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Synthesis, NMR, and conformational studies of methyl α-D-mannopyranoside 2-, 3-, 4-, and 6-monophosphates

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Abstract

The syntheses of methyl α-D-mannopyranoside 2-, 3-, 4-, and 6-phosphate disodium salts are described. ^{1}H, ^{13}C, and ^{31}P NMR spectra of the four monophosphates were recorded, fully assigned, and compared to nonphosphorylated methyl α-D-mannopyranoside in order to obtain chemical shift changes due to phosphorylation. The magnitude of these changes are up to 0.45 ppm for ^{1}H and 3.0 ppm for ^{13}C NMR spectra. The preferred orientation of the phosphate group in the four compounds was also calculated.

Keywords: Sugar phosphates; Synthesis; Conformation; NMR

1. Introduction

Phosphates are substituents in many glycoconjugates in Nature. Analysis of natural oligosaccharides is often hampered by the presence of phosphates because of chromatographic difficulties as well as heterogeneity and the possibility of artefacts. Most analyses have therefore been made on dephosphorylated materials, thereby avoiding the difficulties but also at the same time losing information on the phosphorylation. Since the phosphates are of importance for the biological activity of the glycoconjugates, it is of interest to be able to perform a complete analysis including substitution position and type of all phosphate groups. NMR spectroscopy is an important tool used in structural analysis. To use this technique efficiently on phosphorylated substances, the spectral changes due to phosphorylation need to be investigated. Although several NMR spectra of phosphorylated

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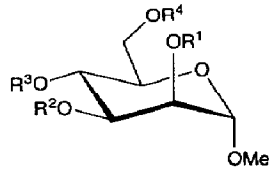
oligosaccharides have been reported and interpreted, only limited investigations on shift changes due to phosphorylation have been made [1]. We have been working on the compilation of NMR data for a computer program (CASPER) [2] that can be used for structural analyses of carbohydrates, and we are also interested in the analyses and syntheses of phosphorylated structures, e.g., from the *Salmonella* Ra core [3]. To be able to extend the CASPER program to phosphorylated structures and to aid in the analyses and syntheses of phosphorylated compounds, all possible monophosphates (2-, 3-, 4-, and 6-) of methyl α-D-mannopyranoside were synthesized and their ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded and fully assigned. Since phosphates in the *Salmonella* Ra core are substituents on heptopyranosides having the L-*glycero*-D-*manno* configuration, methyl α-D-mannopyranoside was chosen as a model substance.

2. Results and discussion

The four selectively protected methyl α-D-mannopyranosides **5–8** [4–7], with a free hydroxyl group in the 2, 3, 4, or 6 position ready for phosphorylation, were synthesized by phase-transfer-catalyzed benzylation [8,9] of methyl 4,6-*O*-benzylidene-α-D-mannopyranoside [10] and methyl 2,3-di-*O*-benzyl-α-D-mannopyranoside [11]. Since benzyl and benzylidene functions were used as hydroxyl protecting groups, benzyl groups were also chosen as phosphate protecting groups in order to achieve only one deprotecting step. Phosphorylation was accomplished by treatment with phosphorus triimidazolate followed by the addition of benzyl alcohol and in situ oxidation with *m*-chloroperoxybenzoic acid [12] to give, directly, the dibenzyl phosphates **9–12** in high yields (91, 88, 89, and 74%, respectively). Deprotection by catalytic hydrogenolysis, followed by ion exchange and pH adjustment, then gave the target compounds **1–4** (69, 74, 71, and 89%, respectively).

Compounds **1–4** were fully assigned with respect to ^{1}H, ^{13}C, and ^{31}P NMR resonances, and the data are given in Tables 1 and 2. Spin–spin coupling constants of interest for the subsequent conformational analysis of the phosphate group as well as the hydroxymethyl group of compound **4** are also tabulated.

On substitution of sugar residues by various groups (e.g., *O*-acetyl groups [13]) or glycosylation by a sugar residue, chemical shift changes are observed. The largest in magnitude is usually observed for the α-position, i.e., the site of substitution, and smaller differences at the adjacent β-positions. For compounds **1–3** which are substituted by a phosphate group at a secondary hydroxyl group, the ^{1}H NMR resonances in the α-position are shifted downfield with a chemical shift difference ($\Delta\delta$) of ~ 0.4 ppm whereas the $\Delta\delta$-value of **4** is lower for the two hydroxymethyl protons. A $\Delta\delta$-value with an absolute magnitude ≥ 0.05 ppm has been used previously [14] as a guide for significant ^{1}H NMR chemical shift differences. Compounds **1** and **2** show significant $\Delta\delta$-values at the β-positions. These are positive with a magnitude of up to 0.14 ppm except for H-3 of **1** for which the $\Delta\delta$-value is -0.06 ppm. The signal from H-4 is also shifted downfield (0.07 ppm), which may be attributed to the presence of the axial phosphate group



1 R^1= $PO(ONa)_2$, R^2= R^3= R^4= H
2 R^2= $PO(ONa)_2$, R^1= R^3= R^4= H
3 R^3= $PO(ONa)_2$, R^1= R^2= R^4= H
4 R^4= $PO(ONa)_2$, R^1= R^2= R^3= H
5 R^1=H, R^2= Bn, R^3, R^4= PhCH
6 R^2= H, R^1= Bn, R^3, R^4= PhCH
7 R^3= H, R^1= R^2= R^4= Bn
8 R^4= H, R^1= R^2= R^3= Bn
9 R^1= $PO(OBn)_2$, R^2= Bn, R^3, R^4= PhCH
10 R^2= $PO(OBn)_2$, R^1= Bn, R^3, R^4= PhCH
11 R^3= $PO(OBn)_2$, R^1= R^2= R^4= Bn
12 R^4= $PO(OBn)_2$, R^1= R^2= R^3= Bn

at C-2. Compound **3** shows for one of the β-positions, H-3, a significant $\Delta\delta$-value similar to those for compounds **1** and **2**. Furthermore, the chemical shifts of H-6a and H-6b have changed, although the δ-values are approximate only. As with **1**,

Table 1
^{1}H NMR data of compounds **1–4** obtained at 70°C relative to internal sodium 3-trimethylsilylpropanoate-d_4 (δ_H 0.00). Chemical shift differences [a] are given in parentheses, $^3J_{H,P}$ in square brackets, and $J_{H\text{-}5,H\text{-}6a}$ and $J_{H\text{-}5,H\text{-}6b}$ in braces

Compound	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	OMe
1	4.89 (0.12)	4.33 (0.39) [8.5]	3.71 (−0.06)	3.74 (0.07)	3.58 (−0.03)	3.78 (0.00)	3.88 (−0.02)	3.43 (0.01)
2	4.77 (0.00)	4.08 (0.14)	4.17 (0.40) [8.5]	3.78 (0.11)	3.65 (0.04)	3.75 (−0.03)	3.89 (−0.01)	3.43 (0.01)
3	4.77 (0.00)	3.94 (0.00)	3.89 (0.12)	4.12 (0.45) [8.5]	3.63 (0.02)	~3.85 (0.07)	~3.85 (−0.05)	3.42 (0.00)
4	4.76 (−0.01)	3.92 (−0.02)	3.78 (0.01)	3.87 (0.20)	3.64 (0.03)	4.07 [b] (0.29) [7.0] {3.9}	3.96 [b] (0.06) [5.6] {2.3}	3.42 (0.00)
α-D-Man-OMe	4.77	3.94	3.77	3.67	3.61	3.78	3.90	3.42

[a] Chemical shift differences are calculated by subtracting the chemical shifts of the methyl mannoside from each compound, i.e., a positive difference indicates a downfield shift.
[b] The assignments of H-6a and H-6b of **4** to *pro-R* and *pro-S*, respectively, are tentative.

Table 2
^{13}C and ^{31}P NMR data of compounds **1–4** obtained at 70°C relative to internal dioxane (δ_C 67.40) or external phosphoric acid (δ_P 0.00). Chemical shift differences [a] are given in parentheses and $^nJ_{C,P}$ in square brackets

Compound	C-1	C-2	C-3	C-4	C-5	C-6	OMe	P
1	101.33	73.23	71.78	68.55	73.67	61.88	55.58	4.79
	(−0.42)	(2.38)	(0.22)	(0.76)	(0.22)	(−0.04)	(0.03)	
	[5.5]	[4.6]	[1.8]					
2	101.58	70.56	74.52	67.88	73.50	62.03	55.57	4.76
	(−0.17)	(−0.29)	(2.96)	(0.09)	(0.05)	(0.11)	(0.02)	
		[3.7]	[4.6]	[2.8]				
3	101.53	70.41	71.80	70.24	72.77	61.80	55.64	5.16
	(−0.22)	(−0.44)	(0.24)	(2.45)	(−0.68)	(−0.12)	(0.09)	
			[<1]	[4.6]	[7.3]			
4	101.95	70.89	71.16	67.25	72.99	63.67	55.66	5.05
	(0.20)	(0.04)	(−0.40)	(−0.54)	(−0.46)	(1.75)	(0.11)	
					[6.4]	[4.6]		
α-D-Man-OMe	101.75	70.85	71.56	67.79	73.45	61.92	55.55	

[a] Chemical shift differences are calculated by substracting the chemical shifts of the methyl mannoside from each compound, i.e., a positive difference indicates a downfield shift.

this may again be attributed to the proximity of the phosphate group to the H-6's of the hydroxymethyl group. No significant β-effect is seen for **4**, but the signal from H-4 shows a large downfield chemical shift (0.20 ppm) which is the largest for **1–4**, except for protons on the substituted carbon. Like the changes in **1** and **3**, the large downfield $\Delta\delta$-value of H-4 in **4** ought to be due to the proximity to the phosphate group. In these three cases, there is a 1,3-relationship between the proton with a chemical shift change and an oxygen atom substituted by a phosphate group. The chemical shift changes may then be due to changes in rotamer populations compared to the hydroxyl group, or the proximity of the phosphate group. The ^1H NMR chemical shift differences of the four lactose monophosphates, as their monosodium salts, previously studied [1] are similar in magnitude although changes due to different stereochemistry are observed. The chemical shift differences for ^{13}C NMR resonances (Table 2) show, for the substitution positions of **1–3**, values of 2.38, 2.96, and 2.45, respectively. The α-position of **4** has a slightly lower $\Delta\delta$-value of 1.75. All other $\Delta\delta$-values are small with only three $\Delta\delta$-values having a magnitude > 0.5 ppm, where the largest is still no more than 0.76 ppm. The ^1H and ^{13}C NMR chemical shifts of **4** are in complete agreement with the methyl α-D-mannopyranoside 6-phosphate synthesized by Meldal et al. [15]. The chemical shift of the ^{31}P NMR resonance of **1–4** is also given in Table 2. The $\Delta\delta$-values of α-carbons for the four lactose monophosphates are larger, up to 4.5 ppm, than for the compounds in this study.

The preferred orientation of the phosphate group can be analysed using Karplus equations of $^3J_{H,P}$ and $^3J_{C,P}$ relationships. Two- and three-bond coupling

constants of ^{1}H and ^{13}C to ^{31}P for **1–4** are given in Tables 1 and 2 as well as $^{3}J_{H\text{-}5,H\text{-}6a}$ and $^{3}J_{H\text{-}5,H\text{-}6b}$ for compound **4**. For the phosphate group, three possible rotamers are assumed and the HCOP dihedral angle θ is taken as reference (for HCOP eclipsed, $\theta = 0°$), except for **4** where the dihedral angle θ is defined by C-5–C-6–O-6–P. The three states are defined as g^+ ($\theta = 60°$), g^- ($\theta = -60°$), and t ($\theta = 180°$). The fractional populations are then defined by P_{g^+}, P_{g^-}, and P_t, with their sum equal to one. Each observed three-bond coupling constant is dependent on the populations of each state and the coupling constant of the state according to:

$$^{3}J_{POCX} = P_{g^-}J_{(g^-)} + P_{g^+}J_{(g^+)} + P_tJ_{(t)} \quad (1)$$

where X = H or C.The magnitude of the vicinal coupling constants in POCC and POCH fragments can be derived from the set of Karplus equations [16–18]:

$$^{3}J_{POCH} = 15.3\cos^2\theta - 6.1\cos\theta + 1.6 \quad (2)$$

$$^{3}J_{POCC} = 6.9\cos^2\theta - 3.4\cos\theta + 0.7 \quad (3)$$

In **1–3**, there are one $^{3}J_{HOCP}$ and two $^{3}J_{CCOP}$ relationships, whereas for **4** the reverse is true. Using the three different three-bond coupling constants for each compound with Eq. 1 together with Eqs. 2 and 3, and that the sum of the fractional populations is equal to one, it is possible to deduce the probability of the different populations of the three states of the phosphate group. The preferred orientations of the hydroxymethyl group can be determined from the $^{3}J_{H\text{-}5,H\text{-}6R}$ and $^{3}J_{H\text{-}5,H\text{-}6S}$ values according to the Karplus equations [19]:

$$^{3}J_{H\text{-}5,H\text{-}6R} = 13.22\cos^2\theta - 0.99\cos\theta + 2.61 - 0.984\cos^2(7.96 + \theta) - 6.396\cos^2(25.87 - \theta) \quad (4)$$

$$^{3}J_{H\text{-}5,H\text{-}6S} = 13.22\cos^2\theta - 0.99\cos\theta + 2.61 - 0.984\cos^2(7.96 + \theta) - 3.198\cos^2(25.87 - \theta) - 3.198\cos^2(25.87 + \theta) \quad (5)$$

The calculated preferences, using the above equations, for different states of the phosphate group of **1–4** and the hydroxymethyl of **4** are given in Table 3. The

Table 3
Preferred orientation [a] of the phosphate group in **1–4** and the hydroxymethyl group [b] of **4**

Compound	P_{g^-}	P_{g^+}	P_t
1	0.5	0.2	0.3
2	0.4	0.3	0.3
3	0.7	0	0.3
4	0.2	0.2	0.6
4 (hydroxymethyl)	0.7	0.3	0

[a] Calculated populations of the phosphate group with respect to the dihedral angle θ defined for **1–3** by HCOP and for **4** by C-5–C-6–O-6–P. P_{g^-} is the population of $\theta = -60°$, for g^+ the angle $\theta = 60°$, and for t the angle $\theta = 180°$.

[b] The dihedral angle ω for the hydroxymethyl group is defined by O-5–C-5–C-6–O-6, and g^-, g^+, and t are $-60°$, 60°, and 180°, respectively.

populations of the *trans* state in **1–3**, where the phosphate is substituted on a secondary hydroxyl group, are all similar. The same approximate populations for the *trans* state were also found for the 3′- and 4′-monophosphates of lactose, i.e., 0.3 and 0.4, respectively. Of the two *gauche* states, g^- is preferred to g^+ in **1** and **2**. In **3** the population of g^+ is even smaller, possibly because of steric interaction with the hydroxymethyl group. In **4**, the hydroxymethyl group populates the two states which the hydroxymethyl group of mannose also populates, although the amount of g^- in the present case is increased from 0.5 [19] to 0.7. For the phosphate group, the *trans* state (with regard to C-5) is the extended conformation and the major conformer. The two *gauche* states are of equal probability. For the lactose monophosphates, the 6′- and 6-phosphate show an approximate population in the *trans* state of 0.6 and 0.8, respectively.

3. Experimental

General methods.—These were as described earlier [20]. NMR spectra for **1–4** were recorded in D_2O at pD ~ 9, to allow the compounds to be present as their disodium salts. Additional pertinent NMR data are given in the tables.

Phase-transfer benzylations.—Following the published procedure [8], the products below were obtained. From methyl 4,6-*O*-benzylidene-α-D-mannopyranoside [10] (2.0 g) after silica gel chromatography (1 : 1 toluene–EtOAc): methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**5**; 0.64 g, 24%); $[\alpha]_D$ +50° (*c* 1.0, $CHCl_3$) (lit. [4] $[\alpha]_D$ +51°); and methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**6**; 1.37 g, 52%); mp 40–44°C (from EtOH), mp 85–87°C (from diethyl ether–light petroleum [bp 40–60°C]); $[\alpha]_D$ +3° (*c* 1.0, $CHCl_3$) {lit. [5] mp 42–44°C (EtOH), $[\alpha]_D$ +2°}.

From methyl 2,3-di-*O*-benzyl-α-D-mannopyranoside [11] (2.93 g) after silica gel chromatography (1 : 1 toluene–EtOAc): methyl 2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (**7**; 1.66 g, 46%); $[\alpha]_D$ 0° (*c* 1.0, $CHCl_3$) (lit. [6] $[\alpha]_D$ +4.5°); and methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (**8**; 0.80 g, 22%); $[\alpha]_D$ +29° (*c* 1.0, $CHCl_3$) (lit. [7] $[\alpha]_D$ +30°).

General procedure for the synthesis of the protected mannopyranoside dibenzyl phosphates.—Phosphorus trichloride (0.2 mL, 2.3 mmol) in CH_2Cl_2 (2 mL) and then triethylamine (1.0 mL, 7.2 mmol) in CH_2Cl_2 (4 mL) were added under N_2 to a cooled (ice bath) solution of imidazole (470 mg, 6.9 mmol) in CH_2Cl_2 (15 mL). A precipitate was formed immediately after the addition of the phosphorus trichloride. The mixture was stirred for 10 min, whereafter the suitably protected mannopyranoside derivative (0.57 mmol) in CH_2Cl_2 (6 mL) was added dropwise. After 40 min, benzyl alcohol (0.75 mL, 7.2 mmol) was added to the mixture, which then became transparent. After stirring for an additional 30 min, *m*-chloroperoxybenzoic acid (590 mg, 3.4 mmol) was added dropwise to the mixture. After a further 90 min, the reaction was quenched by the addition of $Na_2S_2O_3$ (10% aq, 5 mL) and $NaHCO_3$ (satd, aq, 5 mL). The mixture was poured into a separatory

funnel and the phases were separated. The organic phase was washed with water, 1 M HCl, water, sat aq $NaHCO_3$, and water, dried (Na_2SO_4), and concentrated. The residue was purified on a silica gel column to give the mannopyranoside dibenzyl phosphate.

Methyl 3-O-benzyl-4,6-O-benzylidene-2-O-dibenzyloxyphosphoryl-α-D-mannopyranoside (**9**).—Starting from **5** (213 mg, 0.57 mmol) using the procedure described above, **9** (330 mg, 91%) was obtained after silica gel chromatography (two columns; 6:1 toluene–MeOH, and 2:1 light petroleum [bp 40–60°C]–EtOAc); mp 53–56°C; $[\alpha]_D$ −2° (*c* 1.0, $CHCl_3$); ^{13}C NMR data: δ 55.0 (OMe), 63.8–78.4 (C-2–6, Ph*C*H_2), 100.1 (C-1, d), 101.5 (Ph*C*H), 126.1–138.0 (aromatic C). Anal. Calcd for $C_{35}H_{37}O_9P$: C, 66.4; H, 5.9; P, 4.9. Found: C, 67.2; H, 5.8; P, 5.3.

Methyl 2-O-benzyl-4,6-O-benzylidene-3-O-dibenzyloxyphosphoryl-α-D-mannopyranoside (**10**).—Starting from **6** (200 mg, 0.54 mmol), **10** (300 mg, 88%) was obtained (eluent, 3:2 light petroleum [bp 40–60°C]–EtOAc); mp 56–57°C; $[\alpha]_D$ +5° (*c* 1.0, $CHCl_3$); ^{13}C NMR data: δ 54.9 (OMe), 63.8–77.2 (C-2–6, Ph*C*H_2), 100.3 (C-1), 102.1 (Ph*C*H), 126.3–137.7 (aromatic C). Anal. Calcd for $C_{35}H_{37}O_9P$: C, 66.4; H, 5.9; P, 4.9. Found: C, 66.3; H, 5.8; P, 5.0.

Methyl 2,3,6-tri-O-benzyl-4-O-dibenzyloxyphosphoryl-α-D-mannopyranoside (**11**).—Starting from **7** (266 mg, 0.57 mmol), **11** (370 mg, 89%) was obtained (eluent, 6:1 toluene–MeOH); $[\alpha]_D$ +18° (*c* 1.0, $CHCl_3$); ^{13}C NMR data: δ 55.0 (OMe), 69.1–78.2 (C-2–6, Ph*C*H_2), 99.0 (C-1), 127.3–138.5 (aromatic C). Anal. Calcd for $C_{42}H_{45}O_9P$: C, 69.6; H, 6.3; P, 4.3. Found: C, 68.1; H, 6.2; P, 4.1.

Methyl 2,3,4-tri-O-benzyl-6-O-dibenzyloxyphosphoryl-α-D-mannopyranoside (**12**).—Starting from **8** (100 mg, 0.22 mmol), **12** (115 mg, 74%) was obtained (eluent, 3:2 light petroleum [bp 40–60°C]–EtOAc); $[\alpha]_D$ +18° (*c* 1.0, $CHCl_3$); ^{13}C NMR data: δ 54.8 (OMe), 66.8–80.1 (C-2–6, Ph*C*H_2), 99.0 (C-1), 127.5–138.4 (aromatic C). Anal. Calcd for $C_{42}H_{45}O_9P$: C, 69.6; H, 6.3; P, 4.3. Found: C, 68.5; H, 6.3; P, 4.3.

General procedure for the deprotection.—The mannopyranoside dibenzyl phosphate (0.43 mmol) was dissolved in EtOH (20 mL) and hydrogenolyzed over Pd–C (10%) at 400 kPa in a Parr apparatus for 24 h. The mixture was filtered and the filtrate was concentrated. The residue was dissolved in water (5 mL), and the solution washed with diethyl ether and passed through a column of Dowex ion-exchange resin (Na^+ form) whereafter aq NaOH was added to raise the pH in the solution to ~9. Freeze-drying then gave the mannopyranoside disodium phosphate.

Methyl α-D-mannopyranoside 2-(disodium phosphate) (**1**).—Deprotection of **9** (150 mg, 0.24 mmol), using the procedure described above, gave **1** (45 mg, 69%); $[\alpha]_D$ + 26° (*c* 1.0, H_2O); NMR data are presented in Tables 1 and 2.

Methyl α-D-mannopyranoside 3-(disodium phosphate) (**2**).—Deprotection of **10** (270 mg, 0.43 mmol) gave **2** (100 mg, 74%); $[\alpha]_D$ +61° (*c* 1.0, H_2O); NMR data are presented in Tables 1 and 2.

Methyl α-D-mannopyranoside 4-(disodium phosphate) (**3**).—Deprotection of **11** (160 mg, 0.22 mmol) gave **3** (50 mg, 71%); $[\alpha]_D$ +64° (*c* 1.0, H_2O); NMR data are presented in Tables 1 and 2.

Methyl α-D-mannopyranoside 6-(disodium phosphate) (**4**).—Deprotection of **12** (90 mg, 0.12 mmol) gave **4** (35 mg, 89%); $[\alpha]_D$ +35° (*c* 1.0, H_2O); NMR data are presented in Tables 1 and 2.

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