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Stereoselectivity in deoxygenation of 5-hydroxy-5-phosphinyl-hexofuranoses (α-hydroxyphosphonates)

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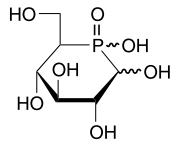
Abstract

The addition of dimethyl phosphonate to six different hexofuranos-5-uloses in the presence of DBU, followed by esterification with methoxalyl chloride and then radical reduction, afforded 5-deoxy-5-dimethoxyphosphinyl-D- and L-hexofuranoses. The stereoselectivity of the deoxygenation and possible transition-state models are discussed.

Keywords: Phospho sugar; Deoxygenation; α-Hydroxyphosphonate

1. Introduction

We have prepared various sugar analogs having a phosphorus atom in the hemiacetal ring (phospho sugars)[1] because of considerable interest in their chemical properties and potential biological activity, as in the case of imino sugars[2] and thio sugars.[3] Regarding phospho sugars of the hexopyranose type, analogs **1** of D-glucose,[4] **2** of D-mannose,[5] **3** of D-galactose,[6] and **4** of L-fucose[7] have been synthesized.



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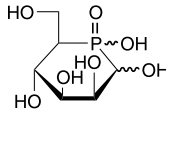

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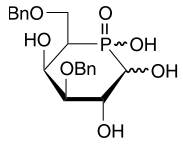

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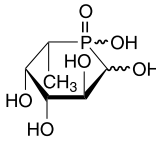

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Although 5-deoxy-5-phosphinyl-D- and L-hexofuranose derivatives are key intermediates in the preparation of hexopyranose-type phospho sugars, only a few methods for stereoselective introduction of a phosphinyl group into the sugar moiety have been reported this far; for example, the addition of a phosphonate to nitroalkenes[8] and α-tosyloxyketones.[7] We have recently employed a new method to introduce a phosphinyl group at C-5 of hexofuranoses; namely, the addition of a phosphonate to hexofuranos-5-ulose derivatives and subsequent deoxygenation of the resulting 5-hydroxy group to afford the corresponding 5-deoxy-5-phosphinyl derivatives.[4c] The exact stereoselectivity on C-5, however, remained essentially unestablished for these reactions. We now report a systematic investigation of the stereoselectivity and synthetic efficiency for dehydroxylation of various α-hydroxyphosphonates (5-hydroxy-5-phosphinyl-hexofuranoses).

2. Results and discussion

As starting materials, the 6-*O*-benzylhexofuranos-5-uloses **8a** (α-D-*xylo*),[4c] **8b** (α-D-*ribo*), **8c** (β-D-*arabino*), **8d** (β-D-*lyxo*), **8e** (α-D-*lyxo*)[5b] were prepared from the corresponding 5,6-diols **5a**–**e** in excellent yields (Scheme 1). Thus, the epoxidation of **5a**–**e** with triphenylphosphine and diethyl azodicarboxylate (DEAD) afforded the 5,6-anhydro derivatives (**6a**–**e**), which were treated with benzyl alcohol and sodium hydride in 1,2-di-

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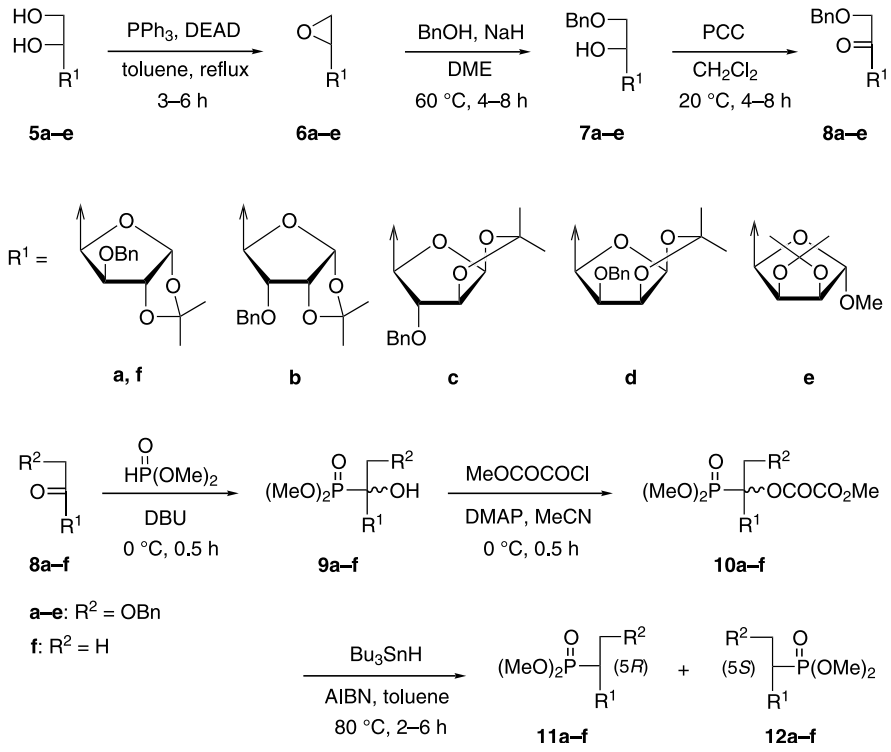

Scheme 1.

methoxyethane (DME) to give the 6-*O*-benzyl compounds (**7a**–**e**), respectively. Oxidation of **7a**–**e** with pyridinium chlorochromate (PCC) gave the corresponding 5-uloses **8a**–**e**. The 6-deoxy-α-D-*xylo*-hexofuranos-5-ulose derivative (**8f**)[9] was prepared by reduction of **6a** with lithium alminum hydride and subsequent oxidation with PCC.

Treatment of **8a**–**f** with dimethyl phosphonate at 0 °C in the presence of DBU, respectively afforded the (5*R*)- and (5*S*)-5-dimethoxyphosphinyl-5-hydroxy compounds (**9a**–**f**) in the yields shown in Table 1. After having examined various modified methods of the Barton–McCombie reaction[10] for the deoxygenation of the 5-hydroxy group of **9**, we found that application of Dolan and MacMillan's procedure[11] was most efficient for our purpose.† Thus, compounds **9a**–**f** were first converted into the 5-*O*-methoxalyl derivatives (**10a**–**f**) by use of methoxalyl chloride in the presence of 4-dimethylaminopyridine (DMAP) and then reduced with tributyltin hydride in the presence of AIBN, affording the corresponding 5-deoxy-5-phosphinyl-D-hexofuranoses (**11a**–**f**) and the L-hexofuranoses (**12a**–**f**), which were separable by column chromatography in the yields and the ratios summarized in Table 1.

The (5*R*)-configuration for **11a**–**f** and the (5*S*)-configuration for **12a**–**f** were assigned on the basis of

Table 1
Yields and ratios of 5-deoxy-5-phosphinyl compounds (**11a**–**f**, **12a**–**f**)

Entry	5-Uloses	5-Hydroxy compounds	5-Deoxy compounds (yields from **9**)	Ratio of **11**:**12**
1	**8a**	(5*R*)-**9a** (64%) (5*S*)-**9a** (27%)	**11a** (50%), **12a** (38%)	57:43
2	**8b**	(5*R*)-**9b** (47%) (5*S*)-**9b** (44%)	**11b** (29%), **12b** (57%)	34:66
3	**8c**	(5*R*)-**9c** (72%) (5*S*)-**9c** (24%)	**11c** (16%), **12c** (68%)	19:81
4	**8d**	(5*R*)-**9d** (68%) (5*S*)-**9d** (24%)	**11d** (29%), **12d** (48%)	38:62
5	**8e**	(5*R*)-**9e** (76%) (5*S*)-**9e** (19%)	**11e** (16%), **12e** (70%)	19:81
6	**8f**	(5*R*)-**9f** (85%) (5*S*)-**9f** (6.6%)	**11f** (24%), **12f** (60%)	28:72

the magnitudes of $J_{4,5}$ values and the presence of the long-range couplings ($^5J_{1,P}$, $^5J_{2,P}$, and $^4J_{3,P}$)[7,8] in the ^{1}H NMR spectra (see, Table 2 and Fig. 1). Thus, the α-D-*gluco* (for **11a**,**f**), β-D-*altro* (for **11c**), β-D-*manno* (for **11d**), and α-D-*manno* (for **11e**) configurations were confirmed by the large values of $J_{4,5}$ (namely an *anti* relationship of H-4/H-5) and the presence of $^5J_{1,P}$ coupling, whereas the β-L-*ido* (for **12a**,**f**), α-L-*galacto* (for **12c**), α-L-*gulo* (for **12d**), and β-L-*gulo* (for **12e**) configurations were confirmed by the large values of $J_{4,5}$ and the presence of $^5J_{2,P}$ coupling. The α-D-*allo* configuration for **11b** was assigned from the small value of $J_{4,5}$ (thus, a *gauche* relationship of H-4/H-5) and the presence of $^5J_{2,P}$ coupling, whereas the β-L-*talo* configuration for **12b** was assigned from the small value of $J_{4,5}$ and the large values of $J_{4,P}$ (thus, an *anti* relationship of H-4/P-5). Meanwhile the C-5 configurations of the (5*R* and 5*S*)-5-hydroxy-5-phoshinyl compounds (**9a**–**f**) were assigned by comparison with the corresponding 5-deoxy compounds (**11a**–**f**,**12a**–**f**), because the similar characteristic tendency of the corresponding coupling constants and the chemical shifts is expected for **9a**–**f** due to almost identical conformations.

Deoxygenation of (5*R*)-**9a** afforded the (5*R*)-5-deoxy product (D-glucofuranose derivative) **11a** (50%) and the (5*S*)-5-deoxy product (L-iodofuranose derivative) **12a** (38%). The epimer (5*S*)-**9a** also gave **11a** and **12a** in almost the same ratio and yields as those from (5*R*)-**9a**. These results indicate that an epimerization takes place at C-5 via a radical intermediate during the reduction of the methoxalyl esters [(5*R*)- and/or (5*S*)-**10**] and therefore the ratios of 5-deoxy products **11** and **12** are not related to the C-5 configuration of the corresponding precursors **9**.

The deoxygenation of other 5-hydroxy compounds (**9b**–**f**) afforded predominantly the corresponding (5*S*)-5-deoxy products (**12b**–**f**) (Table 1, entries 2–6). In order to account for the (5*S*)-diastereoselectivity of the radical reduction of **10**, we propose rotamer **A** (arising from **10b**,**f**) and **A**′ (arising from **10c**,**d**,**e**) of the radical intermediate, from the viewpoint of electronic factors (Fig. 2). That is to say, the opposition of the phosphinyl group and electronegative oxygen atom in the furanose ring diminishes intramolecular electrostatic repulsion.[13] Moreover, the overlapping of the radical p orbital with the best electron-donating σ_{C4-C3} bond stabilizes the transition state by hyperconjugation.[14] Although mechanistic proposals have been reported for the radical-mediated reduction of α-bromo-β-alkoxycarboxylates,[15] no report seems to exist, to the best of our knowledge, for the corresponding β-alkoxyphosphonate derivatives.

The contrary stereoselection of the reduction of **10a** (entry 1) seems to depend upon the steric factor of the substituents on C-3 as well as the conformation of the furanose ring. The 1,2-*O*-isopropylidene-α-D-*xylo*- and *ribo*-furanoses (**a**,**b**,**f** series) have the E_4 conformational preference, whereas the β-D-*arabino*- and *lyxo*-furanoses (**c**,**d** series) are preferentially in the E_1 form, and the 2,3-*O*-isopropylidene-α-D-*lyxo* derivatives (**e** series) exists mainly in the $^{\circ}E$ form.[16] As for the radical intermediates existing in the E_4 form (Fig. 1), the rotamer **A** derived from **10a** is disfavored because of steric hindrance between the bulky R_β (= Bn) and C-6 (= CH_2OBn) groups, whereas **A** derived from **10b** (R_β = H, C-6 = CH_2OBn) and **10f** (R_β = OBn, C-6 = CH_3) involve little steric hindrance. Another possible rotamer **B** was thus proposed as a (5*R*)-predictive model for the reduction of **10a**, taking into account both the electrostatic repulsion between two electronegative groups and the steric repulsion between C-6 and the R_β groups.

In the case of **A**′ derived from **10c**, the effective shielding provided by the R_β (= H) group, which has a *syn*-periplanar relationship with C-5, leads to good stereoselectivity (entry 3). However, in the case of **A**′ derived from **10d**, steric hindrance similar to the **a** series caused interconversion into another rotamer similar to **B** to a considerable extent (but still in favor of the **A**′ form) and lower (5*S*)-selectivity (entry 4). Meanwhile, the rigid dioxolane ring of the **A**′ rotamer derived from **10e** scarcely causes such repulsion with C-6 and the freely rotating 3-*O*-benzyl group, and thus leads to good stereoselectivity (entry 5).

In summary, this work demonstrates a new procedure for the introduction of a C–P bond into sugars and analyzes its stereoselectivity. By using the 5-deoxy-5-phosphinyl-hexofuranoses obtained in this work and their corresponding enantiomers, convenient syntheses of a variety of new phospho sugars are anticipated. We are currently investigating the more detailed mechanism concerning stereoselectivity of the deoxygenation as well as the enhancement of stereoselectivity by using lower reaction temperatures.

3. Experimental

3.1. General methods

All reactions were monitored by TLC (Merck silica gel 60F, 0.25 mm) with an appropriate solvent system [(A) 1:3 and (B) 1:1 EtOAc–hexane, (C) EtOAc, (D) 1:19 MeOH–$CHCl_3$]. Column chromatography was performed with Daiso Silica Gel IR-60/210w. Components were detected by exposing the plates to UV light and/or

[†] Although the deoxygenation of the secondary hydroxy group on the α-carbon of phosphinyl group has been reported,[12] the procedures described were not efficient for the corresponding tertiary hydroxy group in our system.

Table 2
^{1}H and ^{31}P NMR parameters for compounds **9a**–**f**, **11a**–**f**, and **12a**–**f** in $CDCl_3$

Chemical shifts/δ

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	$P(OMe)_2$ [a]	CMe_2	CH_2O-3 [b,c]	CH_2O-6 [b,c]	^{31}P
(5*R*)-**9a**	5.99	4.59	4.43	4.54	(4.93) [d]	3.88	3.82	3.76, 3.74	1.49, 1.33	4.63, 4.60 [e]	4.69, 4.64 [e]	26.3
(5*S*)-**9a**	6.01	4.50	4.25	4.47	(4.58) [d]	3.92	3.79	3.84, 3.80	1.52, 1.32	4.36, 4.15 [e]	4.52, 4.48 [f]	23.6
11a	5.87	4.60	4.08	4.52	2.82	4.00	3.91	3.67, 3.64	1.51, 1.33	4.63, 4.55 [e]	4.59, 4.56 [e]	31.9
12a	5.93	4.53	3.81	4.48	2.67	3.74	3.46	3.755, 3.74	1.52, 1.31	4.50, 4.18 [f]	4.49, 4.31 [f]	32.1
(5*R*)-**9b**	5.79	4.57	4.37	4.49	(2.98) [d]	3.76	3.71	3.77, 3.76	1.58, 1.36	4.74, 4.56 [f]	4.54, 4.48 [f]	25.9
(5*S*)-**9b**	5.75	4.50	4.41	4.43	(3.10) [d]	3.80	3.74	3.79, 3.73	1.58, 1.34	4.68, 4.52[y]	4.53, 4.51 [f]	24.3
11b	5.65	4.38	4.05	4.49	2.64	3.79	3.75	3.74, 3.72	1.58, 1.33	4.66, 4.53 [f]	4.47, 4.38 [f]	30.9
12b	5.77	4.52	4.52	4.49	2.50	3.76	3.69	3.68, 3.60	1.58, 1.35	4.76, 4.60 [f]	4.50, 4.48 [f]	29.7
(5*R*)-**9c**	5.87	4.62	4.60	4.62	(3.50) [d]	3.80	3.80	3.77, 3.76	1.53, 1.34	4.66, 4.625 [f]	4.60, 4.60	25.8
(5*S*)-**9c**	5.91	4.64	4.31	4.69	(3.51) [d]	3.83	3.58	3.78, 3.775	1.57, 1.34	4.56, 4.46 [f]	4.52, 4.52	25.7
11c	5.94	4.64	4.43	4.58	2.61	3.99	3.93	3.67, 3.64	1.44, 1.30	4.59, 4.55 [f]	4.63, 4.59 [f]	31.6
12c	5.87	4.61	4.32	4.46	2.61	3.795	3.78	3.75, 3.73	1.55, 1.33	4.47, 4.45 [f]	4.51, 4.51	30.5
(5*R*)-**9d**	5.74	4.71	4.14	4.15	(4.75) [d]	3.88	3.78	3.84, 3.76	1.54, 1.44	4.67, 4.11 [g]	4.41, 4.56 [f]	23.8
(5*S*)-**9d**	5.67	4.81	4.33	4.08	(5.21) [d]	3.90	3.75	3.73, 3.715	1.51, 1.45	4.84, 4.53 [e]	4.60, 4.55 [f]	26.1
11d	5.65	4.80	4.01	4.19	2.99	3.99	3.93	3.65, 3.61	1.48, 1.41	4.87, 4.46 [e]	4.56, 4.54 [f]	32.1
12d	5.70	4.71	3.76	4.15	2.82	3.77	3.64	3.76, 3.71	1.52, 1.41	4.76, 4.16 [f]	4.49, 4.30 [f]	32.2
(5*R*)-**9e**	4.91	4.57	5.00	4.32	(4.75) [d]	3.88	3.82	3.81, 3.76	1.48, 1.32	(3.26) [h]	4.63, 4.56 [f]	25.2
(5*S*)-**9e**	4.97	4.49	4.85	4.32	(4.36) [d]	3.96	3.85	3.85, 3.80	1.46, 1.23	(3.36) [h]	4.64, 4.58 [f]	24.1
11e	4.81	4.54	4.77	4.29	2.71	3.98	3.94	3.73, 3.71	1.42, 1.31	(3.26) [h]	4.61, 4.55 [f]	31.3
12e	4.88	4.48	4.59	4.29	2.62	3.88	3.82	3.76, 3.74	1.40, 1.25	(3.32) [h]	4.57, 4.51 [f]	32.4
(5*R*)-**9f**	5.99	4.58	4.16	4.48	(5.08) [d]	1.54		3.87, 3.80	1.50, 1.32	4.77, 4.62 [g]		25.5
(5*S*)-**9f**	6.07	4.63	4.22	4.39	(3.91) [d]	1.47		3.86, 3.82	1.51, 1.34	4.70, 4.50 [f]		25.1
11f	5.85	4.59	4.10	4.24	2.64	1.34		3.72, 3.71	1.50, 1.31	4.64, 4.60 [e]		33.5
12f	5.95	4.61	3.87	4.22	2.45	1.06		3.78, 3.74	1.50, 1.32	4.70, 4.45[f]		33.6

Coupling constants/Hz

Compound	$J_{1,2}$	$J_{1,P}$	$J_{2,3}$	$J_{2,P}$	$J_{3,4}$	$J_{3,P}$	$J_{4,5}$	$J_{4,P}$	$J_{5,6}$	$J_{5,6'}$	$J_{5,P}$	$J_{6,6'}$	$J_{6,P}$	$J_{6',P}$
(5*R*)-**9a**	3.7	1.5	0	0	2.8	0		0.5				9.2	25.6	13.4
(5*S*)-**9a**	3.7	0	0	1.8	3.0	1.0		4.0				9.8	7.9	14.5
11a	3.7	1.2	0	0	3.0	0	10.8	5.2	2.8	5.2	19.8	9.2	16.5	28.7
12a	4.0	0	0	2.1	3.1	1.0	10.1	7.0	4.3	4.0	18.6	9.5	10.9	26.2
(5*R*)-**9b**	3.7	0	4.3	1.2	8.6	0.8		14.3				9.8	15.6	12.2
(5*S*)-**9b**	3.7	0	4.0	0	8.5	0		12.2				10.1	12.2	11.0
11b	3.7	0	4.4	1.7	9.1	0.7	2.2	13.4	8.3	3.7	24.2	10.0	7.6	10.0
12b	3.4	0	[i]	0	8.5	0	2.0	33.4	4.6	9.0	21.6	9.7	8.2	7.8
(5*R*)-**9c**	3.7	0.8	[i]	0	[i]	0		[i]				–	17.1	17.1
(5*S*)-**9c**	4.0	0	1.2	1.0	4.3	0		2.5				9.8	9.8	21.4

Table 2 (*Continued*)

Coupling constants/Hz

Compound	$J_{1,2}$	$J_{1,P}$	$J_{2,3}$	$J_{2,P}$	$J_{3,4}$	$J_{3,P}$	$J_{4,5}$	$J_{4,P}$	$J_{5,6}$	$J_{5,6'}$	$J_{5,P}$	$J_{6,6'}$	$J_{6,P}$	$J_{6',P}$
11c	4.0	1.5	0.8	0	1.8	0	10.1	3.7	3.7	3.4	20.5	9.5	28.7	11.9
12c	4.0	0	1.0	1.0	3.1	0	9.2	11.3	5.5	4.0	20.4	9.2	13.1	16.6
(5*R*)-**9d**	4.6	0	4.9	0	4.6	0		3.3				9.8	9.5	18.3
(5*S*)-**9d**	4.9	0	5.4	0	4.2	0		0.5				8.8	27.1	12.1
11d	4.9	1.0	5.3	0	4.3	0	10.1	6.7	2.8	5.2	19.8	9.2	17.7	28.4
12d	4.6	0	5.5	1.1	4.6	0	10.4	6.1	3.4	3.7	18.5	9.8	10.5	29.3
(5*R*)-**9e**	0	2.1	5.8	0	2.8	0		1.0				8.6	26.6	12.8
(5*S*)-**9e**	0	0	5.8	1.0	3.4	0.9		4.2				9.8	10.0	19.8
11e	0	1.5	5.5	0	3.1	0	10.7	5.8	2.8	4.9	19.2	9.2	15.3	29.3
12e	0	0	5.5	1.2	3.1	1.1	10.4	7.3	4.0	3.7	18.3	9.8	10.6	28.1
(5*R*)-**9f**	4.0	1.2	0	0	2.8	0		0					15.6	
(5*S*)-**9f**	4.0	0	0	2.1	3.1	1.0		5.8					15.9	
11f	4.0	1.1	0	0	3.0	0	10.4	5.8	7.3		19.2		18.3	
12f	3.9	0	0	2.4	2.9	1.5	10.6	7.7	7.2		16.0		18.0	

[a] $J_{POMe} = 10.7–11.0$ Hz.
[b] The assignment of CH_2O-3 or -6 signals may have to be interchanged.
[c] Ph: δ 7.24–7.38 (m, 10 H) except for (5*S*)-**9a** [δ 7.12 (dd, 2 H), 7.27–7.33 (m, 8 H)], **12a** [δ 7.18 (dd, 2 H), 7.26–7.32 (m, 8 H)], and (5*R* and 5*S*)-**9f**, **11f**, **12f** [δ 7.26–7.37 (m, 5 H)].
[d] HO-5.
[e] $^2J = 10.7–11.0$ Hz.
[f] $^2J = 11.6–11.9$ Hz.
[g] $^2J = 10.4$ Hz.
[h] MeO-1.
[i] Uncertain because of overlapping with other signals.

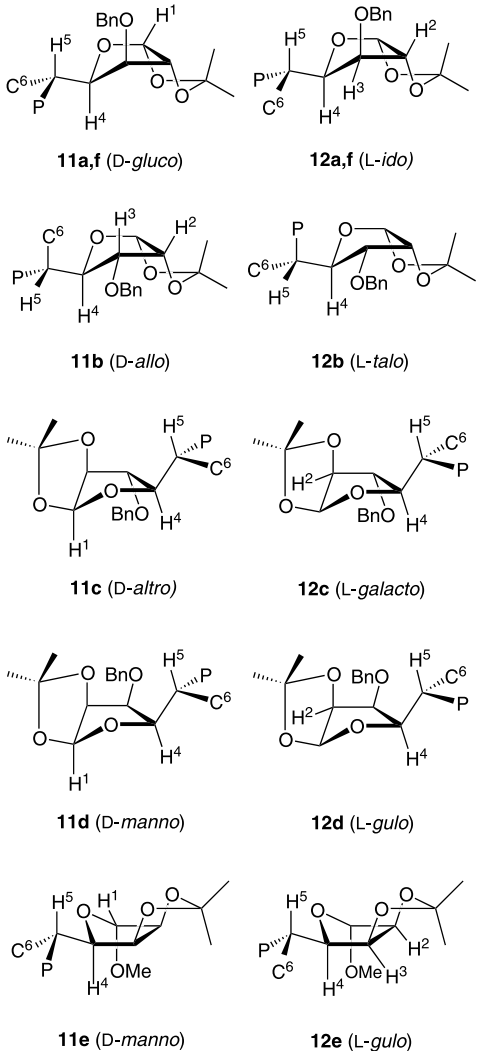

Fig. 1. The most favored conformations for the 5-deoxy-5-phosphinyl-hexofuranoses (**11a**–**f** and **12a**–**f**) and geometrical relationships where couplings between P and H exist.

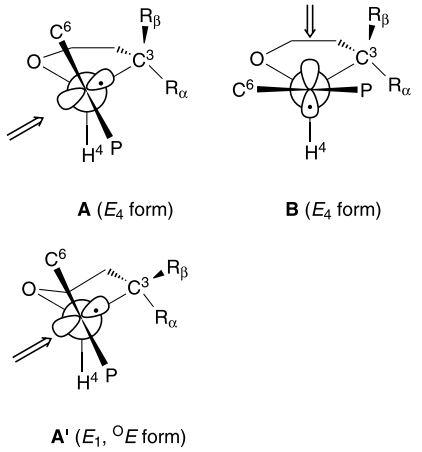

Fig. 2. Plausible conformation for the radical intermediate **A** (from **10b**,**f**), **A′** (from **10c**,**d**,**e**), **B** (from **10a**) and the direction of reduction.

by spraying them with 20% H_2SO_4–EtOAc (with subsequent heating). Optical rotations were measured with a JASCO P-1020 polarimeter in $CHCl_3$. The NMR spectra were measured in $CDCl_3$ with Varian VXR-500 (500 MHz for ^1H) and VXR-200 (81 MHz for ^{31}P) spectrometers at 25 °C. 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 a VG-70SE instrument and are given in terms of m/z (relative intensity) compared with the base peak.

3.2. 3-*O*-Benzyl-1,2-*O*-isopropylidene-β-D-mannofuranose (5d)

To a suspension of 1,2;5,6-di-*O*-isopropylidene-β-D-mannofuranose[17] (360 mg, 1.38 mmol) and NaH (60% in mineral oil, 166 mg, 4.15 mmol) in DME (7.0 mL), benzyl bromide (0.400 mL, 3.36 mmol) at 0 °C was added. The mixture was stirred for 3 h, diluted with satd NH_4Cl (15 mL), and extracted with $CHCl_3$ three times. The combined organic layers were dried (Na_2SO_4), and concentrated in vacuo to give the 3-O-benzyl derivative: R_f 0.35 (A). The residue was dissolved in 70% aqueous AcOH (5.0 mL) and the solution was stirred at rt for 4 h. The mixture was concentrated in vacuo and the residue purified by column chromatography with 1:1 EtOAc–hexane as an eluant to give **5d** (390 mg, 91%) as a colorless syrup: $[\alpha]_D^{22}$ −36.9° (*c* 2.60); R_f 0.11 (B); ^1H NMR: δ 1.34, 1.61 (2s, 3 H each, CMe_2), 2.70 (br s, 2 H, HO-5,6), 3.70 (dd, 1 H, $J_{6,6'}$ 11.5, $J_{5,6'}$ 5.1 Hz, H′-6), 3.83 (dd, 1 H, $J_{5,6}$ 3.9 Hz, H-6), 4.06 (dd, 1 H, $J_{4,5}$ 9.6, $J_{3,4}$ 7.3 Hz, H-4), 4.24 (dd, 1 H, $J_{2,3}$ 5.0 Hz, H-3), 4.40 (ddd, 1 H, H-5), 4.58, 4.87 (2d, 1 H each, ^2J 11.5 Hz, CH_2O-3), 4.64 (t, 1 H, $J_{1,2}$ 4.1 Hz, H-2), 5.73 (d, 1 H, H-1), 7.32–7.39 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.79; H, 7.21.

3.3. 5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-allofuranose (6b)

To a solution of **5b**[18] (603 mg, 1.94 mmol) and triphenylphosphine (612 mg, 2.33 mmol) in dry toluene (12 mL) was added diethyl azodicarboxylate (DEAD, 0.360 mL, 2.32 mmol). The mixture was refluxed for 3 h and evapolated in vacuo. The residue was purified by column chromatography with 1:2 EtOAC–hexane as an eluant to give **6** (525 mg, 93%) as a colorless syrup: $[\alpha]_D^{26}$ +106.3° (*c* 1.28), R_f 0.74 (B); ^1H NMR: δ 1.36, 1.59 (2s, 3 H each, CMe_2), 2.75 (dd, 1 H, $J_{6,6'}$ 4.9, $J_{5,6'}$ 2.8 Hz, H′-6), 2.79 (t, 1 H, $J_{5,6}$ 4.6 Hz, H-6), 3.19 (td, 1 H, $J_{4,5}$ 4.3 Hz, H-5), 3.66 (dd, 1 H, $J_{3,4}$ 8.9 Hz, H-4), 4.21 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-3), 4.57 (t, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.57, 4.75 (2d, 1 H each, ^2J 11.6 Hz, CH_2O-3), 5.75 (d, 1 H, H-1), 7.30–7.42 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.57; H, 6.99.

3.4. 5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-β-D-altrofuranose (6c)

By employing the same procedures as described for **6b**, compound **5c**[19] gave **6c** (92%) as a colorless syrup: $[\alpha]_D^{23}$ −1.83° (*c* 1.66), R_f 0.37 (A); ^{1}H NMR: δ 1.35, 1.55 (2s, 3 H each, CMe_2), 2.66 (dd, 1 H, $J_{6,6'}$ 4.9, $J_{5,6'}$ 2.4 Hz, H′-6), 2.88 (dd, 1 H, $J_{5,6}$ 4.0 Hz, H-6), 3.22 (ddd, 1 H, $J_{4,5}$ 7.0 Hz, H-5), 3.80 (dd, 1 H, $J_{3,4}$ 2.1 Hz, H-4), 4.14 (d, 1 H, $J_{2,3}$ 0 Hz, H-3), 4.57, 4.58 (2d, 1 H each, ^2J 12.0 Hz, CH_2O-3), 4.68 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-2), 5.93 (d, 1 H, H-1), 7.29–7.38 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.59; H, 7.01.

3.5. 5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-β-D-mannofuranose (6d)

By employing the same procedures as those described for **6b**, compound **5d** gave **6d** (89%) as a colorless syrup: $[\alpha]_D^{24}$ +18.1 ° (*c* 1.66), R_f 0.22 (A); ^{1}H NMR: δ 1.35, 1.62 (2s, 3 H each, CMe_2), 2.70 (dd, 1 H, $J_{6,6'}$ 4.9, $J_{5,6'}$ 2.2 Hz, H′-6), 2.87 (dd, 1 H, $J_{5,6}$ 3.9 Hz, H-6), 3.69 (t, 1 H, $J_{4,5}$ 7.3, $J_{3,4}$ 6.8 Hz, H-4), 3.70 (ddd, 1 H, H-5), 4.15 (dd, 1 H, $J_{2,3}$ 4.9 Hz, H-3), 4.62 (dd, 1 H, $J_{1,2}$ 3.9 Hz, H-2), 4.69, 4.81 (2d, 1 H each, ^2J 12.2 Hz, CH_2O-3), 5.70 (d, 1 H, H-1), 7.31 [t, 1 H, $J_{m,p}$ 7.3 Hz, Ph(*p*)], 7.36 [t, 2 H, $J_{o,m}$ 7.3 Hz, Ph(*m*)], 7.42 [d, 2 H, Ph(*o*)]. Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.81; H, 6.95.

3.6. 3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-allofuranose (7b)

To a suspension of sodium hydride (60% in mineral oil, 100 mg, 2.50 mmol) and benzyl alcohol (2.0 mL, 19.3 mmol) in DME (2.0 mL), a solution of **6b** (388 mg, 1.25 mmol) in DME (2.0 mL) at 0 °C was added. The mixture was stirred at 50 °C for 6 h, diluted with saturated NH_4Cl (20 mL), and extracted with $CHCl_3$ three times. The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography with 1:3 EtOAc–hexane as an eluant to give **7b** (462 mg, 92%) as colorless needles: mp 76–77 °C (from 1:1 EtOAc–hexane); $[\alpha]_D^{26}$ +68.9 ° (*c* 1.03); R_f 0.46 (B); ^{1}H NMR: δ 1.35, 1.58 (2s, 3 H each, CMe_2), 2.40 (br s, 1 H, HO-5), 3.52 (dd, 1 H, $J_{6,6'}$ 10.1, $J_{5,6'}$ 7.9 Hz, H′-6), 3.56 (dd, 1 H, $J_{5,6}$ 3.4 Hz, H-6), 3.95 (dd, 1 H, $J_{3,4}$ 8.9, $J_{2,3}$ 4.3 Hz, H-3), 4.08 (dd, 1 H, $J_{4,5}$ 3.7 Hz, H-4), 4.14 (dt, 1 H, H-5), 4.53, 4.55 (2d, 1 H each, ^2J 12.0 Hz, CH_2O-6), 4.54 (t, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.54, 4.74 (2d, 1 H each, ^2J 11.9 Hz, CH_2O-3), 5.73 (d, 1 H, H-1), 7.27–7.36 (m, 10 H, Ph). Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 68.78; H, 7.01.

3.7. 3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-β-D-altrofuranose (7c)

By employing the same procedures as those described for **7b**, compound **6c** gave **7c** (89%) as a colorless syrup; $[\alpha]_D^{23}$ −0.34° (*c* 2.50); R_f 0.29 (A); ^{1}H NMR: δ 1.32, 1.49 (2s, 3 H each, CMe_2), 2.20 (br s, 1 H, HO-5), 3.60 (dd, 1 H, $J_{6,6'}$ 9.5, $J_{5,6'}$ 6.1 Hz, H′-6), 3.71 (dd, 1 H, $J_{5,6}$ 3.4 Hz, H-6), 3.98 (ddd, 1 H, $J_{4,5}$ 8.5 Hz, H-5), 4.10 (dd, 1 H, $J_{3,4}$ 2.0 Hz, H-4), 4.26 (d, 1 H, $J_{2,3}$ 0 Hz, H-3), 4.55, 4.575 (2d, 1 H each, ^2J 11.7 Hz, CH_2O-3), 4.59 (s, 2 H, CH_2O-6), 4.64 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-2), 5.91 (d, 1 H, H-1), 7.27–7.37 (m, 10 H, Ph). Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 69.12; H, 7.04.

3.8. 3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-β-D-mannofuranose (7d)

By employing the same procedures as those described for **7b**, compound **6d** gave **7d** (87%) as a colorless syrup; $[\alpha]_D^{21}$ −18.0° (*c* 1.03); R_f 0.52 (B); ^{1}H NMR: δ 1.32, 1.49 (2s, 3 H each, CMe_2), 2.20 (br s, 1 H, HO-5), 3.60 (dd, 1 H, $J_{6,6'}$ 9.5, $J_{5,6'}$ 6.1 Hz, H′-6), 3.71 (dd, 1 H, $J_{5,6}$ 3.4 Hz, H-6), 3.98 (ddd, 1 H, $J_{4,5}$ 8.5 Hz, H-5), 4.10 (dd, 1 H, $J_{3,4}$ 2.0 Hz, H-4), 4.26 (d, 1 H, $J_{2,3}$ 0 Hz, H-3), 4.55, 4.575 (2d, 1 H each, ^2J 11.7 Hz, CH_2O-3), 4.59 (s, 2 H, CH_2O-6), 4.64 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-2), 5.91 (d, 1 H, H-1), 7.27–7.37 (m, 10 H, Ph). Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 69.21; H, 7.09.

3.9. 3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-5-ulose (8b)

To a suspension of PCC (560 mg, 2.60 mmol) and finely powdered molecular sieves 4A (1.0 g) in dry CH_2Cl_2 (10 mL) was added a solution of **7b** (410 mg, 1.02 mmol) in dry CH_2Cl_2 (4 mL). The mixture was stirred at 25 °C for 4 h. After addition of 2-propanol (2 mL), the mixture was diluted with ether. The precipitates were filtered off through Celite and the filtrate was evaporated in vacuo. The residue was purified by column chromatography with 1:3 EtOAc–hexane as an eluant to give **11** (369 mg, 91%) as a colorless syrup: $[\alpha]_D^{24}$ +41.5° (*c* 1.22), R_f 0.47 (B). ^{1}H NMR: δ 1.35, 1.58 (2s, 3 H each, CMe_2), 3.83 (dd, 1 H, $J_{3,4}$ 9.2, $J_{2,3}$ 4.3 Hz, H-3), 4.29, 4.33 (2d, 1 H each, $J_{6,6'}$ 18.6 Hz, H_2-6), 4.53 (t, 1 H, $J_{1,2}$ 3.4 Hz, H-2), 4.55 (d, 1 H, H-4), 4.57, 4.585 (2d, 1 H each, ^2J 12.2 Hz, CH_2O-6), 4.60, 4.73 (2d, 1 H each, ^2J 12.2 Hz, CH_2O-3), 5.78 (d, 1 H, H-1), 7.29–7.39 (m, 10 H, Ph). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.19; H, 6.68.

3.10. 3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-β-D-*arabino*-hexofuranos-5-ulose (8c)

By employing the same procedures with **8b**, compound **7c** was treated with PCC for 6 h to give **8c** (90%) as a colorless syrup: $[\alpha]_D^{26}$ −3.43° (*c* 1.22); R_f 0.35 (A), 0.69 (B); ^{1}H NMR: δ 1.26, 1.32 (2s, 3 H each, CMe_2), 4.38, 4.70 (2d, 1 H each, $J_{6,6'}$ 18.3 Hz, H_2-6), 4.53 (br s, 1 H, $J_{3,4}$ 0.5, $J_{2,3}$ 0 Hz, H-3), 4.58, 4.63 (2d, 1 H each, ^2J 11.6 Hz, CH_2O-3), 4.59 (s, 2 H, CH_2O-6), 4.62 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-2), 4.62 (br s, 1 H, H-4), 5.98 (d, 1 H, H-1), 7.28–7.37 (m, 10 H, Ph). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.19; H, 6.75.

3.11. 3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-β-D-*lyxo*-hexofuranos-5-ulose (8d)

By employing the same procedures with **8b**, compound **7d** was treated with PCC for 8 h to give **8d** (88%) as a colorless syrup: $[\alpha]_D^{26}$ −54.4 ° (*c* 4.26); R_f 0.49 (A); ^{1}H NMR: δ 1.40, 1.53 (2s, 3 H each, CMe_2), 4.30 (dd, 1 H, $J_{3,4}$ 6.7, $J_{2,3}$ 5.2 Hz, H-3), 4.38, 4.42 (2d, 1 H each, $J_{6,6'}$ 18.0 Hz, H_2-6), 4.47, 4.53 (2d, 1 H each, ^2J 11.9 Hz, CH_2O-6), 4.49, 4.77 (2d, 1 H each, ^2J 11.6 Hz, CH_2O-3), 4.56 (d, 1 H, H-4), 4.69 (dd, 1 H, $J_{1,2}$ 4.3 Hz, H-2), 5.75 (d, 1 H, H-1), 7.26–7.34 (m, 10 H, Ph). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.48; H, 6.73.

3.12. 3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (8f)[9]

By employing the same procedures with **8b**, 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose was treated with PCC for 4 h to give **8f** (97%) as colorless prisms: mp 57–58 °C (from 1:2 EtOAc–hexane); $[\alpha]_D^{26}$ −89.5° (*c* 1.04) [lit.[9a] 91% yield by use of CrO_3–2Py, mp 56–57 °C, $[\alpha]_D^{22}$ −88° (*c* 1.0)]; R_f 0.51 (A); ^{1}H NMR: δ 1.33, 1.47 (2s, 3 H each, CMe_2), 2.23 (s, 3 H, H-6), 4.27 (d, 1 H, $J_{3,4}$ 3.7, $J_{2,3}$ 0 Hz, H-3), 4.48, 4.59 (2d, 1 H each, ^2J 11.9 Hz, CH_2O-3), 4.61 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.63 (d, 1 H, H-4), 6.08 (d, 1 H, H-1), 7.23 [m, 2 H, Ph(*o*)], 7.31 [m, 1 H, Ph(*p*)], 7.33 [m, 2 H, Ph(*m*)].

3.13. The general procedures for preparation of (5*R*)- and (5*S*)-5-dimethoxyphosphinyl-hexofuranoses (9a–f)

DBU (0.44 mL, 2.9 mmol) was dropwise added to a solution of **8** (2.42 mmol) in dimethyl phosphonate (10.0 mL, 109 mmol) at 0 °C and the solution was stirred at this temperature for 30 min under argon. The mixture was treated with saturated NH_4Cl (30 mL) at rt for 4 h and extracted with $CHCl_3$ three times. The combined organic layers were washed with water, dried (Na_2SO_4), and evaporated in vacuo. The residue was separated by column chromatography with a gradient eluant of 1:1 EtOAc–hexane → EtOAc to give (5*R*)-**9** and (5*S*)-**9**.

3.13.1. 3,6-Di-*O*-benzyl-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses (9a).[4c]

(5*R*)-Epimer: Colorless syrup (64% from **8a**); R_f 0.58 (C), (5*S*)-Epimer: Colorless syrup (27% from **8a**); R_f 0.30 (C).

3.13.2. 3,6-Di-*O*-benzyl-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (9b).

(5*R*)-Epimer: Colorless needles (47% from **8b**); mp 107–109 °C (from 2:1 EtOAc–hexane); $[\alpha]_D^{27}$ +37.3 ° (*c* 1.07); R_f 0.26 (C); FAB MS *m*/*z* 509 (M+1; 12), 451 (10), 419 (6), 361 (9), 181 (34), 91 (100). Found: *m*/*z* 509.1960. Calcd for $C_{25}H_{34}O_9P$: M+1, 509.1941. (5*S*)-Epimer: Colorless syrup (44% from **8b**); $[\alpha]_D^{27}$ +41.0° (*c* 1.06); R_f 0.34 (C). FAB MS *m*/*z* 509 (M+1; 18), 451 (10), 419 (9), 361 (6), 181 (24), 91 (100). Found: *m*/*z* 509.1951. Calcd for $C_{25}H_{34}O_9P$: M+1, 509.1941.

3.13.3. 3,6-Di-*O*-benzyl-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-β-D-*arabino*-hexofuranose (9c).

(5*R*)-Epimer: Colorless syrup (72% from **8c**); $[\alpha]_D^{26}$ +7.57° (*c* 1.82); R_f 0.55 (C); FAB MS *m*/*z* 509 (M+1; 15), 451 (14), 419 (9), 361 (8), 181 (31), 91 (100). Found: *m*/*z* 509.1932. Calcd for $C_{25}H_{34}O_9P$: M+1, 509.1941. (5*S*)-Epimer: Colorless prisms (24% from **8c**); mp 95–96 °C (from 3:1 EtOAc–hexane); $[\alpha]_D^{26}$ +15.1° (*c* 1.28); R_f 0.39 (C). Anal. Calcd for $C_{25}H_{33}O_9P$: C, 59.05; H, 6.54. Found: C, 58.08; H, 6.64.

3.13.4. 3,6-Di-*O*-benzyl-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-β-D-*lyxo*-hexofuranose (9d).

(5*R*)-Epimer: Colorless syrup (68% from **8d**); $[\alpha]_D^{20}$ −42.6° (*c* 1.61); R_f 0.46 (C); FAB MS *m*/*z* 509 (M+1; 26), 451 (14), 419 (14), 361 (16), 181 (39), 91 (100). Found: *m*/*z* 509.1969. Calcd for $C_{25}H_{34}O_9P$: M+1, 509.1941. (5*S*)-Epimer: Colorless prisms (24% from **8d**); mp 108–109 °C (from 3:1 EtOAc–hexane); $[\alpha]_D^{24}$ −49.8° (*c* 1.66); R_f 0.32 (C). Anal. Calcd for $C_{25}H_{33}O_9P$: C, 59.05; H, 6.54. Found: C, 59.13; H, 6.41.

3.13.5. Methyl 6-*O*-benzyl-5-dimethoxyphosphinyl-2,3-*O*-isopropylidene-α-D-*lyxo*-hexofuranoside (9e).

(5*R*)-Epimer: Colorless needles (76% from **8e**[5b]); mp 85–86 °C (from 2:1 EtOAc–hexane); $[\alpha]_D^{21}$ +60.8° (*c* 1.70); R_f 0.40 (C). Anal. Calcd for $C_{19}H_{29}O_9P$: C, 52.78, H, 6.76. Found: C, 52.66, H, 6.89. (5*S*)-Epimer: Colorless syrup (19% from **8e**); $[\alpha]_D^{21}$ +36.6° (*c* 1.16); R_f 0.32 (C). Anal. Calcd for $C_{19}H_{29}O_9P$: C, 52.78; H, 6.76. Found: C, 52.59; H, 6.80.

3.13.6. 3-*O*-Benzyl-6-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (9f).

(5*R*)-Epimer: Colorless syrup (85% from **8f**); $[\alpha]_D^{26}$ −16.8° (*c* 1.04); R_f 0.49 (C). Anal. Calcd for $C_{18}H_{27}O_8P$: C, 53.73; H, 6.76. Found: C, 53.66; H, 6.73. (5*S*)-Epimer: Colorless syrup (6.6% from **8f**); $[\alpha]_D^{26}$ −37.6° (*c* 1.05); R_f 0.25

(C). Anal. Calcd for $C_{18}H_{27}O_8P$: C, 53.73; H, 6.76. Found: C, 53.51; H, 6.66.

3.14. General procedures for preparation of the 5-deoxy-5-dimethoxyphosphinyl-hexofuranoses (11a–f and 12a–f)

Methoxalyl chloride (1.00 mL, 10.8 mmol) was added to a solution of **9** (2.16 mmol) and 1,4-dimethylaminopyridine (DMAP, 1.32 g, 10.8 mmol) in dry MeCN (15 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min under argon, and the most of solvent was distilled off in vacuo. The residue was treated with aq NH_4Cl (20 mL) and extracted with $CHCl_3$. The combined organic layer was washed with water, dried (Na_2SO_4) and evaporated in vacuo to give the 5-O-methoxalyl derivative **10** as a pale yellow syrup. The crude **10** was coevaporated with dry toluene and dissolved in the same solvent (15 mL). Tributyltin hydride (0.87 mL, 3.24 mmol) and AIBN (54 mg, 0.33 mmol) were added under argon. The mixture was stirred at 80 °C for 2–6 h and then concentrated in vacuo. The residue was separated by column chromatography with a gradient eluant of 1:1 EtOAc–hexane → EtOAc to give **11** and **12**.

3.14.1. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-D-glucofuranose (11a)[4c]. Colorless syrup (50% from **9a**); R_f 0.60 (C).

3.14.2. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-β-L-idofuranose (12a)[4c]. Colorless syrup (38% from **9a**); R_f 0.38 (C).

3.14.3. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-D-allofuranose (11b). Colorless syrup (29% from **9b**); $[\alpha]_D^{27}$ +40.8° (*c* 1.06); R_f 0.45 (C), 0.30 (D). FAB MS *m/z* 493 (M+1; 18), 435 (22), 237 (11), 185 (16), 91 (100). Found: *m/z* 493.1980. Calcd for $C_{25}H_{34}O_8P$: M+1, 493.1992.

3.14.4. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-β-L-tallofuranose (12b). Colorless needles (57% from **9b**); mp 62–63 °C (from 2:1 EtOAc–hexane); $[\alpha]_D^{27}$ +60.0° (*c* 0.71); R_f 0.42 (C), 0.37 (D). FAB MS *m/z* 493 (M+1; 11), 435 (18), 237 (14), 185 (20), 91 (100). Found: *m/z* 493.1999. Calcd for $C_{25}H_{34}O_8P$: M+1, 493.1992.

3.14.5. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-β-D-altrofuranose (11c). Colorless syrup (16% from **9c**); $[\alpha]_D^{26}$ +6.06° (*c* 1.67); R_f 0.55 (C). FAB MS *m/z* 493 (M+1; 20), 435 (22), 345 (10), 237 (11), 185 (26), 91 (100). Found: *m/z* 493.2011. Calcd for $C_{25}H_{34}O_8P$: M+1, 493.1992.

3.14.6. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-L-galactofuranose (12c). Colorless needles (68% from **9c**); mp 69–70 °C (from 2:1 EtOAc–hexane); $[\alpha]_D^{26}$ +20.9° (*c* 1.21); R_f 0.45 (C). FAB MS *m/z* 493 (M+1; 12), 435 (14), 237 (24), 185 (46), 91 (100). Found: *m/z* 493.1979. Calcd for $C_{25}H_{34}O_8P$: M+1, 493.1992.

3.14.7. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-β-D-mannofuranose (11d). Colorless syrup (29% from **9d**); $[\alpha]_D^{26}$ −38.3° (*c* 1.77); R_f 0.30 (C). FAB MS *m/z* 493 (M+1; 9), 435 (11), 237 (24), 185 (36), 91 (100). Found: *m/z* 493.1998. Calcd for $C_{25}H_{34}O_8P$: M+1, 493.1992.

3.14.8. 3,6-Di-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-L-gulofuranose (12d). Colorless needles (48% from **9d**); mp 70–71 °C (from 2:1 EtOAc–hexane); $[\alpha]_D^{26}$ −47.3° (*c* 1.05); R_f 0.20 (C). FAB MS *m/z* 493 (M+1; 22), 435 (19), 237 (29), 185 (38), 91 (100). Found: *m/z* 493.2012. Calcd for $C_{25}H_{34}O_8P$: M+1, 493.1992.

3.14.9. Methyl 6-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-2,3-*O*-isopropylidene-α-D-mannofuranoside (11e). Colorless prisms (16% from **9e**); mp 65–67 °C (from 2:1 EtOAc–hexane); $[\alpha]_D^{20}$ +49.5 ° (*c* 1.48); R_f 0.45 (C). FAB MS: 417 (M+1; 21), 401 (12), 385 (11), 177 (19), 137 (11), 91 (100). Found: *m/z* 417.1691. Calcd for $C_{19}H_{30}O_8P$: M+1, 417.1679.

3.14.10. Methyl 6-*O*-benzyl-5-deoxy-5-dimethoxyphosphinyl-2,3-*O*-isopropylidene-β-L-gulofuranoside (12e). Colorless syrup (70% from **9e**); $[\alpha]_D^{20}$ +65.8° (*c* 2.81); R_f 0.38 (C). FAB MS: 417 (M+1; 32), 401 (18), 385 (15), 177 (15), 91 (100). Found: *m/z* 417.1682. Calcd for $C_{19}H_{30}O_8P$: M+1, 417.1679.

3.14.11. 3-*O*-Benzyl-5,6-dideoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-α-D-glucofuranose (11f). Colorless syrup (24% from **9f**); $[\alpha]_D^{26}$ −30.5° (*c* 6.47); R_f 0.46 (C). FAB MS *m/z* 387 (M+1; 32), 329 (11), 298 (9), 261 (16), 221 (41), 91 (100). Found: *m/z* 387.1561. Calcd for $C_{18}H_{28}O_7P$: M+1, 387.1573.

3.14.12. 3-*O*-Benzyl-5,6-dideoxy-5-dimethoxyphosphinyl-1,2-*O*-isopropylidene-β-L-idofuranose (12f)[7]. Colorless syrup (60% from **9f**); $[\alpha]_D^{26}$ −37.7° (*c* 2.42) [lit.,[7] $[\alpha]_D^{21}$ −36° (*c* 2.16)]; R_f 0.29 (C).

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