Stereoselectivity in the Preparation of 5,6-Dideoxy-5-dimethoxyphosphinyl-D- and -L-hexofuranoses, and an Efficient Synthesis of 5,6-Dideoxy-5-hydroxyphosphinyl-L-galactopyranose (a P-in-the-Ring L-Fucose Analogue)

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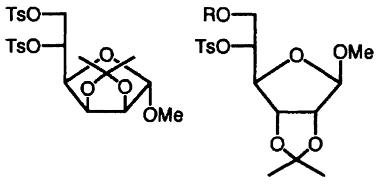
The addition of dimethyl phosphonate to five kinds of 6-*O*-tosyl-hexofuranos-5-uloses **3a**—**e** (α-D-*xylo*, α-D-*ribo*, β-D-*arabino*, α-D-*lyxo*, and β-D-*ribo*) in the presence of DBU, followed by the catalytic hydrogenolysis in the presence of Raney-Ni (W-4), afforded (5*S*)- and (5*R*)-5,6-dideoxy-hexofuranose derivatives in the ratios of 1 : 0—2 : 1, depending upon the kinds of substituents on the β-side of the furanose ring of the intermediate 5,6-dideoxy-hex-5-enofuranoses. A P-in-the-ring sugar analogue of L-fucose type, 5,6-dideoxy-5-hydroxyphosphinyl-L-galactopyranoses, was efficiently prepared from 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-α-L-galactofuranose readily obtained by the selective preparation mentioned above.

5-Deoxy-5-phosphinyl-D- and -L-hexofuranose derivatives are, in many cases, key intermediates in the preparation of the sugar analogues having a phosphorus atom in the hemiacetal ring.[1] An important method of introducing a phosphinyl group onto C-5 of hexofuranoses was accomplished by the reaction of 6-*O*-tosyl-hexofuranos-5-uloses **3** with phosphonate in the presence of DBU.[2—5] This procedure readily gave 5,6-anhydro-5-phosphinyl compounds **4**, which were converted, by the catalytic hydrogenolysis, into the corresponding 5,6-dideoxy-5-phosphinyl derivatives **7** and **8**. The exact stereoselectivity on C-5, however, remained virtually unestablished for these reactions. We now report on our systematic investigation on the stereoselectivity in the preparation of various 5,6-dideoxy-5-phosphinyl-hexofuranoses.

6-*O*-Tosyl-hexofuranos-5-uloses **3a** (α-D-*xylo*),[6] **3b** (α-D-*ribo*),[5] **3c** (β-D-*arabino*),[4] **3d** (α-D-*lyxo*),[7] and **3e** (β-D-*ribo*) were prepared from the corresponding 5,6-diols **1a**—**e** via 6-*O*-tosyl compounds **2a**—**e** (Scheme 1). The mono-*O*-tosylation took place selectively for **1a**—**d**; e.g., **1d** gave 6-*O*-tosyl compound **2d** (90% yield) with the formation of only a trace amount of 5,6-ditosylate **2d′** (2%) (Chart 1). The tosylation of **1e** with 1 equimolar tosyl chloride, however, yielded the 5,6-di-*O*-tosyl derivative **2e′** (10% yield) and the rare 5-*O*-tosyl derivative **2e″** (5%), in addition to the desired compound **2e** (65%) and the recovered diol **1e** (14%). Oxidation of 6-*O*-tosyl compounds **2a**—**e** with pyridinium chlorochromate (PCC) gave the corresponding 5-uloses **3a**—**e**.



2d′ **2e′** R = Ts
2e″ R = H

Chart 1.

Treatment of **3a**—**e** with 1,2-dimethyl phosphonate at −40 °C in the presence of DBU (1 mole equiv) in dimethoxyethane (DME) gave an inseparable mixture of (5*R*)- and (5*S*)-5,6-anhydro compounds **4a**—**e** in the ratios shown in Table 1. In addition to these diastereomers, minor amounts of the enol phosphates **5a**—**e** were also obtained. These appear to be formed as the result of the addition of the phosphonate, followed by a Perkow type rearrangement.[4]

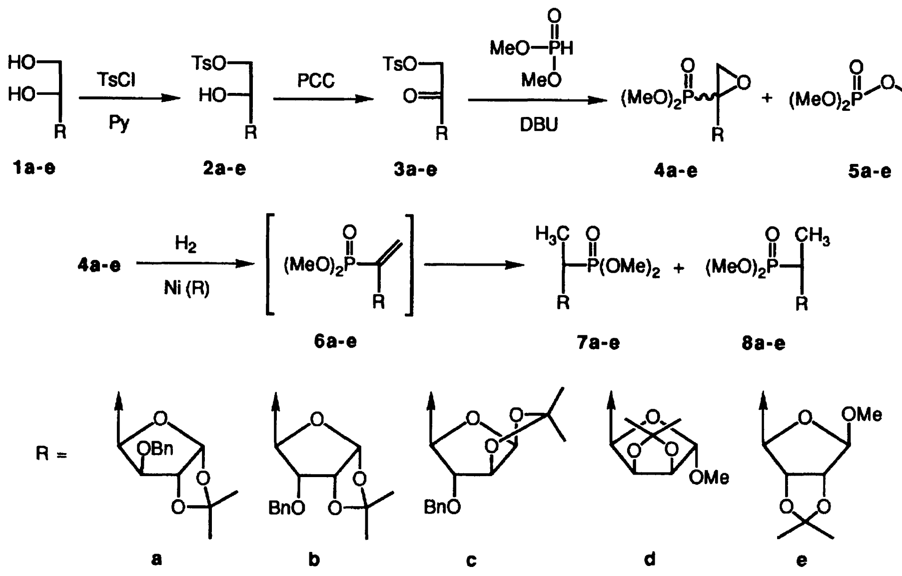
The catalytic hydrogenolysis of **4a**—**e** in the presence of Raney-Ni (W-4) in ethanol afforded (5*S*)-5,6-dideoxy derivatives **7a**—**e** and their (5*R*)-epimers **8b**—**e**, which were separable by column chromatography (except for **7b** and **8b**) in the yields and the ratios summarized in Table 1.

The C-5 configuration of these 5-phosphinyl compounds **7a**—**e** and **8a**—**e** were assigned on the basis of the magnitudes of $J_{4,5}$ values and the presence of the long-range couplings ($^5J_{1,\mathrm{P}}$, $^5J_{2,\mathrm{P}}$, and $^4J_{3,\mathrm{P}}$)[10] (see Table 2 and Fig. 1). Namely, the β-L-*talo* and α-D-*allo* configurations for **7b** and **8b** were confirmed by the small values of $J_{4,5}$ (i.e., a gauche relationship of H-4/H-5) and the large $J_{4,\mathrm{P}}$ value of **7b** (i.e., an anti relationship of H-4/P-5), as well as by the presence of $^5J_{2,\mathrm{P}}$ in **8b**. Similarly, the configurations for **7a** (β-L-*ido*) and **7d** (β-L-*gulo*) were derived from the large values of $J_{4,5}$ (i.e., an anti relationship of H-4/H-5) and the presence of $^5J_{2,\mathrm{P}}$ and $^4J_{3,\mathrm{P}}$, whereas the configura-

Table 1. Yields and Ratios of **7** and **8**

Epoxide	(5*R* : 5*S*)	Product	Yield/% (ratio)
4a	(100 : 0) [a]	**7a** : **8a**	81 (100 : 0)
4b	(55 : 45) [b]	**7b** : **8b**	75 (63 : 37)
4c	(100 : 0) [b]	**7c** : **8c**	79 (85 : 15)
4d	(100 : 0) [b]	**7d** : **8d**	74 (74 : 26)
4e	(94 : 6) [b]	**7e** : **8e**	56 (70 : 30)

a) The (5*R*)-structure of **4a** was determined by X-ray crystallographic analysis (Ref. 8). b) The assignments of (5*R*) to the major isomers are based on Felkin–Anh rule (Ref. 9).



Scheme 1.

Table 2. ^{1}H NMR (500 MHz) Parameters for **7** and **8** in $CDCl_3$

	Chemical shift (δ)										Coupling constant (Hz)										
Compd	H-1	H-2	H-3	H-4	H-5	H-6	$P(OMe)_2$[a]	CMe_2	CH_2O-3[b,c]	${}^{31}P$	$J_{1,2}$	$J_{1,P}$	$J_{2,3}$	$J_{2,P}$	$J_{3,4}$	$J_{3,P}$	$J_{4,5}$	$J_{4,P}$	$J_{5,6}$	$J_{5,P}$	$J_{6,P}$
7a	5.95	4.61	3.87	4.22	2.45	1.06	3.78, 3.74	1.50, 1.32	4.70, 4.45	33.6	3.9	0	0	2.4	2.9	1.5	10.6	7.7	7.2	16.0	18.0
7b	5.77	4.53	4.31	4.10	2.24	1.28	3.70, 3.65	1.57, 1.34	4.75, 4.59	31.4	3.7	0	4.4	0	9.0	0	2.9	27.7	7.5	20.6	17.0
8b	5.72	4.54	3.70	4.36	2.23	1.00	3.74, 3.72	1.59, 1.35	4.79, 4.53	32.6	3.7	0	4.5	1.8	9.2	0	2.6	13.0	7.3	22.6	17.8
7c	5.87	4.60	4.00	4.17	2.34	1.18	3.77, 3.73	1.54, 1.33	4.61, 4.58	31.9	3.9	0	0.8	0	3.4	0	9.0	7.9	7.3	18.9	18.0
8c	5.89	4.63	4.31	4.25	2.40	1.29	3.72, 3.72	1.48, 1.31	4.62, 4.62	31.9	3.8	1.4	0	0	2.3	0	9.4	7.2	7.2	19.6	17.8
7d	4.90	4.53	4.67	4.01	2.43	1.26	3.79, 3.75	1.44, 1.31	(3.33)[d]	33.8	0	0	5.9	1.2	3.5	1.0	10.7	7.5	7.3	15.2	18.0
8d	4.81	4.53	4.73	3.98	2.57	1.35	3.77, 3.75	1.44, 1.31	(3.30)[d]	32.2	0	1.7	5.8	0	3.2	0	10.0	6.5	7.3	18.8	18.1
7e	4.99	4.53	4.69	4.29	2.15	1.23	3.79, 3.77	1.49, 1.32	(3.43)[d]	32.3	0	0	6.0	0	2.1	0	9.3	8.4	7.3	18.0	18.0
8e	4.93	4.56	5.11	4.23	2.13	1.29	3.78, 3.77	1.47, 1.32	(3.38)[d]	31.0	0	2.1	6.0	0	0.5	0	10.7	5.3	7.2	18.5	17.8

a) $J_{POMe}=10.7$ Hz. b) ${}^{2}J_{H,H}=11.6$ Hz. c) Ph: $\delta=7.30$—7.41 (5H, m). d) MeO-1

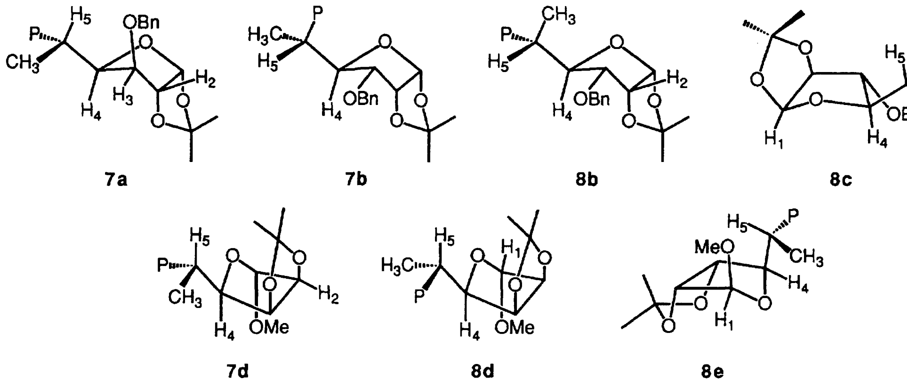
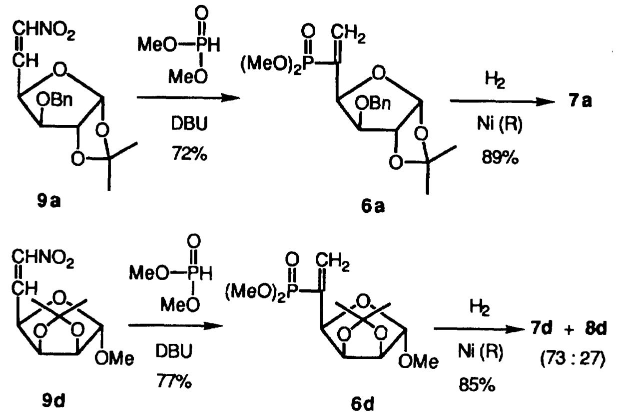


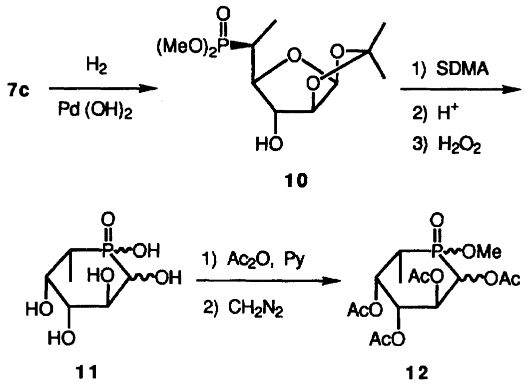
Fig. 1. The most favorable conformations for **7a**, **b**, **d** and **8b**—**e**.

tions for **8c** (β-D-*altro*), **8d** (α-D-*manno*) and **8e** (β-D-*allo*) were derived from the large values of $J_{4,5}$ and the presence of ${}^{5}J_{1,P}$. Therefore, the configurations of their C-5 epimers **7c** and **7e** were assigned to be α-L-*galacto* and α-L-*talo* form, respectively.

Because of above results showed that the product ratios of **7a**—**e** and their corresponding epimers **8a**—**e** were independent of those of the precursors **4a**—**e**, the reduction of **4** was presumed to proceed via certain intermediates such as 5,6-dideoxy-hex-5-enofuranoses **6a**—**e**. Therefore, we studied the catalytic hydrogenation of **6a** and **6d** which were prepared by an alternative route as illustrated in Scheme 2. Namely, treatment of 5,6-dideoxy-6-nitro-α-D-*xylo*-hex-5-enofuranose derivative **9a**[11] with dimethyl phosphonate in the presence of DBU (1.1 mole equiv) gave **6a**. This was then hydrogenated in the presence of Raney-Ni, to yield solely β-L-*ido* compound **7a** in an 89% yield. Similarly,



Scheme 2.



Scheme 3.

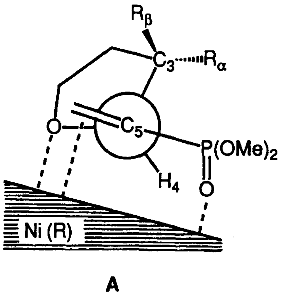
the reduction of **6d**, prepared from the 5,6-dideoxy-6-nitro-α-D-*lyxo*-5-enofuranoside derivative **9d**,[10] gave a mixture of **7d** and **8d** in a ratio of 73 : 27, which turned out to be identical with that directly obtained by the reduction of **4d**.

These results therefore suggest that the preponderant production of the (5*S*)-5-phosphinyl compounds **7a**—**e** proceeds through the following two steps: 1) the deoxygenation of **4a**—**e** gives the olefinic intermediates **6a**—**e**, most likely existing in such a conformation as **A** illustrated in Fig. 2; 2) the hydrogenation of **6a**—**e** occurs at the *re* side where the ring oxygen can assist the adsorption of these molecules to the nickel catalyst. The conformation **A** is supported by the small $J_{4,\mathrm{P}}$ values (4.5 and 4.9 Hz) and the presence of $^5J_{1,\mathrm{P}}$ (0.8 and 1.7 Hz) for **6a** and **6d**. The exact reason for the high stereoselectivity in the hydrogenation of **6a** compared with other intermediates **6b**—**e** remains to be further investigated, although it may depend upon the presence of the substituents on the β-side of the furanose ring as well as the conformation of the furanose ring itself.

An application of the present study was demonstrated by an efficient synthesis of a P-in-the-ring sugar analogue of 6-deoxy-L-galactopyranose (L-fucose) type from **7c** obtained above, as shown in Scheme 3.

Namely, debenzylation of **7c** was effected by the catalytic hydrogenolysis over 20% Pd(OH)$_2$–C to provide compound **10**, which was reduced with sodium dihydridobis(2-methoxyethoxy)aluminate (SDMA). The product was immediately subjected to acid hydrolysis and then oxidation with hydrogen peroxide, affording 5,6-dideoxy-5-hydroxyphosphinyl-L-galactopyranose (**11**) as a diastereomeric mixture. Compound **11** was converted by the well-established method[12] into the 5-deoxy-5-methoxyphosphinyl per-*O*-acetyl compounds **12**. Chromatography of **12** on a column of silica gel with ethyl acetate gave 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-[(*S*)-methoxyphosphinyl]-α-L-galactopyranose (**12a**, 6% overall yield from **10**), its β-anomer **12b** (5%), 5-[(*R*)-methoxyphosphinyl]-α-isomer **12c** (3%), and its β-anomer **12d** (8%).

The precise structures of **12a**—**d** were established by the analysis of their 500-MHz ^{1}H NMR spectra; for all the assignments of the signals, see Table 3. The $^1C_4$ conformation of **12a**—**d** are derived from the large values of $J_{4,\mathrm{P}}$ (35—37 Hz) and $J_{2,3}$ (11 Hz). It is noteworthy that the $J_{4,\mathrm{P}}$ values of **12a**—**d** are considerably larger than those of the corresponding phenylphosphinyl congeners (28—31 Hz).[4,5] As for anomeric orientation of C-1, the large $J_{1,2}$ values (11 Hz) of **12b** and **12d** indicate the axial H-1 configuration, whereas the small $J_{1,2}$ values (3 Hz) of **12a** and **12c** show the equatorial H-1 configuration. With regard to the orientation of the ring P=O group, a downfield shift (0.2—0.3 ppm) of H-2 of **12a** and **12b** compared with those of **12c** and **12d** indicates the axial P=O orientation for the former (**12a, b**) and the equatorial P=O orientation for the latter (**12c, d**).



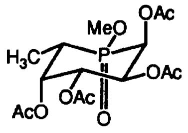
A

Fig. 2. A favorable conformation of **6**.

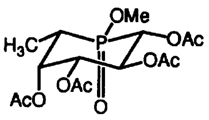
Experimental

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*) AcOEt, (*B*) 2 : 1 AcOEt–hexane, and (*C*) 1 : 1 AcOEt–hexane]. 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. Optical rotations were measured with a Nihon-Bunko DIP-370 polarimeter at 21 °C. The ^{1}H and ^{31}P NMR spectra were measured in CDCl$_3$ with Varian VXR-500 (500-MHz for ^{1}H) and VXR-200 instruments (81-MHz for ^{31}P),

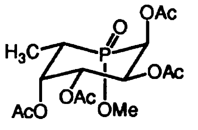
Table 3. ^{1}H NMR (500 MHz) Parameters for **12a**—**d** in $CDCl_3$



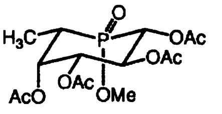
12a



12b



12c



12d

	Chemical shift (δ)									Coupling constant (Hz)										
Compd	H-1	H-2	H-3	H-4	H-5	H-6	POMe	AcO-1,2,3,4[a]	^{31}P	$J_{1,2}$	$J_{1,P}$	$J_{2,3}$	$J_{2,P}$	$J_{3,4}$	$J_{4,5}$	$J_{4,P}$	$J_{5,6}$	$J_{5,P}$	$J_{6,P}$	J_{POMe}
12a	5.70	5.76	5.27	5.54	2.34	1.19	3.69	2.19,2.18,2.01,1.99	39.5	2.8	14.7	10.8	0	2.9	3.0	35.4	7.1	14.3	15.1	10.8
12b	5.29	5.79	4.96	5.48	2.13	1.25	3.74	2.20,2.16,2.00,1.99	39.6	10.6	4.9	10.4	2.1	2.6	3.2	36.7	7.1	14.4	14.8	10.7
12c	5.75	5.44	5.25	5.53	2.51	1.23	3.90	2.19,2.15,2.00,1.99	38.9	3.0	15.6	11.1	0	3.1	3.1	35.8	7.2	14.4	14.6	10.6
12d	5.48	5.59	4.97	5.48	2.25	1.23	3.95	2.11,2.13,2.00,1.98	39.2	10.8	3.5	10.5	1.6	2.8	3.1	37.0	7.2	14.3	14.6	10.5

a) The assignments of acetoxyl groups may have to be interchanged.

respectively; the SC-NMR Lab., Okayama Univ.) at 22 °C. 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 mass spectra were taken on an A. E. I. MS 50 ultra-high resolution instrument and were given in terms of m/z (rel intensity) compared with the base peak.

Methyl 2,3-*O*-Isopropylidene-β-D-allofuranoside (1d).[13] The following modification of the literature procedures[13] was made. A solution of methyl 2,3:5,6-di-*O*-isopropylidene-β-D-allofuranoside[14] (1.07 g, 3.90 mmol) dissolved in 80% aqueous AcOH (10 ml) was stirred for 45 min at 60 °C and then evaporated in vacuo. The residue was purified by column chromatography on silica gel, giving **1d** (865 mg, 95%) as colorless crystals: mp 99—100 °C (from AcOEt–hexane) [lit,[13] mp 100—100.5 °C, 93% yield (by using hydrochloric acid as a catalyst)]; $R_f=0.17$ (*C*); ^{1}H NMR $\delta=1.31$, 1.47 (3H each, 2s, CMe_2), 2.32 (1H, m, HO-6), 3.41 (3H, s, MeO-1), 3.68—3.75 (4H, m, H-4,5,6,6′), 4.27 (1H, br d, $J_{5,OH}=3.7$ Hz, HO-5), 4.57 (1H, d, $J_{2,3}=6.0$, $J_{1,2}\approx0$ Hz, H-2), 4.90 (1H, br d, $J_{3,4}=0.5$ Hz, H-3), 4.96 (1H, s, H-1).

Methyl 2,3-*O*-Isopropylidene-6-*O*-tosyl-α-D-mannofuranoside (2d)[7] **and Its 5,6-Di-*O*-tosyl Derivative (2d′).** To a solution of **1d**[13] (305 mg, 1.30 mmol) in dry pyridine (6.0 ml) at 0 °C was added tosyl chloride (261 mg, 1.37 mmol). The mixture was stirred at 20 °C for 12 h and then water (0.5 ml) was added at 0 °C and then 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 separated by column chromatography (with 1 : 2 AcOEt–hexane), giving **2d** and **2d′**.

2d: Colorless needles (453 mg, 90%); mp 97—98 °C (from AcOEt–hexane); $R_f=0.50$ (*C*); $[\alpha]_D$ +48° (*c* 1.51, $CHCl_3$) [lit,[7] mp 94—95 °C; $[\alpha]_D^{26}$ +4.5° (*c* 1.24, $CHCl_3$)]; ^{1}H NMR $\delta=1.31$, 1.43 (3H each, 2s, CMe_2), 2.45 (3H, s, MeC_6–S), 2.66 (1H, br d, $J_{5,OH}=5.9$ Hz, HO-5), 3.27 (3H, s, MeO-1), 3.90 (1H, dd, $J_{4,5}=7.9$, $J_{3,4}=3.8$ Hz, H-4), 4.15 (1H, br dtd, $J_{5,6'}=5.8$, $J_{5,6}=3.0$ Hz, H-5), 4.19 (1H, dd, $J_{6,6'}=10.2$ Hz, H-6′), 4.31 (1H, dd, H-6), 4.55 (1H, d, $J_{2,3}=5.9$ Hz, H-2), 4.79 (1H, dd, H-3), 4.87 (1H, s, H-1), 7.35, 7.82 (2H each, 2d, $J=8.3$ Hz, C_6H_4–S); MS m/z 373 ($M-CH_3$; 38), 299 (3.5), 252 (13), 240 (7.5), 173 (22), 155 (100).

Found: m/z 373.0949. Calcd for $C_{16}H_{21}O_8S$: $M-CH_3$, 373.0957.

2d′: Colorless syrup (13.9 mg, 2.0%); $R_f=0.67$ (*C*); $[\alpha]_D$ +13° (*c* 1.00, $CHCl_3$); ^{1}H NMR $\delta=1.10$, 1.23 (3H each, 2s, CMe_2), 2.44, 2.45 (3H each, 2s, MeC_6–S), 3.27 (3H, s, MeO-1), 4.17 (1H, dd, $J_{4,5}=6.8$, $J_{3,4}=3.4$ Hz, H-4), 4.30 (1H, dd, $J_{6,6'}=11.1$, $J_{5,6'}=4.7$ Hz, H-6′), 4.43 (1H, d, $J_{2,3}=5.8$, $J_{1,2}\approx0$ Hz, H-2), 4.46 (1H, dd, $J_{5,6}=2.1$ Hz, H-6), 4.47 (1H, dd, H-3), 4.78 (1H, s, H-1), 4.86 (1H, ddd, H-5), 7.29, 7.33, 7.73, 7.76 (2H each, 4d, $J=8.3$ Hz, C_6H_4–S); FAB MS m/z 543 (M+1; 4.5), 511 (10), 357 (3.8), 277 (7.3), 185 (74), 93 (100).

Found: m/z 543.1366. Calcd for $C_{24}H_{31}O_{10}S_2$: M+1, 543.1359.

Methyl 2,3-*O*-Isopropylidene-6-*O*-tosyl-β-D-allofuranoside (2e), Its 5,6-Di-*O*-tosyl (2e′), and 5-*O*-Tosyl Derivative (2e″). By the use of the same procedures as those for **2d**, compound **1e** (206 mg, 0.879 mmol) was treated with tosyl chloride (176 mg, 0.923 mmol) and pyridine (5.0 ml) at 20 °C for 12 h, giving **2e**, **2e′**, **2e″**, and the recovered **1e** (29.5 mg, 14%), after the separation by column chromatography (with 1 : 2 AcOEt–hexane).

2e: Colorless needles (221 mg, 65%); mp 91—92 °C (from AcOEt–hexane); $R_f=0.57$ (*C*); $[\alpha]_D$ −25° (*c* 0.98, $CHCl_3$); ^{1}H NMR $\delta=1.29$, 1.46 (3H each, 2s, CMe_2), 2.45 (3H, s, MeC_6–S), 3.33 (3H, s, MeO-1), 3.34 (1H, br s, HO-5), 3.86 (1H, br td, $J_{4,5}=J_{5,6'}=6.1$, $J_{5,6}=4.4$ Hz, H-5), 4.08 (1H, dd, $J_{6,6'}=10.5$ Hz, H-6′), 4.17 (1H, dd, H-6), 4.18 (1H, br d, $J_{3,4}=0.5$ Hz, H-4), 4.54 (1H, d, $J_{2,3}=6.0$, $J_{1,2}\approx0$ Hz, H-2), 4.82 (1H, br d, H-3), 4.93 (1H, s, H-1), 7.35, 7.81 (2H each, 2d, $J=8.4$ Hz, C_6H_4–S); MS m/z 373 ($M-CH_3$; 30), 357 (1.2), 341 (13), 298 (1.6), 252 (14), 173 (83), 155(100).

Found: m/z 373.0946. Calcd for $C_{16}H_{21}O_8S$: $M-CH_3$, 373.0957.

2e′: Colorless needles (47.9 mg, 10%); mp 94—95 °C (from AcOEt–hexane); $R_f=0.67$ (*C*); $[\alpha]_D$ −25° (*c* 0.73, $CHCl_3$); ^{1}H NMR $\delta=1.25$, 1.42 (3H each, 2s, CMe_2), 2.45, 2.46 (3H each, 2s, MeC_6–S), 3.22 (3H, s, MeO-1), 4.09 (1H, dd, $J_{6,6'}=11.2$, $J_{5,6'}=4.0$ Hz, H-6′), 4.19 (1H, br d, $J_{4,5}=10.4$, $J_{3,4}=0.5$ Hz, H-4), 4.26 (1H, dd, $J_{5,6}=2.1$ Hz, H-6), 4.47 (1H, d, $J_{2,3}=5.9$, $J_{1,2}\approx0$ Hz, H-2), 4.64 (1H, ddd, H-5), 4.68 (1H, br d, H-3), 4.88 (1H, s, H-1), 7.32, 7.34, 7.70, 7.76 (2H each, 4d, $J=8.2$ Hz, C_6H_4–S); FAB MS m/z 543 (M+1; 11), 511 (81), 357 (15), 281 (8.5), 185 (37), 155 (100), 91 (68).

Found: m/z 543.1350. Calcd for $C_{24}H_{31}O_{10}S_2$: M+1, 543.1359.

2e″ Colorless syrup (16.0 mg, 4.7%); $R_f=0.45$ (*C*);

$[\alpha]_D$ −61° (c 1.57, $CHCl_3$); ^{1}H NMR δ=1.24, 1.43 (3H each, 2s, CMe_2), 2.14 (1H, t, $J_{6,OH}$=7.0, $J_{6',OH}$=6.6 Hz, HO-6), 2.46 (3H, s, MeC_6–S), 3.35 (3H, s, MeO-1), 3.80 (1H, ddd, $J_{6,6'}$=13.0, $J_{5,6'}$=4.4 Hz, H-6′), 3.93 (1H, dd, $J_{5,6}$=2.6 Hz, H-6), 4.24 (1H, br d, $J_{4,5}$=10.1, $J_{3,4}$=0.5 Hz, H-4), 4.44 (1H, d, $J_{2,3}$=6.0, $J_{1,2}\approx$0 Hz, H-2), 4.56 (1H, br d, H-3), 4.58 (1H, ddd, H-5), 4.94 (1H, s, H-1), 7.38, 7.84 (2H each, 2d, J=8.2 Hz, C_6H_4–S); FAB MS m/z 389 (M+1; 16), 373 (12), 357 (100), 341 (10), 185 (81), 155 (49), 127 (55), 85 (92).

Found: m/z 389.1285. Calcd for $C_{17}H_{25}O_8S$: M+1, 389.1270.

Methyl 2,3-*O*-Isopropylidene-6-*O*-tosyl-α-D-*lyxo*-hexofuranos-5-ulose (3d).[7] To a solution of **2d** (292 mg, 0.751 mmol) in dry CH_2Cl_2 (3.0 ml) containing finely powdered molecular sieves 3A (0.6 g) was added PCC (325 mg, 1.51 mmol) at 0 °C. The mixture was stirred at 20 °C for 6 h and then 2-propanol (0.8 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 : 2 AcOEt–hexane as an eluent, giving **3d** (280 mg, 96%) as colorless crystals: mp 78—79 °C (from AcOEt–hexane); [lit,[7] mp 79—80 °C, 85% yield (by use of DMSO–Ac_2O for the oxidation)]; R_f=0.60 (C); ^{1}H NMR δ=1.24, 1.33 (3H each, 2s, CMe_2), 2.45 (3H, s, MeC_6–S), 3.33 (3H, s, MeO-1), 4.54 (1H, d, $J_{2,3}$=5.8, $J_{1,2}\approx$0 Hz, H-2), 4.58 (1H, d, $J_{3,4}$=4.1 Hz, H-4), 4.82, 4.91 (1H each, 2d, $J_{6,6'}$=17.1 Hz, H-6,6′), 4.99 (1H, dd, H-3), 5.01 (1H, s, H-1), 7.35, 7.84 (2H each, 2d, J=8.1 Hz, C_6H_4–S); MS m/z 371 (M−CH_3; 23), 343 (1.9), 297 (81), 255 (18), 173 (62), 155 (100).

Found: m/z 371.0790. Calcd for $C_{16}H_{19}O_8S$: M−CH_3, 371.0800.

Methyl 2,3-*O*-Isopropylidene-6-*O*-tosyl-β-D-*ribo*-hexofuranos-5-ulose (3e). The same procedures described as those for **3d** were employed. Thus, **2e** (168 mg) gave **3e** (164 mg, 98%) as a colorless syrup: R_f=0.75 (C); IR (neat) ν 1740 (C=O), 1360 (ν_{as} SO_2), 1170 cm^{-1} (ν_s SO_2); ^{1}H NMR δ=1.30, 1.45 (3H each, 2s, CMe_2), 2.45 (3H, s, MeC_6–S), 3.35 (3H, s, MeO-1), 4.47 (1H, d, $J_{2,3}$=5.9, $J_{1,2}\approx$0 Hz, H-2), 4.55 (1H, br s, $J_{3,4}$=0.5 Hz, H-4), 4.87, 4.97 (1H each, 2d, $J_{6,6'}$=17.1 Hz, H-6,6′), 4.99 (1H, s, H-1), 5.13 (1H, br d, H-3), 7.35, 7.82 (2H each, J=8.2 Hz, C_6H_4–S); MS m/z 371 (M−CH_3; 20), 343 (3.9), 297 (12), 255 (7.3), 173 (88), 155 (100).

Found: m/z 371.0787. Calcd for $C_{16}H_{19}O_8S$: M−CH_3, 371.0800.

The General Procedures for the Preparation of (5*R*)- and (5*S*)-5,6-Anhydro-5-dimethoxyphosphinyl-D- and -L-hexofuranoses (4) and 6-Deoxy-5-*O*-dimethoxyphosphinyl-D-hex-5-enofuranoses (5). To a solution of **3** (0.57 mmol) and dimethyl phosphonate (0.12 ml, 1.3 mmol) in DME (2.0 ml) was dropwise added a solution of DBU (0.090 ml, 0.60 mmol) dissolved in DME (0.5 ml) at −40 °C. The mixture was stirred at the same temp for 2 h and then 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. The residue was separated by silica-gel column chromatography, giving **4** and **5**.

(5*R*)-5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-α-D-*xylo*-hexofuranose (4a):[2] Colorless needles (82% yield from **3a**); mp 107—108 °C (lit,[2] mp 107—108 °C, 70% yield); R_f=0.38 (B); ^{1}H NMR δ=1.30, 1.50 (3H each, 2s, CMe_2), 2.97 (1H, t, $J_{6,6'}$=6.4, $J_{6',P}$=6.3 Hz, H-6′), 3.17 (1H, dd, $J_{6,P}$=3.7 Hz, H-6), 3.74, 3.76 [3H each, 2d, J_{POMe}=10.7, 11.0 Hz, $P(OMe)_2$], 4.36 (1H, d, $J_{3,4}$=3.3, $J_{2,3}\approx$0 Hz, H-3), 4.58 (1H, d, $J_{1,2}$=3.9 Hz, H-2), 4.67 (1H, d, $J_{4,P}\approx$0 Hz, H-4), 4.70, 4.71 (1H each, 2d, ^2J=11.7 Hz, CH_2O-3), 5.89 (1H, d, H-1), 7.26 [1H, t, $J_{m,p}$=7.4 Hz, Ph(p)], 7.33 [2H, t, $J_{o,m}$=7.7 Hz, Ph(m)], 7.41 [2H, d, Ph(o)]; ^{31}P NMR δ=19.8.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-dimethoxyphosphinyl-α-D-*xylo*-hex-5-enofuranose (5a): Colorless syrup (5% from **3a**); R_f=0.48 (B); ^{1}H NMR δ=1.32, 1.49 (3H each, 2s, CMe_2), 3.77, 3.78 [3H each, 2d, J_{POMe}=11.3 Hz, $P(OMe)_2$], 4.10 (1H, d, $J_{3,4}$=3.2, $J_{2,3}\approx$0 Hz, H-3), 4.61 (1H, d, $J_{1,2}$=3.7 Hz, H-2), 4.68 (1H, dt, $J_{4,6}$=$J_{4,6'}$=1.5 Hz, H-4), 5.08 (1H, td, $J_{6,6'}$=2.5, $J_{6',P}$=2.2 Hz, H-6′), 5.14 (1H, dt, $J_{6,P}$=1.5 Hz, H-6), 5.98 (1H, d, H-1), 7.27—7.35 (5H, m, Ph); ^{31}P NMR δ=−5.6.

(5*R*)- and (5*S*)-5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-5-dimethoxyphosphiny-α-D-*ribo*-hexofuranoses (4b): Colorless syrup as a 55 : 45 mixture [92% yield from **3b**[5]]; R_f=0.28 (B); ^{1}H NMR for (5*R*)-isomer δ=1.36, 1.58 (3H each, 2s, CMe_2), 2.96 (1H, dd, $J_{6,6'}$=5.5, $J_{6',P}$=4.3 Hz, H-6′), 3.14 (1H, t, $J_{6,P}$=5.5 Hz, H-6), 3.78, 3.81 [3H each, 2d, J_{POMe}=10.7 Hz, $P(OMe)_2$], 3.79 (1H, dd, $J_{3,4}$=8.9, $J_{2,3}$=4.4 Hz, H-3), 4.44 (1H, d, $J_{4,P}\approx$0 Hz, H-4), 4.52, 4.72 (1H each, 2d, ^2J=11.5 Hz, CH_2O-3), 4.58 (1H, td, $J_{1,2}$=3.7, $J_{2,P}$=1.7 Hz, H-2), 5.80 (1H, d, H-1), 7.31—7.38 (5H, m, Ph), for (5*S*)-isomer δ=1.34, 1.56 (3H each, 2s, CMe_2), 2.99 (1H, dd, $J_{6,6'}$=5.5, $J_{6',P}$=4.3 Hz, H-6′), 3.05 (1H, t, $J_{6,P}$=5.4 Hz, H-6), 3.70, 3.80 [3H each, 2d, J_{POMe}=10.6, 11.0 Hz, $P(OMe)_2$], 3.79 (1H, dd, $J_{3,4}$=8.9, $J_{2,3}$=4.4 Hz, H-3), 4.42 (1H, dd, $J_{4,P}$=2.2 Hz, H-4), 4.52 (1H, t, $J_{1,2}$=3.7 Hz, H-2), 4.61, 4.73 (1H each, 2d, ^2J=11.8 Hz, CH_2O-3), 5.80 (1H, d, H-1), 7.31—7.38 (5H, m, Ph), ^{31}P NMR δ=19.1 [(5*R*)-isomer], 17.5 [(5*S*)-isomer]; MS m/z 385 (M−CH_3; 0.4), 342 (0.6), 309 (5.1), 251 (4.4), 235 (10), 217 (4.5), 207 (18), 181 (12), 165 (13), 91 (100).

Found: m/z 385.1507. Calcd for $C_{17}H_{22}O_8P$: M−CH_3, 385.1052.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-dimethoxyphosphinyl-α-D-*ribo*-hex-5-enofuranose (5b): Colorless syrup (3% yield from **3b**); R_f=0.36 (B); ^{1}H NMR δ=1.36, 1.61 (3H each, 2s, CMe_2), 3.76, 3.78 [3H each, 2d, J_{POMe}=10.8, 11.2 Hz, $P(OMe)_2$], 3.95 (1H, dd, $J_{3,4}$=8.8, $J_{2,3}$=4.3 Hz, H-3), 4.47 (1H, dd, $J_{4,P}$=2.3 Hz, H-4), 4.52 (1H, t, $J_{1,2}$=3.5 Hz, H-2), 4.66, 4.72 (1H each, 2d, ^2J=12.2 Hz, CH_2O-3), 4.98 (1H, t, $J_{6,6'}$=2.5, $J_{6',P}$=2.2 Hz, H-6′), 5.19 (1H, dd, $J_{6,P}$=1.5 Hz, H-6), 5.74 (1H, d, H-1), 7.30—7.37 (5H, m, Ph); ^{31}P NMR δ=−5.5.

(5*R*)-5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-β-D-*arabino*-hexofuranose (4c): Colorless syrup (65% yield from **3c**[4]); R_f=0.38 (B); $[\alpha]_D$ +14° (c 0.97, $CHCl_3$); ^{1}H NMR δ=1.33, 1.56 (3H each, 2s, CMe_2), 3.10 (1H, t, $J_{6,6'}$=5.9, $J_{6',P}$=5.2 Hz, H-6′), 3.19 (1H, dd, $J_{6,P}$=4.4 Hz, H-6), 3.79 [6H, d, J_{POMe}=11.0 Hz, $P(OMe)_2$], 4.25 (1H, dd, $J_{3,4}$=4.4, $J_{2,3}$=1.1 Hz, H-3), 4.36 (1H, t, $J_{4,P}$=5.3 Hz, H-4), 4.61 (1H, dd, $J_{1,2}$=4.0 Hz, H-2), 4.63, 4.64 (1H each, 2d, ^2J=11.7 Hz, CH_2O-3), 5.81 (1H, d, H-1), 7.30—7.36 (5H, m, Ph); ^{31}P NMR δ=19.3; MS m/z 385 (M−CH_3; 4.8), 342 (4.1), 283 (6.0), 251 (3.2), 236 (5.7), 207 (7.8), 193 (3.5), 181 (8.4), 152 (13), 91 (100).

Found: *m/z* 385.1058. Calcd for $C_{17}H_{22}O_8P$: $M-CH_3$, 385.1052.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-dimethoxyphosphinyl-β-D-*arabino*-hex-5-enofuranose (5c): Colorless syrup (3% yield from **3c**); R_f=0.48 (*B*); ^{1}H NMR δ=1.32, 1.49 (3H each, 2s, CMe_2), 3.77, 3.78 [3H each, 2d, J_{POMe}=11.4 Hz, P(OMe)$_2$], 4.21 (1H, d, $J_{3,4}$=2.9, $J_{2,3}\approx0$ Hz, H-3), 4.54 (1H, dt, $J_{4,6}=J_{4,6'}$=1.5 Hz, H-4), 4.62, 4.63 (1H each, 2d, ^2J=11.7 Hz, CH_2O-3), 4.67 (1H, d, $J_{1,2}$=4.1 Hz, H-2), 5.11 (1H, dt, $J_{6,6'}$=2.5, $J_{6',P}$=1.6 Hz, H-6'), 5.14 (1H, q, $J_{6,P}$=2.1 Hz, H-6), 5.96 (1H, d, H-1), 7.29—7.36 (5H, m, Ph); ^{31}P NMR δ=−5.4.

Methyl (5*R*)-5,6-Anhydro-2,3-*O*-isopropylidene-5-dimethoxyphosphinyl-α-D-*lyxo*-hexofuranoside (4d): Colorless syrup (74% yield from **3d**); R_f=0.18 (*B*); $[\alpha]_D$ +50° (*c* 3.54, $CHCl_3$); ^{1}H NMR δ=1.30, 1.48 (3H each, 2s, CMe_2), 2.96 (1H, dd, $J_{6,6'}$=6.4, $J_{6',P}$=5.3 Hz, H-6'), 3.14 (1H, dd, $J_{6,P}$=4.0 Hz, H-6), 3.29 (3H, s, MeO-1), 3.83 [6H, d, J_{POMe}=10.7 Hz, P(OMe)$_2$], 4.41 (1H, br d, $J_{3,4}$=3.8, $J_{4,P}$=0.5 Hz, H-4), 4.53 (1H, d, $J_{2,3}$=6.0, $J_{1,2}\approx0$ Hz, H-2), 4.88 (1H, d, $J_{1,P}$=1.0 Hz, H-1), 4.93 (1H, dd, H-3); ^{31}P NMR δ=19.7; MS *m/z* 310 (12), 309 ($M-CH_3$; 100), 293 (7.9), 266 (3.8), 235 (5.1), 207 (14), 205 (17), 181 (40), 163 (40), 139 (10), 109 (33).

Found: *m/z* 309.0739. Calcd for $C_{11}H_{18}O_8P$: $M-CH_3$, 309.0739.

Methyl 6-Deoxy-2,3-*O*-isopropylidene-5-*O*-dimethoxyphosphinyl-α-D-*lyxo*-hex-5-enofuranoside (5d): Colorless syrup (6% yield from **3d**); R_f=0.31 (*B*); ^{1}H NMR δ=1.30, 1.42 (3H each, 2s, CMe_2), 3.35 (3H, s, MeO-1), 3.84, 3.845 [3H each, 2s, J_{POMe}=11.6 Hz, P(OMe)$_2$], 4.47 (1H, dt, $J_{3,4}$=3.9, $J_{4,6}=J_{4,6'}$=1.4 Hz, H-4), 4.58 (1H, d, $J_{2,3}$=5.9, $J_{1,2}\approx0$ Hz, H-2), 4.82 (1H, dd, H-3), 4.95 (1H, s, H-1), 4.99 (1H, td, $J_{6,6'}=J_{6',P}$=2.2 Hz, H-6'), 5.10 (1H, td, $J_{6,P}$=1.9 Hz, H-6); ^{31}P NMR δ=−5.6; MS *m/z* 324 (M^+; 3.0), 309 (36), 293 (6.4), 266 (5.2), 249 (2.2), 234 (12), 206 (28), 181 (99), 149 (24), 127 (100).

Found: *m/z* 324.0975. Calcd for $C_{12}H_{21}O_8P$: M, 324.0974.

Methyl (5*R*)- and (5*S*)-5,6-Anhydro-2,3-*O*-isopropylidene-5-dimethoxyphosphinyl-β-D-*ribo*-hexofuranoside (4e): Colorless syrup as a 94:6 mixture [77% yield from **2e**]; R_f=0.24 (*B*); ^{1}H NMR for (5*R*)-isomer δ=1.32, 1.49 (3H each, 2s, CMe_2), 2.98 (1H, t, $J_{6,6'}$=5.4, $J_{6',P}$=4.7 Hz, H-6'), 3.09 (1H, t, $J_{6,P}$=5.4 Hz, H-6), 3.37 (3H, s, MeO-1), 3.84, 3.845 [3H each, 2d, J_{POMe}=10.8 Hz, P(OMe)$_2$], 4.48 (1H, br d, $J_{2,3}$=6.0, $J_{1,2}$=0.5 Hz, H-2), 4.74 (1H, dd, $J_{4,P}$=3.3, $J_{3,4}$=1.9 Hz, H-4), 4.82 (1H, dd, H-3), 4.96 (1H, br s, H-1), for (5*S*)-isomer δ=1.31, 1.49 (3H each, 2s, CMe_2), 2.99, 3.16 (2H each, 2t, $J_{6,6'}=J_{6,P}=J_{6',P}$=5.3 Hz, H-6,6'), 3.45 (3H, s, MeO-1), 3.78, 3.84 [3H each, 2d, J_{POMe}=11.9 Hz, P(OMe)$_2$], 4.51 (1H, d, $J_{2,3}$=6.3, $J_{1,2}\approx0$ Hz, H-2), 4.66 (1H, t, $J_{3,4}=J_{4,P}$=2.4 Hz, H-4), 4.70 (1H, dd, H-3), 5.03 (1H, s, H-1); ^{31}P NMR δ=19.8 [(5*R*)-isomer], 19.0 [(5*S*)-isomer]; MS *m/z* 310 (7.0), 309 ($M-CH_3$; 59), 248 (5.6), 234 (15), 221 (15), 205 (24), 181 (47), 161 (26), 149 (40), 93 (100).

Found: *m/z* 309.0738. Calcd for $C_{11}H_{18}O_8P$: $M-CH_3$, 309.0739.

Methyl 6-Deoxy-2,3-*O*-isopropylidene-5-*O*-dimethoxyphosphinyl-β-D-*ribo*-hex-5-enofuranoside (5e): Colorless syrup (4% from **2e**); R_f=0.37 (*B*); $[\alpha]_D$ −38° (*c* 1.09, $CHCl_3$); ^{1}H NMR δ=1.32, 1.50 (3H each, 2s, CMe_2), 3.41 (3H, s, MeO-1), 3.835, 3.84 [3H each, 2d, J_{POMe}=11.3 Hz, P(OMe)$_2$], 4.58 (1H, d, $J_{2,3}$=5.9, $J_{1,2}\approx0$ Hz, H-2), 4.63 (1H, dt, $J_{3,4}$=1.8, $J_{4,6}=J_{4,6'}$=1.0 Hz, H-4), 4.86 (1H, dd, H-3), 4.93 (1H, td, $J_{6,6'}=J_{6',P}$=2.5 Hz, H-6'), 5.05 (1H, s, H-1), 5.05 (1H, td, $J_{6,P}$=2.0 Hz, H-6); ^{31}P NMR δ=−5.6; MS *m/z* 324 (M^+; 3.4), 309 (22), 293 (5.2), 266 (4.7), 234 (14), 206 (25), 181 (94), 149 (17), 127 (100).

Found: *m/z* 324.0976. Calcd for $C_{12}H_{21}O_8P$: M, 324.0974.

General Procedures for the Preparation of 5,6-Dideoxy-5-dimethoxyphosphinyl-hexofuranoses (7a-e and 8a-e). Compound **4** (0.70 mmol) dissolved in ethanol (2 ml) was hydrogenated in the presence of Raney-Ni (W-4) (400 mg) at 20 °C under an atmospheric pressure of H_2. After 4—8 h, the catalyst was filtered off through celite, and the filtrate was evaporated in vacuo. The residue was separated by column chromatography, giving **7** and **8** as a colorless syrup.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-β-L-idofuranose (7a): 81% yield from **4a**; R_f=0.31 (*A*); $[\alpha]_D$ −36° (*c* 2.16, $CHCl_3$); ^{1}H and ^{31}P NMR, see Table 2; FAB MS *m/z* 387 (M+1; 45), 329 (7.8), 298 (8.0), 261 (13), 221 (52), 165 (11), 91 (100).

Found: *m/z* 387.1568. Calcd for $C_{18}H_{28}O_7P$: M+1, 387.1573.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-β-L-talofuranose (7b) and -α-D-allofuranose (8b): 75% yield from **4b** as a 63:37 mixture; R_f=0.25 (*A*); ^{1}H and ^{31}P NMR, see Table 2; MS *m/z* 386 (M^+; 0.2), 371 (0.2), 354 (0.9), 309 (2.1), 277 (4.5), 263 (14), 221 (30), 207 (12), 91 (100).

Found: *m/z* 386.1473. Calcd for $C_{18}H_{27}O_7P$: M, 386.1495.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-α-L-galactofuranose (7c): 67% yield from **4c**; R_f=0.36 (*A*); $[\alpha]_D$ +26° (*c* 1.16, $CHCl_3$); ^{1}H and ^{31}P NMR, see Table 2; MS *m/z* 371 ($M-CH_3$; 2.2), 295 (2.0), 237 (8.0), 221 (11), 167 (27), 138 (19), 91 (100).

Found: *m/z* 371.1255. Calcd for $C_{17}H_{24}O_7P$; $M-CH_3$, 371.1260.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-β-D-altrofuranose (8c): 12% yield from **4c**; R_f=0.49 (*A*); $[\alpha]_D$ +8.8° (*c* 1.97, $CHCl_3$); ^{1}H and ^{31}P NMR, see Table 2.

Methyl 5,6-Dideoxy-2,3-*O*-isopropylidene-5-dimethoxyphosphinyl-β-L-gulofuranoside (7d): 55% yield from **3d**; R_f=0.32 (*A*); $[\alpha]_D$ +65° (*c* 1.15, $CHCl_3$); ^{1}H and ^{31}P NMR, see Table 2; MS *m/z* 295 ($M-CH_3$; 13), 279 (4.4), 250 (3.2), 221 (10), 208 (8.2), 192 (17), 183 (47), 167 (100).

Found: *m/z* 295.0949. Calcd for $C_{11}H_{20}O_7P$: $M-CH_3$, 295.0947.

Methyl 5,6-Dideoxy-2,3-*O*-isopropylidene-5-dimethoxyphosphinyl-α-D-mannofuranoside (8d): 19% yield from **3d**; R_f=0.38 (*A*); $[\alpha]_D$ +56° (*c* 1.44, $CHCl_3$); ^{1}H and ^{31}P NMR, see Table 2.

Methyl 5,6-Dideoxy-2,3-*O*-isopropylidene-5-dimethoxyphosphinyl-α-L-talofuranoside (7e): 39% yield from **3e**; R_f=0.31 (*A*); ^{1}H and ^{31}P NMR, see Table 2;

MS m/z 295 ($M-CH_3$; 22), 279 (5.1), 261 (5.9), 250 (5.0), 220 (18), 193 (13), 167 (100).

Found: m/z 295.0947. Calcd for $C_{11}H_{20}O_7P$: $M-CH_3$, 295.0947.

Methyl 5,6-Dideoxy-2,3-*O*-isopropylidene-5-dimethoxyphosphinyl-β-D-allofuranoside (8e): 17% yield from **3e**; $R_f=0.39$ (*A*); ^{1}H and ^{31}P NMR, see Table 2.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-α-D-*xylo*-hex-5-enofuranose[15] (6a). DBU (0.090 ml, 0.60 mmol) was added at 0 °C to a mixture of compound **9a**[11] (167 mg, 0.520 mmol) and dimethyl phosphonate (0.48 ml, 5.2 mmol), and the mixture was stirred for 3 h at 20 °C. The excess of phosphonate was distilled off at ca. 40 °C (0.2 Torr, 1 Torr=133.322 Pa). The residue was purified on a column of silica gel with 1 : 1 AcOEt–hexane as the eluant, giving **6a** (144 mg, 72%) as colorless needles: mp 114—115 °C (lit,[15] mp 117 °C); $R_f=0.31$ (*C*); ^{1}H NMR $\delta=1.32$, 1.52 (3H each, 2s, CMe$_2$), 3.69, 3.70 [3H each, 2d, $J_{\mathrm{POMe}}=10.9$ Hz, P(OMe)$_2$], 4.13 (1H, d, $J_{3,4}=3.0$ Hz, H-3), 4.55, 4.57 (1H each, 2d, $^2J=11.7$ Hz, CH$_2$O-3), 4.61 (1H, d, $J_{1,2}=3.8$, $J_{2,3}\approx0$ Hz, H-2), 4.88 (1H, ddt, $J_{4,\mathrm{P}}=4.5$, $J_{4,6(E)}=J_{4,6(Z)}=1.6$ Hz, H-4), 5.97 (1H, dd, $^5J_{1,\mathrm{P}}=0.8$ Hz, H-1), 6.27 [1H, dt, $J_{6(Z),\mathrm{P}}=23.4$, $J_{6(E),6(Z)}=1.6$ Hz, H-6(*Z*)], 6.37 [1H, dt, $J_{6(E),\mathrm{P}}=46.4$ Hz, H-6(*E*)], 7.27—7.35 (5H, m, Ph); ^{31}P NMR $\delta=18.0$.

Methyl 5,6-Dideoxy-2,3-*O*-isopropylidene-5-dimethoxyphosphinyl-α-D-*lyxo*-hex-5-enofuranoside (6d). By the same procedures described above for **6a**, compound **9d**[10] (99.7 mg) was converted into **6d** as a colorless syrup: 96.2 mg (77%); $R_f=0.25$ (*C*); $[\alpha]_D$ +21° (*c* 2.67, CHCl$_3$); ^{1}H NMR $\delta=1.26$, 1.36 (3H each, 2s, CMe$_2$), 3.32 (3H, s, MeO-1), 3.72, 3.73 [3H each, 2d, $J_{\mathrm{POMe}}=11.3$ Hz, P(OMe)$_2$], 4.56 (1H, d, $J_{2,3}=5.9$, $J_{1,2}\approx0$ Hz, H-2), 4.64 (1H, ddt, $J_{4,\mathrm{P}}=4.9$, $J_{3,4}=3.6$, $J_{4,6(E)}=J_{4,6(Z)}=1.7$ Hz, H-4), 4.75 (1H, dd, H-3), 4.93 (1H, d, $^5J_{1,\mathrm{P}}=1.7$ Hz, H-1), 6.25 [1H, dt, $J_{6(E),\mathrm{P}}=46.6$, $J_{6(E),6(Z)}=1.9$ Hz, H-6(*E*)], 6.26 [1H, dt, $J_{6(Z),\mathrm{P}}=22.9$ Hz, H-6(*Z*)]; ^{31}P NMR $\delta=18.1$; FAB MS m/z 309 ($M+1$; 100), 293 (10), 277 (31), 219 (18), 191 (13), 177 (11), 165 (12).

Found: m/z 309.1096. Calcd for $C_{12}H_{22}O_7P$: $M+1$, 309.1104.

Hydrogenation of Compounds 6a and 6d. By the use of the same procedures as those for the preparation of **7** and **8** from **4**, compound **6a** was converted into **7a** in an 89% yield.

Similarly, **6d** was converted into a 73 : 27 mixture of **7d** and **8d** in an 85% yield.

5,6-Dideoxy-1,2-*O*-isopropylidene-5-dimethoxyphosphinyl-α-L-galactofuranose (10). Compound **7c** (148 mg, 0.383 mmol) dissolved in ethanol (2 ml) was hydrogenated in the presence of 20% Pd(OH)$_2$–C (80 mg) at 20 °C under atmospheric pressure of H$_2$. After 5 h, the catalyst was filtered off through celite, and the filtrate was evaporated in vacuo. The residue was purified by short-path column chromatography, giving **10** (111 mg, 98%) as a colorless syrup: $R_f=0.13$ (*A*); $[\alpha]_D$ +1.4° (*c* 0.97); ^{1}H NMR $\delta=1.27$ (3H, dd, $J_{6,\mathrm{P}}=18.4$, $J_{5,6}=7.3$ Hz, H-6), 1.36, 1.54 (3H each, 2s, CMe$_2$), 2.50 (1H, dqd, $J_{5,\mathrm{P}}=22.1$, $J_{4,5}=4.6$ Hz, H-5), 3.78, 3.79 [3H each, 2d, $J_{\mathrm{POMe}}=10.5$, 10.7 Hz, P(OMe)$_2$], 3.99 (1H, dt, $J_{3,4}=6.4$, $J_{4,\mathrm{P}}=4.4$ Hz, H-4), 4.12 (1H, br s, HO-3), 4.20 (1H, br dd, $J_{2,3}=1.9$ Hz, H-3), 4.61 (1H, dd, $J_{1,2}=4.1$ Hz, H-2), 5.74 (1H, d, H-1); ^{31}P NMR $\delta=33.6$; MS m/z 281 ($M-CH_3$; 4.8), 237 (1.7), 221 (11), 207 (5.1), 181 (33), 167 (83), 153 (30), 138 (26), 100 (100).

Found: m/z 281.0788. Calcd for $C_{10}H_{18}O_7P$: $M-CH_3$, 281.0790.

1,2,3,4-Tetra-*O*-acetyl-5,6-dideoxy-5-[(*R*)- and (*S*)-methoxyphosphinyl]-α,β-L-galactopyranoses (12a—d). To a solution of **10** (203 mg, 0.685 mmol) in dry benzene (2 ml) was added, with stirring, a solution of SDMA [3.4 M in toluene (1 M=1 mol dm^{-3}), 0.6 ml, 3.0 equiv] in dry benzene (1 ml), in small portions at 5 °C under argon. The stirring was continued at this temp for 1 h. Then water (0.5 ml) was added to decompose excess SDMA and the mixture was centrifuged. The precipitate was extracted with several portions of benzene. The organic layer was combined and evaporated in vacuo, giving 5,6-dideoxy-1,2-*O*-isopropylidene-5-phosphino-α-L-galactofuranose as a colorless syrup.

This syrup was immediately treated with 1 : 1 2-propanol–0.5 M hydrochloric acid (6 ml) at 90 °C for 2 h under argon. After cooling, the reactants were neutralized with Amberlite IRA-93ZU. The resin was filtered off and washed with aq ethanol. The filtrate was evaporated in vacuo. The residue was dissolved in water (3 ml), treated with 30% hydrogen peroxide (0.3 ml) at 20 °C for 12 h, and concentrated in vacuo to give crude 5,6-dideoxy-5-hydroxyphosphinyl-α,β-L-galactopyranoses (**11**) 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 20 °C for 12 h, diluted with a small amount of cold water, and concentrated in vacuo. The residue was dissolved in ethanol and passed through a column of Amberlite IR-120B (30 ml). The eluant was evaporated in vacuo to give a crude 1,2,3,4-tetra-*O*-acetyl-5-hydroxyphosphinyl derivative. This was methylated with ethereal diazomethane in dry CH$_2$Cl$_2$ (3 ml) at 0 °C. After evaporation of the solvent, the residue was separated by column chromatography with a gradient eluent of 2 : 1 AcOEt–hexane→AcOEt, into two fractions.

The faster-eluting fraction [$R_f=0.39$ (*A*)] gave 5-[(*S*)-methoxyphosphinyl]-α-L-galactopyranose **12a** (16.9 mg, 6% from **10**) as a colorless syrup: ^{1}H and ^{31}P NMR, see Table 3; MS m/z 394 (M^+; 2.6), 350 (30), 335 (9.8), 308 (11) 292 (90), 277 (56), 250 (40), 233 (100), 207 (31), 191 (82).

Found: m/z 394.1033. Calcd for $C_{15}H_{23}O_{10}P$: M^+, 394.1029.

The slower-eluting fraction [$R_f=0.28$ (*A*)] gave a colorless syrup (42.3 mg) which consisted of 5-[(*S*)-*P*]-β-L-galactopyranose **12b** (5% from **10**), 5-[(*R*)-*P*]-α-isomer **12c** (3%), and 5-[(*S*)-*P*]-β-isomer **12d** (8%), the relative amount being determined by the integral ratio of ^{31}P NMR signals; ^{1}H and ^{31}P NMR, see Table 3; MS m/z 395 ($M+1$; 3.9), 352 (1.2), 310 (4.5), 293 (38), 277 (3.5), 250 (40), 232 (100), 208 (17), 191 (71).

Found: m/z 395.1110. Calcd for $C_{15}H_{24}O_{10}P$: $M+1$, 395.1107.

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