

## $^1\text{H}$ - AND $^{13}\text{C}$ -N.M.R. SPECTRA OF THE METHYL MONO-, DI-, AND TRI-*O*-ACETYL- $\alpha$ - AND - $\beta$ -D-XYLOPYRANOSIDES\*

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### ABSTRACT

The  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. data for the mono-*O*-acetyl derivatives of methyl  $\alpha$ - and  $\beta$ -D-xylopyranoside are compared with those for the parent compounds, to determine the effect of the acetyl groups on the chemical shifts of the methine protons and the skeletal carbons, and on the one-bond  $^1\text{H}$ - $^{13}\text{C}$ , coupling constants. These substituent effects were used to confirm the assignments in the spectra of the di- and tri-*O*-acetyl derivatives of methyl  $\alpha$ - and  $\beta$ -D-xylopyranoside.

### INTRODUCTION

Several studies on the effect of acylation on the chemical shifts of the skeletal carbons in pyranose rings have been reported in recent years. The investigations covered the tri- and tetra-acetates of  $\alpha$ - and  $\beta$ -D-xylopyranose<sup>1</sup>; eleven partially, and the two (tetra) fully acetylated L-rhamnoses<sup>2</sup>; and a variety of D-glucopyranose derivatives, including seven of the tetraacetates and the two pentaacetates<sup>3</sup>, seven bis- and tris-(3-nitropropionates)<sup>4</sup>, and all of the monomyristates<sup>5</sup> and their methyl pyranosides<sup>6</sup>. We present herein the  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. data for all of the mono-, di-, and tri-*O*-acetyl derivatives of methyl  $\alpha$ - and  $\beta$ -D-xylopyranoside, evaluate the substituent effects, and compare our results with the previously published data.

### RESULTS AND DISCUSSION

The  $^1\text{H}$ -n.m.r. data for the parent xylosides and their derivatives are given in Table I. A number of assignments could be made initially on the basis of a first-order interpretation of the multiplicities of some signals, particularly in the multisubstituted derivatives. Here, the large downfield shifts induced by the acetyl substituents exposed either the whole or a recognizable part of the characteristic multiplets arising from the methine protons. By comparing the spectra from the various compounds and

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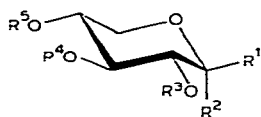
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TABLE I

<sup>1</sup>H-N.M.R. DATA ( $\delta$ ) FOR THE METHYL  $\alpha$ - AND  $\beta$ -D-XYLOPYRANOSIDES (1 AND 9) AND THEIR O-ACETYL DERIVATIVES<sup>a</sup>

H-	O-Acetyl	None (1)	None (9)	2- (2)	2- (10)	3- (3)	3- (11)	4- (4)	4- (12)	2,3- (5)	2,3- (13)	2,4- (6)	2,4- (14)	3,4- (7)	3,4- (15)	2,3,4- (8)	2,3,4- (16)
1	4.55	4.01	4.68 (+0.13)	4.24 (+0.23)	4.59 (+0.04)	4.12 (+0.11)	4.59 (+0.04)	4.09 (+0.08)	4.77 (4.72)	4.43 (4.35)	4.75 (4.72)	4.35 (4.32)	4.66 (4.63)	4.25 (4.20)	4.86 (4.76)	4.59 (4.43)	
2	3.20	2.94	4.45 (+1.25)	4.48 (+1.54)	3.43 (+0.23)	3.09 (+0.15)	3.32 (+0.12)	3.03 (+0.09)	4.65 (4.68)	4.59 (4.63)	4.55 (4.57)	4.57 (4.57)	3.55 (3.55)	3.26 (3.18)	4.80 (4.80)	4.76 (4.72)	
3	3.38	3.11	3.55 (+0.17)	3.32 (+0.21)	4.91 (+1.53)	4.70 (+1.59)	3.60 (+0.22)	3.37 (+0.26)	5.09 (5.08)	4.86 (4.91)	3.80 (3.77)	3.62 (3.58)	5.09 (5.13)	4.94 (4.96)	5.29 (5.30)	5.18 (5.17)	
4	3.34	3.28	3.40 (+0.06)	3.38 (+0.10)	3.49 (+0.15)	3.46 (+0.18)	4.54 (+1.20)	4.52 (+1.24)	3.64 (3.55)	3.59 (3.56)	4.63 (4.60)	4.59 (4.62)	4.75 (4.69)	4.71 (4.70)	4.89 (4.75)	4.85 (4.80)	
5 <sub>ax</sub>	3.25	3.04	3.27 (+0.02)	3.11 (+0.07)	3.33 (+0.08)	3.14 (+0.10)	3.31 (+0.06)	3.15 (+0.11)	3.37 (3.35)	3.25 (3.21)	3.35 (3.33)	3.26 (3.22)	3.42 (3.39)	3.36 (3.25)	3.45 (3.41)	3.49 (3.32)	
5 <sub>eq</sub>	3.46	3.71	3.50 (+0.04)	3.77 (+0.06)	3.51 (+0.05)	3.77 (+0.06)	3.56 (+0.10)	3.79 (+0.08)	3.60 (3.55)	3.82 (3.83)	3.63 (3.60)	3.87 (3.85)	3.65 (3.61)	3.90 (3.85)	3.74 (3.65)	3.97 (3.91)	

<sup>a</sup>From the signal of tetramethylsilane for solutions in dimethyl sulfoxide-*d*<sub>6</sub>. Spectra were obtained with a Varian HA-100D spectrometer, and were analyzed with the spin-simulation program (SIMEQ) with a Varian FT-80A system. Values in parentheses for the monacetates are the acetylation-induced shifts obtained by subtracting the proton chemical-shift for the parent D-xyloside from that of the equivalent proton in the acetate. These values were then used to estimate the chemical shifts for the di- and tri-acetate derivatives (in parentheses). The average values of the coupling constants for the  $\alpha$ -D anomers (1-8) were  $J_{1,2}$  3.4,  $J_{2,3}$  9.8,  $J_{3,4}$  9.4,  $J_{4,5}$  6.0,  $J_{4,6}$  10.5, and  $J_{5,6}$  11.4 Hz (standard deviation <0.2 Hz); and for the  $\beta$ -D anomer (9-16)  $J_{1,2}$  7.5,  $J_{2,3}$  9.3,  $J_{3,4}$  9.1,  $J_{4,5}$  5.3,  $J_{4,6}$  10.0, and  $J_{5,6}$  11.4 Hz (standard deviation <0.3 Hz). The hydroxyl protons appeared in the range  $\delta$  4.9-5.6, either as broad singlets or as resolved doublets with splittings of 4.5-6.5 Hz. Chemical shifts for the acetoxy protons were in the range  $\delta$  1.96-2.03.

 $\alpha$  - Series

- 1  $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}, \text{R}^2 = \text{OMe}$
- 2  $\text{R}^1 = \text{R}^4 = \text{R}^5 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^3 = \text{Ac}$
- 3  $\text{R}^1 = \text{R}^3 = \text{R}^5 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^4 = \text{Ac}$
- 4  $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^5 = \text{Ac}$
- 5  $\text{R}^1 = \text{R}^5 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^3 = \text{R}^4 = \text{Ac}$
- 6  $\text{R}^1 = \text{R}^4 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^3 = \text{R}^5 = \text{Ac}$
- 7  $\text{R}^1 = \text{R}^3 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^4 = \text{R}^5 = \text{Ac}$
- 8  $\text{R}^1 = \text{H}, \text{R}^2 = \text{OMe}, \text{R}^3 = \text{R}^4 = \text{P}^5 = \text{Ac}$

 $\beta$  - Series

- 9  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}$
- 10  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{H}, \text{R}^3 = \text{Ac}$
- 11  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^3 = \text{R}^5 = \text{H}, \text{R}^4 = \text{Ac}$
- 12  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}, \text{R}^5 = \text{Ac}$
- 13  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^5 = \text{H}, \text{R}^3 = \text{R}^4 = \text{Ac}$
- 14  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^4 = \text{H}, \text{R}^3 = \text{R}^5 = \text{Ac}$
- 15  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^3 = \text{H}, \text{R}^4 = \text{R}^5 = \text{Ac}$
- 16  $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{H}, \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{Ac}$

observing the changes occurring in the more complex subspectra due to the different substitution patterns, it was possible to estimate the shifts of the remaining protons and, by trial and error, to eventually fit a simulated spectrum in all cases. Since the coupling constants for the compounds in an anomeric series were quite similar, only the average values, and their overall standard deviation are given. First-order coupling constants ( $J_{1,2}$ ,  $J_{2,3}$ , and  $J_{3,4}$ ) reported for the mono- and di-*O*-myristoyl derivatives of methyl  $\alpha$ - and  $\beta$ -D-glucopyranoside by Yoshimoto *et al.*<sup>6</sup> were also nearly constant. The results for the xylopyranoside derivatives support the conclusion of these authors that the conformation of the pyranose ring is altered very little, if at all, by the introduction of an acyl group at any position.

The chemical-shift data for the monoacetate derivatives reported in Table I show that the introduction of an acetoxy group at C-2, -3, or -4 in either anomer causes a large downfield shift of the signals for the methine protons ( $\Delta\delta + 1.20$  to  $+1.59$ ). Vicinal protons were shifted by smaller amounts ( $\Delta\delta + 0.08$  to  $+0.26$ ). Parallel results were observed for the 2- and 3-mono-*O*-myristoyl derivatives of methyl 4,6-*O*-benzylidene- $\alpha$ - and  $\beta$ -D-glucopyranoside<sup>6</sup>; the induced shifts of the methine protons in the  $\alpha$ -D anomer were  $\Delta\delta + 1.25$  for H-2, and  $\Delta\delta + 1.46$  for H-3, and for the  $\beta$ -D-anomer,  $\Delta\delta + 1.53$  for H-2 and  $\Delta\delta + 1.57$  for H-3.

The chemical shifts for the di- and tri-*O*-acetylxylopyranosides were calculated by adding the appropriate induced shifts observed in the mono-*O*-acetyl compounds to the observed shifts of the equivalent protons in the parent xyloside. Agreement between the observed and calculated values were good, demonstrating the additivity of the substituent effects. The average deviation was  $\delta 0.04$  for the  $\alpha$ -, and  $0.05$  for the  $\beta$  series. Maximum deviations ( $\delta 0.14$  for the  $\alpha$ -, and  $0.17$  for the  $\beta$ -D anomer) occurred in the values for the triacetates.

The  $^{13}\text{C}$ -chemical shift data are given in Table II, and the one-bond  $^{13}\text{C}$ - $^1\text{H}$  coupling constants in Table III. No attempt was made to determine long-range  $^{13}\text{C}$ - $^1\text{H}$  couplings because of the complexity of the multiplets in the high-resolution spectra. Assignment of the signals in the spectra of the monoacetates was readily achieved by comparing the shapes and positions of the multiplets recorded under

TABLE II

<sup>13</sup>C CHEMICAL SHIFTS ( $\delta$ ) FOR METHYL  $\alpha$ - AND  $\beta$ -D-XYLOPYRANOSIDES (1 AND 9) AND THEIR O-ACETYL DERIVATIVES<sup>a</sup>

C- O-Acetyl																
None (1)	None (2)	2- (2)	2- (10)	3- (3)	3- (11)	4- (4)	4- (12)	2,3- (5)	2,3- (13)	2,4- (6)	2,4- (14)	3,4- (7)	3,4- (15)	2,3,4- (8)	2,3,4- (16)	
1	100.09	104.57	96.83 (-3.26)	101.76 (-2.81)	99.80 (-0.29)	104.32 (-0.25)	99.96 (-0.13)	104.44 (-0.13)	96.54 (96.54)	101.28 (101.51)	96.69 (96.70)	101.39 (101.63)	99.67 (99.67)	104.11 (104.19)	96.43 (96.41)	100.87 (100.38)
2	71.88	73.12	73.28 (+1.40)	73.55 (+0.43)	69.60 (-2.28)	70.96 (-2.16)	71.81 (-0.07)	73.25 (+0.13)	70.71 (71.00)	71.35 (71.39)	72.89 (73.21)	73.21 (73.68)	69.38 (69.53)	70.85 (71.09)	70.24 (70.93)	70.70 (71.52)
3	73.37	76.44	70.60 (-2.77)	74.15 (-2.29)	75.43 (+2.06)	77.52 (+1.08)	70.06 (-3.31)	73.02 (-3.42)	72.28 (72.66)	75.18 (75.23)	67.34 (67.29)	70.46 (70.73)	72.04 (72.12)	74.15 (74.10)	68.98 <sup>b</sup> (69.35)	71.48 (71.81)
4	69.90	69.50	69.94 (+0.04)	69.62 (+0.12)	67.58 (-2.32)	67.52 (-1.98)	71.75 (+1.85)	71.58 (+2.08)	67.43 (67.62)	67.39 (67.64)	71.41 (71.79)	71.28 (71.70)	69.11 (69.43)	69.31 (69.60)	68.67 <sup>b</sup> (69.47)	68.73 (69.72)
5	61.61	65.54	61.40 (-0.21)	65.66 (+0.12)	61.34 (-0.27)	65.37 (-0.17)	57.88 (-3.73)	61.89 (-3.65)	61.22 (61.13)	65.30 (65.49)	57.89 (57.67)	61.69 (62.01)	57.83 (57.61)	61.77 (61.72)	57.78 (57.40)	61.48 (61.84)
OCH <sub>3</sub>	54.49	55.87	54.50 (+0.01)	55.80 (-0.07)	54.59 (-0.10)	56.01 (+0.14)	54.74 (+0.25)	56.01 (+0.14)	54.56 (54.40)	55.01 (55.94)	54.77 (54.75)	55.92 (55.94)	54.88 (54.64)	56.13 (56.15)	54.88 (54.65)	56.08 (56.08)

<sup>a</sup>From the signal of tetramethylsilane for solutions in dimethyl sulfoxide-*d*<sub>6</sub>. Data accuracy  $\pm 0.3$  Hz. Values in parentheses for the monoacetates are the acetylation-induced shifts obtained by subtracting the carbon chemical-shift for the parent D-xylopyranoside from that of the equivalent carbon atom in the acetate. These values were then used to estimate the chemical shifts for the di- and tri-acetates (in parentheses). Acetoxy resonances; CH<sub>3</sub> in the range  $\delta$  20.30–21.03, CO<sub>2</sub>  $\delta$  169.06–170.16. <sup>b</sup>These assignments may be reversed; peaks overlapped in high resolution spectra.

TABLE III

 $^{13}\text{C}$ - $^1\text{H}$  COUPLING CONSTANTS ( $^1J_{\text{CH}}$ , Hz) FOR METHYL  $\alpha$ - AND  $\beta$ -D-XYLOPYRANOSIDES (1 AND 9) AND THEIR *O*-ACETYL DERIVATIVES<sup>a</sup>

<i>O</i> -Acetyl	<i>C</i> -1	<i>C</i> -2	<i>C</i> -3	<i>C</i> -4	<i>C</i> -5
None (1)	167.3	142.4	144.6	143.1	146
None (9)	159.4	142.5	141.1	143.2	140.0
2- (2)	168.9	146.3	144	143	146
2- (10)	160.0	151.3	141	143.8	140.6
3- (3)	168.1	141.9	151	144.4	146
3- (11)	159.0	143.8	148	145.6	141
4- (4)	168.1	145.0	143.7	148.2	149
4- (12)	158.8	142.5	142	148.2	141.9
2,3- (5)	171.3	150.7	153.9	146.6	148
2,3- (13)	161.9	152.5	150.7	146.2	141.9
2,4- (6)	170.0	143.2	140	148.6	150.1
2,4- (14)	162.8	150.0	142	147.6	146
3,4- (7)	170.6	143.7	153.7	153.8	143.9
3,4- (15)	161.3	144.4	149.7	150.6	150.6
2,3,4- (8)	173.2	152.2	154	153.0	146.0
1,3,4- (16)	165.3	153.1	153.2	153.3	143.1
					150.6
					148
					144.1
					151.0

<sup>a</sup>For solutions in dimethyl sulfoxide-*d*<sub>6</sub>. First-order spacings measured between centroids of signals. Data accuracy  $\pm 0.3$  Hz. Three significant figures only are given where signals were partially obscured by overlap. These values are probably within  $\pm 1$  Hz.  $^nJ_{\text{CH}}$  for the acetoxy carbons were in the ranges:  $\text{CH}_3$ ,  $^1J$  129.1–129.9,  $\text{CO}_2$ ,  $^2J$  6.6–7.0, and  $^3J$  3.1–4.1 Hz.

high-resolution conditions with those from the parent xylosides. As expected<sup>6</sup>, the introduction of an acetyl group resulted in a down-field shift of the resonance from the substituted carbon atom, with a concomitant increase of 3.9 to 8.8 Hz in the  $^{13}\text{C}$ - $^1\text{H}$  splitting, and a large up-field shift of the signals from the adjacent carbon atoms. The substituent-induced shifts derived from the monoacetate-shift data were then used to estimate the chemical shifts for the di- and tri-acetate derivatives. Initial assignments of the  $^{13}\text{C}$ -spectral resonances, based on the calculated chemical-shifts, were readily confirmed by the size of the one-bond  $^{13}\text{C}$ - $^1\text{H}$  splittings and the shape of the multiplets observed in the high-resolution spectra. Once again, the additivity of the substituent effects was demonstrated by the agreement of the observed and calculated shifts. The average deviation for the skeletal carbons was  $\delta$  0.25 in the  $\alpha$ , and 0.31 in the  $\beta$  series; and the maximum deviations occurred in the values for the triacetates ( $\delta$  + 0.80 for the  $\alpha$ -, and + 0.99 for the  $\beta$ -D anomer).

The induced shifts for the carbon atoms adjacent to an acetoxyl group in the xylosides (downfield by  $\delta$  0.43 to 2.08) differ from those reported by Utile and Vottero<sup>1</sup> for the corresponding carbon atoms of the *O*-acetyl-D-xylopyranoses, which were either down-field by a much smaller amount ( $\delta$  + 0.12 to +0.41) or significantly up-field ( $\delta$  - 0.36 to - 0.97). This is not surprising in view of their different approach to determining the effects of acetylation, that is by subtracting the observed shifts of the various triacetate derivatives from those of the corresponding tetraacetate (a procedure used earlier for the tetra- and penta-*O*-acetyl-D-glucopyranoses, giving similar results<sup>3</sup>). The presence of three or more acetoxyl groups on the pyranose ring should lead to considerable steric interaction, altering the orientation of the groups, and thereby affecting the shielding of the adjacent carbon atoms, as compared to the interaction observed for the mono-*O*-acetyl-D-xylopyranosides. (Similar conclusions were drawn from the n.m.r. study of a number of partially and fully acetylated L-rhamnopyranoses<sup>2</sup>). As for the D-xylosides, the carbon atoms in 1,3-relationship to an acetyl substituent in the xylopyranoses exhibited large up-field shifts that were generally greater for the  $\alpha$ - than for the  $\beta$ -D anomer.

The overall substituent-induced shifts observed for the mono-*O*-acetyl-D-xylosides are similar in direction and amount to those reported by Yoshimoto *et al.*<sup>5,6</sup> for C-1 to -5 of the 2-, 3-, and 4-mono-*O*-myristoyl- $\alpha$ - and - $\beta$ -D-glucopyranoses, and their methyl pyranosides (all in pyridine solution). In contrast to the results for the D-xylo- and D-gluco-pyranose compounds<sup>1,3</sup> described herein, Yoshimoto *et al.*<sup>5,6</sup> found that the induced shifts observed for the 2-, 3-, 4-, and 6-mono-*O*-acyl-D-glucopyranoses were similar in trends and values to those of the corresponding methyl D-glucopyranosides. These substituent effects were shown to be additive for a large number of assorted di- and tri-*O*-acyl-D-glucoses in various solvents (including the *O*-3-nitropropionyl derivatives in acetone studied by Pfeffer *et al.*<sup>4</sup>). However, calculated <sup>13</sup>C-chemical shifts for the per-*O*-acetyl- $\alpha$ -D-glucopyranose in pyridine, deviated from the observed values by  $\delta$  1.2 to 2.6, owing once again to the steric interaction of the accumulated acyl groups.

Calculation (in this laboratory, using the myristoyl shift data and the <sup>13</sup>C-shift values for the parent D-glucose derivative in pyridine) of shift values for the tetraacetate derivatives studied by Komura *et al.*<sup>3</sup> (for solutions in chloroform) showed similar deviations. If, however, the shifts for the tetra- and penta-acetates were calculated by using the shifts for the parent pyranose compound in deuterium oxide or acetone solution, the deviations were reduced to a range of  $\delta$  0.1 to 1.5.

It is apparent, from the results presented and reviewed here, that the acylation-induced shifts derived from the study of monoacylated monosaccharides facilitate the structural elucidation of monomeric pyranoses or pyranosides having multiple acyl substituents, provided allowance is made for a decreasing substituent additivity in the more acylated sugars. Not only are they useful for the initial tentative assignment of the carbon or proton resonances, but, when used in conjunction with C-H

TABLE IV

MELTING POINTS (m.p.) AND SPECIFIC ROTATIONS ( $[\alpha]_D$ ) OF THE METHYL  $\alpha$ - AND  $\beta$ -D-XYLOPYRANOSIDES (1 AND 9) AND THEIR *O*-ACETYL DERIVATIVES<sup>a</sup>

Compound	m.p. (degrees)	$[\alpha]_D^{21b}$ (degrees)
1	91	+152.8
2		+156.4
3	125	+164.2
4	75	+132.4
5	106	+121.4
6		+128.7
7	96	+161.8
8	85	+120.4
9	156	-65.3
10	98	-59.3
11	115	-39.3
12	116	-90.5
13	85	-77.3
14	68	-70.9
15	115	-28.2
16	115	-65.1

<sup>a</sup>Recrystallizing media were: 1, 2-propanol-water; 16, water; 11, benzene; 8 and 9, ethanol; other compounds from ethyl acetate-pentane, except for 2 and 6, which did not crystallize. <sup>b</sup>Concentrations, c, 2.0, chloroform; except for 1 and 9, which were 10.0, water.

or H-H coupling data (constants and multiplicities), they can lead to rapid unequivocal assignments, as in the spectra of the methyl di- and tri-*O*-acetyl-D-xylopyranosides reported herein.

#### EXPERIMENTAL

*Preparation of xylopyranosides.* — The methyl mono- and di-*O*-acetyl-D-xylopyranosides (2-7 and 10-15, with the exception of 14) were initially obtained<sup>7</sup> by preparative chromatography on silicic acid columns of the acetate mixtures produced in transesterification reactions between the methyl  $\alpha$ - and  $\beta$ -D-xylopyranosides (1 and 9) and their tri-*O*-acetyl derivatives (8 and 16).

Compound 14 was obtained by synthesis<sup>7</sup>. The acetates were recrystallized (with two exceptions) to give constant melting points (Thomas-Hoover capillary apparatus) which are listed with the optical rotations (Rudolph Model 80 polarimeter) in Table IV. Synthetic procedures have since been developed for all of the mono- and di-acetates, and will be reported later.

*N.m.r. spectra.* —  $^{13}\text{C}$ -N.m.r. spectra (25.16 MHz) were recorded with a Varian XL-100/15 Fourier-transform spectrometer at 29° for solutions (0.4 mL) in a 5-mm tube (sample concentration, 100 g/L of dimethyl sulfoxide-*d*<sub>6</sub>). The experimental conditions were: spectral width, 5120 Hz, acquisition time, 0.8 or 1.6 s, flip

angle  $\sim 41^\circ$ , time constant  $-0.8$  s, internal  $^2\text{H}$ -lock to solvent. The conditions of  $^1\text{H}$ -irradiation at 100 MHz were:  $\gamma\text{H}_2/2\pi \sim 3800$  Hz, continuous broad-band irradiation by 0 to  $180^\circ$  phase modulation at 150 Hz (proton-decoupled spectrum); or irradiation only applied for 1.6 s between data-acquisition periods (high-resolution spectrum).

$^1\text{H}$ -N.m.r. spectra (100 MHz) were recorded with a Varian HA-100D spectrometer at  $28^\circ$  using the solutions from the  $^{13}\text{C}$ -n.m.r. experiments. Spectra were recorded after a 1:3 dilution (33 g/L), and after addition of deuterium oxide to remove coupling with the hydroxyl protons. The latter spectra were simulated with the program SIMEQ on the Varian FT-80 NMR system.

#### REFERENCES

- 1 J.-P. UTILLE AND P. J. A. VOTTERO, *Carbohydr. Res.*, **85** (1980) 289–297.
- 2 V. POZSGAY AND A. NESZMÉLYI, *Carbohydr. Res.*, **80** (1980) 196–202.
- 3 H. KOMURA, A. MATSUNO, Y. ISHIDO, K. KUSHIDA, AND K. AOKI, *Carbohydr. Res.*, **65** (1978) 271–277.
- 4 P. E. PFEFFER, K. M. VALENTINE, B. G. MOYER, AND D. L. GUSTINE, *Carbohydr. Res.*, **73** (1979) 1–8.
- 5 K. YOSHIMOTO, Y. ITATANI, AND Y. TSUDA, *Chem. Pharm. Bull.*, **28** (1980) 2065–2076.
- 6 K. YOSHIMOTO, Y. ITATANI, K. SHIBATA, AND Y. TSUDA, *Chem. Pharm. Bull.*, **28** (1980) 208–219.
- 7 T. McEWAN, Ph.D. Thesis, Dalhousie University, Halifax, N.S., 1966.