 8.

TABLE II

^{1}H-N.M.R. COUPLING-CONSTANTS (Hz) OF D-XYLOBIOSES **1–7**, **9**, **11**, AND **12**

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'a}$	$J_{4',5'b}$	$J_{5'a,5'b}$
1	7.25	9.00	9.00	5.37	9.30	12.00	3.75	10.00	9.75	5.47	11.50	11.06
2	6.75	8.25	8.25	5.00	8.50	11.75	6.00	7.75	7.75	4.50	7.50	12.00
3	5.50	6.50	6.50	4.00	6.50	12.50	3.75	10.00	10.00	6.00	11.00	11.00
4	5.50	6.50	6.50	4.00	6.50	12.50	3.75	10.00	10.00	6.00	11.00	11.00
5	6.00	7.25	7.25	4.50	7.00	12.00	6.25	7.75	7.75	4.50	7.75	12.00
6	6.00	7.25	7.25	4.50	7.00	12.00	6.25	7.75	7.75	4.50	7.75	12.00
7	5.50	7.00	6.65	4.00	6.50	12.50	6.00	7.55	7.30	4.60	7.20	12.00
9	7.00	8.25	8.25	5.00	9.00	12.00	3.75	10.00	10.00	6.00	11.00	11.00
11	7.00	8.50	8.50	5.00	9.50	12.00	6.00	7.50	7.50	4.50	3.00	12.00
12	7.25	8.50	8.60	4.85	8.85	11.80	6.00	8.00	7.85	4.70	8.25	11.80

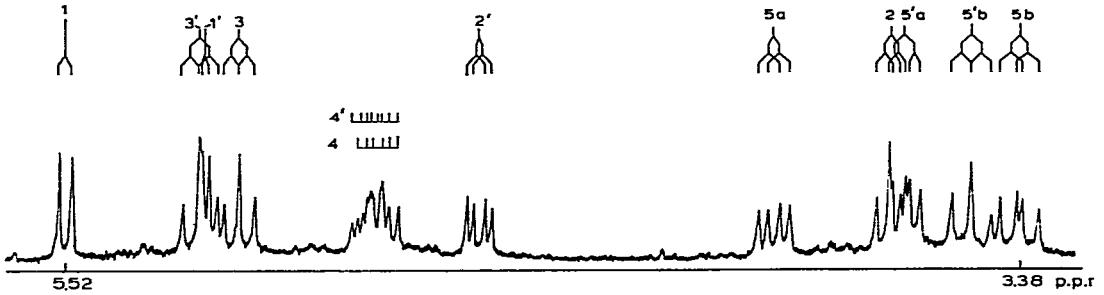

Fig. 1. ^{1}H-N.m.r. spectrum of 1,3,4-tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-β-D-xylopyranose (1).

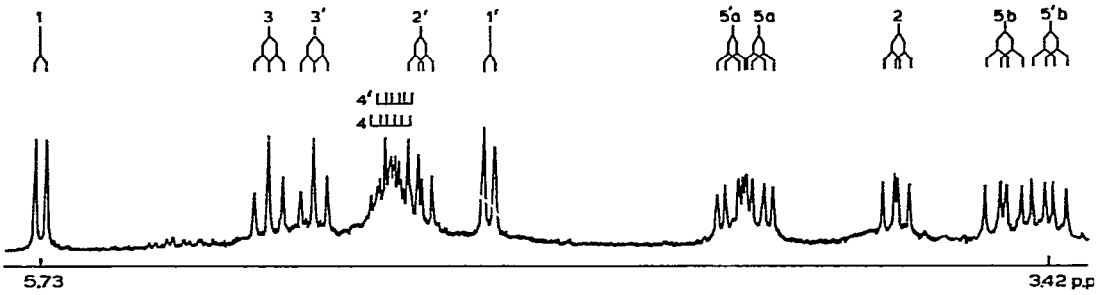

Fig. 2. ^{1}H-N.m.r. spectrum of 1,3,4-tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose (2).

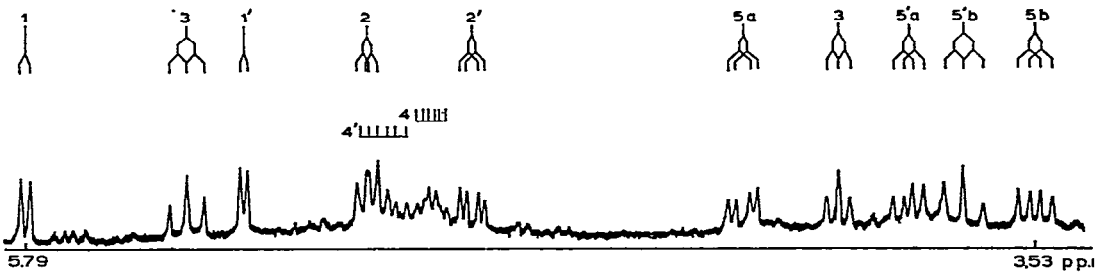

Fig. 3. ^{1}H-N.m.r. spectrum of 1,2,4-tri-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-β-D-xylopyranose (3).

Comparison of the spectra of the six hexa-*O*-acetyl disaccharides showed a good similarity between the chemical shifts of the protons belonging to nonreducing residues for disaccharides having a β-D linkage (slightly perturbed, neighbouring glycoside linkage), whereas for compounds having an α-D linkage differences of δ 0.15–0.20 were observed. It is known that, for α-D-linked disaccharides, the rotational angle ϕ around the C-1′–O bond of the glycoside linkage may be less restricted than that of the β-D-linked disaccharides, which allows a wider environment. The differences

Fig. 4. ^{1}H-N.m.r. spectrum of 1,2,4-tri-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-xylopyranose (5).

reported herein for the proton chemical shifts of the nonreducing unit of α-D-xylobioses may suggest an "exo-anomeric effect"[7].

For each glycoside linkage (C-1′→O-x), the position of the H-x signal relative to those of H-5 and -5′ is characteristic of the glycoside linkage; for the β-D configuration, the H-x signal is located between those of H-5′a and -5a, and H-5b and -5′b; for the α-D configuration, it is located between that of H-5a and those of the group H-5′a, -5b, and -5′b. The proton H-5′b exhibited a signal similar to a triplet ($J_{4',5'b} \simeq J_{5'a,5'b}$) for the α-D, and a doublet of doublets for the β-D configuration. The chemical shifts of H-1′ or H-x, or of both, are not very characteristic of the nature of the (C-1′→O-x) linkage, when compared to those observed in ^{13}C-n.m.r. spectroscopy.

^{13}C-N.m.r. — The signals of the carbon atoms were assigned by a selective, heteronuclear-decoupling technique on the basis of ^{1}H-n.m.r. data (Table III). By

TABLE III

^{13}C-CHEMICAL SHIFTS (δ)[a] OF REDUCING XYLOBIOSES **1–12**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-1′*	*C-2′*	*C-3′*	*C-4′*	*C-5′*
1	93.84	74.38	72.34	68.98	63.06	95.40	71.07	69.13	68.98	58.74
2	92.80	76.61	72.77	68.65	62.97	100.86	70.13	70.68	68.77	61.73
3	91.81	69.45	73.70	69.01	61.61	96.00	71.05	69.21	69.01	59.03
4	91.98	69.72	74.08	69.23	61.73	96.15	70.91	71.41	68.84	59.08
5	92.07	70.13	76.90	68.62	62.36	101.03	70.25	70.81	68.62	61.83
6	92.05	70.03	77.22	68.60	62.36	101.01	70.18	72.73	68.36	61.78
7	92.22	70.40	76.71	68.87	62.41	101.18	72.70	71.22	71.51	61.78
8[b]	92.00	70.15	73.21	72.97	64.30	96.51	70.86	69.08	69.01	58.82
9	91.95	70.03	73.11	73.02	64.21	96.44	70.69	68.82	70.57	57.48
10[b]	92.41	70.13	72.19	74.33	63.50	99.74	70.66	70.78	68.57	61.83
11	92.22	70.01[c]	72.02	74.25	63.33	99.43	70.10[c]	69.91	69.91	61.15
12	92.34	70.01	72.17	74.55[c]	63.45	100.06	70.61	74.47[c]	67.97	64.76

[a]From the signal of an internal standard of Me_4Si for solutions in chloroform-*d*; Spectra are given in ref. 8. [b]See ref. 6. [c]Chemical-shift values of C-2 and -2′ for **11**, and C-4 and -3′ for **12** may be transposed.

TABLE IV

CHEMICAL SHIFTS (δ) INDUCED BY SUBSTITUTION WITH CHLOROACETYL[a] OR ACETYL[b] GROUPS

Compound	*Substituent*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*
4 (α-D)	3'-$OCOCH_2Cl$	+0.17	+0.27	+0.38	+0.22	+0.12	+0.15	−0.14	+2.20	−0.17	+0.05
6 (β-D)	3'-	−0.02	−0.10	+0.32	−0.02		−0.02	−0.07	+1.92	−0.26	−0.05
9 (α-D)	4'-	−0.05	−0.12	−0.10	+0.05	−0.09	−0.07	−0.17	−0.26	+1.56	−0.34
11 (β-D)	4'-	−0.19	−0.12	−0.17	−0.08	−0.17	−0.31	−0.56	−0.87	+1.34	−0.68
5 (β-D)	3'-OAc	−0.15	−0.27	+0.19	−0.25	−0.05	−0.15	−2.45	−0.41	−2.89	+0.05
10 (β-D)	4'-	+0.07	+0.12	+0.02	−0.22	+0.05	−0.32	+0.05	−3.69	+0.60	−2.93

[a]Difference between the shift position of a particular carbon atom in any *O*-chloroacetyl-D-xylobiose derivative and the resonance of the equivalent carbon atom in the parent hexa-*O*-acetyl-D-xylobiose. [b]Difference between the shift position of a particular carbon atom in hexa-*O*-acetyl-D-xylobioses **5** and **10** and the resonance of the equivalent carbon atom in the respective parent penta-*O*-acetyl-D-xylobioses **7** and **12**.

use of 62.86-MHz spectroscopy, it was possible to assign almost all the peaks, some tentative interpretations being confirmed on the basis of ester-group effects.

It is well known that substitution of an acetyl group by a more electronegative group, such as the trichloroacetyl group[9], produces a general deshielding effect on the corresponding ring carbon-atom, and a shielding effect on the two neighboring ring carbon-atoms, as was observed for an octa-*O*-acetylgentiobiose derivative[10]. Esterification by a chloroacetyl group showed, in smaller magnitudes, an α effect in the range of δ +1.3-2.2 and a slight β effect of less than δ −0.7 (Table IV). The influence of the substituent located in the nonreducing residue takes place through bonding electrons rather than space, as no modification of the chemical shifts for the carbon atoms of the reducing part of the disaccharide was observed.

On the other hand, comparison (Table IV) of the chemical shifts of carbon atoms of hexa-*O*-acetyl disaccharides with those of homologous penta-*O*-acetyl derivatives (free hydroxyl group in the nonreducing unit of **7** and **10**) corroborates the effects that have been observed for *O*-acetyl groups in the D-xylopyranose series[11] and for L-rhamnose acetates[12].

The availability of all these reducing disaccharides allowed a comparison between the chemical shifts of the signals of C-1′ atoms, the glycoside configuration, and the nature of the linkage C-1′–O–C-x (Table V). Each C-1 and -1′ showed a specific shift relative to the glycoside linkage, with a set of values for the α-D configuration between δ 95.40 and 96.51 and for the β-D configuration between δ 99.74 and 101.03. However, it should be made clear that signals for C-1′ atoms involved in the β-D-(1′→2) and β-D-(1′→3) linkages (**2** and **5**) are separated by not more than δ 0.17. Nevertheless, taking into account the general pattern of the C-1′ signals, these signals

TABLE V

^{13}C-CHEMICAL SHIFTS OF C-1′ FOR A C-1′–O–C-x LINKAGE[a]

Compound	*Linkage*	*C-1′α*	*C-1′β*	*C-x*
1	(1′→2)	95.40		74.38
2			100.86	76.61
3	(1′→3)	96.00		73.70
4		96.15		74.08
5			101.03	76.90
6			101.01	77.22
7			101.18	76.71
8	(1′→4)	96.51		72.97
9		96.44		73.02
10			99.74	74.33
11			99.43	74.25
12			100.06	74.55

[a]For **1–2**, x = 2; for **3–7**, x = 3; for **8–12**, x = 4.

may be used to identify the nature of the glycoside linkages in oligo- or poly-D-xylose structures as per-*O*-acetyl derivatives.

As could be expected, substitution at O-2, -3, and -4 of the reducing unit by a D-xylopyranosyl residue resulted in a great downfield shift of the corresponding signal (see Table V). These signals, which are generally more difficult to observe than those of the C-1 atoms in analysis of mixtures of oligosaccharides or polysaccharides of complex structures, may ,however, bring complementary information and confirmation of the assignments.

EXPERIMENTAL

General methods. — The ^{1}H- and ^{13}C-n.m.r. spectra were recorded with a Kameca apparatus at the Centre Grenoblois de Résonance Magnétique (France). The disaccharides were examined in solution in chloroform-*d* at 20°. Chemical shifts were measured relative to the signal of tetramethylsilane, used as internal reference. For ^{1}H-n.m.r. spectroscopy, attribution of the signals was made by selective irradiation or Indor experiments; the chemical shifts and coupling constants were measured on a 600-Hz scale-width for spectra recorded at 250 MHz with tubes of 5-mm o.d. Proton-decoupled, ^{13}C-n.m.r. spectra were obtained at 62.86 MHz with tubes of 8-mm o.d. by Fourier-transform experiments (16 k memory; pulse width, 13 μs, $\simeq$90°; acquisition time, 0.6; spectral windows, $\simeq$200 p.p.m.; and enlargement, $\simeq$50 p.p.m.). Attribution of ^{13}C signals was made by selective, heteronuclear-decoupling experiments.

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