Synthesis of 2-Amino-2,5,6-trideoxy-5-phenylphosphinyl-L-galactopyranose. The P-in-the-Ring Analogue of L-Fucosamine

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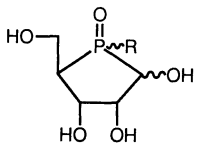
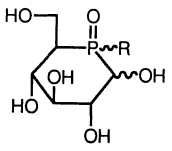
3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-allofuranose was led to methyl (5*R* and 5*S*)-3-*O*-benzyl-5,6-dideoxy-5-[(methoxy)phenylphosphinyl]-D-*ribo*-hexofuranoside (**9**) in a 4 step sequence (55% overall yield). Methyl (5*R* and 5*S*)-2-acetamido-2,5,6-trideoxy-5-[(methoxy)phenylphosphinyl]-D-*arabino*-hexofuranoside (**12**) was prepared from **9** in 4 steps involving a C-2 inversion (62% overall yield). Compound **12** was then converted, in 2 steps, into the title compound, which was characterized as the peracetyl derivatives.

We have prepared various sugar analogues having a phosphorus atom in the hemiacetal ring[1] because of a significant interest in their chemical and biochemical properties. Thus, a large number of P-in-the-ring sugar analogues were synthesized, such as those of D-ribofuranose **1**,[2] D-glucopyranose **2**,[3] and 6-deoxy-L-galactopyranose (L-fucose) **3**.[4] However, no such analogues of an amino sugar type have been reported yet, whereas some 2-amino-2,6-dideoxyhexoses have long been known to occur in nature; for instance, L-fucosamine (**4**) has been identified as a component of the antigenic lipopolysaccharide of the Pseudomonas species.[5] We wish to describe herein a convenient synthesis of 2-amino-2,5,6-trideoxy-5-phenylphosphinyl-L-galactopyranose (a P-in-the-ring analogue of **4**) as the first example of an amino sugar type by employing phenylphosphinyl as a model functional group.



1 (R = Ph, Et, OH)



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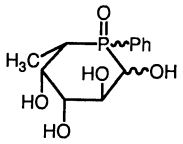
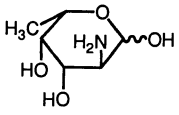
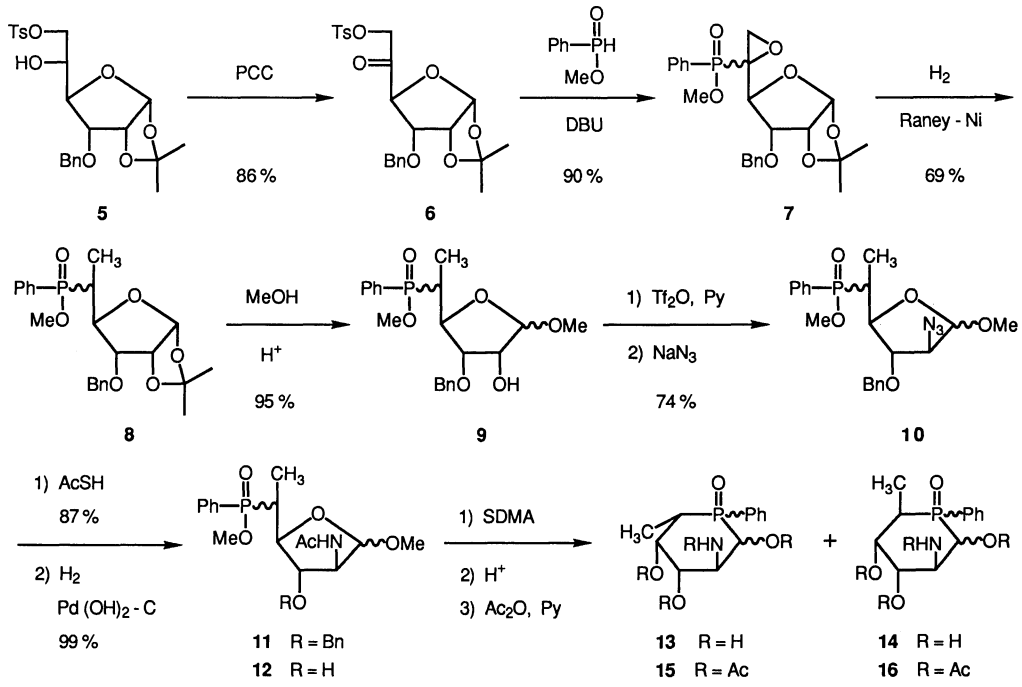


3



4

Treatment of 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-allofuranose (**5**)[6] with pyridinium chlorochromate (PCC) gave the 5-ulose derivative **6** (Scheme 1). The reaction of **6** with methyl phenylphosphinate in 1,2-dimethoxyethane in the presence of DBU yielded 5,6-



Scheme 1.

anhydro-5-[(methoxy)phenylphosphinyl] compound **7**. Hydrogenation of **7** in the presence of Raney Ni (W-4) in ethanol afforded the 5,6-dideoxy derivative **8**.

Compound **8** was treated with methanol in the presence of acidic ion-exchange resin to give methyl glycoside **9**. It was then led to the 2-*O*-trifluoromethanesulfonate to introduce an azido group with C-2 inversion, affording methyl D-*arabino*-hexofuranoside **10**. Azide **10** was easily led to the 2-acetamido derivative **11** upon treatment with thiolacetic acid or by hydrogenation in the presence of 10% Pd on carbon, followed by acetylation. Debenzylation of **11** by catalytic hydrogenation over 20% $Pd(OH)_2$–C provided furanoside **12**.

Then, compound **12** was reduced with sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA), followed by acid hydrolysis, to afford a mixture of 2,5,6-trideoxy-2-amino-5-phenylphosphinyl-L-galactopyranose (**13**) and D-altropyranose (**14**). These were converted into their tetraacetyl derivatives, which were purified by column chromatography over silica gel with 19 : 1 (v/v) ethyl acetate–ethanol, thus affording 2-acetamido-1,3,4-tri-*O*-acetyl-2,5,6-trideoxy-5-[(*R*)-phenylphosphinyl]-α-L-galactopyranose (**15a**, 7.2% overall yield from **12**), its β-anomer **15b** (5.2%), 2-acetamido-1,3,4-tri-*O*-acetyl-2,5,6-trideoxy-5-[(*S*)-phenylphosphinyl]-α-D-altropyranose (**16a**, 1.0%), its β-anomer **16b** (5.5%), and 5-[(*R*)-*P*]-α-isomer **16c** (1.6%).

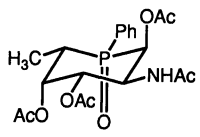
The precise structures of **15a, b** and **16a—c** were established by analysis of their 500-MHz ^1H NMR spectra; for all the assignments of the signals, see Table 1. The $^1C_4$ conformation of **15a, b** and **16c** are derived from the large values of $J_{4,P}$ (26—29 Hz) and $J_{2,3}$ (ca. 11 Hz) and small values of $J_{2,P}$ (0—4 Hz).[4] In contrast, the opposite magnitudes ($J_{4,P}$=ca. 4, $J_{2,3}$=3—5, $J_{2,P}$=24—27 Hz) of **16a, b** suggest the $^4C_1$ conformation. The small $J_{5,P}$ values for **15a, b** and **16a, b** indicate the axial orientation of H-5 and the ring P=O group,[3,4] whereas the equatorial H-5 orientation of **16c** is assigned by the large $J_{5,P}$ value. Since a similar argument can be applied to $J_{1,P}$ values, the anomeric orientation at C-1 is readily perceived by these values as well as those of $J_{1,2}$. It is noteworthy that a considerable downfield shift (δ=1.6—2.0) is observed for the signals of axial HN-2 group (for **16a, b**) in the vicinity of axial P=O group compared with those of equatorial HN-2 group (for **15a, b** and **16c**).

Although improvement of the yields of the final ring enlargement reactions and isolation of other minor isomers of **15** and **16** remain to be done, the present work demonstrates a convenient way for preparation of the P-in-the-ring analogue of 2-amino-2,6-dideoxyhexoses and this scheme is expected to be readily applicable for preparation of various other amino sugar analogues.

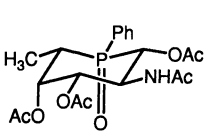
Experimental

Melting points were determined with a Yanagimoto MP-S3 instrument and are uncorrected. All reactions were monitored by TLC (Merck silica gel 60F, 0.25 mm) with an appropriate solvent system [(*A*) 1 : 1 AcOEt–hexane, (*B*) 19 : 1 AcOEt–EtOH, or (*C*) 19 : 1 $CHCl_3$–MeOH]; components were detected by exposing the plates to UV light and/or by spraying them with 20% sulfuric acid–ethanol, with subsequent heating. Column chromatography was performed by Wako C-200 silica gel. The IR spectra were taken with a Hitachi 260-10S

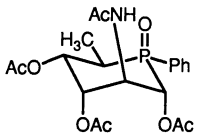
Table 1. ^1H and ^{31}P NMR Parameters for **15a, b** and **16a—c** in $CDCl_3$



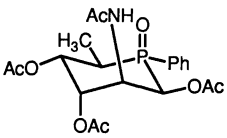
15a



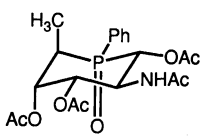
15b



16a



16b



16c

Compd	Chemical shifts/δ									
	H-1	H-2	H-3	H-4	H-5	H-6	NH-2	Ac-1,2,3,4[a]	Ph(*o,m,p*)[b]	^{31}P
15a	5.70	5.36	5.30	5.71	2.66	1.17	5.50	2.27, 2.06, 1.92, 1.91	7.73, 7.51, 7.63	29.2
15b	5.58	5.11	5.31	5.64	2.31	1.14	5.53	2.26, 2.05, 1.97, 1.91	7.77, 7.52, 7.59	29.8
16a	5.16	4.84	5.45	5.63	2.98	1.12	7.17	2.16, 2.08, 2.03, 1.97	7.79, 7.56, 7.65	38.9
16b	5.78	4.85	5.57	5.54	2.55	1.08	7.49	2.23, 2.10, 2.03, 1.92	7.75, 7.57, 7.65	37.0
16c	5.96	5.22	5.41	5.42	2.71	1.05	5.47	2.26, 2.08, 2.00, 1.93	7.73, 7.52, 7.59	32.3

Compd	Coupling constants/Hz										
	$J_{1,2}$	$J_{1,P}$	$J_{2,3}$	$J_{2,P}$	$J_{2,NH}$	$J_{3,4}$	$J_{3,P}$	$J_{4,5}$	$J_{4,P}$	$J_{5,6}$	$J_{5,P}$	$J_{6,P}$
15a	2.5	10.5	11.4	0	8.7	2.6	0	2.6	27.6	7.3	6.5	14.8
15b	11.7	3.3	10.8	4.4	8.9	2.5	0	2.5	28.9	7.1	3.0	14.4
16a	2.9	9.1	3.0	24.3	8.5	3.0	1.0	11.9	4.2	7.1	4.5	15.5
16b	4.8	3.2	4.7	27.0	8.5	2.6	1.5	12.0	3.6	7.0	3.1	15.1
16c	11.4	3.0	10.6	3.5	9.6	2.5	0	4.0	26.1	8.0	19.4	16.4

a) The assignment of acetyl signals may be interchanged. b) *J* values for *P*-Ph: $J_{P,o}$=12.5, $J_{P,m}$=3.5, $J_{P,p}$=1.5, $J_{o,m}$=$J_{m,p}$=7.5 and $J_{o,p}$=1.5 Hz.

infrared spectrophotometer. The ^1H and ^{31}P NMR spectra were measured in $CDCl_3$ with Varian VXR-500 and VXR-200 instruments (500 and 81 MHz, respectively, the SC-NMR Lab., Okayama Univ. at 21 °C) or with a Hitachi R-1900 instrument (90 MHz, FT). Chemical shifts are reported as δ values relative to tetramethylsilane (internal standard for ^1H) and 85% phosphoric acid (external standard for ^{31}P). The mass spectra were taken on an A.E.I. MS 50 ultrahigh resolution instrument and were given in terms of m/z (rel intensity) compared with the base peak.

3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-*ribo*-hexofuranos-5-ulose (6). To a suspension of **5**[6] (1.10 g, 2.38 mmol) and finely powdered molecular sieves 3A (2.4 g) in dry CH_2Cl_2 (20 ml) was added PCC (1.54 g, 7.14 mmol) at 0 °C. The mixture was stirred at 20 °C for 6 h and then 2-propanol (6 ml) was added at 0 °C. The mixture was stirred at 20 °C for 1 h and diluted with ether. The precipitates were filtered off through celite. The filtrate was evaporated in vacuo and the residue was purified by short-path column chromatography with 1 : 1 AcOEt–hexane as an eluant, giving **6** (0.99 g, 90%) as a colorless syrup: R_f=0.59 (*A*); IR (neat) ν 1740 (C=O), 1350 (ν_{as} SO_2), 1170 cm^{-1} (ν_s SO_2); ^1H NMR (500 MHz) δ=1.35, 1.57 (3H each, 2s, CMe_2), 2.43 (3H, s, MeC_6-S), 3.84 (1H, dd, $J_{3,4}$=9.1, $J_{2,3}$=4.2 Hz, H-3), 4.52 (1H, t, $J_{1,2}$=3.5 Hz, H-2), 4.53 (1H, d, H-4), 4.64, 4.71 (1H each, 2d, J=12.0 Hz, CH_2O-3), 4.84, 4.86 (1H each, 2d, $J_{6,6'}$=17.7 Hz, H-6,6'), 5.77 (1H, d, H-1), 7.33, 7.81 (2H each, 2d, J=8.1 Hz, C_6H_4-S), 7.32—7.37 (5H, m, Ph).

(5*R* and 5*S*)-5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α-D-*ribo*-hexofuranoses (7). To a solution of **6** (2.89 g, 6.24 mmol) and methyl phenylphosphinate (1.24 ml, 9.34 mmol) in DME (20 ml) was dropwise added a solution of DBU (0.98 ml, 6.57 mmol) in DME (7.0 ml) at −40 °C. The mixture was stirred at the same temp for 1 h and then concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and saturated aq $NaHCO_3$ was added. After having been stirred at 20 °C overnight, the organic layer was separated and the aq layer was extracted twice with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed in a column of silica gel, giving **7** (2.43 g, 87%) as a colorless syrup: R_f=0.15 (*A*); ^{31}P NMR δ=32.1, 33.1, 35.2, and 36.1 (in a ratio of 18 : 35 : 31 : 16, respectively); ^1H NMR (500 MHz) for the two major components of **7** δ=1.32, 1.35,* 1.44, 1.58* (6H, 4s, CMe_2), 2.95,* 2.97 (1H, d,* dd, $J_{6',P}$=4.9,* 4.1, $J_{6,6'}$=5.7 Hz, H-6'), 2.95,* 3.26 (1H, d,* t, $J_{6,P}$=4.9,* 4.8 Hz, H-6), 3.63, 3.74* (1H, 2dd, $J_{3,4}$=8.8, 8.5,* $J_{2,3}$=4.4 Hz, H-3), 3.78,* 3.80 (3H, 2d, J_{POMe}=10.8 Hz, POMe), 4.30, 4.59* (1H, 2d, $J_{4,P}$=2.5, 4.2* Hz, H-4), 4.42, 4.48,* 4.63, 4.71* (2H, 4d, J=11.3 Hz, CH_2O-3), 4.51, 4.54* (1H, 2td, $J_{1,2}$=3.7, $^5J_{2,P}$=1.5 Hz, H-2), 5.70,* 5.71 (1H, 2d, H-1), 7.30—7.57 [8H, m, Ph-*C*, Ph(*m*,*p*)-*P*], 7.83,* 7.91 [2H, m, $J_{o,P}$=12.2, $J_{o,m}$=7.1, $J_{o,P}$=1.4 Hz, Ph(*o*)-*P*], for the two minor components of **7** δ=1.29, 1.36,* 1.46, 1.56* (6H, 4s, CMe_2), 2.33, 3.01* (1H, 2dd, $J_{6'P}$=6.2, 2.6,* $J_{6,6'}$=5.2, 5.6* Hz, H-6'), 2.87, 3.26* (1H, 2t, $J_{6,P}$=5.2, 4.8* Hz, H-6), 3.56, 3.78* (3H, 2d, J_{POMe}=10.8 Hz, POMe), 3.75—3.80 (1H, m, H-3), 3.91, 4.57* (1H, dd, m,* $J_{4,P}$=15.1, $J_{3,4}$=8.1 Hz, H-4), 4.48, 4.57* (1H, 2m, H-2), 4.56, 4.57,* 4.71, 4.74* (2H, 4d, J=12.0 Hz, CH_2O-3), 5.21, 5.86* (1H, 2d, $J_{1,2}$=3.4 Hz, H-1), 7.30—7.57 [8H, m, Ph-*C*, Ph(*m*,*p*)-*P*], 7.71, 7.79* [2H, m, Ph(*o*)-*P*].

* For another diastereomer with regard to the phosphorus atom; the assignment of some of the δ values may have to be interchanged.

(5*R* and 5*S*)-3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α-D-*ribo*-hexofuranoses (8). Compound **7** (832 mg, 1.86 mmol) dissolved in ethanol (8 ml) was hydrogenated in the presence of Raney-Ni (W-4) (1.65 g) at 20 °C under an atmospheric pressure of H_2. After 8 h, the catalyst was filtered off through celite, and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel to give **8** (555 mg, 69%) as a colorless syrup: R_f=0.11 (*A*); ^1H NMR (90 MHz) δ=0.97, 1.01 (3H, 2dd, $J_{6,P}$=16.5, $J_{5,6}$=7.3 Hz, H_3-6), 1.25, 1.29, 1.32, 1.37, 1.48, 1.50 (6H, 6s, CMe_2), 2.20—2.50 (1H, m, H-5), 3.59, 3.64, 3.66, 3.67 (3H, 4d, J_{POMe}=11.8 Hz, POMe), 3.90—4.35 (2H, m, H-3,4), 4.40—4.80 (3H, m, H-2, CH_2O-3), 5.53, 5.68, 5.74 (1H, 3d, $J_{1,2}$=3.5 Hz, H-1), 7.33 (5H, m, Ph-*C*), 7.35—7.80 (5H, m, Ph-*P*); ^{31}P δ=46.4, 35.7, 45.1 (33 : 31 : 35); MS m/z 432 (M^+; 0.4), 341(29), 326(7), 309(6), 283(15), 213(24), 184(33), 155(51), 91(100). Found: m/z 432.1709. Calcd for $C_{23}H_{29}O_6P$: M, 432.1703.

Methyl (5*R* and 5*S*)-3-*O*-Benzyl-5,6-dideoxy-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α(and β)-D-*ribo*-hexofuranosides (9). A mixture of **8** (455 mg, 1.05 mmol) and Amberlite IR-120B (H^+) ion exchange resin (2 ml) in abs methanol (8 ml) was refluxed for 2 h. After cooling, the resin was filtered off and the filtrate was evaporated in vacuo. The residue was purified by column chromatography with a gradient eluant of $CHCl_3$→ 5% MeOH–$CHCl_3$, giving **9** (407 mg, 95%) as a colorless syrup: R_f=0.40—0.36 (*C*); ^1H NMR (90 MHz) δ=1.07, 1.10, 1.25 (3H, 3dd, $J_{6,P}$=17.4, $J_{5,6}$=7.3 Hz, H_3-6), 2.05—2.45 (1H, m, H-5), 2.80—3.20 (1H, m, HO-2), 3.02, 3.17, 3.20, 3.33 (3H, 4s, MeO-1), 3.60, 3.62, 3.64, 3.66 (3H, 4d, J_{POMe}=11.7 Hz, POMe), 3.75—4.40 (3H, m, H-2,3,4), 4.50—4.71 (3H, m, H-1, CH_2O-3), 7.30—7.85 (5H, m, Ph-*P*), 7.33 (5H, m, Ph-*C*).

Methyl (5*R* and 5*S*)-2-Azido-3-*O*-benzyl-2,5,6-trideoxy-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α(and β)-D-*arabino*-hexofuranosides (10). To a solution of **9** (377 mg, 0.928 mmol), 4-dimethylaminopyridine (6.0 mg, 0.05 mmol) and dry pyridine (0.30 ml, 3.7 mmol) in CH_2Cl_2 (5 ml) was added trifluoromethanesulfonic anhydride (0.30 ml, 1.8 mmol) at −40 °C over a period of 30 min. The stirring was continued at this temp for 1 h and then water (0.5 ml) was added. The organic layer was separated and aq layer was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated in vacuo. The residue was dissolved in DMF (2.5 ml) and sodium azide (300 mg, 4.6 mmol) was added. The mixture was stirred at 40 °C for 36 h. The precipitate was filtered off and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and washed with water, dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed on silica gel using 5% methanol–chloroform as the eluant, giving **10** (295 mg, 74%) as a colorless syrup: R_f=0.40 (*C*); IR (neat) ν 2100 cm^{-1} (N_3); ^1H NMR (90 MHz) δ=0.98, 1.04, 1.23, 1.48 (3H, 4dd, $J_{6,P}$=16.3, $J_{5,6}$=7.5 Hz, H_3-6), 2.05—2.45 (1H, m, H-5), 3.03, 3.20, 3.32, 3.33, 3.35 (3H, 5s, MeO-1), 3.60, 3.62, 3.63, 3.65, 3.68 (3H, 5d, J_{POMe}=11.0 Hz, POMe), 3.70—3.95 (1H, m, H-3), 3.95—4.40 (2H, m, H-2,4), 4.50—4.95 (3H, m, H-1, CH_2O-3), 7.30—7.85 (5H, m, Ph-*P*), 7.33 (5H, m, Ph-*C*); MS m/z 400 ($M-CH_3O$; 0.6), 316(3), 251(25), 155(42), 91(100). Found: m/z 400.1426. Calcd for $C_{20}H_{23}N_3O_4P$: $M-CH_3O$, 400.1426.

Methyl (5*R* and 5*S*)-2-Acetamido-3-*O*-benzyl-2,5,6-trideoxy-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α(and β)-D-*arabino*-hexofuranosides (11). A. A mixture of azide **10** (456 mg, 1.06 mmol) and thioacetic acid (0.47 ml, 6.6 mmol) was stirred

at room temp for 30 h under argon. The excess thioacetic acid was removed under reduced pressure. The resulting syrup was chromatographed in a column of silica gel, giving **11** (411 mg, 87%) as a colorless syrup: R_f=0.33—0.28 (*C*). Recrystallization of this mixture from AcOEt–hexane gave one pure diastereomer as colorless prisms (62 mg): Mp 190—191 °C; ^{1}H NMR (500 MHz) δ=1.21 (3H, dd, $J_{6,P}$=16.4, $J_{5,6}$=7.3 Hz, H_3-6), 1.99 (3H, s, AcN-2), 2.28 (1H, dquint, $J_{5,P}$=14.7, $J_{4,5}$=7.0 Hz, H-5), 3.15 (3H, s, MeO-1), 3.64 (3H, d, J_{POMe}=10.9 Hz, POMe), 3.94 (2H, m, H-3,4), 4.51, 4.71 (1H each, 2d, J=11.1 Hz, CH_2O-3), 4.58 (1H, ddd, $J_{2,NH}$=8.8, $J_{2,3}$=6.1, $J_{1,2}$=4.9 Hz, H-2), 4.71 (1H, d, H-1), 6.06 (1H, d, NH-2), 7.31 (5H, m, Ph-*C*), 7.43 [2H, m, $J_{o,m}$=$J_{m,p}$=7.5, $J_{m,P}$=3.3 Hz, Ph(*m*)-*P*], 7.51 [1H, m, $J_{o,p}$=$J_{p,P}$=1.4 Hz, Ph(*p*)-*P*], 7.75 [2H, m, $J_{o,P}$=11.4 Hz, Ph(*o*)-*P*]; ^{31}P NMR δ=45.5; MS *m*/*z* 416 (M−CH_3O; 0.3), 356 (M−$PhCH_2$; 0.2), 341(3), 324(5), 296(7), 254(10), 184(28), 155(34), 91(100). Found: *m*/*z* 416.1621. Calcd for $C_{22}H_{27}NO_5P$: M−CH_3O, 416.1627.

B. Compound **10** (33 mg, 0.076 mmol) dissolved in ethanol (0.3 ml) was hydrogenated in the presence of 10% Pd–C (40 mg) at 20 °C under an atmospheric pressure of H_2. After 4 h, the catalyst was filtered off through celite, and the filtrate was evaporated in vacuo to give 2-amino-2-deoxy derivative as a colorless syrup. This was dissolved in dry pyridine (0.06 ml) and acetic anhydride (0.03 ml) was added at 0 °C. After stirring at 20 °C overnight, cold water was added. The mixture was evaporated in vacuo and the residue was chromatographed on silica gel to give **11** (28 mg, 82%).

Methyl (5*R* and 5*S*)-2-Acetamido-2,5,6-trideoxy-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α(and β)-D-*arabino*-hexofuranosides (12). Compound **11** (110 mg, 0.246 mmol) dissolved in ethanol (2 ml) was hydrogenated in the presence of 20% $Pd(OH)_2$–C (80 mg) at room temp under an atmospheric pressure of H_2. After 6 h, the catalyst was filtered off through celite, and the filtrate was evaporated in vacuo. The residue was purified by short-path column chromatography to give **12** as a colorless syrup (87 mg, 99%): R_f=0.15 (*C*); ^{1}H NMR (90 MHz) δ=0.92, 1.11, 1.22, 1.28 (3H, 4dd, $J_{6,P}$=16.5, $J_{5,6}$=7.5 Hz, H_3-6), 1.97, 1.98, 2.00 (3H, 3s, AcN-2), 2.05—2.45 (1H, m, H-5), 3.20, 3.25, 3.30 (3H, 3s, MeO-1), 3.25—3.50 (1H, m, HO-3), 3.59, 3.64, 3.69 (3H, 3d, J_{POMe}=11.0 Hz, POMe), 3.70—4.25 (2H, m, H-3,4), 4.25—4.80 (2H, m, H-1,2), 6.10—6.35 (1H, m, NH-2), 7.35—7.80 (5H, m, Ph-*P*).

2-Acetamido-1,3,4-tri-*O*-acetyl-2,5,6-trideoxy-5-[(*R* and *S*)-phenylphosphinyl]-α(and β)-L-galactopyranoses (15) and D-Altropyranoses (16). To a solution of **12** (192 mg, 0.537 mmol) in dry benzene (3 ml) was added, with stirring, a solution of SDMA (3.4 M in toluene, 0.75 ml, 4.8 equiv) in dry benzene (2 ml), in small portions at 5 °C under argon. The mixture was stirred at this temp for 2 h, and then water (0.5 ml) was added. The mixture was centrifuged and the precipitate was extracted with several portions of benzene. The organic layers were combined and evaporated in vacuo. The residue was immediately treated with 1 : 1 2-propanol–0.5 M hydrochloric acid (6.0 ml) (1 M=1 mol dm^{-3}) at 90 °C for 3 h under argon. After cooling, the reactants were neutralized with Amberlite IRA-45. The resin was filtered off and washed with aq ethanol. The filtrate was evaporated in vacuo to give a mixture of 2-amino-2,5,6-trideoxy-5-[(*R* and *S*)-phenylphosphinyl]-α(and β)-L-galactopyranoses (**13**) and D-altropyranoses (**14**) as a colorless syrup.

This was dissolved in dry pyridine (4.0 ml) and acetic anhydride (2.0 ml) at 0 °C. The mixture was stirred at 20 °C overnight, diluted with a small amount of cold water, and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and evaporated in vacuo, giving a mixture of tetraacetates **15** and **16**, which were separated by column chromatography with a gradient eluant of AcOEt→19 : 1 AcOEt–EtOH into three fractions A—C.

Fraction A [R_f=0.36 (*B*)] gave a colorless syrup (15.3 mg) which consisted of 5-[(*S*)-phenylphosphinyl]-α-D-altropyranose **16a** (1.0% from **12**) and its 5-[(*S*)-*P*]-β-*altro* isomer **16b** (5.5%), the relative amounts being determined by the integral ratio of ^{31}P signals: ^{1}H and ^{31}P NMR, see Table 1: MS *m*/*z* 440 (M+1; 3), 397(7), 380(58), 338(17), 320(36), 277(48), 259(100), 236(21), 195(27), 125(77). Found: *m*/*z* 440.1473. Calcd for $C_{20}H_{27}NO_8P$: M+1, 440.1473.

Fraction B [R_f=0.21 (*B*)] gave 5-[(*R*)-*P*]-α-L-*galacto* isomer **15a** as a colorless syrup: 17.0 mg (7.2% from **12**): ^{1}H and ^{31}P NMR, see Table 1; MS *m*/*z* (M^+; 7), 396(23), 380(100), 338(32), 320(66), 277(65), 259(43), 236(36), 195(36), 125(79). Found: *m*/*z* 439.1405. Calcd for $C_{20}H_{26}NO_8P$: M, 439.1396.

Fraction C [R_f=0.10 (*B*)] gave a colorless syrup (16.0 mg) which consisted of 5-[(*R*)-*P*]-β-L-*galacto* isomer **15b** (5.2% from **12**) and 5-[(*R*)-*P*]-β-D-*altro* isomer **16c** (1.6%): ^{1}H and ^{31}P NMR, see Table 1; MS *m*/*z* 439 (M^+; 12), 397(38), 380(50), 338(41), 320(48), 277(78), 251(89), 236(45), 203(77), 125(100). Found: *m*/*z* 439.1398. Calcd for $C_{20}H_{26}NO_8P$: M, 439.1396.

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