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Synthesis of 5-Deoxy-5-phenylphosphino- and 5-Phenylphosphinyl-D-glucopyranoses

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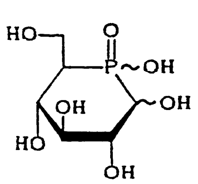
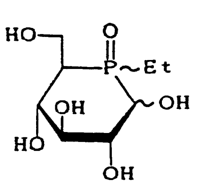
(5*R* and 5*S*)-3-*O*-Acetyl-5-deoxy-1,2-*O*-isopropylidene-5-[(methoxy)phenylphosphinyl]-6-*O*-(tetrahydro-2-pyranyl)-α-D-*xylo*-hexofuranoses (**7**) were prepared from 3-*O*-acetyl-5,6-dideoxy-6-nitro-α-D-*xylo*-hex-5-enofuranose in 4 steps. Reduction of **7** with sodium dihydridobis(2-methoxyethoxy)aluminate followed by acid hydrolysis provided the title compounds, among which the 5-deoxy-5-phenylphosphino-D-glucoses are the first example of hexopyranose analogs having a phosphinidene group in place of hemiacetal ring-oxygen. These compounds were converted into 1,2,3,4,6-penta-*O*-acetates, whose structures were established by spectroscopy.

In the chemical modification of sugar compounds, various sugar analogs containing phosphorus as the ring heteroatom have been prepared.[1] As for analogs of D-glucopyranose type, 5-deoxy-5-hydroxyphosphinyl- (**1**)[2] and 5-ethylphosphinyl-D-glucopyranoses (**2**)[3] have been reported. In this paper we wish to describe the synthesis of hitherto unreported 5-deoxy-5-arylphosphino- and 5-arylphosphinyl-D-glucopyranose analogs by taking phenyl as a model functional group. Besides, the former compound becomes the first hexopyranose analog having a phosphinidene group in the hemiacetal ring.[4]



1



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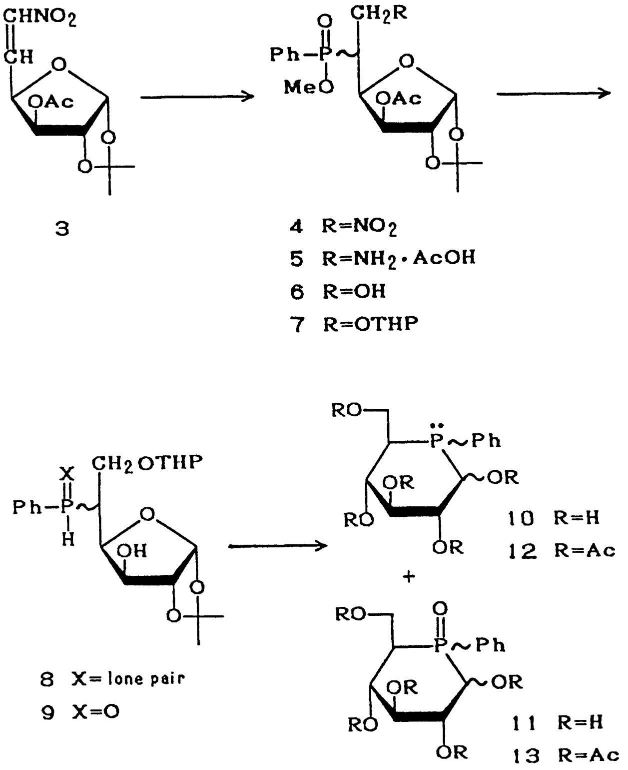


Scheme 1.

Results and Discusion

The addition reaction of methyl hydrogenphenylphosphinate to 3-*O*-acetyl-5,6-dideoxy-6-nitro-α-D-*xylo*-hex-5-enofuranose (**3**)[5] in the presence of triethylamine (TEA) at 25 °C gave an inseparable mixture (9 : 9 : 1 : 1) of two major D-"gluco" and two minor L-"ido" furanoses (**4**) in a 85% yield (Scheme 1). The assignments of the configuration of the products were made by comparison of their spectral data with those of other 5-phosphinyl compounds having similar structures;[2,6] see the Experimental section. Catalytic hydrogenation of **4** over palladium hydroxide on carbon [to convert it into 6-amino derivatives (**5**)], followed by diazotization and then hydrolysis, gave (5*R* and 5*S*)-3-*O*-acetyl-5-deoxy-1,2-*O*-isopropylidene-5-[(methoxy)-phenylphosphinyl]-α-D-*xylo*-hexofuranose (**6**). Compound **6** was converted into 6-*O*-(tetrahydro-2-pyranyl) derivatives (**7**) by treatment with dihydropyran in the presence of pyridinium *p*-toluenesulfonate (PPTS).

Compound **7** was then subjected to the reduction with sodium dihydridobis(2-methoxyethoxy)aluminate (SDMA), giving an unstable colorless syrup. This was found to consist exclusively of compounds having a 5-phenylphosphino structure (**8**) on the basis of the characteristic ^{31}P NMR data (δ=−53.4 and −51.5); judging from the presence of a very weak ^{31}P NMR signal (δ=30.1), only an extremely small proportion (<5%) of a 5-phenylphosphinyl compound (**9**) appeared to be present among the above reduction products. This presents a rather unexpected contrast to the fact that when the 5-[(ethyl)methoxyphosphinyl] congener of **7** was subjected to the SDMA reduction, its 5-

ethylphosphinyl derivative was exclusively obtained.[3] The reason for this difference has remained to be studied.

The phenylphosphino intermediate **8** was hydrolyzed in ethanolic 0.25 M hydrochloric acid (1 M=1 mol dm^{-3}) to effect the ring transposition, affording 5-deoxy-5-phenylphosphino-D-hexopyranose (**10**) and a minor proportion of their 5-phenylphosphinyl derivatives (**11**) as well (Scheme 1). Despite the attempted inert atmosphere during the procedure, **11** is presumably derived either from the oxidized intermediate **9** before the ring enlargement or from compound **10**; both **8** and **10** would become liable to suffer autoxidation upon prolonged heating at 90 °C.

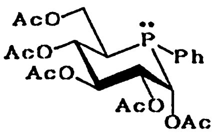
Because of the difficulty in separation and purification, compounds **10** and **11** were converted into the corresponding per-*O*-acetyl derivatives (**12** and **13**, respectively) by the usual method for characterization. By purification in a column of silica gel, the following penta-*O*-acetyl compounds were isolated: 5-[(*R*)-phenylphosphino]-α-D-glucopyranose (**12a**, 2.0% overall yield from **7**), its β-anomer **12b** (9.9%), 5-[(*S*)-phenylphosphinyl]-α-D-glucopyranose (**13a**, 4.5%), and its β-anomer (**13b**, 5.3%). Besides these compounds, a small amount (ca. 2%) of three additional products were obtained as an inseparable mixture (ca. 1 : 1 : 1). The products were presumed to be the two remaining diastereomers of **13a,b** (namely, 5-[(*R*)-phenylphosphinyl]-α,β- isomers) and an L-idopyranose on the basis of ^{31}P NMR data, although the exact structures of these extremely minor products remained unestablished.

Structures of the final products **12a,b** and **13a,b** were established on the basis of high-resolution mass spectrometry and ^{1}H and ^{31}P NMR spectral data (see, Table 1). As large $J_{4,5}$ values (11.1—11.6 Hz) of **12a,b** and **13a,b** are characteristic coupling constants for an axial–axial conformation of H-4 and H-5, all of these compounds have D-glucopyranose configuration with $^4C_1$(D) conformation. With regard to the anomeric orientation of C-1, small $J_{1,2}$ values (2.2 and 2.8 Hz) of **12a** and **13a** indicate α-configuration, whereas large $J_{1,2}$ values (10.8 and 11.2 Hz) of **12b** and **13b** indicate β-configuration. The anti connection of H–C$_1$–P=O for **12b** and **13b** is confirmed by the smaller $J_{1,\mathrm{P}}$ values (5.0 and 3.0 Hz) compared with the corresponding parameters (9.3 and 10.6 Hz) of **12a** and **13a** having this group in the gauche connections.[3] The H-2, H-4, and H-6′ signals of **13a,b** appear at a considerably downfield compared with those of **12a,b**. This can be explained by deshielding effect of the axial P=O bond at 1,3-diaxial positions, while the axial P-lone pair does not exert such an effect. The precise NMR parameters summarized in Table 1 are thought to be of value in determining the structures of other sugar analogs having similar constituents.

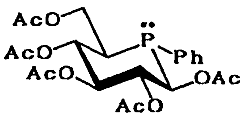
It should be noticed that while the precursor **7** was a ca. 9 : 1 mixture of D-gluco and L-idofuranose, the final, isolated products **12a,b** and **13a,b** all possessed D-glucopyranose configuration. This indicates that no epimerization apparently takes place at C-5 of **7** by the strongly basic reagent SDMA during the reduction to yield phosphine **8**.[7]

Although yields of some of the steps of the reaction scheme have to be improved, the present work thus demonstrates a possible way for preparation of 5-deoxy-5-arylphosphino- and 5-arylphosphinyl-D-glucopyranoses from an appropriate intermediate. Extension of this work including studies of reactivities of the phosphinidene functional group of **12a,b**, as well as biological evaluation of all products, is in progress.

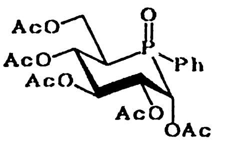
Table 1. ^{1}H and ^{31}P NMR Parameters for **12a,b** and **13a,b** in CDCl$_3$



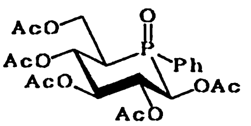
12a



12b



13a



13b

Compd	Chemical shifts (δ)											
	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	Ac-1,2,3,4,6[a]	Ph(*o*)	Ph(*m*)	Ph(*p*)	^{31}P
12a	5.76	5.33	5.52	5.49	3.30	4.29	3.97	1.85, 2.04, 2.02, 1.95, 1.93	7.55	7.42	7.42	−30.7
12b	5.78	5.44	5.26	5.42	2.65	4.16	3.88	1.82, 2.03, 2.01, 1.97, 1.84	7.64	7.43	7.43	−32.6
13a	5.68	5.72	5.59	5.73	3.19	4.37	4.32	1.56, 2.08, 2.06, 2.05, 1.96	7.77	7.54	7.61	27.3
13b	5.65	5.81	5.42	5.69	2.81	4.32	4.31	1.46, 2.06, 2.04, 1.98, 1.87	7.79	7.55	7.62	26.1

	Coupling constants/Hz												
	$J_{1,2}$	$J_{1,\mathrm{P}}$	$J_{2,3}$	$J_{2,\mathrm{P}}$	$J_{3,4}$	$J_{4,5}$	$J_{4,\mathrm{P}}$	$J_{5,6}$	$J_{5,6'}$	$J_{5,\mathrm{P}}$	$J_{6,\mathrm{P}}$	$J_{6',\mathrm{P}}$	$J_{6,6'}$
12a	2.2	9.3	10.1	3.2	9.6	11.1	3.2	4.7	4.4	3.9	13.2	9.4	11.8
12b	10.8	5.0	9.6	4.6	10.0	11.5	3.8	4.9	3.9	4.2	13.3	10.3	11.8
13a	2.8	10.6	10.5	0	9.7	11.6	1.9	7.4	6.2	5.4	11.6	14.8	11.6
13b	11.2	3.0	9.8	2.9	9.9	11.6	2.5	6.8	6.8	3.3	14.1	14.1	—

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

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) 1:1, (C) 2:1 AcOEt–hexane, and (D) 5:3:1 2-propanol–AcOEt–H_2O]; components were detected by spraying the plates with 20% sulfuric acid–ethanol, with subsequent heating. Column chromatography was performed by Wako C-200 silica gel. 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 (81 MHz for ^{31}P) instrument (the SC-NMR Lab., Okayama Univ.) at 21 °C, except for compound **7** [which was measured with Hitachi R600 (60 MHz) instrument]. 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 ultrahigh resolution instrument and were given in terms of m/z (rel intensity) compared with the base peak.

(5*R* and 5*S*)-3-*O*-Acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-6-nitro-α-*xylo*-hexofuranoses (4). TEA (0.10 ml, 0.72 mmol) was added dropwise at 0 °C to a mixture of **3**[5] (464 mg, 1.70 mmol) and methyl hydrogenphenylphosphinate (1.41 g, 9.04 mmol) in benzene (2 ml). The mixture was stirred for 3 h at 25 °C and then poured into saturated aq $NaHCO_3$. The resulting solution was stirred overnight and extracted three times with CH_2Cl_2. The extracts were washed with saturated aq NaCl, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified in a column of silica gel with AcOEt–hexane as an eluant, giving an inseparable mixture [9:9:1:1 (two D-gluco and two L-ido isomers)] of **4** as a colorless syrup, the ratio being determined by ^{1}H and ^{31}P NMR: 620 mg (85%); R_f=0.28 (B); ^{1}H NMR (500 MHz) for two D-gluco isomers δ=1.25, 1.28*, 1.45, 1.48* (3H each, 4s, CMe_2), 1.70, 2.09* (3H, 2s, AcO-3), 3.58, 3.61* (1H, 2m, H-5, their splitting patterns uncertain because of overlapping with other proton signals), 3.60, 3.67* (3H, 2d, J_{POMe}=11.1 Hz, POMe), 4.39, 4.48* (1H, 2d, $J_{1,2}$=3.8, 3.6* Hz, H-2), 4.50, 4.59* (1H, 2ddd, $J_{4,5}$=9.7, 9.1*, $J_{4,P}$=5.7, 7.4*, $J_{3,4}$=2.8, 2.9* Hz, H-4), 4.51, 4.87* (1H, 2td, $J_{6',P}$=14.9, 15.2*, $J_{6,6'}$=14.9, 15.0*, $J_{5,6'}$=4.9, 5.4* Hz, H-6′), 4.77, 4.89* (1H, 2ddd, $J_{6,P}$=12.2, 13.7*, $J_{5,6}$=6.4, 7.0* Hz, H-6), 4.99, 5.25* (1H, 2d, H-3), 5.74, 5.78* (1H, 2d, H-1), 7.54, 7.54* [2H, m, Ph(*m*)], 7.63, 7.64* [1H, 2m, Ph(*p*)], 7.74, 7.78* [2H, 2m, Ph(*o*)], * for another diastereomer with regard to the phosphorus atom (the assignment of some of the δ values may have to be interchanged); ^{31}P NMR δ=39.1 and 38.0 (D-gluco), 39.4 and 38.6 (L-ido isomers); MS m/z 430 (M+1; 1.0), 414 (24), 354 (33), 340 (28), 312 (13), 293 (18), 265 (38), 258 (55), 211 (44), 173 (31), 155 (100). Found: m/z 430.1273. Calcd for $C_{18}H_{25}NO_9P$: M+1, 430.1267.

(5*R* and 5*S*)-3-*O*-Acetyl-5-deoxy-1,2-*O*-isopropylidene-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-α-D-*xylo*-hexofuranoses (6). Compound **4** (585 mg, 1.36 mmol) dissolved in a mixture of ethanol (3 ml) and acetic acid (0.15 ml, 2.6 mmol) was hydrogenolyzed in the presence of 20% $Pd(OH)_2$ on carbon (630 mg, 0.90 mmol) at 20 °C under atmospheric pressure of H_2. After 24 h, the catalyst was filtered off and the filtrate was evaporated in vacuo, giving 6-ammonio-hexofuranose acetate derivatives **5** as a colorless syrup: R_f=0.49 (D).

To a stirred solution of **5** in water (15 ml) was added, at 0 °C, acetic acid (0.20 ml, 3.5 mmol) and then sodium nitrite (384 mg, 3.57 mmol). After 2 h, the mixture was twice extracted with $CHCl_3$. The combined organic layers were washed with aq $NaHCO_3$ and then water, dried (Na_2SO_4), and evaporated in vacuo. The residue was separated by column chromatography (with AcOEt as an eluant), giving two fractions.[#]

The faster-eluting fraction [R_f=0.27 (A)] gave a colorless syrup which was one D-gluco isomer of **6** [but contained a minor amount (<10%) of an L-ido isomer]: 138 mg (25% from **4**): ^{1}H NMR (500 MHz) δ=1.30, 1.53 (3H each, 2s, CMe_2), 2.08 (3H, s, AcO-3), 2.63 (1H, dddd, $J_{5,P}$=13.9, $J_{4,5}$=10.9, $J_{5,6}$=5.1, $J_{5,6'}$=4.0 Hz, H-5), 3.60 (3H, d, J_{POMe}=11.0 Hz, POMe), 3.90 (1H, ddd, $J_{6',P}$=23.5, $J_{6,6'}$=11.9 Hz, H-6′), 3.91 (1H, ddd, $J_{6,P}$=7.0 Hz, H-6), 4.05 (1H, m, HO-6), 4.50 (1H, d, $J_{1,2}$=3.9, $J_{2,3}\approx$0 Hz, H-2), 4.77 (1H, ddd, $J_{4,P}$=5.0 Hz, $J_{3,4}$=2.8 Hz, H-4), 5.34 (1H, d, H-3), 5.85 (1H, d, H-1), 7.52 [2H, m, $J_{o,m}$=$J_{m,p}$=7.5, $J_{m,P}$=3.5 Hz, Ph(*m*)], 7.61 [1H, m, $J_{o,p}$=$J_{p,P}$=1.4 Hz, Ph(*p*)], 7.71 [2H, m, $J_{o,P}$=11.7 Hz, Ph(*o*)]; ^{31}P NMR δ=42.0.

The slower-eluting fraction [R_f=0.20 (A)] gave a colorless syrup which was mainly the other D-gluco isomer **6** [but contained a minor amount (<10%) of another L-ido isomer]: 144 mg (27% from **4**); ^{1}H NMR (500 MHz) δ=1.26, 1.42 (3H each, 2s, CMe_2), 1.96 (3H, s, AcO-3), 2.75 (1H, ddt, $J_{5,P}$=17.1, $J_{4,5}$=10.8, $J_{5,6}$=5.5, $J_{5,6'}$=5.4 Hz, H-5), 3.64 (3H, d, J_{POMe}=11.2 Hz, POMe), 3.68 (1H, m, HO-6), 4.04 (1H, ddd, $J_{6,6'}$=11.8, $J_{6',P}$=10.7 Hz, H-6′), 4.08 (1H, ddd, $J_{6,P}$=10.2 Hz, H-6), 4.38 (1H, ddd, $J_{4,P}$=6.0, $J_{3,4}$=2.7 Hz, H-4), 4.42 (1H, d, $J_{1,2}$=3.9, $J_{2,3}\approx$0 Hz, H-2), 5.08 (1H, d, H-3), 5.79 (1H, d, H-1), 7.53 [2H, m, Ph(*m*)], 7.61 [1H, m, Ph(*p*)], 7.74 [2H, m, Ph(*o*)]; ^{31}P NMR δ=42.0; MS m/z 401 (M+1; 1.0), 385 (16), 325 (13), 283 (21), 253 (25), 229 (54), 211 (20), 199 (37), 173 (34), 155 (100). Found: m/z 401.1353. Calcd for $C_{18}H_{26}NO_8P$: M+1, 401.1365.

(5*R* and 5*S*)-3-*O*-Acetyl-5-deoxy-1,2-*O*-isopropylidene-5-[(*R* and *S*)-(methoxy)phenylphosphinyl]-6-*O*-(tetrahydro-2-pyranyl)-α-D-*xylo*-hexofuranose (7). A solution of **6**[#] (140 mg, 0.350 mmol) and dihydropyran (0.10 ml, 1.1 mmol) in dry CH_2Cl_2 (1.5 ml) containing PPTS (50 mg, 0.20 mmol) was stirred for 10 h at 20 °C. The solution was diluted with ether, washed with half-saturated brine, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography (with 3:1 AcOEt–hexane), giving **7** (154 mg, 90%) as a colorless syrup: R_f=0.45—0.30 (A); ^{1}H NMR (60 MHz) δ=1.25—1.65 [6H, m, C–$(CH_2)_3$–C–O-6], 1.28, 1.35, 1.45, 1.48 (6H, 4s, CMe_2), 1.96, 2.01, 2.06, 2.10 (3H, 4s, AcO-3), 2.45—2.85 (1H, m, H-5), 3.47, 3.50, 3.59 (3H, 3d, J_{POMe}=11.0 Hz, POMe), 3.50—4.15 (4H, m, CH_2–O–C–O-6, H_2-6), 4.25—4.65 (2H, m, H-4, CH–O-6), 4.45 (1H, d, $J_{1,2}$=4.0 Hz, H-2), 5.34 (1H, d, $J_{3,4}$=2.8 Hz, H-3), 5.80 (1H, d, H-1), 7.45—7.70, [3H, m, Ph(*m,p*)], 7.70—7.90 [2H, m, Ph(*o*)]; MS m/z 481 (M^+; 0.6), 469 (1.7), 401 (15), 385 (19), 325 (18), 283 (27), 253 (20), 229 (41), 199 (34), 173 (42), 155 (100). Found: m/z 484.1843. Calcd for $C_{23}H_{33}O_9P$: M, 483.1862.

1,2,3,4,6-Penta-*O*-acetyl-5-deoxy-5-phenylphosphino- (12) and 5-Phenylphosphinyl-α,β-D-glucopyranoses (13). To a solution of **7** (264 mg, 0.545 mmol) in dry benzene (5 ml) was added, with stirring, a solution of SDMA (3.4 M toluene

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[#] Because the separation of the two fractions of **6** was rather difficult and each fraction was expected to give the same mixture of **8** and/or **9** after the SDMA reduction (Ref. 8), the combined fractions of **6** were used for the practical preparation of **7**.

solution, 0.50 ml, 1.7 mmol) in dry benzene (2 ml) in small portions at 5 °C under an argon atmosphere. The stirring was continued at this temp for 1 h. Then, water (0.5 ml) was added and the mixture was stirred for 30 min. The precipitate was centrifuged and washed with several portions of benzene. The organic layers were combined and evaporated in vacuo, giving the 5-phenylphosphino derivative **8** as a colorless syrup: R_f=0.78—0.70 (A): ^{31}P NMR δ=−53.4, −51.5; besides these strong signals, a weak signal (less than a 5% relative intensity) was observed at δ=30.1 most likely assignable to **9**.

The above syrup (mostly **8**) was immediately treated with a mixture of ethanol (5 ml) and 0.5 M hydrochloric acid (5 ml) at 90 °C for 3 h under an argon atmosphere. After cooling, the reactants were neutralized with weakly basic ion-exchange resin Amberlite IRA-45. The resin was filtered off and washed with water, and the filtrate was evaporated in vacuo to give a mixture of 5-deoxy-5-phenylphosphino- [**10**, R_f=0.74 (D), major] and 5-phenylphosphinyl-D-glucopyranoses [**11**, R_f=0.58 (D), minor] as a colorless syrup.

This was acetylated with acetic anhydride (1 ml) in dry pyridine (2 ml) for 12 h at 20 °C and then the mixture was concentrated in vacuo. The residue was separated by column chromatography with a gradient eluant of 1 : 1 AcOEt–hexane→AcOEt, into three fractions A—C.

Fraction A [R_f=0.56 (C)] gave a chromatographically inseparable mixture (31.3 mg) consisting of 5-[(*R*)-phenylphosphino]-α-D-glucopyranose **12a** (2.0% from **7**) and its β-isomer **12b** (9.9%). Pure compound **12b** was obtained by recrystallization of the above mixture from 1 : 1 AcOEt–hexane: colorless prisms, mp 148—149 °C; ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 483 (M+1; 0.8), 440 (4.1), 381 (100), 339 (27), 321 (12), 279 (32), 261 (12), 237 (23), 219 (28), 125 (22). Found: C, 54.35; H, 5.58%; *m/z* 483.1420. Calcd for $C_{22}H_{27}O_{10}P$: C, 54.77; H, 5.64%. Calcd for $C_{22}H_{28}O_{10}P$: (M+1), 483.1420.

Fraction B [R_f=0.20 (C)] gave colorless crystals (26.7 mg) which consisted of 5-[(*S*)-phenylphosphinyl]-α-D-glucopyranose **13a** (4.5% from **7**) and its β-isomer **13b** (5.3%); mp 226—228 °C (1 : 1 mixture, from AcOEt); ^{1}H and ^{31}P NMR, see Table 1; MS *m/z* 499 (M+1; 3.8), 456 (5.2), 397 (70), 355 (100), 337 (18), 295 (60), 253 (39), 234 (45), 159 (36), 125 (47). Found: C, 53.22; H, 5.54%; *m/z* 499.1382. Calcd for $C_{22}H_{27}O_{11}P$: C, 53.02; H, 5.46%. Calcd for $C_{22}H_{28}O_{11}P$: (M+1), 499.1369.

Fraction C [R_f=0.15—0.10 (C)] gave an inseparable mixture of products as a colorless syrup (5 mg, ca. 2% from **7**); ^{31}P NMR δ=24.5, 25.8, 26.3; for their structures, see the main text.

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8) The SDMA reduction of similar sugar analogs bearing either an [(*R*)- or [(*S*)-(alkoxy)phenylphosphinyl] group is known to accompany epimerization of the phosphorus atom to give an identical [(*R*,*S*)-phenylphosphinyl] derivative: T. Hanaya, N. Shigetoh, and H. Yamamoto, *Bull. Chem. Soc. Jpn.*, **61**, 2499 (1988), and references cited therein.