Synthesis of 5,6-Dideoxy-5-phenylphosphinyl-L-galactopyranoses. The P-in-Ring Sugar Analogs of L-Fucose

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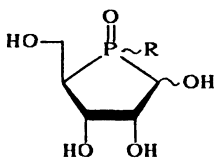
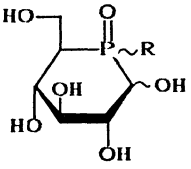
1,2-*O*-Isopropylidene-3-*O*-methyl-6-*O*-tosyl-β-D-*arabino*-hexofuranos-5-ulose (**9a**) and its 3-*O*-benzyl congener (**9b**) were prepared from 1,2:5,6-di-*O*-isopropylidene-β-D-altrofuranose in 4 steps. Addition of methyl phenylphosphinate to **9a** and **9b** in the presence of DBU, followed by reduction with Raney Ni, afforded (5*R* and 5*S*)-5,6-dideoxy-1,2-*O*-isopropylidene-5-[(methoxy)phenylphosphinyl]-3-*O*-methyl-β-D-*arabino*-hexofuranose (**11a**) and 3-*O*-benzyl congener (**11b**), respectively. The latter compound (**11b**) was debenzylated to 3-*O*-unsubstituted hexofuranose **11d**. By reduction with sodium dihydrobis(2-methoxyethoxy)aluminate, followed by acid hydrolysis, these key intermediates **11a**, **11b**, and **11d** provided the title L-fucoses **13** (together with a minor proportion of D-altropyranoses **14**) having as phenylphosphinylidene group in place of the ring oxygen. Compounds **13** and **14** were converted into per-*O*-acetyl derivatives for structural and conformational analysis by spectroscopy.

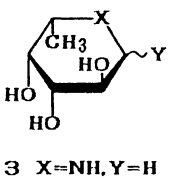
Sugar analogues having a phosphorus atom in the hemiacetal ring have been prepared in recent years;[1] e.g., those corresponding to D-ribofuranoses **1**[2] and D-glucopyranoses **2**.[3] These P-in-ring sugars have drawn interest in view of their physicochemical properties as well as potential biological activity. In the mean time, 1,5-imino-L-fucitol (**3**)[4] and 5-thio-L-fucose (**4**)[5] were synthesized and both compounds have been proven to inhibit L-fucosidase. We describe herein a detailed synthetic study on the first P-in-ring L-fucose analogues by placing phenylphosphinylidene in the hemiacetal ring as a model functional group.[6]



1 R=Et, Ph, OH



2 R=Et, OH



3 X=NH, Y=H
4 X=S, Y=OH

Results and Discussion

1,2:5,6-Di-*O*-isopropylidene-β-D-altrofuranose (**5**)[7] (available from D-glucose) served as the starting material for preparation of the important key intermediate, 3-*O*-substituted 1,2-*O*-isopropylidene-6-*O*-tosyl-β-D-*arabino*-hexofuranos-5-uloses (**9a—c**), by the sequence illustrated in Scheme 1.

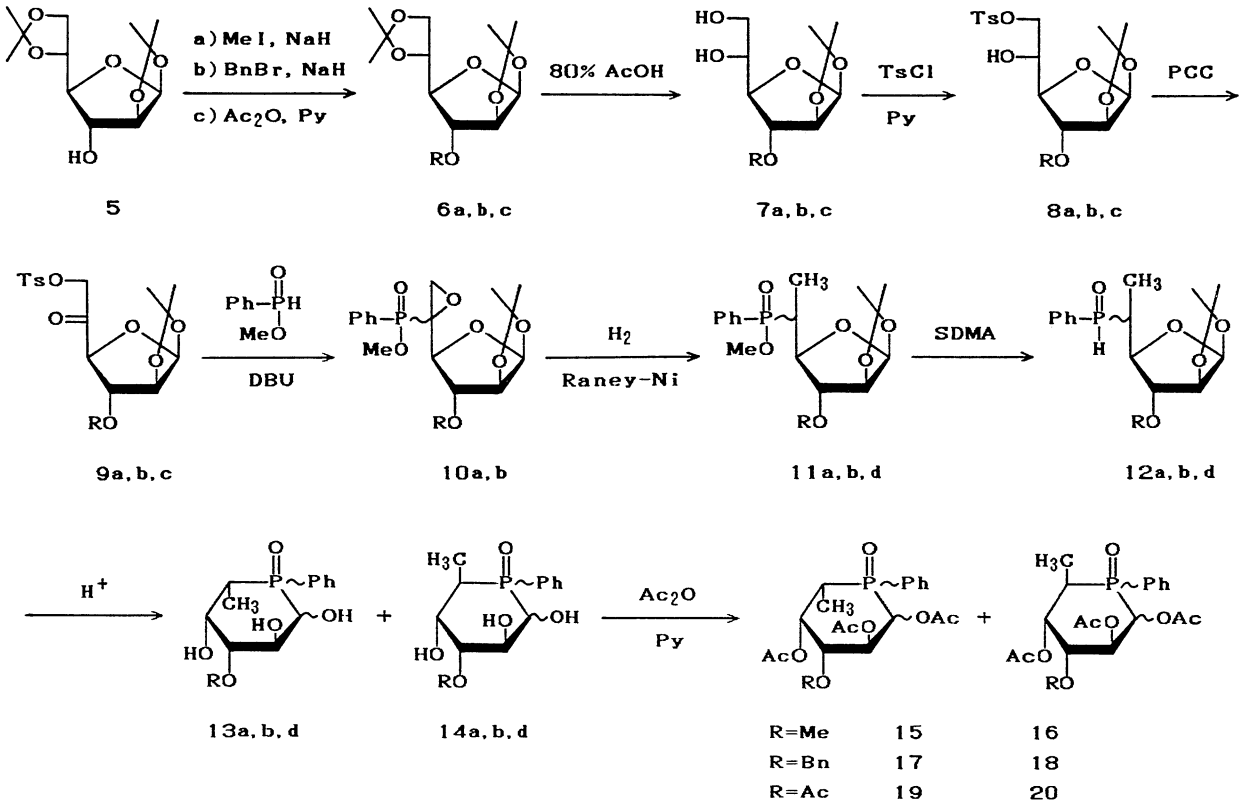
Thus, 3-*O*-methylation of **5** using NaH–MeI in 1,2-dimethoxyethane (DME) was found to furnish a higher yield of 3-*O*-methyl derivative **6a** than that by the previously reported method (MeI–Ag_2O in DMF).[8] The selective deprotection of **6a** with acid afforded 1,2-*O*-isopropylidene-3-*O*-methyl-β-D-altrofuranose (**7a**),[8] which was then treated with tosyl chloride in pyridine to give the 6-*O*-tosyl derivative **8a**. Oxidation of **8a** with pyridinium chlorochromate (PCC) in dichloromethane in the presence of molecular sieves (3A) gave 3-*O*-methyl-5-ulose **9a** in 95% yield.

The reaction of **9a** with methyl phenylphosphinate in DME in the presence of DBU gave 5,6-anhydro-5-[(methoxy)phenylphosphinyl] compound (**10a**) as a mixture of the diastereomers with regard to C-5 and P atom. Hydrogenation of **10a** in the presence of Raney-Ni (W-4) in ethanol afforded the 5,6-dideoxy derivative **11a**.

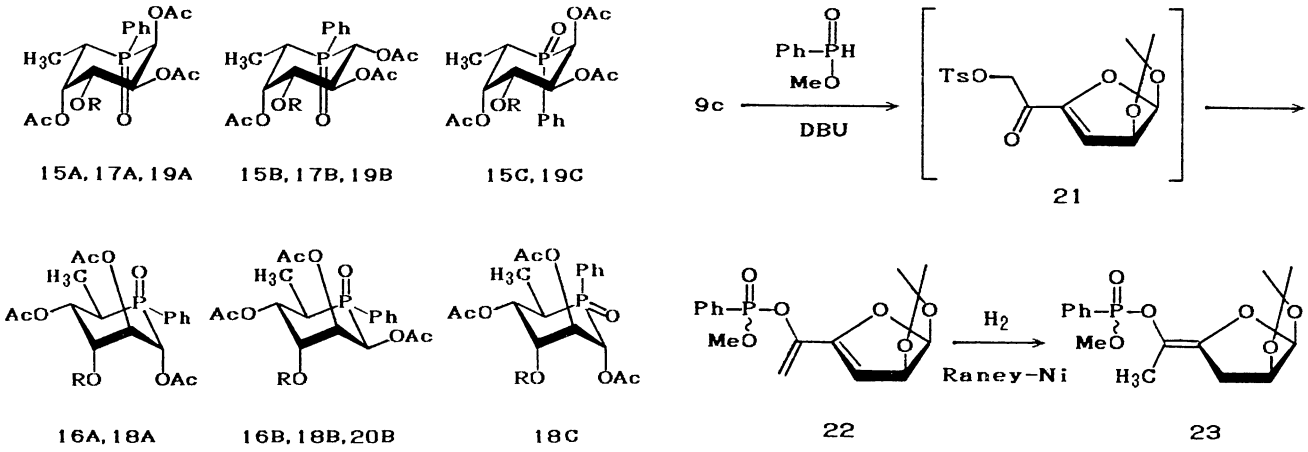
Compound **11a** was reduced with dihydrobis(2-methoxyethoxy)aluminate (SDMA) to give the unstable 5,6-dideoxy-5-phenylphosphinyl derivative **12a**, which was immediately treated with ethanolic 0.5 M hydrochloric acid (1 M=1 mol dm^{-3}) at 90 °C, thus affording a crude mixture of 5,6-dideoxy-3-*O*-methyl-5-phenylphosphinyl-L-galacto- (L-fucose, **13a**) and -D-altropyranoses (**14a**) as shown in Scheme 1.

These products were characterized after having been converted into the corresponding tri-*O*-acetyl derivatives **15** and **16** by the usual method. By purification in a silica-gel column, the presence of the following five diastereomers was confirmed, although some of the minor products were not completely separable (see the Experimental section): 5,6-dideoxy-5-[(*R*)-phenylphosphinyl]-α-L-galactopyranose (**15A**, 9.8% overall yield from **11a**), the β-anomer **15B** (2.1%), the 5-[(*S*)-*P*]-α-isomer **15C** (7.1%), 5,6-dideoxy-5-[(*S*)-phenylphosphinyl]-α-D-altropyranose (**16A**, 2.1%), the β-anomer **16B** (9.1%). Structures and the preferable conformations of these products were established on the basis of high-resolution mass spectrometry and 500 MHz ^1H NMR spectral data (see below).

Similarly, synthesis of 3-*O*-benzyl congeners **13b** and **14b** was performed by the sequence of **5**→**6b**→**7b**→**8b**→**9b**→**10b**→**11b**→**12b**→**13b** and **14b**. The unambiguous structural assignments of **13b** and **14b** were



Scheme 1. Synthesis of 5,6-dideoxy-5-phenylphosphinyl-L-galacto- and -D-altropyranoses. a: R=Me. b: R=Bn. c: R=Ac. d: R=H.



Scheme 2.

made by converting them into their triacetates **17** and **18**, which were separated into five diastereomers: **17A** (4.4% overall yield from **11b**), **17B** (1.1%), **18A** (1.3%), **18B** (9.3%), and **18C** (4.4%).

These successful synthesis of 3-*O*-alkyl-L-fucose analogues **13a** and **13b** prompted us to prepare 3-*O*-unsubstituted compound **13d**. Thus, following the synthetic scheme analogous to that used for **9a**, **b**, we prepared 3-*O*-acetyl-5-ulose **9c** from **5** by the sequence of **5**→**6c**[9]→**7c**→**8c**→**9c**. However, when **9c** was treated with methyl phenylphosphinate and DBU in DME as in the cases of **9a** and **9b**, the main product turned out to be the enol phosphonate **22**. This is presumably formed from **9c** as the result of the prior elimination of AcOH by the action of DBU to give an activated α-tosyloxycarbonyl compound **21**, which in turn undergoes the Perkow[10] type reaction with methyl phenylphosphinate to afford **22** as illustrated in Scheme 2. Although many examples are well known for the Perkow reactions of α-halo-, α-acetoxy-,[11] and α-tosyloxycarbonyl compounds[12] with trialkyl phosphites, the reactions with alkyl phosphinate appear to be rare, to our knowledge. The catalytic hydrogen-

ation of **22** in the presence of Raney-Ni afforded hex-4-enofuranose **23**.

Therefore, we turned our attention to another approach for preparation of **13d:** namely, from **11b** in stead of **9c**. Debenzylation of **11b** by catalytic hydrogenation over 20% $Pd(OH)_2$–C in ethanol smoothly provided **11d**. By the same procedures described above, compound **11d** was converted into a mixture of **13d** and **14d** via **12d** (Scheme 1). The structures of **13d** and **14d** were similarly established by derivatization into tetraacetates **19** and **20** that were separated by column chromatography into four diastereomers: **19A** (11% overall yield from **11d**), **19B** (2.7%), **19C** (4.2%), and **20B** (3.5%).

^{1}H NMR Spectral Analysis of Per-*O*-acetyl-5,6-dideoxy-5-phenylphosphinyl-L-galactopyranoses (15A—C, 17A,B, 19A—C) and D-Altropyranoses (16A,B, 18A—C, 20B). For structural assignments of these new products **15—20**, the chemical shift of each proton signal of their NMR spectra and the dependence of the $^2J_{H,P}$, $^3J_{H,P}$, and $^3J_{H,H}$ values on their dihedral angles were carefully taken into consideration. The precise parameters thereby obtained for the these compounds are summarized in Table 1. Since the parameters for 5,6-dideoxy-5-phosphinyl-L-galacto- and -D-altropyranoses have been obtained for the first time in the present study, some characteristic features of **15—20** are discussed here in detail. These parameters are instructive in determining the structures of other similar phosphinyl-in-ring sugar analogues, preparation of which is currently under investigation.

(1) A series of compounds **15**, **17**, and **19** characteristically show small values of $J_{4,5}$ (2.3—3.0 Hz) and $J_{2,P}$ (0—4 Hz) and large values of $J_{2,3}$ (9.8—10.9 Hz) and $J_{4,P}$ (28—31 Hz), whereas another series of compounds **16**, **18**, and **20** exhibit opposite magnitudes of the

Table 1. ^{1}H NMR (500 MHz) Parameters for **15—20** in $CDCl_3$

Compd	Chemical shift (δ)											
	H-1	H-2	H-3	H-4	H-5	H-6	MeO-3 (CH_2O-3)[c]	Ac-1,2,4[a] (Ac-1,2,3,4)	Ph(*o*)	Ph(*m*)	Ph(*p*)[b]	^{31}P
5,6-Dideoxy-5-phenylphosphinyl-L-galactopyranoses												
15A	5.77	5.85	3.68	5.87	2.61	1.19	3.46	2.23, 2.00, 1.95	7.75	7.51	7.59	30.9
15B	5.62	5.90	3.50	5.79	2.30	1.17	3.44	2.24, 2.04, 1.95	7.76	7.51	7.58	33.2
15C	6.17	5.57	3.74	5.61	2.73	1.28	3.43	2.24, 2.11, 1.65	7.76	7.51	7.58	30.9
17A	5.78	5.90	3.92	5.89	2.59	1.19	(4.76, 4.54)	2.23, 1.96, 1.89	7.74	7.49	7.58 d)	30.4
17B	5.57	5.96	3.70	5.80	2.30	1.16	(4.75, 4.49)	2.25, 1.97, 1.96	7.74	7.50	7.57 d)	32.7
19A	5.80	5.95	5.39	5.76	2.72	1.15		(2.23, 2.03, 1.97, 1.95)	7.75	7.52	7.59	30.5
19B	5.64	6.05	5.16	5.66	2.29	1.12		(2.25, 2.02, 2.00, 1.95)	7.76	7.53	7.61	30.4
19C	6.24	5.65	5.41	5.49	2.82	1.30		(2.26, 2.06, 1.98, 1.61)	7.94	7.57	7.62	30.1
5,6-Dideoxy-5-phenylphosphinyl-D-altropyranoses												
16A	5.37	5.49	3.80	5.60	3.02	1.16	3.60	2.18, 2.09, 1.96	7.80	7.51	7.59	35.2
16B	5.69	5.77	3.85	5.64	2.70	1.10	3.61	2.23, 2.13, 1.94	7.76	7.51	7.57	30.1
18A	5.38	5.50	4.01	5.58	3.10	1.15	(4.74, 4.63)	2.20, 2.07, 1.97	7.80	7.51	7.59 d)	35.0
18B	5.82	5.77	4.04	5.59	2.76	1.09	(4.86, 4.67)	2.22, 1.98, 1.96	7.76	7.50	7.57 d)	29.9
18C	5.94	5.75	3.89	5.60	3.16	1.23	(4.83, 4.67)	2.07, 1.97, 1.73	7.96	7.53	7.59 d)	33.2
20B	5.70	5.59	5.57	5.66	2.59	1.14		(2.25, 2.24, 2.00, 1.96)	7.76	7.53	7.61	29.6

Compd	Coupling constant (Hz)									
	$J_{1,2}$	$J_{1,P}$	$J_{2,3}$	$J_{2,P}$	$J_{3,4}$	$J_{3,P}$	$J_{4,5}$	$J_{4,P}$	$J_{5,6}$	$J_{5,P}$	$J_{6,P}$
5,6-Dideoxy-5-phenylphosphinyl-L-galactopyranoses											
15A	2.9	11.8	10.4	0	2.8	0	2.7	27.9	7.3	6.7	14.8
15B	11.1	2.7	9.9	2.3	2.8	0	2.5	29.1	7.2	5.0	14.7
15C	3.1	8.6	9.8	4.2	2.8	0	2.9	29.6	7.3	21.2	14.6
17A	2.9	11.7	10.4	0	3.0	0	3.0	27.9	7.3	6.6	15.0
17B	11.0	2.8	9.9	2.4	2.8	0	2.3	29.5	7.2	5.0	14.5
19A	2.9	11.7	10.9	0	3.0	0	2.9	28.2	7.3	5.9	15.0
19B	11.1	2.8	10.4	2.3	2.7	0	2.8	29.3	7.3	5.0	14.7
19C	3.0	9.6	10.7	0	2.8	0	2.5	30.7	7.3	20.7	14.2
5,6-Dideoxy-5-phenylphosphinyl-D-altropyranoses											
16A	3.4	9.6	4.7	20.1	2.3	1.0	11.5	6.4	7.2	6.1	14.9
16B	3.5	0.5	5.2	24.9	2.3	1.8	12.0	4.1	7.2	4.1	14.8
18A	3.4	9.5	4.5	20.2	2.2	1.2	11.8	6.8	7.2	6.5	14.9
18B	3.5	0.5	5.0	24.7	2.3	1.8	12.3	4.0	7.1	4.1	15.0
18C	3.9	13.8	5.1	27.6	2.2	1.8	12.7	3.2	7.2	20.9	15.3
20B	3.5	0.8	5.0	25.3	2.5	1.8	12.1	4.0	7.2	4.1	14.8

a) The assignments of acetoxyl groups may have to 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. c) $^2J_{CH_2}$=11.9 Hz. d) C–Ph: δ=7.29—7.41 (5H, m).

corresponding coupling constants, namely relatively large values of $J_{4,5}$ (11.5—12.7 Hz) and $J_{2,P}$ (20—28 Hz) and small values of $J_{2,3}$ (4.5—5.2 Hz) and $J_{4,P}$ (3.2—6.8 Hz). By applying the arguments similar to these employed for distinction between 5-deoxy-5-phosphinyl-L-gulo- and -D-mannopyranoses,[13] the above two series of compounds **15,17,19** and **16,18,20** can be assigned to have structures of L-galactopyranose predominantly in the $^1C_4$(L) conformation and D-altropyranose in the $^4C_1$(D) conformation, respectively.

(2) As the H-5 of **15—20** is all in axial position, the magnitudes of $J_{5,P}$ values establishes the orientation of the ring P=O group in these compounds. The small values of $J_{5,P}$ (4.1—6.7 Hz) are indicative of the anti orientation of H-C(5)-P=O for **15—19A,B** and **20B**. On the other hand, because of the large values of $J_{5,P}$ (20.7—21.2 Hz), the equatorial P=O orientation is assigned to **15C**, **18C**, and **19C**. The orientation of the ring P=O group in these compounds should also be derived by examining the δ values of H-2 for **15**, **17**, and **19** and of H-4 for **16**, **18**, and **20**, although care must be taken when the inclination of the axially oriented *P*-phenyl ring exerts an anisotropic effect on H-2 and/or H-4 of 1,3-diaxial position.[14] An appreciable downfield shift (0.3—0.4 Hz) is observed for **15A,B**, **17A,B**, and **19A,B** (compared with the chemical shifts of **15C** and **19C**), thus confirming the axial orientation of the ring P=O for the compounds of the former group (**A** and **B**).

(3) The anomeric orientation of C-1 is derived from the values of $J_{1,P}$ and $J_{1,2}$ and also in some cases the δ values of H-5. Namely, the small values of $J_{1,P}$ (0.5—2.8 Hz) of **15—20B** and the large $J_{1,P}$ values (8.6—13.8 Hz) of **15—19A,C** suggest respectively the anti and gauche connection of H-C(1)-P=O for these compounds. The large value of $J_{1,2}$ (11 Hz) of **15—20B** confirms the axial H-1 orientation for **15B**, **17B**, and **19B**, whereas the smaller $J_{1,2}$ value (3 Hz) points out the equatorial H-1 configuration for **15A,C**, **17A**, and **19A,C** in the L-galactopyranose series. For a series of the D-altropyranoses whose H-2 are in the equatorial position and thus $J_{1,2}$ values are all similar and small (ca. 3.5 Hz), an appreciable downfield shift (0.3—0.4 ppm) of H-5 caused by the axially situated AcO group on C-1 can be used for distinction between the α-anomers (**16A** and **18A,C**) and β-anomers (**16B**, **18B**, and **20B**).

Present work thus demonstrates a possible way for preparation of 5,6-dideoxy-5-phosphinyl-L-galactopyranoses from appropriate intermediates. Extension of this work including preparative studies on improved product ratios of the L-fucose type analogues in conection with other kinds of substituents at P-5 and O-3 of the precursors **11** and **12**, as well as biological evaluation of the compounds, is in progress.

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 (*A*) 1:1 AcOEt–hexane or (*B*) AcOEt as the eluant; components were detected by exposing the plates to a UV light (254 nm) and/or by spraying them with 20% sulfuric acid–ethanol, with subsequent heating. Column chromatography was performed on Wako C-200 silica gel. Optical rotation were measured with a Nihon-Bunko DIP-4 polarimeter at 25 °C. The IR spectra were taken with a Hitachi 260-105 infrared spectrophotometer. The ^{1}H 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-600 (60 MHz, FT) spectrometer. Chemical shifts are reported as δ values relative to tetramethylsilane (internal standard for ^{1}H) and 85% phosphoric acid (external standard for ^{31}P). The assignments of all signals obtained at 500 MHz were made by employing a first-order analysis with the aid of decoupling technique and, if necessary, two-dimensional COSY measurements; the parameters were confirmed by a computer-assisted simulation analysis. 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.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-methyl-β-D-altrofuranose (6a)[8] and Its 3-*O*-Benzyl Congener (6b). The following procedures resulted in a better yield of **6a** than the reported method using MeI–Ag_2O.[8] Thus, to a solution of **5**[7] (1.35 g, 5.19 mmol) in DME (10 ml) was added, with stirring, sodium hydride [500 mg, 60% in mineral oil (which was washed with DME), 2.4 equiv] in small portions at 0 °C under an argon atmosphere. To this suspension was dropwise added methyl iodide (1.00 ml, 16.1 mmol) at 0 °C. The mixture was stirred at 25 °C for 2 h and then methanol (8 ml) was added at 0 °C. The mixture was stirred at 25 °C for 0.5 h and evaporated in vacuo. The residue was dissolved in CH_2Cl_2, washed with water, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography, giving **6a** (1.37 g, 96%) as a colorless syrup (cf. lit,[8] 88% yield): R_f=0.73 (*A*).

The procedures similar to those for **6a** from **5** were employed for preparation of **6b**. Thus, **5** (510 mg, 1.96 mmol) was treated with sodium hydride (60% in oil, 200 mg, 2.6 equiv) and benzyl bromide (0.47 ml, 3.95 mmol) at 25 °C for 3 h. Purification by column chromatography gave **6b** (625 mg, 91%) as a colorless syrup: R_f=0.80 (*A*); $[\alpha]_D$+4.0° (*c* 1.20, $CHCl_3$); ^{1}H NMR (500 MHz) δ=1.31, 1.51 (3H each, 2s, Me_2C-O-1,2), 1.35, 1.43 (3H each, 2s, Me_2C-O-5,6), 3.99 (1H, dd, $J_{6,6'}$=8.8, $J_{5,6'}$=4.9 Hz, H-6′), 4.03 (1H, dd, $J_{4,5}$=9.3, $J_{3,4}$=1.6 Hz, H-4), 4.11 (1H, dd, $J_{5,6}$=6.2 Hz, H-6), 4.19 (1H, d, $J_{2,3}\approx$0 Hz, H-3), 4.25 (1H, ddd, H-5), 4.58, 4.60 (1H each, 2d, ^2J=11.7 Hz, CH_2O-3), 4.64 (1H, d, $J_{1,2}$=3.8 Hz, H-2), 5.89 (1H, d, H-1), 7.34 (5H, m, Ph); MS *m/z* 335 (M-CH_3; 2.7), 292 (1.5), 249 (4.1), 221 (2.5), 163 (2.5), 129 (3.0), 105 (12), 91 (100). Found: *m/z* 335.1494. Calcd for $C_{18}H_{23}O_6$: M-CH_3, 335.1494.

General Procedures for the Preparation of 3-*O*-Substituted 1,2-*O*-Isopropylidene-β-D-altrofuranoses (7a—c). A mixture of **6** (4.78 mmol) and 80% aqueous acetic acid (15 ml) was stirred at 60 °C for 2 h. The solution was evaporated in vacuo and the residue was purified by use of column

chromatography on silica gel, giving **7**.

3-*O*-Methyl Derivative (7a):[8] Colorless syrup (83% from **6a**, lit,[8] 79%); R_f=0.14 (*A*).

3-*O*-Benzyl Derivative (7b): Colorless needles (85% from **6b**); mp 68—69 °C (from AcOEt–hexane); R_f=0.23 (*A*); $[\alpha]_D$+4.2° (*c* 1.33, $CHCl_3$); ^1H NMR (500 MHz) δ=1.33, 1.52 (3H each, 2s, CMe_2), 2.15 (2H, br s, HO-5,6), 3.72 (1H, dd, $J_{6,6'}$=11.3, $J_{5,6'}$=5.4 Hz, H-6′), 3.76 (1H, dd, $J_{5,6}$=3.9 Hz, H-6), 3.91 (1H, ddd, $J_{4,5}$=7.5 Hz, H-5), 4.05 (1H, dd, $J_{3,4}$=2.9 Hz, H-4), 4.21 (1H, d, $J_{2,3}\approx$0 Hz, H-3), 4.60, 4.62 (1H each, 2d, ^2J=11.6 Hz, CH_2O-3), 4.67 (1H, d, $J_{1,2}$=4.1 Hz, H-2), 5.89 (1H, d, H-1), 7.35 (5H, m, Ph); MS *m/z* 310 (M^+; 0.1), 295 (1.8), 249 (4.7), 221 (3.5), 193 (2.5), 163 (3.1), 91 (100). Found: *m/z* 310.1419. Calcd for $C_{16}H_{22}O_6$: M, 310.1416.

3-*O*-Acetyl Derivative (7c): Colorless needles (84% from **6c**[9]); mp 85—86 °C (from AcOEt–hexane); R_f=0.13 (*A*); $[\alpha]_D$−196° (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz) δ=1.31, 1.52 (3H each, 2s, CMe_2), 2.10 (3H, s, AcO-3), 2.28 (2H, br s, HO-5,6), 3.73 (1H, dd, $J_{6,6'}$=11.5, $J_{5,6'}$=4.7 Hz, H-6′), 3.82 (1H, dd, $J_{5,6}$=3.7 Hz, H-6), 3.93 (1H, ddd, $J_{4,5}$=9.1 Hz, H-5), 4.04 (1H, dd, $J_{3,4}$=1.3 Hz, H-4), 4.63 (1H, d, $J_{1,2}$=3.9, $J_{2,3}\approx$0 Hz, H-2), 5.28 (1H, d, H-3), 5.92 (1H, d, H-1); MS *m/z* 247 ($M-CH_3$; 29), 231 (2.3), 201 (49), 187 (4.5), 173 (28), 143 (100), 127 (33), 113 (41). Found: *m/z* 247.0819. Calcd for $C_{10}H_{15}O_7$: $M-CH_3$, 247.0818.

General Procedures for the Preparation of 3-*O*-Substituted 1,2-*O*-Isopropylidene-6-*O*-tosyl-β-D-altrofuranoses (8a—c). To a solution of **7** (8.30 mmol) in dry pyridine (40 ml) was added tosyl chloride (1.8 g, 9.5 mmol) at 0 °C. The mixture was stirred at 25 °C for 8 h and then water (2 ml) was added at 0 °C. The mixture was evaporated in vacuo. The residue was dissolved in CH_2Cl_2, washed with water, dried (Na_2SO_4), and evaporated in vacuo. The residue was chromatographed on silica gel to give **8**.

3-*O*-Methyl Derivative (8a): Colorless syrup (86% from **7a**); R_f=0.48 (*A*); $[\alpha]_D$+33° (*c* 0.89, $CHCl_3$); ^1H NMR (500 MHz) δ=1.29, 1.43 (3H each, 2s, CMe_2), 2.05 (1H, br s, HO-5), 2.45 (3H, s , MeC_6-*S*), 3.38 (3H, s, MeO-3), 3.88 (1H, dd, $J_{4,5}$=8.5, $J_{3,4}$=1.7 Hz, H-4), 3.98 (1H, d, $J_{2,3}\approx$0 Hz, H-3), 4.04 (1H, m, H-5), 4.06, 4.30 (1H each, 2m, H-6,6′), 4.54 (1H, d, $J_{1,2}$=3.9 Hz, H-2), 5.82 (1H, d, H-1), 7.35, 7.80 (2H each, 2d, *J*=8.5, C_6H_4-*S*); MS *m/z* 373 ($M-CH_3$; 13), 345 (2.7), 327 (1.4), 281 (4.6), 245 (10), 215 (5.3), 173 (93), 155 (30), 91 (41), 87 (100). Found: *m/z* 373.0951. Calcd for $C_{16}H_{21}O_8S$: $M-CH_3$, 373.0958.

3-*O*-Benzyl Derivative (8b): Colorless syrup (95% from **7b**); R_f=0.80 (*A*); $[\alpha]_D$+8.7° (*c* 1.71, $CHCl_3$); ^1H NMR (500 MHz) δ=1.28, 1.43 (3H each, 2s, CMe_2), 2.44 (3H, s, MeC_6-*S*), 2.63 (1H, br s, HO-5), 3.99 (1H, dd, $J_{4,5}$=7.1, $J_{3,4}$=1.5 Hz, H-4), 4.05—4.07 (2H, m, H-5,6′), 4.21 (1H, d, $J_{2,3}\approx$0 Hz, H-3), 4.31 (1H, m, H-6), 4.56, 4.58 (1H each, 2d, ^2J=11.7 Hz, CH_2O-3), 4.62 (1H, d, $J_{1,2}$=3.9 Hz, H-2), 5.85 (1H, d, H-1), 7.30—7.35 (5H, m, Ph-C), 7.33, 7.79 (2H each, 2d, *J*=8.3 Hz, C_6H_4-*S*); MS *m/z* 449 ($M-CH_3$; 0.1), 295 (1.2), 249 (5.4), 221 (2.5), 193 (1.5), 163 (2.7), 91 (100). Found: *m/z* 449.1299. Calcd for $C_{22}H_{25}O_8S$: $M-CH_3$, 449.1270.

3-*O*-Acetyl Derivative (8c): Colorless syrup (88% from **7c**); R_f=0.50 (*A*); ^1H NMR (60 MHz) δ=1.28, 1.43 (3H each, 2s, CMe_2), 2.10 (3H, s, AcO-3), 2.46 (3H, s, MeC_6-*S*), 3.00 (1H, m, HO-5), 4.05—4.35 (3H, m, H-4,6,6′), 4.60 (1H, d, $J_{1,2}$=4.0, $J_{2,3}\approx$0 Hz, H-2), 5.35 (1H, d, $J_{3,4}$=1.5 Hz, H-3), 5.89 (1H, d, H-1), 7.35, 7.80 (2H each, 2d, *J*=8.5 Hz, C_6H_4-*S*).

General Procedures for the Preparation of 3-*O*-Substituted 1,2-*O*-Isopropylidene-6-*O*-tosyl-β-D-*arabino*-hexofuranos-5-uloses (9a—c). To a stirred suspension of **8** (0.59 mmol) and finely powdered molecular sieves 3A (500 mg) in dry CH_2Cl_2 (2 ml) was added PCC (254 mg, 1.18 mmol) at 0 °C. The mixture was stirred at 25 °C for 4 h and then 2-propanol (0.5 ml) was added at 0 °C. The mixture was stirred at 25 °C for 1 h and diluted with ether. The precipitates were filtered off through activated carbon. The filtrate was evaporated in vacuo and the residue was purified by short-path chromatography with 1:1 AcOEt–hexane as an eluant, giving **9**.

3-*O*-Methyl Derivative (9a): Colorless syrup (95% from **8a**); R_f=0.55 (*A*); $[\alpha]_D$+2.4° (*c* 1.47, $CHCl_3$); IR (neat) ν 1740 (C=O), 1360 (ν_{as} SO_2), 1170 cm^{-1} (ν_s SO_2); ^1H NMR (500 MHz) δ=1.24, 1.25 (3H each, 2s, CMe_2), 2.45 (3H, s, MeC_6-*S*), 3.40 (3H, s, MeO-3), 4.24 (1H, br s, $J_{3,4}$=0.5, $J_{2,3}\approx$0 Hz, H-3), 4.52 (1H, br s, H-4), 4.55 (1H, d, $J_{1,2}$=3.9 Hz, H-2), 4.95, 5.26 (1H each, 2d, $J_{6,6'}$=17.7 Hz, H-6,6′), 5.95 (1H, d, H-1), 7.35, 7.83 (2H each, 2d, *J*=8.5 Hz, C_6H_4-*S*); MS *m/z* 386 (M^+; 0.5), 371 (9.0), 343 (11), 313 (2.1), 255 (13), 185 (2.2), 173 (100), 155 (23), 145 (11), 115 (25), 91 (39). Found: *m/z* 386.1036. Calcd for $C_{17}H_{22}O_8S$: M, 386.1036.

3-*O*-Benzyl Derivative (9b): Colorless syrup (86% from **8b**); R_f=0.49 (*A*); $[\alpha]_D$−6.1° (*c* 2.60, $CHCl_3$); IR (neat) ν 1740 (C=O), 1360 (ν_{as} SO_2), 1170 cm^{-1} (ν_s SO_2); ^1H NMR (500 MHz) δ=1.24, 1.26 (3H each, 2s, CMe_2), 2.45 (3H, s, MeC_6-*S*), 4.47 (1H, br s, $J_{3,4}$=0.5, $J_{2,3}\approx$0 Hz, H-3), 4.58 (2H, s, CH_2O-3), 4.60 (1H, br s, H-4), 4.62 (1H, d, $J_{1,2}$=3.9 Hz, H-2), 4.95, 5.25 (1H each, 2d, $J_{6,6'}$=17.6 Hz, H-6,6′), 5.98 (1H, d, H-1), 7.30—7.35 (5H, m, Ph), 7.35, 7.83 (2H each, 2d, *J*=8.3 Hz, C_6H_4-*S*); MS *m/z* 447 ($M-CH_3$; 0.2), 230 (2.9), 172 (1.9), 155 (18), 122 (7.4), 105 (31), 91 (100). Found: *m/z* 447.1120. Calcd for $C_{22}H_{23}O_8S$: $M-CH_3$, 447.1114.

3-*O*-Acetyl Derivative (9c): Colorless syrup (97% from **8c**); R_f=0.45 (*A*); $[\alpha]_D$−2.1° (*c* 1.54, $CHCl_3$); IR (neat) ν 1740 (C=O), 1730 (ester C=O), 1355 (ν_{as} SO_2), 1170 cm^{-1} (ν_s SO_2); ^1H NMR (500 MHz) δ=1.23, 1.25 (3H each, 2s, CMe_2), 2.09 (3H, s, AcO-3), 2.45 (3H, s, MeC_6-*S*), 4.56 (1H, d, $J_{1,2}$=3.9, $J_{2,3}\approx$0 Hz, H-2), 4.59 (1H, br s, $J_{3,4}$=0.5 Hz, H-4), 4.95, 5.21 (1H each, 2d, $J_{6,6'}$=17.4 Hz, H-6,6′), 5.55 (1H, br s, H-3), 5.98 (1H, d, H-1), 7.35, 7.83 (2H each, 2d, *J*=8.2 Hz, C_6H_4-*S*); MS *m/z* 399 ($M-CH_3$; 0.4), 201 (5.4), 185 (1.2), 161 (1.4), 149 (5.1), 43 (100). Found: *m/z* 399.0749. Calcd for $C_{17}H_{19}O_9S$: $M-CH_3$, 399.0750.

(5*R* and 5*S*)-5,6-Anhydro-1,2-*O*-isopropylidene-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-3-*O*-methyl-β-D-*arabino*-hexofuranoses (10a) and Their 3-*O*-Benzyl Congeners (10b). To a solution of **9a** (123 mg, 0.322 mmol) and methyl phenylphosphinate (0.065 ml, 0.49 mmol) in DME (1 ml) was dropwise added a solution of DBU (74 mg, 0.49 mmol) in DME (1 ml) at −40 °C. The mixture was stirred at the same temp for 1 h and the concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and saturated aq $NaHCO_3$ was added. After stirring at 25 °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 **10a** (65 mg, 55%) as a colorless syrup: R_f=0.27 (*A*); ^1H NMR (60 MHz) δ=1.31, 1.51 (3H each, 2s, CMe_2), 2.75, 3.20 (1H each, 2m, H-6,6′), 3.13, 3.36 (3H, 2s, MeO-3), 3.70, 3.78 (3H, 2d, J_{POMe}=10.8 Hz, POMe), 3.80—4.10 (1H, m, H-3), 4.25—4.55 (2H, m, H-2,4),

5.18, 5.25 (1H, 2d, $J_{1,2}$=4.0 Hz, H-1), 7.40—8.05 (5H, m, Ph); MS *m/z* 370 (M^+; 0.9), 355 (19), 340 (9.2), 312 (5.5), 294 (6.4), 281 (16), 253 (12), 227 (100), 211 (20), 155 (76). Found: *m/z* 370.1174. Calcd for $C_{17}H_{23}O_7P$: M, 370.1181.

By the use of the same procedures described above, **9b** (2.86 g, 6.18 mmol) was treated with methylphenylphosphinate (1.65 ml, 12.4 mmol) and DBU (1.0 ml, 6.7 mmol) at −40 °C for 1 h. Purification by column chromatography gave **10b** (1.37 g, 50%) as a colorless syrup: R_f=0.43 (*A*); ^{1}H NMR (60 MHz) δ=1.28, 1.50 (3H each, 2s, CMe_2), 2.75, 3.17 (1H each, 2m, H-6,6′), 3.68, 3.70 (3H, 2d, J_{POMe}=10.8 Hz, POMe), 4.00—4.60 (3H, m, H-2,3,4), 4.54 (2H, s, CH_2O-3), 5.67, 5.75 (1H, 2d, $J_{1,2}$=4.0 Hz, H-1), 7.30 (5H, s, Ph-C), 7.30—8.00 (5H, m, Ph-P); MS *m/z* 431 (M−CH_3; 2.5), 355 (3.1), 340 (4.8), 297 (6.8), 281 (7.2), 253 (3.6), 227 (8.4), 198 (15), 156 (34), 91 (100). Found: *m/z* 431.1254. Calcd for $C_{22}H_{24}O_7P$: M−CH_3, 431.1260.

(5*R* and 5*S*)-5,6-Dideoxy-1,2-*O*-isopropylidene-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-β-D-*arabino*-hexofuranoses (11d) and 3-*O*-Methyl and 3-*O*-Benzyl Derivatives (11a and 11b). Compound **10a** (256 mg, 0.691 mmol) dissolved in ethanol (2 ml) was hydrogenated in the presence of Raney-Ni (W-4) (730 mg) at 24 °C under an atmospheric pressure of H_2. After 4 h, the mixture was centrifuged to remove the catalyst; the precipitate was twice extracted with ethanol. The combined organic layers were evaporated in vacuo. The residue was chromatographed on silica gel to give **11a** (108 mg, 44%) as a pale yellow syrup: R_f=0.31—0.24 (*B*); ^{1}H NMR (60 MHz) δ=1.11 (3H, dd, $J_{6,P}$=17.0, $J_{5,6}$=7.4 Hz, H$_3$-6), 1.32, 1.40, 1.48 (6H, 3s, CMe_2), 2.10—2.65 (1H, m, H-5), 3.37, 3.40 (3H, 2s, MeO-3), 3.65, 3.68, 3.76 (3H, 3d, J_{POMe}=10.8 Hz, POMe), 3.90—4.55 (3H, m, H-2,3,4), 5.60—5.85 (1H, m, H-1), 7.35—7.95 (5H, m, Ph).

By the same procedures described above, **10b** (247 mg, 0.553 mmol) was treated with Raney-Ni (W-4) (600 mg) for 7 h under H_2. Purification by column chromatography gave **11b** (98 mg, 41%) as a colorless syrup: R_f=0.36—0.26 (*B*); ^{1}H NMR (500 MHz) for the two predominant components of **11b** δ=1.06, 1.21* (3H, 2dd, $J_{6,P}$=17.5, $J_{5,6}$=7.0 Hz, H-6), 1.25, 1.30,* 1.45, 1.50* (6H, 4s, CMe_2), 2.45,* 2.50 (1H, 2dq, $J_{5,P}$=14.5,* 14.7, $J_{4,5}$=7.7,* 8.2 Hz, H-5), 3.62,* 3.64 (3H, 2d, J_{POMe}=11.0 Hz, POMe), 3.92, 4.32* (1H, 2ddd, $J_{4,P}$=6.8, 5.9,* $J_{3,4}$=4.0 Hz, H-4), 4.02, 4.08* (1H, 2d, $J_{2,3}$≈0 Hz, H-3), 4.54, 4.59,* 4.62, 4.62* (2H, 4d, *J*=11.7 Hz, CH_2O-3), 4.58 (1H, d, $J_{1,2}$=3.8 Hz, H-2), 5.81,* 5.84 (1H, 2d, H-1), 7.36 (5H, m, Ph-C), 7.46 [2H, m, Ph(*m*)-P], 7.55 [1H, m, Ph(*p*)-P], 7.73, 7.76* [2H, 2m, Ph(*o*)-P], *for another diastereomer (the assignment of some of the δ values may have to be interchanged); MS *m/z* 432 (M^+; 0.3), 417 (2.8), 341 (5.2), 326 (7.4), 303 (2.1), 283 (7.5), 267 (8.9), 213 (23), 184 (28), 155 (29), 91 (100). Found: *m/z* 432.1699. Calcd for $C_{23}H_{29}O_6P$: M, 432.1702.

Compounds **11b** (103 mg, 0.238 mmol) dissolved in ethanol (1 ml) was hydrogenated in the presence of 20% $Pd(OH)_2$–C (80 mg) at 25 °C under an atmospheric pressure of H_2. After 1.5 h, the catalyst was filtered off through celite, and the filtrate was evaporated in vacuo. The residue was purified by column chromatography, giving **11d** (78 mg, 96%) as a colorless syrup: R_f=0.25—0.19 (*B*); ^{1}H NMR (60 MHz) δ=0.96, 1.19 (3H, 2dd, $J_{6,P}$=17.4, $J_{5,6}$=7.4 Hz, H$_3$-6), 1.36, 1.40, 1.45 (6H, 3s, CMe_2), 2.00—2.75 (1H, m, H-5), 3.20—3.50 (1H, m, HO-3, D_2O exchangeable), 3.59, 3.67 (3H, 2d, J_{POMe}=10.8 Hz, POMe), 3.95—4.75 (3H, m, H-2,3,4), 5.72 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 7.30—7.95 (5H, m, Ph-P); MS *m/z* 342 (M^+; 1.6), 327 (6.1), 295 (1.2), 267 (3.4), 239 (2.9), 213 (61), 173 (9.8), 155 (52), 100 (100). Found: *m/z* 342.1235. Calcd for $C_{16}H_{23}O_6P$: M, 342.1232.

1,2,4-Tri-*O*-acetyl-5,6-dideoxy-3-*O*-methyl-[(*R* and *S*)-phenylphosphinyl]-L-galactopyranoses (15) and -D-Altropyranoses (16). To a solution of **11a** (227 mg, 0.637 mmol) in dry benzene (3 ml) was added, with stirring, a solution of SDMA (3.4 M in toluene, 0.5 ml, 2.5 equiv) in dry benzene (1 ml), in small portions at 5 °C under an argon atmosphere. The mixture was stirred at this temp for 1.5 h, and then water (1 ml) was added to decompose excess SDMA. The mixture was centrifuged and the precipitate was extracted with several portions of benzene. The organic layers were combined and evaporated in vacuo, giving (5*R* and 5*S*)-5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-5-[(*R* and *S*)-phenylphosphinyl]-β-D-*arabino*-hexofuranoses (**12a**) as a colorless syrup.

The syrup was immediately treated with 1:1 ethanol–0.5 M hydrochloric acid (6 ml) at 90 °C for 3 h under an argon atmosphere. 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 5,6-dideoxy-3-*O*-methyl-5-[(*R* and *S*)-phenylphosphinyl]-α, β-L-galactopyranoses (**13a**) and -D-altropyranoses (**14a**) as a colorless syrup.

This was dissolved in dry pyridine (4 ml) and acetic anhydride (2 ml) at 0 °C. The mixture was stirred at 25 °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 triacetates **15** and **16**, which were separated by column chromatography with a gradient eluant of 3:1 AcOEt–hexane→AcOEt into four fractions A—D.

Fraction A [R_f=0.44 (*B*)] gave 5-[(*R*)-phenylphosphinyl]-α-L-galactopyranose (**15A**) as colorless needles: 26.7 mg (9.8% from **11a**); mp 260—261 °C (from AcOEt–hexane); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 369 (M–Ac; 1.1), 353 (11), 338 (3.6), 327 (1.2), 312 (21), 279 (8.8), 269 (19), 251 (27), 211 (40), 182 (21), 169 (24), 129 (70), 85 (100). Found: *m/z* 369.1098. Calcd for $C_{17}H_{22}O_7P$: M−CH_3CO, 369.1103.

Fraction B [R_f=0.38 (*B*)] gave 5-[(*S*)-*P*]-α-D-altropyranose **16A** as a colorless syrup: 5.4 mg (2.1% from **11a**); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 413 (M+1; 0.7), 412 (M^+; 0.2), 353 (11), 311 (13), 269 (11), 251 (22), 183 (10), 169 (24), 115 (38), 85 (100). Found: *m/z* 412.1311. Calcd for $C_{19}H_{25}O_8P$: M, 412.1287.

Fraction C [R_f=0.30 (*B*)] gave a colorless syrup (29.5 mg) which consisted of 5-[(*R*)-*P*]-β-D-altro isomer **16B** (9.1% from **11a**) and 5-[(*R*)-*P*]-β-L-galacto isomer **15B** (2.1%), the relative amounts being determined by the intensity ratio of their MeO-3 signals: ^{1}H and ^{31}P NMR, see Table 1.

Fraction D [R_f=0.25 (*B*)] gave 5-[(*S*)-*P*]-α-L-galacto isomer **15C** as a colorless syrup: 18.6 mg (7.1% from **11a**); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 353 (M−AcO; 4.9), 311 (5.9), 292 (2.5), 269 (10), 251 (12), 169 (19), 129 (11), 85 (100). Found: *m/z* 353.1154. Calcd for $C_{17}H_{22}O_6P$: M−AcO, 353.1154.

1,2,4-Tri-*O*-acetyl-3-*O*-benzyl-5,6-dideoxy-5-[(*R* and *S*)-phenylphosphinyl]-α,β-L-galactopyranoses (17) and -D-Altropyranoses (18). By the same procedures described for **15** and **16**,

compound **11b** (266 mg, 0.615 mmol) was converted into a mixture of triacetates **17** and **18** via **12b** and **13b/14b**. This was separated by column chromatography into four fractions A—D.

Fraction A [R_f=0.61 (*B*)] gave 5-[(*R*)-phenylphosphinyl]-α-D-altropyranose (**18C**) as a colorless syrup: 14.6 mg (4.4% from **11b**); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 489 (M+1; 0.1), 429 (7.5), 387 (1.3), 327 (3.2), 323 (29), 280 (5.4), 221 (11), 125 (13), 91 (100). Found: *m/z* 489.1680. Calcd for $C_{25}H_{30}O_8P$: M+1, 489.1678.

Fraction B [R_f=0.55 (*B*)] gave 5-[(*R*)-*P*]-α-L-galacto isomer **17A** as colorless needles: 18.3 mg (6.1% from **11b**); mp 242—244 °C (from AcOEt–hexane); $[\alpha]_D$−78° (*c* 0.56, $CHCl_3$); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 429 (M−AcO; 1.3), 323 (51), 280 (15), 263 (15), 238 (12), 221 (26), 125 (14), 91 (100). Found: *m/z* 429.1452. Calcd for $C_{23}H_{26}O_6P$: M−AcO, 429.1467. Anal. ($C_{25}H_{29}O_8P$) C, H.

Fraction C [R_f=0.45 (*B*)] gave a colorless syrup (7.2 mg) which consisted of 5-[(*R*)-*P*]-β-L-galacto isomer **17B** (1.1% from **11b**) and 5-[(*S*)-*P*]-α-D-altro isomer **18A** (1.3%), the relative amounts being determined from the integral ratio of ^{31}P signals: ^{1}H and ^{31}P NMR, see Table 1.

Fraction D [R_f=0.38 (*B*)] gave 5-[(*S*)-*P*]-β-D-altro isomer (**18B**) as colorless needles: 27.8 mg (9.3% from **11b**); mp 268—269 °C (from AcOEt–hexane); $[\alpha]_D$−28° (*c* 0.64, $CHCl_3$); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 429 (M−AcO; 14), 387 (3.0), 369 (1.3), 327 (5.0), 280 (5.3), 125 (10), 91 (100). Found: *m/z* 429.1463. Calcd for $C_{23}H_{26}O_6P$: M−AcO, 429.1467.

1,2,3,4-Tetra-*O*-acetyl-5,6-dideoxy-5-[(*R* and *S*)-phenylphosphinyl]-α,β-L-galactopyranoses (19) and -D-Altropyranoses (20). By the same procedures described above, compound **11d** (264 mg, 0.771 mmol) was converted into a mixture of tetraacetates **19** and **20** via **12d** and **13d/14d**. This was separated by column chromatography into four fractions A—D.

Fraction A [R_f=0.60 (*B*)] gave 5-[(*R*)-phenylphosphinyl]-α-L-galactopyranose (**19A**) as a colorless syrup: 36.6 mg (11% from **11d**); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 441 (M+1; 1.6), 398 (7.4), 381 (13), 356 (10), 339 (73), 296 (24), 279 (86), 253 (19), 237 (100), 209 (29), 184 (25), 159 (25), 141 (31), 125 (73). Found; *m/z* 441.1297. Calcd for $C_{20}H_{26}O_9P$: M+1, 441.1314.

Fraction B [R_f=0.53 (*B*)] gave a colorless syrup (10.3 mg, 3.0% from **11d**) which consisted of three isomers among **19** and **20**, the exact structures of which, however, have remained unassignable; ^{31}P NMR δ=34.4, 33.0, and 31.0 (1:1:2).

Fraction C [R_f=0.48 (*B*)] gave a colorless syrup (21.0 mg) which consisted of 5-[(*R*)-*P*]-β-L-galacto isomer **19B** (2.7% from **11d**) and 5-[(*S*)-*P*]-β-D-altro isomer **20B** (3.5%), the relative amounts being determined from the integral ratio of ^{31}P signals; ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 441 (M+1; 2.7), 398 (6.2), 381 (10), 356 (7.5), 339 (88), 296 (23), 279 (59), 237 (100), 209 (26), 184 (24), 159 (21), 141 (27), 125 (60). Found: *m/z* 441.1302. Calcd for $C_{20}H_{26}O_9P$: M+1, 441.1314.

Fraction D [R_f=0.43 (*B*)] gave 5-[(*S*)-*P*]-α-L-galacto isomer **19C** as a colorless syrup: 14.3 mg (4.2% from **11d**); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 441 (M+1; 0.7), 440 (M^+; 0.7), 398 (6.9), 381 (11), 356 (7.1), 339 (85), 296 (24), 279 (55), 237 (100), 209 (30), 184 (23), 159 (27), 142 (33), 125 (74). Found: *m/z* 440.1255. Calcd for $C_{20}H_{25}O_9P$; M, 440.1236.

3,6-Dideoxy-1,2-*O*-isopropylidene-5-*O*-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α-L-*glycero*-hexa-3,5-dienofuranoses (22). The procedures similar to those for **10a** from **9a** were eomployed. Thus, **9C** (333 mg, 0.803 mmol) was treated with methyl phenylphosphinate (0.20 ml, 1.5 mmol) and DBU (0.14 ml, 0.94 mmol) at −40 °C for 1 h. Purification of the crude product by column chromatography gave **22** (227 mg, 83%) as an inseparable mixture (1:1 epimers with respect to the phosphorus atom): Colorless syrup; R_f=0.46 (*A*); ^{1}H NMR (500 MHz) δ=1.29, 1.40,* 1.42, 1.43* (6H, 4s, CMe_2), 3.84, 3.86* (3H, 2d, J_{POMe}=11.2 Hz, POMe), 5.20, 5.24,* 5.24, 5.27* (2H, 4t, $J_{6,6'}$=$J_{6,P}$=2.3 Hz, H-6,6′), 5.31, 5.34* (1H, 2dd, $J_{1,2}$=5.2, $J_{2,3}$≈2.5 Hz, H-2), 5.41, 5.43* (1H, 2d, H-3), 6.075, 6.08* (1H, 2d, H-1), 7.48, 7.49* [2H, 2m, Ph(*m*)], 7.58, 7.59* [1H, 2m, Ph(*p*)], 7.83, 7.83* [2H, 2m, Ph(*o*)], *for another diastereomer (the assignment of some of the δ values may have to be interchanged).

3,6-Dideoxy-1,2-*O*-isopropylidene-5-*O*-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α-L-*glycero*-hex-4-enofuranoses (23). The procedures similar to those for **11a** from **10a** were employed. Thus, **22** (79 mg, 0.233 mmol) was treated with Raney-Ni(W-4) (70 mg) under H_2 for 5 h. Purification of the crude product by column chromatography gave **23** (35 mg, 44%) as an inseparable mixture (1:1) of *P*-epimers: Colorless syrup; R_f=0.40 (*A*); ^{1}H NMR (500 MHz) δ=1.35, 1.36,* 1.40,* 1.42 (6H, 4s, CMe_2), 1.87,* 2.02 (3H, 2t, $J_{3S,6}$=$J_{6,P}$=2.0 Hz, H_3-6), 2.51, 2.71* (1H, 2dddq, $J_{3R,3S}$=17.1, $J_{2,3S}$=5.7, $J_{3S,P}$= 3.7 Hz, H-3S), 2.87, 2.92* (1H, 2br d, $J_{3R,P}$=0.5 Hz, $J_{2,3R}$≈0 Hz, H-3R), 3.79, 3.795* (3H, 2d, J_{POMe}=11.2 Hz, POMe), 4.67, 4.72* (1H, 2dd, $J_{1,2}$=3.6 Hz, H-2), 5.92, 5.93* (1H, 2d, H-1), 7.47, 7.47* [2H, m, $J_{o,m}$=$J_{m,p}$=7.5, $J_{m,P}$=4.4 Hz, Ph(*m*)], 7.57, 7.57* [1H, m, $J_{o,p}$=$J_{p,P}$=1.5 Hz, Ph(*p*)], 7.82, 7.82* [2H, m, $P_{o,P}$=13.6 Hz, Ph(*o*)], *for another diastereomer.

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