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SYNTHESIS OF 2-ACETAMIDO-2,5-DIDEOXY-5-PHOSPHORYL-D-GLUCOPYRANOSE DERIVATIVES: NEW PHOSPHA-SUGAR ANALOGS OF *N*-ACETYL-D-GLUCOSAMINE

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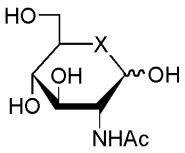
Abstract – Starting with *N*-acetyl-D-glucosamine, methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-*xylo*-hexofuranosid-5-ulose (**18**) was prepared in 7 steps. The addition reaction of dimethyl phosphonate to **18**, followed by deoxygenation of its 5-hydroxy group, provided the 5-deoxy-5-dimethoxyphosphoryl-D-glucofuranoside derivative (**21a**). The hydride reduction of **21a**, followed by the action of hydrochloric acid and then hydrogen peroxide, afforded the first D-glucosamine analog (**23**) having a phosphoryl group in the hemiacetal ring. This was converted into the per-*O*-acetylated *N*-acetyl-D-glucosamine phospha-sugar (**25**), while the same treatment of the 5-deoxy-5-dimethoxyphosphoryl-L-idose dimethyl acetal derivative (**13b**) afforded the *N*-acetyl-L-idosamine phospha-sugar (**29**).

INTRODUCTION

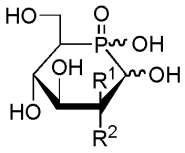
Various sugar analogs containing nitrogen,[1] sulfur,[2] or phosphorus[3] as a ring heteroatom have been prepared because of the wide interest in their chemical and biochemical properties. Heteroatom-in-the-ring sugar analogs of 2-amino- and 2-acetamido-2-deoxyhexopyranoses, which widely occur as a component of many natural products, have also attracted considerable interest. Azasugar (**1**)[4] and thiasugar analogs (**2**)[5] of *N*-acetyl-D-glucosamine, for example, have been prepared and *N*-acetyl-glucosaminidase inhibitory activity of the former has been reported.

In view of such a chemical modification by heteroatoms, we have prepared various sugar analogs having

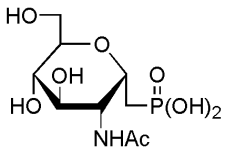
a phosphorus atom in the ring (phospha-sugar); *e.g.*, D-glucopyranose (**3**)[6] and D-mannopyranose analogs (**4**).[7] These phospha-sugar analogs are expected to be of interest in view of potential biological activities, such as glycosidase inhibitory activities[8] and antitumor activities against leukemia cells.[9] Meanwhile, as synthetic *N*-acetyl-D-glucosamine analogs having phosphorus attached to a sugar-carbon atom, the isosteric phosphonate analog of 1-phosphate (**5**)[10] and the cyclic phosphonate analog (**6**)[11] have been prepared. We describe herein the first synthetic route to the *N*-acetyl-D-glucosamine phospha-sugar (**25**), by using our effective procedure[12] to introduce a phosphoryl group onto a sugar skeleton; namely addition of a phosphonate to an appropriate hexos-5-ulose derivative and the subsequent deoxygenation.



1 X = NH
2 X = S



3 R^1 = H, R^2 =OH
4 R^1 = OH, R^2 =H



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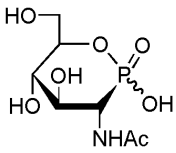

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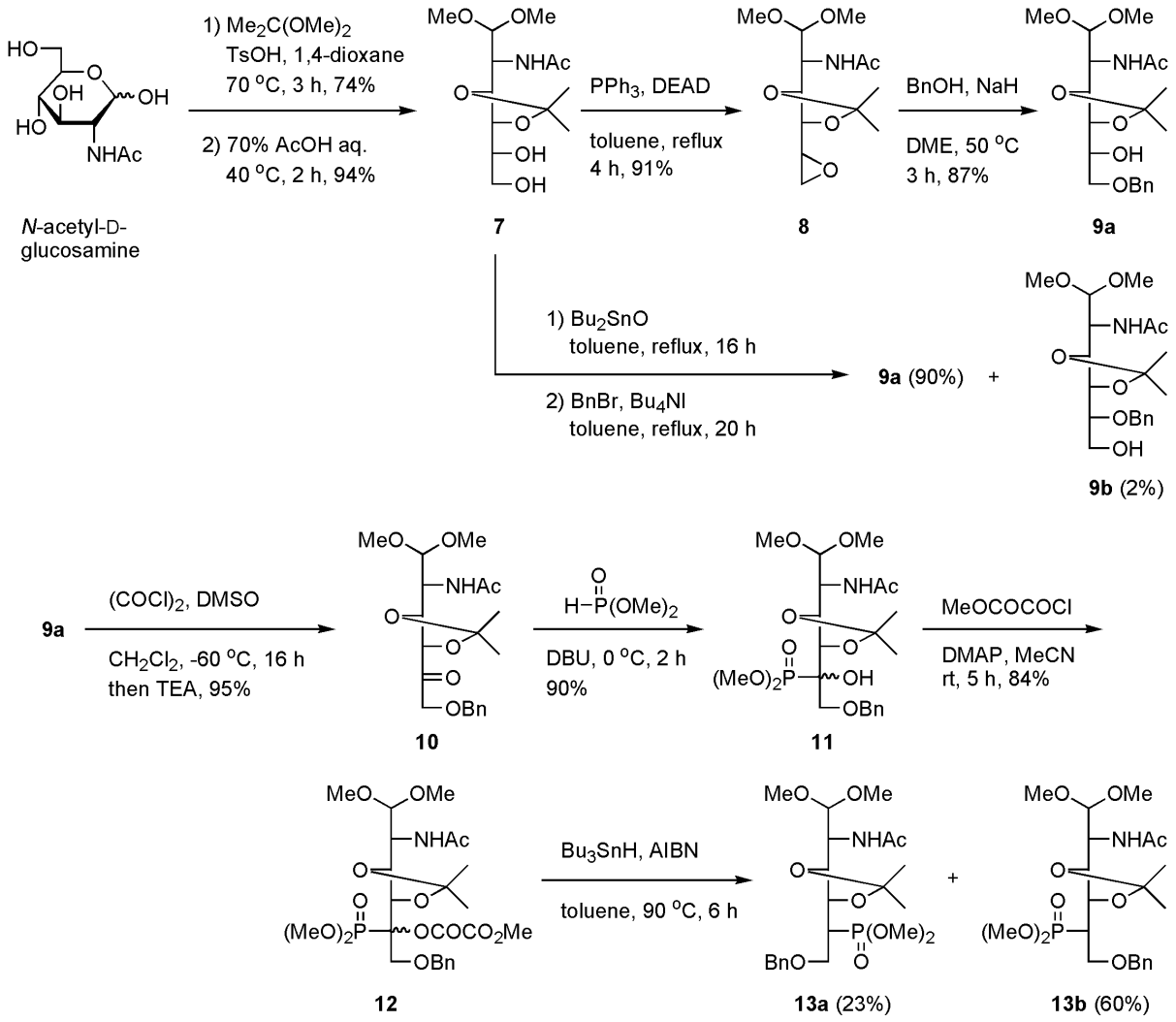
RESULTS AND DISCUSSION

For the preparation of the key 5-deoxy-5-dimethylphosphoryl-D-glucose precursors (**13a** and **21a**), two synthetic routes by starting with open-chain and furanose derivatives (**7** and **15**) of *N*-acetyl-D-glucosamine were employed (Scheme 1 and 3).

First, 2-acetamido-2-deoxy-3,4-*O*-isopropylidene-D-glucose dimethyl acetal (**7**) (available from *N*-acetyl-D-glucosamine in 2 steps)[13] served as the starting material for preparation of the 5-ulose intermediate (**10**) to introduce a phosphoryl group, as illustrated in Scheme 1. The epoxidation of **7** under Mitsunobu's conditions afforded the 5,6-anhydro derivative (**8**) (91%), which was then treated with benzyl alcohol and sodium hydride in 1,2-dimethoxyethane (DME) to give the 6-*O*-benzyl compound (**9a**) in 87% yield. As an alternative way for preparation of **9a**, the 5,6-diol **7** was treated with dibutyltin oxide in refluxed toluene to give 5,6-*O*-stannylene acetal, which was subjected to the benzylation with benzyl bromide in the presence of tetrabutylammonium iodide in the same solvent,[14] providing the 6-*O*-benzyl derivative (**9a**) (90% yield) together with a trace amount of the 5-*O*-benzyl isomer (**9b**) (2%). Swern oxidation of **9a** with oxalyl chloride-DMSO afforded the D-*xylo*-hexos-5-ulose dimethyl acetal (**10**) in 95%.

The addition reaction of dimethyl phosphonate to **10** in the presence of DBU gave the (5*R*)- and (5*S*)-5-*C*-dimethoxyphosphoryl-D-*xylo*-hexose derivatives (**11**) (26% and 54%, respectively).[15] The diastereomeric mixture of **11** was converted to the methoxalyl esters (**12**) with methoxalyl chloride in the presence of 4-dimethylaminopyridine (DMAP) in 84% yield and then reduced with tributyltin hydride in the presence of AIBN, affording a 72:28 mixture of 5-deoxy products. On structural assignment of the resulting two separable diastereoisomers by ^{1}H-NMR, it turned out that the major isomer was not the

expected 5-deoxy-5-dimethoxyphosphoryl-D-glucose derivative (**13a**) (23%) but the L-idose isomer (**13b**) (60%).



Scheme 1

The large $J_{3,4}$ values (8.5 and 8.2 Hz) of **13a,b** indicate an *anti* relationship of H-3/H-4 for both isomers. The D-*gluco* configuration for **13a** was assigned on the basis of the small $J_{4,P}$ (9.9 Hz) and $J_{4,5}$ (4.1 Hz) values and the presence of a long range coupling, $^{4}J_{3,P}$ (1.5 Hz)[12,16] (Figure 1). Similarly, the L-*ido* configuration for **13b** was derived from the relatively large $J_{4,P}$ (18.2 Hz) and small $J_{4,5}$ (5.3 Hz) values.

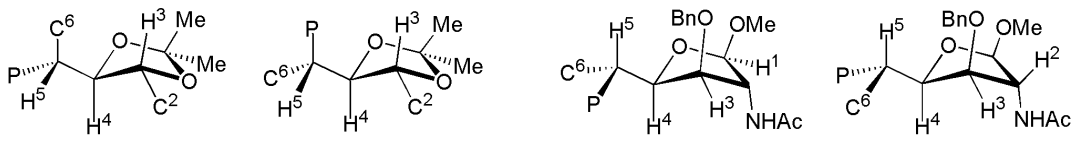
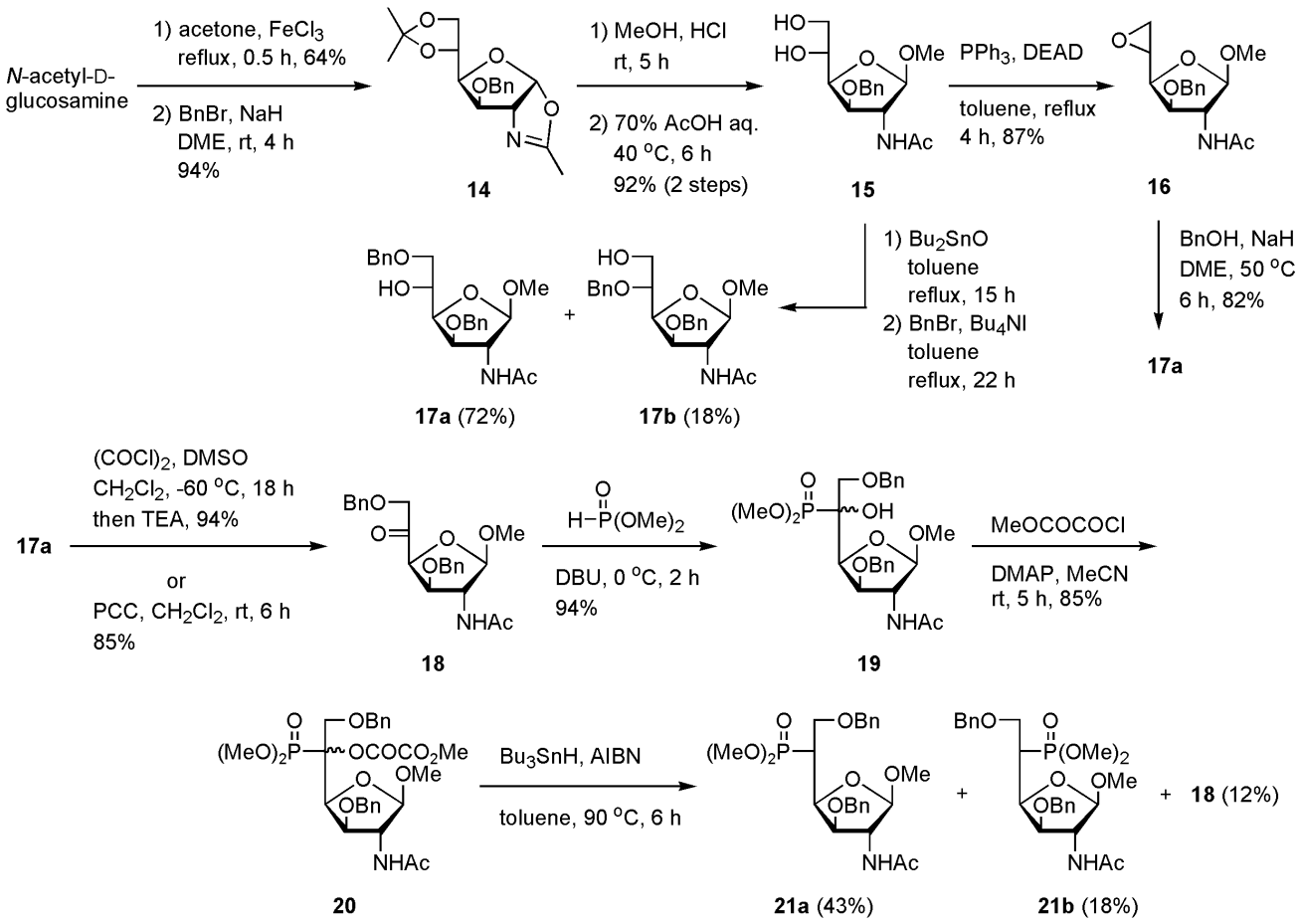


Figure 1. The most favorable conformations for **13a,b** and **21a,b**.

Alternatively, methyl 2-acetamido-3-*O*-benzyl-2-deoxy-D-glucofuranose (**15**) was prepared from *N*-acetyl-D-glucosamine in 4 steps via **14** with a slight modification of reported procedures[4,17] (Scheme 2). The epoxidation of **15** under Mitsunobu's conditions afforded the 5,6-anhydro derivative (**16**) (87%), which was then treated with benzyl alcohol and sodium hydride to give the 6-*O*-benzyl compound (**17a**) in 82% yield. Meanwhile, benzylation of **15** by way of the 5,6-*O*-stannylene acetal resulted in production of the 6-*O*-benzyl derivative (**17a**) (72% yield) and its 5-*O*-benzyl isomer (**17b**) (18%) with less selectivity than that from **7**. Oxidation of **17a** with oxalyl chloride-DMSO afforded the D-*xylo*-hexofuranosid-5-ulose (**18**) in 94% yield, while the same reaction with PCC gave **18** in 85%.



Scheme 2

The addition reaction of dimethyl phosphonate to **18** in the presence of DBU provided the (5*R*)- and (5*S*)-5-dimethoxyphosphoryl-D-*xylo*-hexofuranoside derivatives (**19**) (69% and 25%, respectively).[15] The diastereomeric mixture of **19** was converted to the methoxalyl esters (**20**) in 85% yield, which were then reduced with tributyltin hydride, affording the 5-deoxy-5-dimethoxyphosphoryl-D-glucofuranoside derivative (**21a**) (43%) and its L-idofuranoside isomer (**21b**) (18%) together with dephosphorylated product **18** (12%). The D-*gluco* configuration for **21a** was assigned on the basis of the large $J_{4,5}$ value

(9.4 Hz) and the presence of a long-range coupling $^{5}J_{1,P}$ (1.2 Hz), whereas the L-*ido* configuration for **21b** was derived from the large $J_{4,5}$ value (10.6 Hz) and the presence of $^{4}J_{3,P}$ (1.2 Hz) and $^{5}J_{2,P}$ (1.5 Hz) (Figure 1).[12,16]

Although the reduction from the open-chain 5-*O*-methoxalyl compound (**12**) preferentially gave the 5-deoxy-L-ido isomer (**13b**), the same reaction from the furanoside form (**20**) afforded 5-deoxy-D-gluco isomer (**21a**) as a major product. As this reaction proceeds via a radical intermediate formed by a homolytic cleavage of the O–C-5 bond, ratios of the 5-deoxy products (**13a**:**13b** and **21a**:**21b**) are not correlated to the diastereomeric ratios of the 5-*O*-methoxalyl precursors.[12] As for the predominant production of the L-ido isomer (**13b**) from **12**, we propose the rotamer **A** of the radical intermediate from the viewpoint of electronic factors (Figure 2). Namely, the opposition of the 5-phosphoryl group and electronegative 4-*O* atom diminishes their intramolecular electrostatic repulsion.[18] Moreover, the alignment of the σ_{C4-C5} bond with the radical p orbital stabilizes the transition state by hyperconjugation. Meanwhile, as for the predominant production of the D-gluco isomer (**21a**) from **20**, another possible rotamer **B** was proposed, taking into account both the electrostatic repulsion between two electronegative groups and the steric repulsion between C-6 and the 3-*O*-benzyl group.[19]

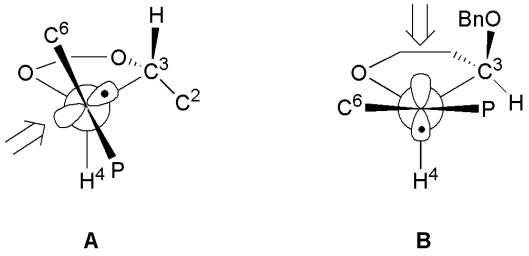
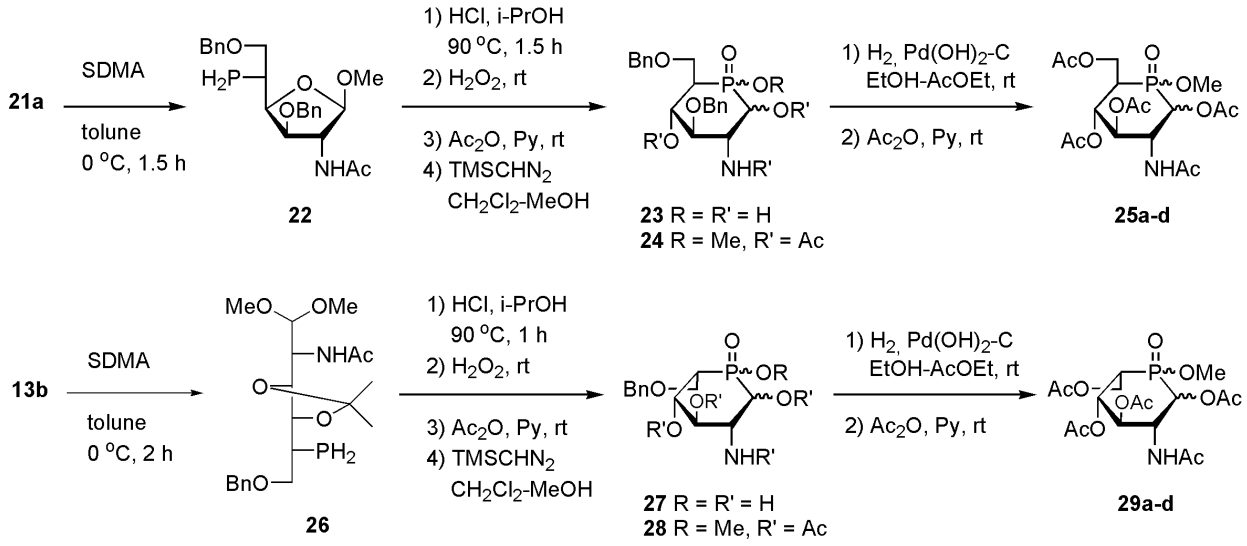


Figure 2. The most plausible conformations for the radical intermediates **A** (from **12**) and **B** (from **20**) and directions of the reduction.

The major product (**21a**) was then reduced with sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA) to give the 5-phosphino derivative (**22**), which was immediately treated with hydrochloric acid at 90 °C and then oxidized with hydrogen peroxide to afford 2-amino-3,6-di-*O*-benzyl-2,5-dideoxy-5-hydroxyphosphoryl-α,β-D-glucopyranoses (**23**) (Scheme 3).

For the purpose of purification and characterization, compounds **23** were converted to the corresponding 1,2,4-triacetyl-5-methoxyphoshoryl derivatives (**24**) by treatment with acetic anhydride-pyridine and then trimethylsilyldiazomethane. Debenzylation of **24** by the catalytic hydrogenation over 20% $Pd(OH)_2$-C, followed by acetylation, afforded the fully acetylated *N*-acetyl-D-glucosamine phospha-sugar (**25**). By purification on a silica gel column, the 5-deoxy-5-[(*R*)-methoxyphosphoryl]-α-D-glucopyranose (**25a**)

(7.5% overall yield from **21a**), its β-anomer (**25b**) (2.7%), 5-[(*S*)-methoxyphosphoryl]-α-D-glucopyranose (**25c**) (19%), and its β-anomer (**25d**) (2.3%) were obtained.



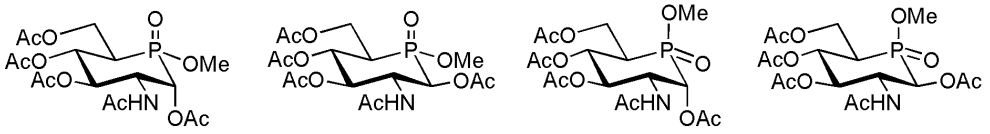
Scheme 3

The similar treatment of the L-idose dimethyl acetal derivative (**13b**) afforded 2-amino-3,6-di-*O*-benzyl-2,5-dideoxy-5-hydroxyphosphoryl-α,β-L-idopyranoses (**27**) via 5-phosphino compound **26**. The L-idopyranose analogs **27** were also converted to *N*-acetyl-L-idosamine phospha-sugar (**29**) via **28**: the 5-deoxy-5-[(*R*)-methoxyphosphoryl]-β-L-idopyranose (**29a**) (3.4% overall yield from **13b**), its α-anomer (**29b**) (8.3%), 5-[(*S*)-methoxyphosphoryl]-β-L-glucopyranose (**29c**) (5.4%), and its α-anomer (**29d**) (3.0%).

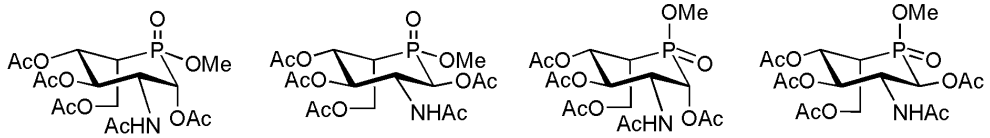
The precise structures of **25a–d** and **29a–d** were established by the analysis of their ^{1}H-NMR spectra; for all the assignments of the signals, see Table 1. The D-glucopyranose configuration of **25a-d** are derived from the large values of $J_{4,5}$ (11–12 Hz). As for anomeric orientation of C-1, the large $J_{1,2}$ values (10.5 Hz) of **25b,d** indicate the axial H-1 orientation, whereas the small $J_{1,2}$ values (2.6 Hz) of **25a,c** show the equatorial H-1 configuration.[3] With regard to the orientation of the ring P=O group, a downfield shift (0.2–0.3 ppm) of H-2,4 for **25a,b** compared with those of **25c,d** indicates the axial P=O orientation for the former and the equatorial P=O orientation for the latter. In contrast, the small values of $J_{4,5}$ (5–6 Hz) for **29a–d** indicate the L-idopyranose structure and their structural assignments were made by similar characteristic tendency of the corresponding $J_{1,2}$ values and H-2,4 chemical shifts for **25a-d**.

Present work thus demonstrates a convenient way for preparation of 2-acetamido-2,5-dideoxy-5-phosphoryl-D-glucopyranose from appropriate intermediates. Extension of this work including applications of these findings in synthesizing other phospha-sugar analogs, as well as biological

evaluation of *N*-acetyl-D-glucosamine phospha-sugars, is anticipated to be highly of interest.



25a **25b** **25c** **25d**



29a **29b** **29c** **29d**

Table 1. ^{1}H and ^{31}P NMR Parameters for Compounds **25a–d** and **29a–d** in $CDCl_3$

Compound	Chemical shifts / δ										
	H-1	H-2	H-3	H-4	H-5	H-6	H'-6	POMe	HN-2 [a]	Ac-1,2,3,4,6, [b]	^{31}P
25a	5.45	4.85	5.19	5.56	2.57	4.43	4.35	3.75	5.68	2.23, 2.08, 2.05, 2.04, 1.91	38.79
25b	5.11	4.79	4.97	5.52	2.42	4.44	4.41	3.85	5.60	2.15, 2.09, 2.07, 2.03, 1.92	37.25
25c	5.58	4.59	5.14	5.39	2.65	4.62	4.24	3.93	5.72	2.25, 2.07, 2.04, 2.04, 1.91	37.29
25d	5.27	4.57	5.00	5.37	2.43	4.59	4.31	3.97	5.65	2.14, 2.08, 2.03, 2.02, 1.92	35.48
29a	5.45	4.67	5.35	5.52	2.98	4.56	4.36	3.84	c	2.20, 2.11, 2.08, 2.07, 1.95	37.50
29b	5.48	4.56	5.31	5.33	2.83	4.43	4.40	3.98	5.48	2.24, 2.15, 2.08, 2.04, 1.92	36.96
29c	5.54	4.67	5.28	5.30	2.91	4.56	4.46	3.90	c	2.22, 2.10, 2.09, 2.04, 1.96	36.85
29d	5.79	4.45	5.69	5.25	2.59	4.50	4.35	3.97	6.09	2.22, 2.06, 2.01, 1.91, 1.85	36.85

	Coupling constants / Hz												
	$J_{1,2}$	$J_{1,P}$	$J_{2,3}$	$J_{2,P}$	$J_{3,4}$	$J_{4,5}$	$J_{4,P}$	$J_{5,6}$	$J_{5,6'}$	$J_{5,P}$	$J_{6,6'}$	$J_{6,P}$	$J_{6',P}$	J_{POMe}
25a	2.6	13.2	11.2	0	9.6	12.2	1.8	5.9	4.7	13.8	12.0	16.4	12.9	10.9
25b	10.5	5.6	10.6	2.4	9.6	11.0	2.0	5.0	6.0	13.0	11.8	14.5	16.0	11.0
25c	2.6	14.1	11.1	0	9.7	11.7	1.8	4.4	3.5	13.9	12.0	22.0	10.0	10.6
25d	10.5	3.0	10.0	2.5	9.8	12.0	2.0	5.0	4.1	12.5	11.8	20.0	11.5	10.6
29a [d]	5.3	11.2	10.0	c	10.8	5.3	c	4.1	7.6	25.5	11.7	c	10.1	10.9
29b	11.4	4.4	9.5	3.5	8.8	5.9	c	2.9	2.9	25.2	11.7	9.2	0	10.6
29c [e]	3.5	10.8	9.5	c	8.5	5.0	c	4.7	7.3	21.4	11.7	c	10.9	10.9
29d	11.2	5.0	10.2	c	10.6	5.9	1.0	3.2	4.1	25.2	11.5	c	7.9	10.6

[a] $J_{2,NH}$ = 8.5–8.8 Hz. [b] The assignment of acetyl signals may be interchanged. [c] Uncertain because of overlapping with other signals. [d] $J_{1,5}$ = 0.8 Hz. [e] $J_{1,5}$ = 1.5 Hz.

EXPERIMENTAL

All reactions were monitored by TLC (Merck silica gel 60F, 0.25 mm) with an appropriate solvent system [(*A*) AcOEt and (*B*) 1:9 EtOH-AcOEt]. Column chromatography was performed with Daiso Silica Gel IR-60/210w. Components were detected by exposing the plates to UV light and/or spraying them with 20% sulfuric acid–ethanol (with subsequent heating). Optical rotations were measured with a Jasco P-1020 polarimeter in $CHCl_3$. The NMR spectra were measured in $CDCl_3$ with Varian 600-System (600 MHz for ^1H, 151 MHz for ^{13}C, 243 MHz for ^{31}P) spectrometer at 23 °C. Chemical shifts are reported as δ values relative to $CHCl_3$ (7.26 ppm as an internal standard for ^1H), $CDCl_3$ (77.0 ppm as an internal standard for ^{13}C), and 85% phosphoric acid (0 ppm as an external standard for ^{31}P). The assignments of ^{13}C signals were made with the aid of 2D HSQC measurements. The MS spectra were measured on a VG-70SE instrument.

2-Acetamido-5,6-anhydro-2-deoxy-3,4-*O*-isopropylidene-D-glucose dimethyl acetal (8).

To a solution of **7** [13] (300 mg, 0.976 mmol) and triphenylphosphine (310 mg, 1.18 mmol) in dry toluene (10 mL) was added DEAD (40% in toluene, 0.470 mL, 1.18 mmol). The mixture was refluxed for 4 h and evaporated in vacuo. The residue was purified by column chromatography with AcOEt as an eluant to give **8** (257 mg, 91%) as colorless needles: mp 102–103 °C (from AcOEt-hexane): R_f = 0.39 (*A*); $[\alpha]_D^{22}$ +4.55 (*c* = 1.28, $CHCl_3$); ^1H-NMR δ = 1.41, 1.42 (3H each, s, CMe_2), 2.03 (3H, s, NAc), 2.69 (1H, dd, $J_{6,6'}$ = 4.7, $J_{5,6'}$ = 2.6 Hz, H'-6), 2.83 (1H, t, $J_{5,6}$ = 4.1 Hz, H-6), 3.79 (1H, td, $J_{4,5}$ = 4.7 Hz, H-5), 3.36, 3.42 (3H each, 2s, MeO-1), 3.69 (1H, dd, $J_{3,4}$ = 7.9 Hz, H-4), 4.21 (1H, dd, $J_{2,3}$ = 2.1 Hz, H-3), 4.26 (1H, ddd, $J_{2,NH}$ = 9.7, $J_{1,2}$ = 5.9 Hz, H-2), 4.40 (1H, d, H-1), 5.85 (1H, d, HN-2); ^{13}C NMR δ = 23.36 (CH_3CO), 26.66 and 26.85 (CMe_2), 45.04 (C-6), 49.46 (C-2), 51.39 (C-5), 53.28 and 55.52 (MeO-1), 75.77 (C-3), 77.10 (C-4), 103.03 (C-1), 109.91 (CMe_2), 169.96 (CH_3CO). Anal. Calcd for $C_{13}H_{23}NO_6$: C, 53.97; H, 8.01. Found: C, 53.90; H, 8.04.

2-Acetamido-6-*O*-benzyl-2-deoxy-3,4-*O*-isopropylidene-D-glucose dimethyl acetal (9a) and its 5-*O*-benzyl analog (9b).

A. From 8. To a suspension of sodium hydride (60% in mineral oil, 560 mg, 14.0 mmol) and benzyl alcohol (2.20 mL, 21.3 mmol) in DME (5.0 mL) was added a solution of **8** (2.02 g, 6.98 mmol) in DME (5.0 mL) at 0 °C. The mixture was stirred at 50 °C for 3 h, diluted with saturated NH_4Cl (20 mL), and extracted with $CHCl_3$ three times. The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography with 3:1 AcOEt-hexane as an eluant to give **9a** (2.44 g, 88%) as colorless needles.

B. From 7. To a solution of **7** (1.85 g, 6.02 mmol) in toluene (50 mL) was added dibutyltin oxide (1.80

g, 7.23 mmol) and then the suspension was refluxed under Dean-Stark trap for 16 h. After removal of the trap, benzyl bromide (1.40 mL, 11.8 mmol) and tetrabutylammonium iodide (1.10 g, 2.98 mmol) were added and the mixture was refluxed for 20 h. The mixture was evaporated in vacuo and the residue was separated by column chromatography on silica gel to give **9a** (2.15 g, 90%) and **9b** (45 mg, 2%).

9a: Colorless needles: 97–99 °C (from AcOEt-hexane); R_f = 0.44 (*A*); $[\alpha]_D^{20}$ +13.3 (*c* = 1.23, $CHCl_3$); ^{1}H NMR δ = 1.37 (6H, s, CMe_2), 2.03 (3H, s, NAc), 3.10 (1H, br s, HO-5), 3.32, 3.39 (3H each, 2s, MeO-1), 3.55 (1H, dd, $J_{6,6'}$ = 9.8, $J_{5,6'}$ = 5.8 Hz, H'-6), 3.65 (1H, t, $J_{3,4}$ = 8.2, $J_{4,5}$ = 8.0 Hz, H-4), 3.70 (1H, dd, $J_{5,6}$ = 2.8 Hz, H-6), 3.79 (1H, ddd, H-5), 4.27 (1H, dd, $J_{2,3}$ = 1.5 Hz, H-3), 4.42 (1H, d, $J_{1,2}$ = 6.7 Hz, H-1), 4.47 (1H, ddd, $J_{2,NH}$ = 9.5 Hz, H-2), 4.58 (2H, s, CH_2O-6), 5.85 (1H, d, HN-2), 7.27 [1H, t, $J_{m,p}$ = 7.4 Hz, Ph(*p*)], 7.34–7.38 [4H, m, Ph(*o,m*)]. Anal. Calcd for $C_{20}H_{31}NO_7$: C, 60.44; H, 7.86. Found: C, 60.61; H, 7.90.

9b: Colorless syrup; R_f = 0.41 (*A*); ^{1}H NMR δ = 1.38, 1.39 (3H each, s, CMe_2), 2.03 (3H, s, NAc), 2.90 (1H, br s, HO-6), 3.28, 3.38 (3H each, 2s, MeO-1), 3.69 (1H, m, H-5), 3.72–3.76 (2H, m, H,H'-6), 3.90 (1H, d, $J_{3,4}$ = 8.5, $J_{4,5}$ = 4.4 Hz, H-4), 4.36 (1H, ddd, $J_{2,NH}$ = 9.7, $J_{1,2}$ = 6.5, $J_{2,3}$ = 1.2 Hz, H-2), 4.37 (1H, dd, H-3), 4.40 (1H, d, H-1), 4.67, 4.71 (1H each, 2d, ^2J = 11.7 Hz, CH_2O-5), 5.88 (1H, d, HN-2), 7.28 [1H, t, $J_{m,p}$ = 7.5 Hz, Ph(*p*)], 7.34 [2H, t, $J_{o,m}$ = 7.5 Hz, Ph(*m*)], 7.38 [2H, d, Ph(*o*)].

2-Acetamido-6-*O*-benzyl-2-deoxy-3,4-*O*-isopropylidene-D-*xylo*-hexos-5-ulose dimethyl acetal (10).

To a solution of oxalyl chloride (1.70 mL, 19.5 mmol) in CH_2Cl_2 (4.0 mL) was added DMSO (2.80 mL, 39.4 mmol) in CH_2Cl_2 (8.0 mL) at –60 °C. After stirring for 30 min, a solution of **9a** (2.56 g, 6.44 mmol) in CH_2Cl_2 (8 mL) was added. The mixture was stirred for 16 h and then TEA (9.0 mL, 64.4 mmol) was added. The mixture was stirred for 1 h, diluted with $CHCl_3$, and washed with sat. NaCl. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed with water, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography with AcOEt to give **10** (2.41 g, 95%) as colorless needles: mp 96–97 °C (from AcOEt-hexane); R_f = 0.46 (*A*); $[\alpha]_D^{20}$ –1.41 (*c* = 1.62, $CHCl_3$); ^{1}H NMR δ = 1.32, 1.43 (3H each, 2s, CMe_2), 2.04 (3H, s, NAc), 3.34, 3.40 (3H each, 2s, MeO-1), 4.23 (1H, d, $J_{3,4}$ = 7.3 Hz, H-4), 4.33, 4.46 (1H each, 2d, $J_{6,6'}$ = 18.5 Hz, H_2-6), 4.38 (1H, d, $J_{1,2}$ = 5.9 Hz, H-1), 4.45 (1H, dd, $J_{2,3}$ = 1.8 Hz, H-3), 4.49 (1H, ddd, $J_{2,NH}$ = 9.7 Hz, H-2), 4.59, 4.63 (1H each, 2d, ^2J = 11.7 Hz, CH_2O-6), 5.79 (d, 1H, HN-2), 7.27 [1H, t, $J_{m,p}$ = 7.4 Hz, Ph(*p*)], 7.34–7.38 [4H, m, Ph(*o,m*)]; ^{13}C NMR δ = 23.37 (CH_3CO), 25.88 and 26.64 (CMe_2), 49.77 (C-2), 53.36 and 55.05 (MeO-1), 72.61 (CH_2O-6), 73.28 (C-6), 75.64 (C-3), 80.33 (C-4), 102.87 (C-1), 111.02 (CMe_2), 127.99 [Ph(*p*)], 128.07 [Ph(*o*)], 128.48 [Ph(*m*)], 137.04 [Ph(*ipso*)], 170.15 (CH_3CO), 205.67 (C-5). Anal. Calcd for $C_{20}H_{29}NO_7$: C, 60.74; H, 7.39. Found: C, 60.61; H, 7.42.

(5*R*)- and (5*S*)-2-Acetamido-6-*O*-benzyl-2-deoxy-5-*C*-dimethoxyphosphoryl-3,4-*O*-isopropylidene-D-*xylo*-hexose dimethyl acetals (11).

To a solution of **10** (2.10 g, 5.31 mmol) in dimethyl phosphonate (25 mL) was added DBU (1.60 mL, 10.7 mmol) at 0 °C under argon. After stirring for 2 h at 0 °C, the mixture was treated with saturated NH_4Cl at rt for 0.5 h and then extracted with $CHCl_3$ three times. The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated in vacuo. The residue was separated by column chromatography with 1:9 EtOH-AcOEt to give (5*R*)-**11** (958 mg, 36%) and (5*S*)-**11** (1.44 g, 54%).

(5*R*)-**11**: Colorless syrup; R_f = 0.30 (*B*); $[\alpha]_D^{22}$ +4.17 (*c* = 1.37, $CHCl_3$); ^{1}H NMR δ = 1.36, 1.38 (3H each, 2s, CMe_2), 2.05 (3H, s, NAc), 3.30, 3.33 (3H each, 2s, MeO-1), 3.80, 3.82 (3H each, 2d, J_{POMe} = 10.6 Hz, POMe), 3.85 (1H, dd, $J_{6',P}$ = 10.9, $J_{6,6'}$ = 9.9 Hz, H-6'), 3.87 (1H, dd, $J_{6,P}$ = 13.8 Hz, H-6'), 4.02 (1H, t, $J_{4,P}$ = 8.5, $J_{3,4}$ = 8.2 Hz, H-4), 4.06 (1H, br s, HO-5), 4.37 (1H, d, $J_{1,2}$ = 6.5 Hz, H-1), 4.49 (1H, ddd, $J_{2,NH}$ = 9.7, $J_{2,3}$ = 1.1 Hz, H-2), 4.59, 4.66 (1H each, 2d, ^2J = 11.9 Hz, CH_2O-6), 4.70 (1H, dt, $^3J_{3,P}$ = 1.0 Hz, H-3), 5.84 (1H, d, HN-2), 7.27 [1H, t, $J_{m,p}$ = 7.6 Hz, Ph(*p*)], 7.33 [2H, t, $J_{o,m}$ = 7.5 Hz, Ph(*m*)], 7.37 [2H, d, Ph(*o*)]; ^{31}P NMR δ = 24.77.

(5*S*)-**11**: Colorless needles; mp 121–123 °C (from AcOEt); R_f = 0.40 (*B*); $[\alpha]_D^{22}$ +12.8 (*c* = 0.97, $CHCl_3$); ^{1}H NMR δ = 1.37, 1.44 (3H each, 2s, CMe_2), 1.98 (3H, s, NAc), 3.28, 3.36 (3H each, 2s, MeO-1), 3.72-3.82 (3H, m, H_2-6, HO-5), 3.75, 3.80 (3H each, 2d, J_{POMe} = 10.6 Hz, POMe), 4.03 (1H, dd, $J_{4,P}$ = 19.1, $J_{3,4}$ = 8.8 Hz, H-4), 4.39 (1H, d, $J_{1,2}$ = 6.5 Hz, H-1), 4.46 (1H, ddd, $J_{2,NH}$ = 9.7, $J_{2,3}$ = 1.2 Hz, H-2), 4.57, 4.65 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-6), 4.79 (1H, dd, H-3), 5.88 (1H, d, HN-2), 7.26 [1H, t, $J_{m,p}$ = 7.5 Hz, Ph(*p*)], 7.32 [2H, t, $J_{o,m}$ = 7.5 Hz, Ph(*m*)], 7.37 [2H, d, Ph(*o*)]; ^{31}P NMR δ = 24.75. Anal. Calcd for $C_{22}H_{36}NO_{10}P$: C, 52.27; H, 7.18. Found: C, 52.47; H, 7.13.

(5*R*)- and (5*S*)-2-Acetamido-6-*O*-benzyl-2-deoxy-5-*C*-dimethoxyphosphoryl-5-*O*-methoxalyl-3,4-*O*-isopropylidene-D-*xylo*-hexose dimethyl acetals (12).

Methoxalyl chloride (0.330 mL, 3.59 mmol) was added to a solution of **11** (40:60 diastereomeric mixture, 936 mg, 1.79 mmol) and DMAP (608 mg, 4.98 mmol) in dry MeCN (10 mL) at 0 °C. The mixture was stirred at rt for 5 h under argon and then concentrated in vacuo. The residue was treated with saturated NH_4Cl and extracted with $CHCl_3$. The combined organic layers were washed with water, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography with AcOEt to give an inseparable mixture (40:60) of (5*R*)- and (5*S*)-**12** (889 mg, 84%) as a colorless syrup: R_f = 0.45 (*B*).

(5*R*)-**12**: ^{1}H NMR δ = 1.40, 1.42 (3H each, 2s, CMe_2), 2.03 (1H, s, NAc), 3.29, 3.30 (3H each, 2s, MeO-1), 3.80, 3.81 (3H each, 2d, J_{POMe} = 11.0 Hz, POMe), 3.89 (3H, s, CO_2Me), 4.21 (1H, dd, $J_{6',P}$ = 15.9, $J_{6,6'}$ = 9.7 Hz, H'-6), 4.28 (1H, dd, $J_{6,P}$ = 8.2 Hz, H-6), 4.30 (1H, d, $J_{1,2}$ = 6.5 Hz, H-1), 4.38 (1H, dd,

$J_{3,4}$ = 8.2, $J_{4,P}$ = 7.4 Hz, H-4), 4.56, 4.60 (1H each, 2d, ^2J = 11.7 Hz, CH_2O-6), 4.60 (1H, ddd, $J_{2,NH}$ = 10.0, $J_{2,3}$ = 1.0 Hz, H-2), 4.80 (1H, dd, H-3), 5.77 (1H, d, HN-2), 7.26 [1H, t, $J_{m,p}$ = 7.4 Hz, Ph(*p*)], 7.29–7.34 [4H, m, Ph(*o,m*)] ; ^{31}P NMR δ = 19.08.

(5*S*)-**12**: ^{1}H NMR δ = 1.42, 1.49 (3H each, 2s, CMe_2), 2.04 (1H, s, NAc), 3.16, 3.18 (3H each, 2s, MeO-1), 3.77, 3.80 (3H each, 2d, J_{POMe} = 10.9 Hz, POMe), 3.89 (3H, s, CO_2Me), 4.01 (1H, dd, $J_{6,6'}$ = 10.6, $J_{6,P}$ = 2.9 Hz, H'-6), 4.16 (1H, dd, $J_{3,4}$ = 7.9, $J_{4,P}$ = 5.3 Hz, H-4), 4.28 (1H, d, $J_{1,2}$ = 6,5 Hz, H-1), 4.37 (1H, t, $J_{6,P}$ = 10.2 Hz, H-6), 4.47, 4.63 (1H each, 2d, ^2J = 11.7 Hz, CH_2O-6), 4.58 (1H, ddd, $J_{2,NH}$ = 10.0, $J_{2,3}$ = 1.0 Hz, H-2), 4.69 (1H, dd, H-3), 5.79 (1H, d, HN-2), 7.24-7.30 (5H, m, Ph) ; ^{31}P NMR δ = 19.16. Anal. Calcd for $C_{25}H_{38}NO_{13}P$: C, 50.76; H, 6.47. Found: C, 50.60; H, 6.51.

2-Acetamido-6-*O*-benzyl-2,5-dideoxy-5-dimethoxyphosphoryl-3,4-*O*-isopropylidene-D-glucose dimethyl acetal (13a) and its L-idose analog (13b).

To a solution of **12** (900 mg, 1.51 mmol) in toluene (6 mL), a solution of AIBN (130 mg, 0.792 mmol) and tributyltin hydride (0.850 mL, 3.16 mmol) in dry toluene (7 ml) was dropwise added at 90 °C under argon. The mixture was stirred at the same temperature for 6 h and then concentrated in vacuo. The residue was separated by column chromatography with 1:9 EtOH-AcOEt to give **13a** (169 mg, 23%) and **13b** (442 mg, 60%).

13a: Colorless syrup; R_f = 0.28 (*B*); $[\alpha]_D^{24}$ +1.79 (*c* = 2.47, $CHCl_3$); ^{1}H NMR δ = 1.33, 1.39 (3H each, 2s, CMe_2), 2.02 (3H, s, NAc), 2.47 (1H, dddd, $J_{5,P}$ = 23.8 Hz, $J_{5,6}$ = 6.8, $J_{4,5}$ = 4.1, $J_{5,6'}$ = 3.2, H-5), 3.30, 3.31 (3H each, 2s, MeO-1), 3.725, 3.73 (3H each, 2d, J_{POMe} = 10.9 Hz, POMe), 3.79 (1H, ddd, $J_{6',P}$ = 15.6, $J_{6,6'}$ = 10.0 Hz, H'-6), 3.89 (1H, ddd, $J_{6,P}$ = 7.6 Hz, H-6), 4.04 (1H, ddd, $J_{4,P}$ = 9.9, $J_{3,4}$ = 8.5 Hz, H-4), 4.33 (1H, d, $J_{1,2}$ = 5.9 Hz, H-1), 4.35 (1H, ddd, $J_{2,NH}$ = 8.5, $J_{2,3}$ = 1.5 Hz, H-2), 4.46 (1H, dt, $^4J_{3,P}$ = 1.5 Hz, H-3), 4.49, 4.55 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-6), 5.77 (1H, d, HN-2), 7.26 [1H, t, $J_{m,p}$ = 7.5 Hz, Ph(*p*)], 7.34–7.38 [4H, m, Ph(*o,m*)]; ^{13}C NMR δ = 23.35 (*C*H_3CO), 26.88 and 27.07 (C*Me*$_2$), 39.36 (d, $^1J_{5,P}$ = 136.9 Hz, C-5), 48.15 (C-2), 52.69 and 52.73 [2d, $^2J_{C,P}$ = 6.7 Hz, $P(OMe)_2$], 52.95 and 54.93 (MeO-1), 64.94 (C-6), 73.10 (CH_2O-6), 74.32 (d, $^2J_{4,P}$ = 2.8 Hz, C-4), 76.76 (d, $^3J_{3,P}$ = 8.4 Hz, C-3), 103.36 (C-1), 108.62 (*C*Me_2), 127.54 [Ph(*p*)], 127.71 [Ph(*o*)], 128.25 [Ph(*m*)], 137.89 [Ph(*ipso*)], 169.79 (CH_3*C*O); ^{31}P NMR δ = 30.31.

13b: Colorless needles: mp 97–99 °C, R_f = 0.38 (*B*); $[\alpha]_D^{24}$ +16.6 (*c* = 2.12, $CHCl_3$); ^{1}H NMR δ = 1.38, 1.41 (3H each, 2s, CMe_2), 1.99 (3H, s, NAc), 2.52 (1H, dddd, $J_{5,P}$ = 22.0, $J_{5,6'}$ = 7.6, $J_{4,5}$ = 5.3, $J_{5,6}$ = 3.8 Hz, H-5), 3.28, 3.34 (3H each, 2s, MeO-1), 3.71, 3.72 (3H each, 2d, J_{POMe} = 11.0 Hz, POMe), 3.75 (1H, ddd, $J_{6',P}$ = 15.3, $J_{6,6'}$ = 10.0 Hz, H'-6), 3.85 (1H, ddd, $J_{6,P}$ = 13.8 Hz, H-6), 4.04 (1H, ddd, $J_{4,P}$ = 18.2, $J_{3,4}$ = 8.2 Hz, H-4), 4.35 (1H, d, $J_{1,2}$ = 6.2 Hz, H-1), 4.40 (1H, dd, $J_{2,NH}$ = 9.7, $J_{2,3}$ = 1.7 Hz, H-2), 4.53 (1H, dd, H-3), 4.54 (2H, s, CH_2O-6), 5.78 (1H, d, HN-2), 7.26 [1H, t, $J_{m,p}$ = 7.4 Hz, Ph(*p*)], 7.33 [2H, t, $J_{o,m}$ =

7.4 Hz, Ph(*m*)], 7.36 [2H, d, Ph(*o*)]; ^{13}C NMR δ = 23.36 (*C*H$_3$CO), 26.89 and 27.06 (C*Me*$_2$), 40.56 (d, $^1J_{5,P}$ = 138.6 Hz, C-5), 48.58 (C-2), 52.37 and 52.56 [2d, $^2J_{C,P}$ = 6.7 Hz, P(OMe)$_2$], 52.85 and 55.21 (MeO-1), 66.63 (C-6), 72.93 (CH$_2$O-6), 74.17 (d, $^2J_{4,P}$ = 4.5 Hz, C-4), 77.42 (d, $^3J_{3,P}$ = 7.3 Hz, C-3), 103.50 (C-1), 108.74 (*C*Me$_2$), 127.52 [Ph(*p*)], 127.71 [Ph(*o*)], 128.24 [Ph(*m*)], 137.87 [Ph(*ipso*)], 169.72 (CH$_3$*C*O); ^{31}P NMR δ = 29.51. Anal. Calcd for $C_{22}H_{36}NO_9P$: C, 53.98; H, 7.41. Found: C, 54.11; H, 7.37.

Methyl 2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucofuranoside (15).[5]

The following modification of the literature procedures[4] was made. The oxazoline **14** [17] (3.93 g, 11.8 mmol) was dissolved in dry MeOH (40 mL) containing 4M HCl (in dioxane, 0.032 mL). The mixture was stirred at rt for 5 h and neutralized with Amberlite-IRA96SB at 0 °C. The resin was filtered off and the filtrate was evaporated in vacuo to give a crude syrup (4.25 g) of methyl 2-acetamido-3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside: R_f = 0.59 (*A*).

The above syrup was dissolved in 70% aqueous acetic acid (50 ml) and the mixture was stirred at 40 °C for 6 h. Then the mixture was concentrated in vacuo and the residue was purified by column chromatography with 1:9 MeOH-$CHCl_3$ to give **15** (3.52 g, 92% from **14**) as colorless needles: mp 121–122 °C (from AcOEt) (lit.,[5] mp 123 °C, 47% yield); R_f = 0.14 (*A*); ^{1}H NMR δ = 2.00 (3H, s, NAc), 2.15, 2.90 (1H each, 2br s, HO-5,6), 3.36 (3H, s, MeO-1), 3.69 (1H, dd, $J_{6,6'}$ = 11.5, $J_{5,6'}$ = 5.1 Hz, H'-6), 3.83 (1H, dd, $J_{5,6}$ = 2.9 Hz, H-6), 4.02 (1H, ddd, $J_{4,5}$ = 9.3 Hz, H-5), 4.08 (1H, dd, $J_{3,4}$ = 6.4, $J_{2,3}$ = 0.9 Hz, H-3), 4.20 (1H, dd, H-4), 4.50 (1H, d, $J_{2,NH}$ = 7.9, $J_{1,2}$ = 0 Hz, H-2), 4.62, 4.92 (1H each, 2d, ^2J = 11.9 Hz, CH$_2$O-3), 4.80 (1H, s, H-1), 5.68 (1H, d, HN-2), 7.32 [1H, m, Ph(*p*)], 7.34–7.36 [4H, t, Ph(*o,m*)]; ^{13}C NMR δ = 23.21 (*C*H$_3$CO), 55.52 (MeO-1), 59.50 (C-2), 64.14 (C-6), 70.62 (C-5), 71.82 (CH$_2$O-3), 79.83 (C-4), 82.63 (C-3), 107.90 (C-1), 128.25 [Ph(*p*)], 128.25 [Ph(*o*)], 128.75 [Ph(*m*)], 137.08 [Ph(*ipso*)], 169.61 (CH$_3$*C*O).

Methyl 2-acetamido-5,6-anhydro-3-*O*-benzyl-2-deoxy-β-D-glucofuranoside (16).

By use of the same procedures described for **8** from **7**, compound **15** (2.90 g, 8.91 mmol) was treated with triphenylphosphine (2.83 g, 10.8 mmol) and DEAD (40% in toluene, 4.30 mL, 10.8 mmol) in toluene (60 mL) to give **16** (2.38 g, 87%) as colorless needles: mp 209–210 °C (from AcOEt-hexane); R_f = 0.36 (*A*); ^{1}H NMR δ = 1.97 (3H, s, NAc), 2.73 (1H, dd, $J_{6,6'}$ = 5.0, $J_{5,6'}$ = 2.6 Hz, H'-6), 2.90 (1H, dd, $J_{5,6}$ = 4.1 Hz, H-6), 3.41 (ddt, 1H, $J_{4,5}$ = 6.7 Hz, H-5), 3.41 (3H, s, MeO-1), 3.84 (1H, t, $J_{3,4}$ = 6.5, H-4), 4.23 (dd, $J_{2,3}$ = 2.1 Hz, H-3), 4.40 (dt, 1H, $J_{2,NH}$ = 7.6, $J_{1,2}$ = 1.2 Hz, H-2), 4.71, 4.81 (1H each, 2d, ^2J = 12.3 Hz, CH$_2$O-3), 4.83 (1H, d, H-1), 5.53 (1H, d, HN-2), 7.27 [1H, t, $J_{m,p}$ = 7.4 Hz, Ph(*p*)], 7.34 [2H, t, $J_{o,m}$ = 7.4 Hz, Ph(*m*)], 7.39 [2H, d, Ph(*o*)]; ^{13}C NMR δ = 23.24 (*C*H$_3$CO), 55.79 (MeO-1), 59.12 (C-2), 45.66 (C-6), 49.78 (C-5),

55.69 (MeO-1), 60.55 (C-2), 72.02 (CH_2O-3), 81.94 (C-4), 82.68 (C-3), 107.84 (C-1), 127.69 [Ph(*p*)], 127.79 [Ph(*o*)], 128.36 [Ph(*m*)], 137.78 [Ph(*ipso*)], 169.60 (CH_3CO). Anal. Calcd for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89. Found: C, 62.62; H, 6.93.

Methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucofuranoside (17a) and its 3,5-di-*O*-benzyl analog (17b).

A. From 16. By use of the same procedures described for **9a** from **8**, compound **16** (1.70 g, 5.53 mmol) was treated with benzyl alcohol (2.0 mL, 19.4 mmol) and sodium hydride (60% in mineral oil, 580 mg, 14.5 mmol) in DME (10 mL) to give **17a** (1.88 g, 82%).

B. From 15. To a solution of **15** (1.84 g, 5.65 mmol) in toluene (60 ml) was added dibutyltin oxide (1.72 g, 6.91 mmol) and then the suspension was refluxed under Dean-Stark trap for 15 h. After removal of the trap, benzyl bromide (1.35 mL, 11.4 mmol) and tetrabutylammonium iodide (1.05 g, 2.84 mmol) were added and the mixture was refluxed for 22 h. The mixture was evaporated in vacuo and the residue was separated by column chromatography on silica gel to give **17a** (1.70 g, 72%) and **17b** (430 mg, 18%).

17a: Colorless needles; mp 103–105 °C (from AcOEt-hexane); R_f = 0.42 (*A*); $[\alpha]_D^{26}$ –122.6 (*c* = 1.04, $CHCl_3$); ^{1}H NMR δ = 1.98 (3H, s, NAc), 2.92 (1H, d, $J_{5,OH}$ = 3.5 Hz, HO-5), 3.32 (3H, s, MeO-1), 3.63 (1H, dd, $J_{6,6'}$ = 10.3, $J_{5,6'}$ = 5.3 Hz, H'-6), 3.70 (1H, dd, $J_{5,6}$ = 3.1 Hz, H-6), 4.04 (1H, dd, $J_{3,4}$ = 6.2, $J_{2,3}$ = 0.9 Hz, H-3), 4.14 (ddt, 1H, $J_{4,5}$ = 8.8 Hz, H-5), 4.23 (dd, 1H, H-4), 4.47 (dd, 1H, $J_{2,NH}$ = 7.6, $J_{1,2}$ = 0 Hz, H-2), 4.54, 4.59 (1H each, 2d, ^2J = 12.3 Hz, CH_2O-6), 4.59, 4.87 (1H each, 2d, ^2J = 12.3 Hz, CH_2O-3), 4.77 (1H, s, H-1), 5.72 (1H, d, HN-2), 7.26–7.36 (10H, m, Ph). Anal. Calcd for $C_{23}H_{29}NO_6$: C, 66.49; H, 7.04. Found: C, 66.60; H, 6.99.

17b: Colorless syrup; R_f = 0.30 (*A*); ^{1}H NMR δ = 1.99 (3H, s, NAc), 3.05 (1H, br s, HO-6), 3.40 (3H, s, MeO-1), 3.80 (1H, d, $J_{6,6'}$ = 12.0, $J_{5,6'}$ = 3.0 Hz, H'-6), 3.92 (1H, dd, $J_{5,6}$ = 3.5 Hz, H-6), 3.99 (1H, dt, $J_{4,5}$ = 8.8 Hz, H-5), 4.03 (1H, dd, $J_{3,4}$ = 5.0, $J_{2,3}$ = 0.9 Hz, H-3), 4.28 (dd, 1H, H-4), 4.46, 4.52 (1H each, 2d, ^2J = 11.2 Hz, CH_2O-5), 4.50 (1H, d, $J_{2,NH}$ = 7.6, $J_{1,2}$ = 0 Hz, H-2), 4.59, 4.88 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-3), 4.84 (1H, s, H-1), 5.58 (d, 1H, HN-2), 7.26–7.36 (10H, m, Ph). Anal. Calcd for $C_{23}H_{29}NO_6$: C, 66.49; H, 7.04. Found: C, 66.68; H, 7.01.

Methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-*xylo*-hexofuranosid-5-ulose (18).

A. Oxidation with oxalyl chloride-DMSO. By use of the same procedures described for **10** from **9a**, compound **17a** (1.54 g, 3.71 mmol) was treated with oxalyl chloride (0.960 mL, 11.2 mmol) and DMSO (1.60 mL, 22.5 mmol) in CH_2Cl_2 (20 mL) to give **18** (1.44 g, 94%) as a colorless syrup: R_f = 0.37 (*A*); ^{1}H NMR δ = 1.99 (1H, s, NAc), 3.44 (3H, s, MeO-1), 4.28 (1H, d, $J_{3,4}$ = 6.2, $J_{2,3}$ = 0 Hz, H-3), 4.31, 4.37 (1H

each, 2d, $J_{6,6'}$ = 17.9 Hz, H_2-6), 4.33, 4.49 (1H each, 2d, ^2J = 11.7 Hz, CH_2O-6), 4.46 (1H, d, $J_{2,NH}$ = 7.3, $J_{1,2}$ = 0 Hz, H-2), 4.53, 4.77 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-3), 4.84 (1H, d, H-4), 4.95 (1H, s, H-1), 5.70 (1H, d, HN-2), 7.22–7.38 (10H, m, Ph); ^{13}C NMR δ = 23.10 (CH_3CO), 56.07 (MeO-1), 58.92 (C-2), 71.94 (CH_2O-3), 73.19 (CH_2O-6), 74.23 (C-6), 83.28 (C-3), 85.89 (C-4), 109.33 (C-1), 127.78 and 127.83 [Ph(*p*)], 127.86 and 128.09 [Ph(*o*)], 128.32 and 128.37 [Ph(*m*)], 137.11 and 137.36 [Ph(*ipso*)], 169.91 (CH_3CO), 205.11 (C-5). Anal. Calcd for $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58. Found: C, 66.54; H, 6.61.

B. Oxidation with PCC. To a suspension of PCC (1.38 g, 6.40 mmol) and finely powdered MS3A (2.0 g) in dry CH_2Cl_2 (20 mL) was added a solution of **17a** (1.10 g, 2.65 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred at rt for 6 h and then 2-propanol (5.0 mL) was added at 0 °C. The mixture was stirred for 30 min, diluted with ether, and filtered. The filtrate was evaporated in vacuo and the residue was purified by column chromatography to give **18** (930 mg, 85%).

Methyl (5*R*)- and (5*S*)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-5-*C*-dimethoxyphosphoryl-β-D-*xylo*-hexofuranosides (19).

By use of the same procedures described for **11** from **10**, compound **18** (1.37 g, 3.31 mmol) was treated with dimethyl phosphonate (15 mL) and DBU (0.75 mL, 5.0 mmol) to give (5*R*)-**19** (1.20 g, 69%) and (5*S*)-**19** (430 mg, 25%).

(5*R*)-**19**: Colorless prisms; mp 144–145 °C (from AcOEt); R_f = 0.35 (*B*); $[\alpha]_D^{26}$ –75.3 (*c* = 1.04, $CHCl_3$); ^{1}H NMR δ = 2.01 (3H, s, NAc), 3.39 (3H, s, MeO-1), 3.64, 3.68 (3H each, 2d, J_{POMe} = 10.7 Hz, POMe), 3.75 (1H, dd, $J_{6',P}$ = 12.5, $J_{6,6'}$ = 8.9 Hz H'-6), 3.90 (1H, dd, $J_{6,P}$ = 26.2 Hz, H-6), 4.28 (1H, d, $J_{3,4}$ = 4.9, $J_{2,3}$ = 0 Hz, H-3), 4.48 (1H, d, $J_{2,NH}$ = 7.4, $J_{1,2}$ = 0 Hz, H-2), 4.56, 4.90 (1H each, 2d, ^2J = 11.0 Hz, CH_2O-3), 4.59 (1H, d, $J_{4,P}$ = 0 Hz, H-4), 4.60, 4.63 (1H each, 2d, ^2J = 11.9 Hz, CH_2O-6), 4.86 (1H, d, $^5J_{1,P}$ = 1.0 Hz, H-1), 4.99 (1H, s, HO-5), 5.75 (1H, d, HN-2), 7.26-7.39 (10H, m, Ph); ^{31}P NMR δ = 26.21. Anal. Calcd for $C_{25}H_{34}NO_9P$: C, 57.36; H, 6.55. Found: C, 57.47; H, 6.52.

(5*S*)-**19**: Colorless syrup; R_f = 0.26 (*B*); $[\alpha]_D^{26}$ –74.0 (*c* = 3.47, $CHCl_3$); ^{1}H NMR δ = 2.01 (3H, s, NAc), 3.44 (3H, s, MeO-1), 3.55 (2H, dd, $J_{6',P}$ = 25.9, $J_{6,6'}$ = 9.2 Hz H'-6), 3.77, 3.85 (3H each, 2d, $J_{P,H}$ = 10.5 Hz, MeOP), 3.79 (2H, dd, $J_{6,P}$ = 10.9 Hz, H-6), 4.05 (1H, d, $J_{3,4}$ = 4.9, $J_{2,3}$ = 0 Hz, H-3), 4.26, 4.42 (1H each, 2d, ^2J = 11.9 Hz, CH_2O-6), 4.29 (1H, br s, HO-5), 4.30, 4.75 (1H each, 2d, ^2J = 11.6 Hz, CH_2O-3), 4.45 (1H, d, $J_{2,NH}$ = 7.3, $^5J_{2,P}$ = 1.2, $J_{1,2}$ = 0 Hz, H-2), 4.66 (1H, t, $J_{4,P}$ = 4.6 Hz, H-4), 4.95 (1H, s, H-1), 6.32 (1H, d, HN-2), 7.24–7.35 (10H, m, Ph); ^{31}P NMR δ = 24.84.

Methyl (5*R*)- and (5*S*)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-5-*C*-dimethoxyphosphoryl-5-*O*-methoxalyl-α-D-*xylo*-hexofuranosides (20).

By use of the same procedures described for **12** from **11**, compound **19** (74:26 diastereomeric mixture,

660 mg, 1.26 mmol) was treated with methoxalyl chloride (0.240 mL, 2.51 mmol) and DMAP (433 mg, 3.54 mmol) to give an inseparable diastereomeric mixture (74:26) of **20** (654 mg, 85%) as a colorless syrup: R_f = 0.40 (*B*).

(5*R*)-**20**: ^{1}H NMR δ = 1.96 (3H, s, NAc), 3.32 (3H, s, MeO-1), 3.70-3.82 (2H, m, H-6, 6'), 3.73, 3.79 (3H each, 2d, J_{POMe} = 11.2 Hz, POMe), 3.81 (3H, s, COOMe), 3.97 (1H, dd, $J_{3,4}$ = 5.3, $J_{2,3}$ = 1.2 Hz, H-3), 4.48 (1H, dd, $J_{2,NH}$ = 7.9, $J_{1,2}$ = 0 Hz, H-2), 4.51, 4.73 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-3 or 6), 4.54, 4.75 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-3 or 6), 4.85 (1H, d, $^5J_{1,2}$ = 1.1 Hz, H-1), 5.25 (1H, dd, $J_{4,P}$ =8.8 Hz, H-4), 5.97 (1H, d, HN-2), 7.25–7.38 (10H, m, Ph). Anal. Calcd for $C_{25}H_{34}NO_9P$: C, 57.36; H, 6.55. Found: C, 57.47; H, 6.52.

(5*S*)-**20**: ^{1}H NMR δ = 1.99 (3H, s, NAc), 3.25 (3H, s, MeO-1), 3.70-3.82 (2H, m, H-6, 6'), 3.70, 3.76 (3H each, 2d, J_{POMe} = 11.2 Hz, POMe), 3.87 (3H, s, COOMe), 4.07, 4.64 (1H each, 2d, ^2J = 10.9 Hz, CH_2O-3 or 6), 4.09, 4.68 (1H each, 2d, ^2J = 10.9 Hz, CH_2O-3 or 6), 4.13 (1H, dd, $J_{3,4}$ = 5.0, $J_{2,3}$ = 1.0 Hz, H-3), 4.45 (1H, dd, $J_{2,NH}$ = 9.4, $J_{1,2}$ = 0 Hz, H-2), 4.83 (1H, s, H-1), 5.13 (1H, dd, $J_{4,P}$ = 3.5 Hz, H-4), 5.92 (1H, d, HN-2), 7.25–7.38 (10H, m, Ph).

Methyl 2-acetamido-3,6-di-*O*-benzyl-2,5-dideoxy-5-dimethoxyphosphoryl-β-D-glucofuranoside (21a) and its α-L-idofuranoside analog (21b).

To a solution of **20** (695 mg, 1.14 mmol) in toluene (5 mL), a solution of AIBN (101 mg, 0.625 mmol) and tributyltin hydride (0.610 mL, 2.27 mmol) in dry toluene (3 ml) was dropwise added at 90 °C under argon. The mixture was stirred at the same temperature for 6 h and then concentrated in vacuo. The residue was separated by column chromatography with 1:9 EtOH-AcOEt into three fractions A–C.

Fraction A [R_f = 0.68 (*B*)] gave a pale yellow syrup which mainly consisted of **18** (53.5 mg, 12%).

Fraction B [R_f = 0.30 (*B*)] gave **21a** (249 mg, 43%) as colorless needles: mp 113–115 °C (from AcOEt); $[\alpha]_D^{29}$ –52.0 (*c* = 1.07, $CHCl_3$); ^{1}H NMR δ = 2.00 (3H, s, NAc), 2.89 (1H, dddd, $J_{5,P}$ = 19.5, $J_{4,5}$ = 9.4, $J_{5,6'}$ = 5.3, $J_{5,6}$ = 3.2 Hz, H-5), 3.35 (3H, s, MeO-1), 3.58, 3.64 (3H each, 2d, J_{POMe} = 10.9 Hz, POMe), 3.90–3.96 (2H, m, H,H'-6), 3.96 (d, 1H, $J_{3,4}$ = 4.2, $J_{2,3}$ = 0 Hz, H-3), 4.43 (1H, dd, $J_{2,NH}$ = 7.6, $J_{1,2}$ = 1.2 Hz, H-2), 4.50, 4.84 (1H each, 2d, ^2J = 11.7 Hz, CH_2O-3), 4.54, 4.58 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-6), 4.55 (1H, ddd, $J_{4,P}$ = 7.3 Hz, H-4), 4.79 (1H, d, $^5J_{1,P}$ = 1.2 Hz, H-1), 5.94 (1H, d, HN-2), 7.25–7.37 (10H, m, Ph); ^{13}C NMR δ = 23.19 (CH_3CO), 37.50 (d, $^1J_{5,P}$ = 136.9 Hz, C-5), 52.21 (d, $^2J_{C,P}$ = 6.7 Hz, POMe), 52.80 (d, $^2J_{C,P}$ = 6.2 Hz, POMe), 55.79 (MeO-1), 59.12 (C-2), 66.96 (d, $^2J_{6,P}$ = 8.4 Hz C-6), 71.61 (CH_2O-3), 73.35 (CH_2O-6), 77.82 (d, $^2J_{4,P}$ = 5.6 Hz, C-4), 82.30 (d, $^3J_{3,P}$ = 2.3 Hz, C-3), 108.33 (C-1), 127.44 and 127.48 [Ph(*p*)], 127.60 and 127.83 [Ph(*o*)], 128.17 and 128.22 [Ph(*m*)], 138.02 and 138.19 [Ph(*ipso*)], 169.75 (CH_3CO); ^{31}P NMR δ = 32.25. Anal. Calcd for $C_{25}H_{34}NO_8P$: C, 59.16; H, 6.75. Found: C, 59.04; H, 6.78.

Fraction C [R_f = 0.25 (*B*)] gave **21b** (105 mg, 18%) as a colorless syrup; $[\alpha]_D^{29}$ –92.6 (*c* = 2.79, $CHCl_3$); ^{1}H NMR δ = 2.01 (3H, s, NAc), 2.70 (1H, dddd, $J_{5,P}$ = 18.2, $J_{4,5}$ = 10.6, $J_{5,6'}$ = 3.5, $J_{5,6}$ = 2.9 Hz, H-5), 3.31 (1H, ddd, $J_{6',P}$ = 31.7, $J_{6,6'}$ = 9.7 Hz, H'-6), 3.40 (3H, s, MeO-1), 3.68 (1H, d, $J_{3,4}$ = 4.4, $^4J_{3,P}$ = 1.2, $J_{2,3}$ = 0 Hz, H-3), 3.69 (1H, ddd, $J_{6,P}$ = 10.7 Hz, H-6), 3.70, 3.75 (3H each, 2d, J_{POMe} = 10.9 Hz, POMe), 4.15, 4.29 (1H each, 2d, ^2J = 12.0 Hz, CH_2O-6), 4.40, 4.80 (1H each, 2d, ^2J = 11.7 Hz, CH_2O-3), 4.41 (1H, dd, $J_{2,NH}$ = 7.3, $^5J_{2,P}$ = 1.5, $J_{1,2}$ = 0 Hz, H-2), 4.48 (1H, ddd, $J_{4,P}$ = 7.0 Hz, H-4), 4.89 (1H, s, H-1), 6.19 (1H, d, HN-2), 7.20–7.33 (10H, m, Ph); ^{13}C NMR δ = 23.10 (CH_3CO), 38.43 (d, $^1J_{5,P}$ = 142.5 Hz, C-5), 52.22 (d, $^2J_{C,P}$ = 7.3 Hz, POMe), 52.80 (d, $^2J_{C,P}$ = 6.2 Hz, POMe), 55.73 (MeO-1), 58.76 (C-2), 66.36 (d, $^2J_{6,P}$ = 7.3 Hz C-6), 70.84 (CH_2O-3), 73.07 (CH_2O-6), 78.35 (d, $^2J_{4,P}$ = 3.9 Hz, C-4), 80.44 (d, $^3J_{3,P}$ = 11.8 Hz, C-3), 108.38 (C-1), 127.66 and 127.75 [Ph(*p*)], 127.77 and 128.25 [Ph(*o*)], 128.25 and 128.60 [Ph(*m*)], 137.34 and 137.74 [Ph(*ipso*)], 169.89 (CH_3CO); ^{31}P NMR δ = 33.29. Anal. Calcd for $C_{25}H_{34}NO_8P$: C, 59.16; H, 6.75. Found: C, 58.98; H, 6.72.

2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2,5-dideoxy-5-methoxyphosphoryl-D-glucopyranoses (25a–d).

To a solution of **21a** (103 mg, 0.203 mmol) in dry toluene (2.0 mL) was added, with stirring, a solution of 0.34 M SDMA in toluene (2.5 mL, 0.85 mmol) in small portions at –5 °C under argon. The stirring was continued at this temperature for 1.5 h and diluted with benzene. Then, water (0.10 mL) was added to decompose excess SDMA and the mixture was centrifuged. The precipitate was extracted with several portions of benzene. The organic layers were combined and evaporated in vacuo, giving the 5-deoxy-5-phosphino derivative (**22**) as a colorless syrup: R_f = 0.44 (*B*).

This syrup was immediately treated with 1:1 2-propanol–0.5 M hydrochloric acid (3.0 mL) at 90 °C for 1 h under argon. After cooling, the mixture was evaporated in vacuo. The residue was dissolved in MeOH (1.0 mL), treated with 30% hydrogen peroxide (0.6 mL, 5.9 mmol) at rt for 12 h and then concentrated in vacuo. The residue was dissolved in MeOH (1.0 mL), treated with propylene oxide (0.5 mL) at rt for 2 h, and evaporated in vacuo to give crude 5-deoxy-5-hydroxyphosphoryl-D-glucopyranose derivatives (**23**) as a colorless syrup.

This was dissolved in dry pyridine (1.5 mL), and acetic anhydride (0.6 mL, 6.3 mmol) was added at 0 °C. The mixture was stirred at rt for 15 h, diluted with a small amount of cold water, and concentrated in vacuo. The residue was dissolved in methanol and passed through a column of Amberlite IR-120(H^+) (10 mL). The eluent was evaporated in vacuo and the residue was methylated with (trimethylsilyl)diazomethane (2M in ether, 0.40 mL, 0.80 mmol) in dry CH_2Cl_2 (1.0 mL) at rt for 3 h. After evaporation of the solvent, the residue was purified by column chromatography with 1:1 EtOH-AcOEt to give an inseparable mixture of the 2-acetamido-3,6-*O*-dibenzyl-2,5-dideoxy-5-methoxyphosphoryl derivatives (**24**) as a colorless syrup: R_f = 0.30–0.25 (*B*).

The compounds **24** dissolved in 1:1 EtOH-AcOEt (2.0 mL) was hydrogenated in the presence of 20% $Pd(OH)_2$-C (3.0 mg) at rt under atmospheric pressure of hydrogen. After 24 h, the catalyst was filtered off and the filtrate was evaporated in vacuo. The residue was acetylated again with dry pyridine (1.0 mL) and acetic anhydride (0.20 mL). The mixture was evaporated in vacuo and the residue was sepalated by column chromatography with a gradient eluent of AcOEt to 1:9 EtOH-AcOEt into two fractions.

The faster-elutiong fraction [R_f = 0.36–0.32 (*B*)] gave a colorless syrup (17.5 mg), which consisted of the 5-[(*R*)-methoxyphosphoryl]-α-D-glucopyranose (**25a**) (7.5% from **21a**) and its 5-[(*S*)-P]-α-isomer (**25c**) (11.6%), the ratio being estimated by 1H NMR: ^{1}H and ^{31}P NMR, see Table 1. HRMS (FAB): *m/z* calcd for $C_{17}H_{27}NO_{11}P$ $[M + H]^+$ 452.1322, found 452.1333.

The slower-eluting fraction [R_f = 0.34–0.30 (*B*)] gave a colorless syrup (11.2 mg) which consisted of **25c** (7.2% from **21a**), 5-[(*R*)-P]-β-isomer (**25b**) (2.7%), and its 5-[(*S*)-P]-β-isomer (**25d**) (2.3%), the ratio being estimated by ^{1}H NMR: ^{1}H and ^{31}P NMR, see Table 1.

2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2,5-dideoxy-5-methoxyphosphoryl-L-idopyranoses (29a–d).

The procederes similar to those for preparation of compounds **25** from **21a** were employed. Thus, compound **13b** (101 mg, 0.206 mmol) were converted into the diasteromeric L-idopyranoses (**29**) via intermediates **26**, **27**, and **28**. The crude product **29** was separated by column chromatography into two fractions.

The faster-eluting fraction [R_f = 0.26–0.22 (*B*)] gave a colorless syrup (10.2 mg), which consisted of the 5-[(*R*)-methoxyphosphoryl]-β-L-idopyranose (**29a**) (3.4% from **13a**), its 5-[(*R*)-P]-α-isomer (**29b**) (4.3%), and 5-[(*S*)-P]-β-isomer (**29c**) (3.2%), the ratio being estimated by ^{1}H NMR: ^{1}H and ^{31}P NMR, see Table 1. HRMS (FAB): *m/z* calcd for $C_{17}H_{27}NO_{11}P$ $[M + H]^+$ 452.1322, found 452.1311.

The slower-eluting fraction [R_f = 0.24–0.20 (*B*)] gave a colorless syrup (8.5 mg) which consisted of **29b** (4.0% from **13b**), its 5-[(*S*)-P]-β-isomer (**29c**) (2.2%), and 5-[(*S*)-P]-α-isomer (**29d**) (3.0%), the ratio being estimated by ^{1}H NMR: ^{1}H and ^{31}P NMR, see Table 1.

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