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SYNTHESIS, AND X-RAY STRUCTURAL ANALYSIS, OF 1,2,3,4-TETRA-*O*-ACETYL-5,6-DIDEOXY-5-*C*-[(*S*)-PHENYLPHOSPHINYL]-α- AND -β-L-IDOPYRANOSE

SABURO INOKAWA*, KEIZO YAMAMOTO, HEIZAN KAWAMOTO, HIROSHI YAMAMOTO,
Department of Chemistry, Faculty of Science, Okayama University, Okayama 700 (Japan)

MITSUJI YAMASHITA,
Department of Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432 (Japan)

AND PETER LUGER**
Institut für Kristallographie der Freien Universität Berlin, D-1 Berlin 33 (West Germany)

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ABSTRACT

The title compounds and two diastereoisomers were prepared from (5*RS*)-3-*O*-benzyl-5,6-dideoxy-5-*C*-[(*RS*)-(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses upon reduction with sodium dihydrobis(2-methoxyethoxy)-aluminate, followed by hydrolysis with mineral acid, and acetylation with acetic anhydride–pyridine. Among these products, the two readily crystallized compounds were determined by X-ray crystallographic analysis to be 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-α- and -β-L-idopyranose-$^4C_1$.

INTRODUCTION

Sugar analogs having a phosphorus atom in the hemiacetal ring are interesting not only from the viewpoint of their physicochemical properties but also from that of the potential utility of their biological activities. However, only a few reports have so far been published concerning such sugars.

We previously reported[1] the synthesis of 1,2,4-tri-*O*-acetyl-5,6-dideoxy-3-*O*-methyl-5-*C*-[(*S*)-phenylphosphinyl]-β-D-glucopyranose, and now describe a new approach to the preparation of (5*RS*)-5,6-dideoxy-5-*C*-[(*RS*)-phenylphosphinyl]hexopyranoses, starting from (5*RS*)-5,6-anhydro-3-*O*-benzyl-5-*C*-[(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose[2,3], and also the X-ray crystallographic analysis of the 1,2,3,4-tetraacetates of these sugars.

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*To whom correspondence should be addressed with respect of the synthesis.
**To whom correspondence should be addressed with respect of the X-ray analysis.

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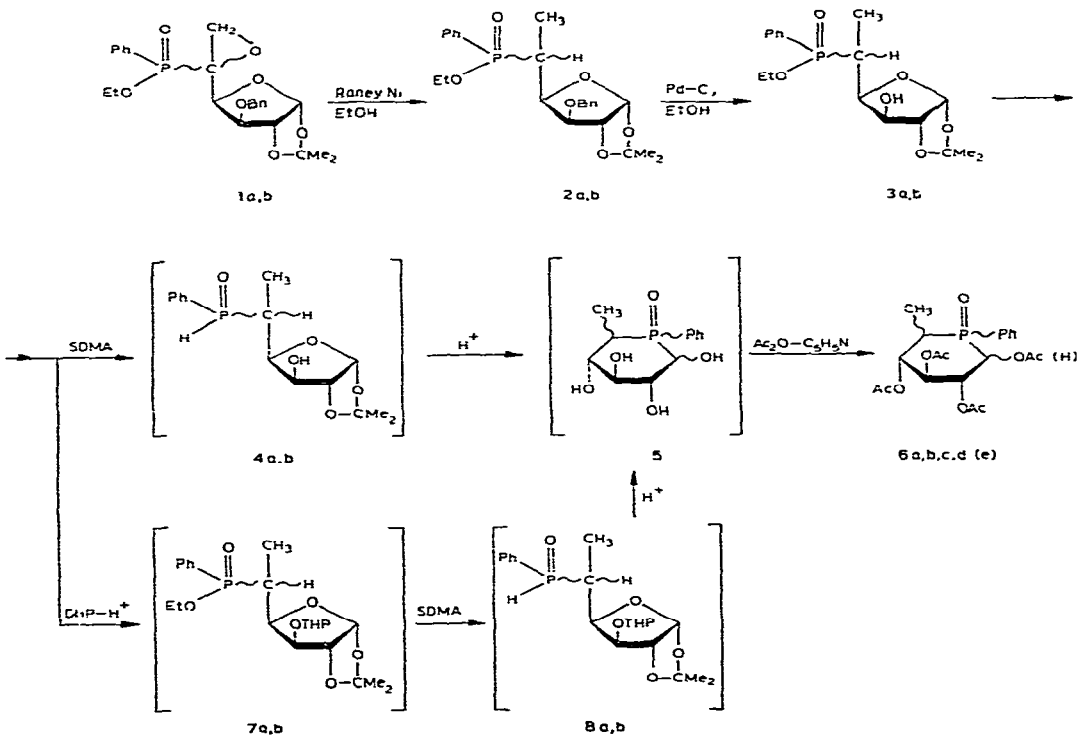
RESULTS AND DISCUSSION

Synthesis. — (*RS*)-3-*O*-Benzyl-5,6-dideoxy-5-*C*-[(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses[3] (**2a,b**) were prepared in 81% yield by hydrogenolysis of (5-*RS*)-5,6-anhydro-3-*O*-benzyl-5-*C*-[(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses[2-4] (**1a,b**) in the presence of Raney Ni (W-4) in ethanol at room temperature. The syrupy products were separated, by preparative t.l.c. using 1:1 ethyl acetate–benzene as the eluant, into **2a** and **2b** in the molar



ratio of 1:1. The structures of **2a** and **2b** were derived from the n.m.r.- and mass-spectral data, although the configuration of C-5 of these compounds could not be assigned. Compounds **2a** and **2b** were hydrogenated in ethanol in the presence of 10% Pd-on-carbon at room temperature, to afford (5*RS*)-5,6-dideoxy-5-*C*-[(ethoxy)-phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses (**3a,b**) in 87% yield. As reduction with sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA) is known[4-6] to cause epimerization at C-5, the phosphinates **3a** and **3b** were, without separation, treated with an excess of SDMA in benzene at 5°, affording (5*RS*)-5,6-dideoxy-1,2-*O*-isopropylidene-5-*C*-(phenylphosphinyl)-α-D-*xylo*-hexofuranoses (**4a, b**), along with a small proportion of byproducts (apparently formed by elimination of the phosphinate group).

Because of their facile air-oxidation, **4a** and **4b** were, without further purification, hydrolyzed by refluxing in aqueous ethanol containing hydrochloric acid. Neutralization of the acid with a weakly basic, anion-exchange resin, followed by the usual processing, afforded syrupy (5*RS*)-5,6-dideoxy-5-*C*-[(*RS*)-phenylphosphinyl]-hexopyranoses (**5**) (expected to be a mixture of the eight diastereoisomers theoretically possible with respect to C-1, C-5, and the P atom), the structural assignment of which was made after acetylation with acetic anhydride–pyridine. The crude, peracetylated products **6** were separated, by preparative t.l.c. on silica gel using ethyl acetate as the eluant, into three fractions, referred to as **6a,b**, **6c**, and **6d,e** (2:1:2) according to the R_F values. The combined yield of **6** was 35%, based on **3a,b**. Fraction **6a,b** gave two crystalline compounds, **6a** and **6b** (1:1), after fractional recrystallization from ethyl acetate–hexane. The next fraction afforded a single product (**6c**), whereas the last fraction gave crystalline compounds **6d** and **6e**; the latter (**6e**) was, however, obtained only once, in 7% yield (see later).

Elemental analyses of **6a**, **b**, **c**, and **d** all showed the molecular formula $C_{20}H_{25}O_9P$, and their ^{1}H-n.m.r. spectra exhibited a methyl signal and four acetyl peaks, but no P–H signal, indicating that the phosphorus atom was situated in the hemiacetal ring, as in (5*RS*)-1,2,3,4-tetra-*O*-acetyl-[(*RS*)-phenylphosphinyl]hexopyranoses (**6**). Most of the coupling constants of the n.m.r. signals due to H-1, H-2, H-3, H-4, and the P atom of these products could not be determined, because of the

TABLE I

CRYSTAL DATA FOR 1,2,3,4-TETRA-*O*-ACETYL-5,6-DIDEOXY-5-*C*-[(*S*)-PHENYLPHOSPHONYL]-β-L-IDOPYRANOSE (**6a**) AND -α-L-IDOPYRANOSE (**6b**) (E.S.D. VALUES IN PARENTHESES)

Property	**6a**	**6b**
Formula	$C_{20}H_{25}O_9P$	$C_{20}H_{25}O_9P$
Lattice constants	a = 0.8552(3)	1.6175(5)
(nm, degrees)	b = 1.5754(5)	1.3199(4)
	c = 0.8528(4)	1.0988(4)
	β = 92.83(3)	
Cell volume (nm^3)	V = 1.1475	2.3459
Formula units/cell	Z = 2	4
Space group	$P2_1$	$P2_12_12_1$
Linear absorption coefficient (CuKα, cm^{-1})	μ = 14.65	14.33
Total number of reflections	1990	2232
Unobserved (I $<2\sigma$)	74	44
X-Ray density ($mg.m^{-3}$)	1.266	1.239
a[a]	0.9	0.8
b	1.5	6.5
R value	3.6%	3.7%
R_ω[b]	5.0%	4.4%

[a]The function refined was $\Sigma\omega(|Fo| - |Fc|)^2$, with ω = x.y, and x = 1 for sin θ > a, and x = sin θ/a otherwise; y = 1 for |Fo| < b, and y = b/|Fo| otherwise. [b]$R\omega = [\Sigma\omega(|Fo| - |Fc|)^2/\Sigma\omega Fo^2]^{\frac{1}{2}}$.

TABLE II

FRACTIONAL COORDINATES OF **6a** AND **6b** (E.S.D. VALUES IN PARENTHESES)

Atom	**6a**			**6b**		
	X	*Y*	*Z*	*X*	*Y*	*Z*
C 1	.7724(4)	.3866(2)	.0600(4)	.7297(2)	.2304(2)	.7127(2)
O 1	.9298(3)	.3976(2)	.0126(3)	.7203(1)	.1220(2)	.7198(2)
C 11	1.0407(5)	.3442(3)	.0760(6)	.7468(3)	.0673(3)	.6223(4)
O 11	1.0122(5)	.2900(3)	.1680(7)	.7790(2)	.1040(2)	.5365(3)
C 12	1.1954(6)	.3627(4)	.013(1)	.7294(7)	−.0432(4)	.6440(9)
C 2	.6738(4)	.3422(2)	−.0713(4)	.6448(2)	.2776(2)	.6971(2)
O 2	.7450(3)	.2608(2)	−.1026(3)	.6104(1)	.2376(2)	.5866(2)
C 21	.6847(5)	.1949(2)	−.0342(5)	.5396(3)	.1833(3)	.5953(4)
O 21	.5702(6)	.1996(2)	.0406(8)	.5013(2)	.1756(4)	.6867(4)
C 22	.7754(6)	.1159(3)	−.0545(6)	.5193(5)	.1389(7)	.4749(8)
C 3	.6601(4)	.3914(2)	−.2253(4)	.6498(2)	.3931(2)	.6828(2)
O 3	.5603(3)	.3492(2)	−.3328(3)	.5651(1)	.4282(2)	.6773(2)
C 31	.6100(7)	.3266(3)	−.4770(5)	.5377(2)	.4681(3)	.5722(3)
O 31	.7413(6)	.3362(3)	−.5110(5)	.5784(2)	.4736(3)	.4828(3)
C 32	.479(1)	.2973(5)	−.5861(7)	.4497(3)	.5025(5)	.5839(6)
C 4	.5781(4)	.4765(3)	−.2021(4)	.6887(2)	.4466(2)	.7917(2)
O 4	.5557(3)	.5146(2)	−.3548(3)	.6914(1)	.5521(1)	.7549(2)
C 41	.4141(5)	.5434(4)	−.3956(5)	.6990(2)	.6215(2)	.8439(3)
O 41	.3070(5)	.5355(6)	−.3148(4)	.6990(2)	.6012(2)	.9494(2)
C 42	.4102(9)	.5848(5)	−.5538(6)	.7082(5)	.7256(3)	.7928(5)
C 5	.6666(4)	.5388(2)	−.0928(4)	.7763(2)	.4112(2)	.8259(2)
C 6	.8202(5)	.5710(3)	−.1574(5)	.8425(2)	.4407(3)	.7337(3)
P 5	.67744(8)	.4882(—)	.09840(9)	.77194(4)	.27633(5)	.85783(6)
C 51	.8022(4)	.5504(3)	.2301(4)	.8766(2)	.2314(2)	.8702(3)
C 52	.8978(5)	.5121(4)	.3444(5)	.9154(3)	.2458(4)	.9794(4)
C 53	.9835(6)	.5614(5)	.4531(6)	.9980(3)	.2163(6)	.9930(5)
C 54	.9708(7)	.6491(5)	.4495(7)	1.0399(3)	.1720(4)	.9011(5)
C 55	.8739(8)	.6869(4)	.3356(8)	1.0010(3)	.1544(4)	.7935(4)
C 56	.7885(6)	.6389(3)	.2251(6)	.9196(2)	.1851(4)	.7775(4)
O 50	.5196(3)	.4697(2)	.1556(3)	.7186(1)	.2514(2)	.9634(2)
H 1	.779(5)	.350(3)	.155(5)	.763(2)	.253(2)	.649(3)
H 121	1.272(7)	.311(4)	.018(7)	.752(6)	−.051(6)	.736(8)
H 122	1.20(1)	.380(6)	−.08(1)	.671(4)	−.052(5)	.650(6)
H 123	1.243(8)	.404(5)	.083(8)	.756(4)	−.081(5)	.586(6)
H 2	.563(5)	.332(3)	−.042(4)	.611(2)	.264(2)	.768(3)
H 221	.821(7)	.093(4)	.039(7)	.561(3)	.149(4)	.409(5)
H 222	.68(1)	.064(8)	−.10(1)	.517(4)	.080(5)	.495(6)
H 223	.849(7)	.116(4)	−.131(7)	.464(4)	.169(5)	.461(6)
H 3	.769(6)	.396(3)	−.273(5)	.676(2)	.415(2)	.610(3)
H 321	.384(8)	.271(5)	−.530(8)	.434(4)	.523(6)	.515(7)
H 322	.44(1)	.342(7)	−.65(1)	.417(4)	.439(5)	.595(6)
H 323	.524(7)	.257(5)	−.669(8)	.440(3)	.555(4)	.657(5)
H 4	.477(4)	.466(2)	−.160(4)	.654(2)	.443(2)	.863(3)
H 421	.32(1)	.633(7)	−.56(1)	.702(4)	.778(5)	.849(6)
H 422	.419(8)	.545(5)	−.615(9)	.750(4)	.733(5)	.737(6)
H 423	.52(1)	.601(8)	−.58(1)	.668(4)	.740(5)	.731(6)
H 5	.581(6)	.586(4)	−.080(6)	.789(2)	.445(3)	.910(3)
H 61	.788(8)	.595(5)	−.282(8)	.840(3)	.510(4)	.720(4)
H 62	.891(8)	.533(5)	−.160(8)	.895(3)	.420(3)	.763(4)
H 63	.87(1)	.603(9)	−.08(1)	.833(2)	.418(3)	.654(4)
H 52	.911(7)	.450(4)	.351(7)	.885(3)	.272(4)	1.045(5)
H 53	1.055(7)	.531(4)	.538(8)	1.028(4)	.242(5)	1.064(6)
H 54	1.023(8)	.681(5)	.553(8)	1.095(3)	.160(4)	.909(5)
H 55	.864(6)	.746(4)	.332(7)	1.027(3)	.122(3)	.719(4)
H 56	.72(1)	.667(6)	.14(1)	.897(4)	.174(5)	.694(6)

poor resolution at 60 MHz. Therefore, the exact configurations, as well as the conformations, of **6a**, **b**, **c**, and **d** were not established from the n.m.r. data. The structure of **6e** was tentatively assigned to a (5*RS*)-2,3,4-tri-*O*-acetyl-1,5,6-trideoxy-5-*C*-[(*RS*)-phenylphosphinyl]-D-*xylo*-hexopyranose on the evidence of the ^{1}H-n.m.r. and mass spectra. The configurations of C-5 and the P atom of **6e** still remain uncertain, and the mechanism for the fluctuating formation of such a further-reduced, phosphorus-containing sugar is not yet known.

X-Ray structural analysis. — Among the four compounds **6a**, **b**, **c**, and **d**, compounds **6a** (m.p. 199°) and **6b** (m.p. 215°) gave, by recrystallization from ethyl acetate–hexane, crystals of good quality, suitable for X-ray measurements. Precise lattice-constants and three-dimensional, intensity data were measured on a DEC PDP 15/40 controlled Stoe four-circle diffractometer with Ni-filtered CuKα radiation (λ = 154.18 pm). A summary of the crystallographic data is given in Table I.

Phase determination was made by a direct method (MULTAN[7]). The refinement with least-squares techniques was executed with the corresponding programs of the XRAY 76 program system[8]. The intensity data for both compounds were corrected for absorption, and for the anomalous scattering of phosphorus. All hydrogen atoms were located from difference syntheses. During the refinement, which was made with anisotropic temperature-factors for the heavy atoms, and with isotropic temperature-factors for hydrogen atoms, a weighting scheme was applied that made wΔF independent of |F|. After convergence of all parameters, final *R*-values of 3.6% for **6a** and

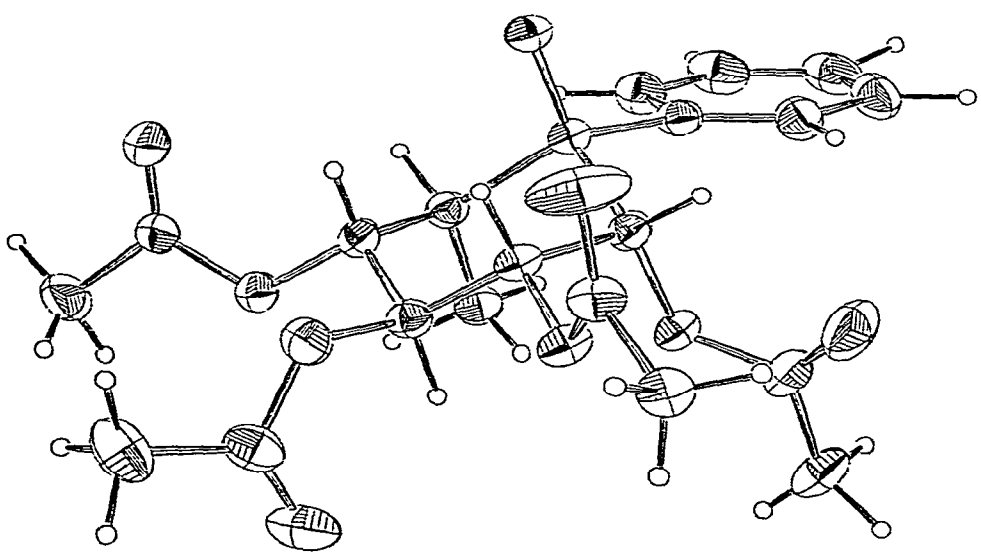


Fig. 1. ORTEP[9] representation of a molecular model of 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-β-L-idopyranose (**6a**). Thermal ellipsoids are plotted at a 20% probability level.

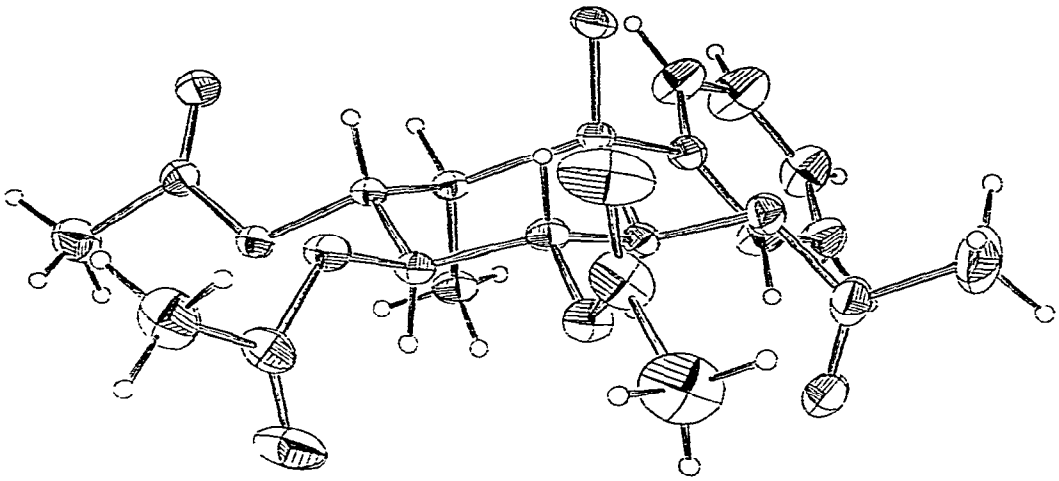


Fig. 2. ORTEP[9] representation of a molecular model of 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-α-L-idopyranose (**6b**). Thermal ellipsoids are plotted at a 20% probability level.

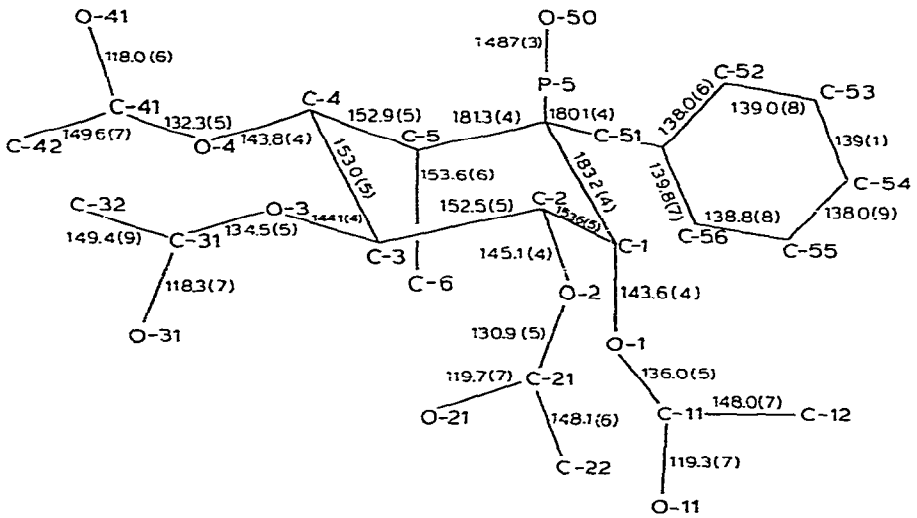


Fig. 3. Atom-numbering scheme, and bond lengths (pm), for **6a** (e.s.d. values in parentheses).

3.7% for **6b** were obtained. Fractional coordinates of all atoms are given in Table II*.

As Figs. 1 and[9] 2 show, compounds **6a** and **6b** are 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-β- and -α-L-idopyranose, respectively. The pyranoses are in the $^4C_1$(L) conformation. In **6a**, the substituents at C-1 and C-5 are linked axially, and those at C-2, C-3, and C-4 and the phenyl group at P, equatori-

*A complete, atom list, with the temperature parameters included, and a list of observed and calculated structure-factors can be obtained on request from Elsevier Scientific Publishing Company, BBA data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/216/*Carbohydr. Res.*, 106 (1982) 31–42.

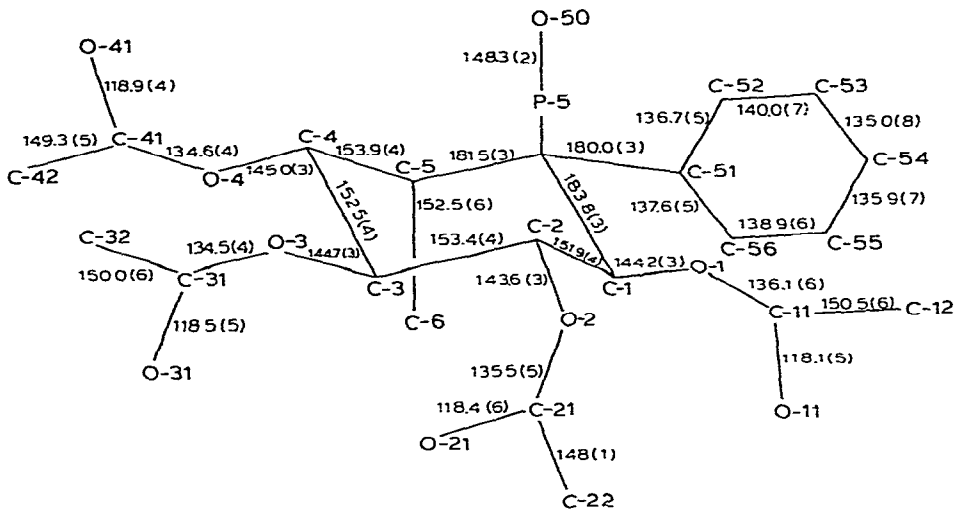


Fig. 4. Atom-numbering scheme, and bond lengths (pm), for **6b** (e.s.d. values in parentheses).

TABLE III

BOND ANGLES OF **6a** AND **6b** (E.S.D. VALUES IN PARENTHESES)

Bond	*Angle (degrees)*		*Bond*	*Angle (degrees)*	
	6a	**6b**		**6a**	**6b**
O-1–C-1–C-2	109.8(3)	108.5(2)	O-1–C-1–P-5	112.0(2)	108.7(2)
C-2–C-1–P-5	107.2(2)	107.4(2)	C-1–O-1–C-11	117.3(3)	116.8(2)
O-1–C-11–O-11	122.9(4)	123.3(3)	O-1–C-11–C-12	110.6(4)	109.3(5)
O-11–C-11–C-12	126.4(5)	127.4(5)	C-1–C-2–O-2	108.4(3)	107.2(2)
C-1–C-2–C-3	114.4(3)	111.8(2)	O-2–C-2–C-3	107.8(3)	107.4(2)
C-2–O-2–C-21	116.2(3)	117.5(3)	O-2–C-21–O-21	122.6(4)	123.2(4)
O-2–C-21–C-22	113.2(3)	109.4(5)	O-21–C-21–C-22	124.2(4)	127.3(5)
C-2–C-3–O-3	107.2(3)	105.8(2)	C-2–C-3–C-4	110.5(3)	113.7(2)
O-3–C-3–C-4	106.6(3)	106.0(2)	C-3–O-3–C-31	118.5(3)	118.3(2)
O-3–C-31–O-31	123.1(5)	123.5(3)	O-3–C-31–C-32	111.5(5)	111.0(3)
O-3i–C-31–C-32	125.3(5)	125.5(4)	C-3–C-4–O-4	106.9(3)	103.8(2)
C-3–C-4–C-5	115.2(3)	115.5(2)	O-4–C-4–C-5	108.9(3)	109.4(2)
C-4–O-4–C-41	117.4(3)	116.9(2)	O-4–C-41–O-41	122.4(5)	123.7(3)
O-4–C-41–C-42	111.5(4)	111.2(3)	O-41–C-41–C-42	126.1(5)	125.0(3)
C-4–C-5–C-6	113.6(3)	114.0(2)	C-4–C-5–P-5	105.5(2)	108.0(2)
C-6–C-5–P-5	117.5(3)	114.0(2)	C-1–P-5–C-5	103.1(2)	99.8(1)
C-1–P-5–O-50	107.8(2)	112.9(1)	C-1–P-5–C-51	109.5(2)	107.8(1)
C-5–P-5–O-50	112.0(1)	113.1(1)	C-5–P-5–C-51	108.9(2)	107.5(1)
O-50–P-5–C-51	114.9(2)	114.5(1)	P-5–C-51–C-52	121.0(3)	116.8(3)
P-5–C-51–C-56	118.5(3)	124.4(2)	C-52–C-51–C-56	120.2(4)	118.7(3)
C-51–C-52–C-53	120.1(5)	119.5(4)	C-52–C-53–C-54	120.2(5)	121.3(5)
C-53–C-54–C-55	119.3(6)	119.5(4)	C-54–C-55–C-56	121.3(6)	119.9(4)
C-51–C-56–C-55	118.8(5)	121.0(4)			

TABLE IV

CHOICE OF TORSION ANGLES FOR **6a** AND **6b** (E.S.D. VALUES IN PARENTHESES)

Sequence	*Angle (degrees)*	
	6a	**6b**
C-1–C-2–C-3–C-4	−62.2(3)	−60.3(3)
C-2–C-3–C-4–C-5	64.7(4)	56.9(3)
C-3–C-4–C-5–P-5	−63.7(3)	−58.2(2)
C-4–C-5–P-5–C-1	56.3(2)	57.3(2)
C-5–P-5–C-1–C-2	−55.7(3)	−62.1(2)
P-5–C-1–C-2–C-3	60.6(3)	65.3(2)
O-1–C-1–P-5–C-5	64.8(3)	−179.3(2)
C-6–C-5–P-5–C-1	−71.5(3)	−70.5(2)
O-50–P-5–C-1–C-2	62.9(3)	58.2(2)
C-51–P-5–C-1–C-2	−171.5(2)	−174.3(2)
C-52–C-51–P-5–C-5	−144.8(3)	81.9(3)
C-56–C-51–P-5–C-5	41.7(4)	−97.4(3)
O-11–C-11–O-1–C-1	−.3(6)	2.8(5)
O-21–C-21–O-2–C-2	5.4(6)	7.2(6)
O-31–C-31–O-3–C-3	14.3(7)	2.1(5)
O-41–C-41–O-4–C-4	−3.3(8)	−4.3(5)

ally. In **6b**, the substituent at C-5 is linked axially, and those at C-1, C-2, C-3, and C-4, and the phenyl group at P, equatorially.

The atom-numbering scheme and the average bond-lengths are given in Figs. 3 and 4. Bond angles and a choice of torsion angles are listed in Tables I–IV.

The geometry of the pyranoid ring is that of a regular chair, which is indicated by the Cremer–Pople[11,12] puckering parameters (Q = 67 pm, $\theta = 6.1°$, $\phi = 346.5°$ for **6a**, and Q = 69 pm, $\theta = 12.5°$, $\phi = 20.0°$ for **6b**). The acetyl groups have the usual orientation, *i.e.*, the C=O (carbonyl) bond is almost *syn*-parallel to the corresponding C–H bond of the pyranoid ring. The configuration of P in 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-6-*C*-nitro-5-*C*-[(*R*)-phenylphosphinyl]-β-L-idopyranose (**9**) had been X-ray-crystallographically established[10] as (*R*), but that of P in **6a** and **6b** turns out to be (*S*). In the exocyclic bonding (P-5–O-50 and P-5–C-50), there is no difference between **9** and **6a,b**, but, in the endocyclic bonding (C-5–P-5 and C-1–P-5), the bond lengths in **6a** and **b** are longer, by 1.7–0.11 pm, than those in **9**, which is, however, in the range of only 2 or 3 times δ. There are no significant differences in the bond angles.

In **6a** (the β anomer), the plane of the phenyl ring is almost perpendicular to the P-5–O-50 bond, which is indicated by the torsion angle O-50–P-5–C-51–C-52 = 88.6°. However, in **6b** (the α anomer), the torsion angle is significantly smaller (−44.7°), so that close contact been the phenyl ring and the equatorial acetoxyl group on C-1 is avoided.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Silica gel B-5F and C-200 (Wako Pure Chemical Industries, Ltd., Japan) were used for t.l.c. and column chromatography. All reactions were monitored by t.l.c., and products were detected with sulfuric acid–ethanol or cobalt(II) chloride–acetone as the indicator. Optical rotations were determined with a Yanagimoto OR-10 polarimeter. I.r. spectra were recorded with a Nihon–Bunko IR-S spectrometer. ^{1}H-N.m.r. spectra were recorded, for solutions in $CDCl_3$, with a Hitachi–Perkin–Elmer R-20A (60 MHz) at 27°. Chemical shifts are reported as δ values relative to tetramethylsilane (δ 0.00) as the internal standard.

Materials. — (5*RS*)-5,6-Anhydro-3-*O*-benzyl-5-*C*-[(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose was prepared from D-glucose in eight steps[1]. The product was a mixture of the *gluco* (**1a**) and *ido* derivative (**1b**), but was used without separation.

(5RS)-*3-O-benzyl-5,6-dideoxy-5-C-[(ethoxy)phenylphosphinyl]-1,2-O-isopropylidene-α-D-xylo-hexofuranose*[2] (**2a,b**). — Compound **1a,b** (2.06 g) in ethanol (12 mL) was hydrogenated in the presence of Raney Ni (W-4; 2.0 g) for 23 h at room temperature. The mixture was centrifuged to remove the catalyst, the supernatant liquor was evaporated *in vacuo*, and the residue (1.96 g) was separated into two fractions, **2a** (810 mg) and **2b** (810 mg), by preparative t.l.c., using 1 : 1 (v/v) ethyl acetate–benzene as the eluant; each fraction was extracted into ethanol (total yield 81%).

Compound **2a** (upper band); $[\alpha]_D^{25}$ −24.1° (*c* 1.23, $CHCl_3$); ^{1}H-n.m.r.: δ 0.98 (dd, 3 H, $J_{5,6}$ 7.5, $J_{6,P}$ 16.5 Hz, H_3-6), 1.18–1.40 (m, 9 H, POCMe, CMe_2), 2.46 (m, 1 H, H-5), 3.58–4.60 (m, 7 H, H-2,3,4, CH_2Ph, $POCH_2C$), 5.79 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), and 7.24–8.00 (m, 10 H, CPh, PPh); *m/z* 446 (M^+).

Compound **2b** (lower band): $[\alpha]_D^{25}$ −53.2° (*c* 1.11, $CHCl_3$); ^{1}H-n.m.r.: δ 0.90 (dd, 3 H, $J_{5,6}$ 7.5, $J_{6,P}$ 17.3 Hz, H_3-6), 1.15–1.42 (m, 9 H, POCMe, CMe_2), 2.36 (m, 1 H, H-5), 3.61–4.76 (m, 7 H, H-2,3,4, CH_2Ph, $POCH_2C$), 5.89 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), and 7.28–8.00 (m, 10 H, CPh, PPh); *m/z* 446 (M^+).

(5RS)-*5,6-Dideoxy-5-C-[(ethoxy)phenylphosphinyl]-1,2-O-isopropylidene-α-D-xylo-hexofuranose* (**3a,b**). — Compound **2a,b** (1.5 g) in ethanol (8 mL) was hydrogenated in the presence of Pd-on-carbon (720 mg) for 24 h at room temperature. The mixture was centrifuged to remove the catalyst, the supernatant liquor was evaporated *in vacuo*, and the residue was chromatographed on a column of silica gel with ethyl acetate as the eluant, giving **3a,b** (1.04 g, 87%) as a colorless oil.

Similarly, compounds **2a** and **2b** gave **3a** and **3b**, respectively.

Compound **3a**: $[\alpha]_D^{25}$ −0.51° (*c* 1.18, $CHCl_3$): ^{1}H-n.m.r.: δ 1.01–1.42 (m, 12 H, H_3-6, POCMe, CMe_2), 2.60 (m, 1 H, H-5), 3.68–4.50 (m, 5 H, H-2,3,4, $POCH_2C$), 5.87 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), and 7.37–8.02 (m, 5 H, PPh); *m/z* 356 (M^+).

Compound **3b**: $[\alpha]_D^{25}$ −46.1° (*c* 1.17, $CHCl_3$); ^{1}H-n.m.r.: δ 0.93–1.40 (m, 12 H, H_3-6, POCMe, CMe_2), 2.65 (m, 1 H, H-5), 3.60–4.55 (m, 5 H, H-2,3,4, $POCH_2C$), 5.95 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), and 7.37–7.96 (m, 5 H, PPh); *m/z* 356 (M^+).

(5RS)-*5,6-Dideoxy-5-C-(phenylphosphinyl)-1,2-O-isopropylidene-3-O-(tetrahydropyran-2-yl)*-α-D-xylo-*hexofuranose* (**7a,b**). — A mixture of **3a,b** (652 mg), dihydropyran (802 mg), and crystalline *p*-toluenesulfonic acid (22 mg) in 1,4-dioxane (6 mL) was stirred for 22 h at room temperature. The acid was neutralized with Amberlite IRA-45 anion-exchange resin, the solution evaporated *in vacuo*, and the residue (850 mg) chromatographed on a column of silica gel with ethyl acetate as the eluant, giving **7a,b** (734 mg, 91%) as a colorless oil; R_F 0.36 (EtOAc); ^{1}H-n.m.r.: δ 0.83–1.75 (m, 18 H, H_3-6, POCMe, CMe_2, THP), 2.50 (m, 1 H, H-5), 3.16–4.84 (m, 8 H, H-2,3,4, $POCH_2C$, THP), 5.83, 5.91 (d, d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), and 7.38–8.19 (m, 5 H, PPh).

Anal. Calc. for $C_{22}H_{33}O_7P \cdot H_2O$: C, 57.63; H, 7.69. Found: C, 58.01; H, 7.83.

1,2,3,4-Tetra-O-acetyl-5,6-dideoxy-5-C-[(RS)-phenylphosphinyl]idopyranoses (**6a, b, c,** *and* **d**) *and* (5RS)-*2,3,4-tri-O-acetyl-1,5,6-trideoxy-5-C-[(RS)-phenylphosphinyl]*-D-xylo-*hexopyranose* (**6e**) *from* **2a,b**. — To a solution of **2a,b** (306 mg) in dry benzene (8 mL) was slowly added SDMA (70% in toluene; 0.6 mL) diluted with toluene (7 mL), with stirring, during 30 min. Then, a small amount of water was added at 0°, the mixture was centrifuged to remove aluminum hydroxide, and the precipitate was washed with benzene. The organic layers were combined, and evaporated *in vacuo*, to afford (5RS)-*5,6-dideoxy-1,2-O-isopropylidene-5-C-(phenylphosphinyl)*-α-D-xylo-*hexofuranose* (**4a,b**) as a pale-yellow oil. Immediately, to a solution of the **4a,b** in ethanol (2 mL) was added oxygen-free 0.5M hydrochloric acid (20 mL), and the mixture was refluxed under argon for 4 h at 110° (bath). The acid was neutralized with Amberlite IRA-45 anion-exchange resin, and the solution was evaporated *in vacuo*, to afford (5RS)-*5,6-dideoxy-5-C-[(RS)-phenylphosphinyl]*-D-xylo-*hexopyranose* (**5**) (205 mg) as a pale-yellow oil.

Treatment of the crude **5** with acetic anhydride (0.6 mL) in pyridine (1.0 mL) in the usual way gave an oil (226 mg) of the tetraacetates (**6a, b, c,** and **d**). By preparative t.l.c. using ethyl acetate as the eluant, this oil was separated into three fractions, **6a-b, 6c,** and **6d-e**, according to their R_F values; each fraction was eluted with ethanol, and the combined yield was 35% in the ratios of 2:1:2. The fraction **6a-b** was separated, by fractional recrystallization from ethyl acetate–hexane, into two crystalline compounds **6a** (m.p. 199°) and **6b** (m.p. 215°) (ratio 1:1). After standing in the refrigerator, **6c** and **6d** (**6e**) crystallized. Fractional recrystallization of **6d-e** from the same mixed solvent gave two crystalline compounds, **6d** and **6e**.

1,2,3,4-Tetra-O-acetyl-5,6-dideoxy-5-C-[(S)-phenylphosphinyl]-β-L-idopyranose (**6a**); R_F 0.49 (EtOAc); m.p. 199°, $[\alpha]_D^{23}$ +18.4° (*c* 0.93, EtOH); ^{1}H-n.m.r.: δ1.36 (dd, 3 H, $J_{5,6}$ 8.0, $J_{6,P}$ 14.0 Hz, H_3-6), 1.98, 2.08, 2.09, 2.15 [s, 12 H, $(OAc)_4$], 3.05 (m, 1 H, H-5), 5.67 (m, 1 H, H-3), 5.76 (m, 1 H, H-2), 5.78 (m, 1 H, H-4), 6.09 (m, 1 H, H-1), and 7.5–8.1 (m, 5 H, PPh).

Anal. Calc. for $C_{20}H_{25}O_9P$: C, 54.55; H, 5.72. Found: C, 54.12; H, 5.77.

1,2,3,4-Tetra-O-acetyl-5,6-dideoxy-5-C-[(S)-phenylphosphinyl]-α-L-idopyranose (**6b**): R_F 0.49 (EtOAc); m.p. 215°, $[\alpha]_D^{23}$ −7.1° (*c* 0.73, EtOH); ^{1}H-n.m.r.: δ 1.10 (dd, 3 H, $J_{5,6}$ 7.6, $J_{6,P}$ 16.8 Hz, H_3-6), 1.95, 2.01, 2.06, 2.06 [s, 12 H, $(OAc)_4$], 2.79

(m, 1 H, H-5), 5.55 (m, 1 H, H-3), 5.76 (m, 1 H, H-4), 5.80 (m, 1 H, H-2), 6.11 (m, 1 H, H-1), and 7.5–7.8 (m, 5 H, PPh).

Anal. Calc. for $C_{20}H_{25}O_9P$: C, 54.55; H, 5.72. Found: C, 54.50; H, 5.81.

Compound **6c**: R_F 0.36 (EtOAc); m.p. 138°, $[\alpha]_D^{23}$ −31.8° (*c* 0.76, EtOH); ^{1}H-n.m.r.: δ 1.50 (dd, 3 H, $J_{5,6}$ 7.6, $J_{6,P}$ 14.3 Hz, H_3-6), 2.03, 2.07, 2.12, 2.20 [s, 12 H, $(OAc)_4$], 3.09 (m, 1 H, H-5), 5.10 (m, 1 H, H-4), 5.24 (m, 1 H, H-2), 5.49 (m, 1 H, H-3), 5.95 (m, 1 H, H-1, and 7.62–8.00 (m, 5 H, PPh)).

Anal. Calc. for $C_{20}H_{25}O_9P$: C, 54.55; H, 5.72. Found: C, 54.45; H, 5.83.

Compound **6d**: R_F 0.22 (EtOAc); m.p. 168°, $[\alpha]_D^{23}$ −10.3° (*c* 0.78, EtOH); ^{1}H-n.m.r.: δ 1.56 (dd, 3 H, $J_{5,6}$ 7.5, $J_{6,P}$ 13.7 Hz, H_3-6), 2.01, 2.02, 2.13, 2.23 [s, 12 H, $(OAc)_4$], 3.20 (m, 1 H, H-5), 4.91 (m, 1 H, H-2), 5.04 (m, 1 H, H-4), 5.65 (m, 1 H, H-3), 6.15 (m, 1 H, H-1), and 7.65–7.94 (m, 5 H, PPh).

Anal. Calc. for $C_{20}H_{25}O_9P$: C, 54.55; H, 5.72. Found: C, 54.21; H, 5.82.

(5RS)-*2,3,4-Tri-O-acetyl-1,5,6-trideoxy-5-C-*[(RS)-*phenylphosphinyl*]-D-xylo-*hexopyranose* (**6e**): R_F 0.22 (EtOAc); m.p. 158°; ^{1}H-n.m.r.: δ 1.04 (dd, 3 H, $J_{5,6}$ 7.5, $J_{6,P}$ 16.9 Hz, H_3-6), 2.04, 2.05, 2.07 [s, 9 H, $(OAc)_3$], 2.77 (m, 1 H, H-5), 5.4, 5.5, 5.6 (m, 3 H, H-2,3,4), 5.7 (m, 2 H, H_2-1), and 7.54–7.72 (m, 5 H, PPh): *m/z* 382 (M^+).

Compounds **6a**, **b**, **c**, *and* **d** *from* **7a**, **b**, — As already described, (5*RS*)-5,6-dideoxy-1,2-*O*-isopropylidene-5-*C*-(phenylphosphinyl)-3-*O*-(tetrahydropyran-2-yl)-D-*xylo*-hexofuranose (**8a,b**) was prepared by treating **7a,b** (730 mg) in dry benzene (12 mL) with SDMA (0.83 mL) in dry benzene (10 mL). The crude product was immediately dissolved in a mixture of ethanol (2 mL) and 0.5M hydrochloric acid (20 mL), and the whole was refluxed for 5 h at 110° (bath). After processing as already described, compound **5** (429 mg) was obtained as a pale-yellow oil; this was acetylated with acetic anhydride–pyridine, to afford the tetraacetate (480 mg) as a yellow oil. The oil was similarly separated by preparative t.l.c. into **6a**, **b**, **c**, and **d** (1:1:1:2) (397 mg; 55% combined yield).

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