Carbohydrate Research, 113 (1983) 31–43
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

FORMATION AND X-RAY STRUCTURAL ANALYSIS OF 2,3,4-TRI-*O*-ACETYL-1,5-ANHYDRO-5,6-DIDEOXY-5-*C*-[(*S*)-PHENYLPHOSPHINYL]-L-IDITOL: A FURTHER MECHANISTIC STUDY OF THE RING ENLARGEMENT OF (5*RS*)-5-DEOXY-5-*C*-[(*RS*)-PHOSPHINYL]-α-D-*xylo*-HEXOFURANOSES TO GIVE 5-DEOXY-5-*C*-[(*RS*)-PHOSPHINYL]-α,β-L-IDOPYRANOSES

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(Received June 24th, 1982; accepted for publication, September 1st, 1982)

ABSTRACT

The minor byproduct formed during the ring enlargement of (5*RS*)-5,6-dideoxy-5-*C*-[(*RS*)-(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses to 5,6-dideoxy-5-*C*-[(*RS*)-phenylphosphinyl]-α,β-L-idopyranose was determined by X-ray crystallographic analysis to be 2,3,4-tri-*O*-acetyl-1,5-anhydro-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-L-iditol-$^4C_1$. This unique, ring enlargement was closely examined, and a possible pathway for the formation of these 5-deoxy-5-phosphinyl-L-*ido* derivatives is discussed.

INTRODUCTION

We have previously described[1] the synthesis of 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-α-L-idopyranose (**4**), its β anomer (**5**), and their 5-*C*-[(*R*)-phenylphosphinyl] epimers (**7** and **8**) by the sequence **1**→**3**→**4** + **5** + **7** + **8**. The structures of these idopyranoses were established by X-ray crystallographic analysis (for **4** and **5**)[1], and also by 400-MHz, ^{1}H-n.m.r.-spectral analysis[2] of **4**, **5**, **7**, and **8**. It was also reported[1,2] that the preparation of the L-idopyranoses **4**, **5**, **7**, and **8** from **1** was accompanied (only once) by formation of a small amount of a byproduct, to which a tentative structure, (5*RS*)-2,3,4-tri-*O*-acetyl-1,5-anhydro-5,6-dideoxy-5-*C*-[(*RS*)-phenylphosphinyl]-D-*xylo*-hexitol, was assigned on the evidence of its mass and ^{1}H-n.m.r. spectra. We now describe the precise structure of this byproduct, along with significant features of its formation, with regard to the unique, ring enlargement of the D-*xylo*-hexofuranoses to the L-*ido* derivatives.

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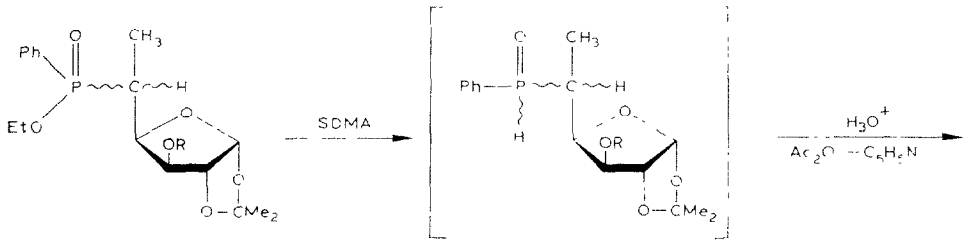

1a,b R = H
2a,b R = THP
THP = tetrahydropyran-2-yl

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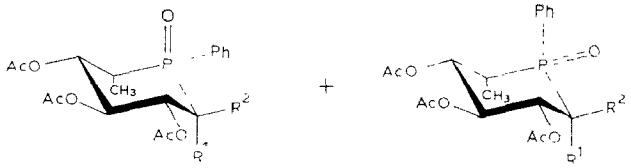


4 R^1 = H, R^2 = OAc
5 R^1 = OAc, R^2 = H
6 R^1 = R^2 = H

7 R^1 = H, R^2 = OAc
8 R^1 = OAc, R^2 = H

Synthesis and reaction pathway. — Reduction of (*5RS*)-5,6-dideoxy-5-*C*-[(*RS*)-(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses (**1**) with sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA) was closely re-examined by individual use of the (*5R*) and (*5S*) compounds (**1a** and **1b**, or *vice versa*), which had previously[1] been separated in a column of silica gel. After acid hydrolysis to effect the ring transposition, and derivatization to the per-*O*-acetyl

TABLE I

YIELDS OF THE 5-DEOXY-5-*C*-PHOSPHINYL-L-IDOPYRANOSES AND -IDITOL FROM 5-DEOXY-5-*C*-PHOSPHINYL-α-D-*xylo*-HEXOFURANOSES

Starting material	*Mol. equiv. of SDMA added*[a]	*Reaction conditions* *Time*[a] *(h)*	*Temp. (°C)*	*Yield*[b] *(%)* **4**	**5**	**7**	**8**	**6**	*Total*
1a	4.0	3	0	4.3	4.3	4.6	7.9	3.6	24.2
1b	3.5	4	0	4.5	4.5	5.7	8.5	3.9	27.1
1a,b[c]	5.0	2	−20–0	5.8	5.8	8.1	10.5	4.9	35.1
2a,b[c]	2.0	1	0	10	10	12	22	0	54

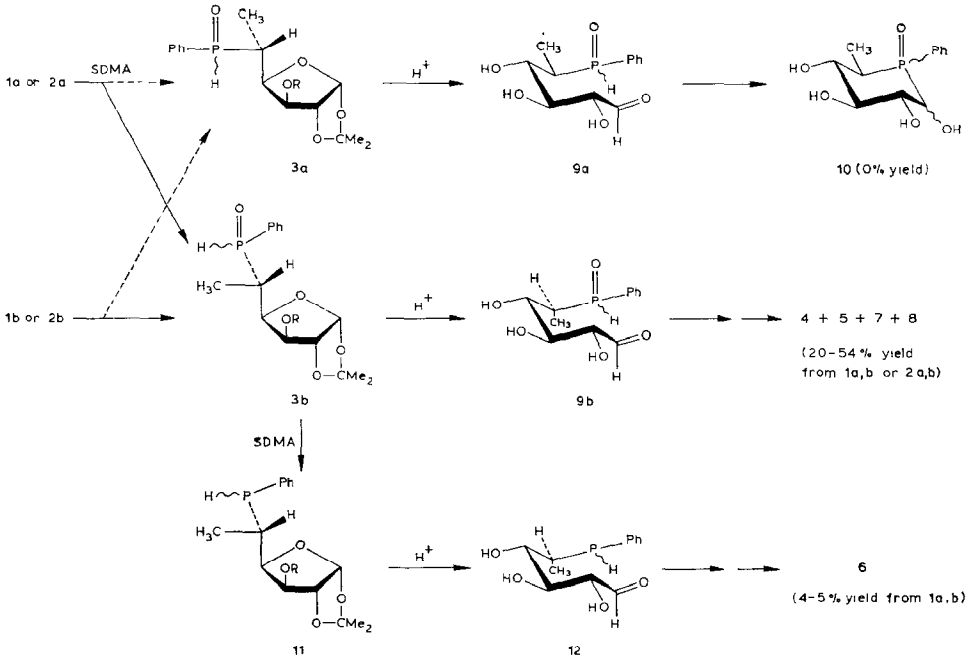
[a]The reaction was quenched by adding water when the starting material disappeared (t.l.c.). [b]Yield refers to pure (t.l.c.) products isolated after acid hydrolysis and per-*O*-acetylation (except for compounds **4** and **5**, which were a mixture). [c]A 1:1 mixture of **1a** and **1b** (or **2a** and **2b**).

compounds, the products were separated by preparative t.l.c. on silica gel, and identified by their spectral analysis; the reaction conditions and the yield of each product are summarized in Table I.

Although the precise configuration of C-5 of the two starting materials, **1a** and **1b**, could not be assigned[1], both compounds were found to give almost the same proportions of the L-idopyranoses **4**, **5**, **7**, and **8** and the byproduct (**6**); it should be noted that no P sugar of the D-*gluco* type was formed from **1a** or **1b**. This was presumed to be caused by epimerization at C-5 with the strongly basic reductant SDMA, as had been observed in a similar hexofuranose system[3] (for further discussion, see later). Accordingly, use, as the starting material, of a 1:1 mixture of **1a** and **1b**, which was available from its 5,6-anhydro-3-benzyl precursor[1,4] also resulted in the same ratio; the total yield was slightly improved, presumably due to the addition of SDMA (to **1a,b**) at a lower temperature (−20°, instead of under ice-cooling).

Because of the presence of a free hydroxyl group at C-3 in the starting material (**1a,b**), an excess of SDMA had to be used for this reduction. Moreover, an appreciable proportion of phosphorus-free byproducts, apparently formed by elimination of the phosphinate group, was produced during the reduction, most probably by the excess of SDMA.

However, it was now found that such disadvantages were overcome by protecting the HO-3 group of **1a,b** with a tetrahydropyran-2-yl group. Thus, when

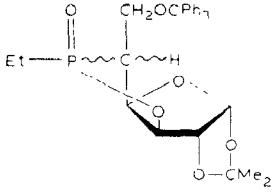


Scheme 1. A possible pathway for the formation of 5-deoxy-5-*C*-phosphinyl-L-idopyranoses (4, 5, 7, and 8), and -iditol (6) from precursors 1a,b and 2a,b.

compound[1] **2a,b** was subjected to reduction with 2 mol equiv. of SDMA, no elimination reaction of the phosphinate group was observed, and the yields of the products **4**, **5**, **7**, and **8** were significantly increased, as recorded in Table 1. It is also noteworthy that, on employing **2a,b** as the starting material, no byproduct **6** was formed.

The molecular composition ($C_{18}H_{23}O_7P$) of this byproduct (**6**) was now confirmed by elemental analysis and the high-resolution mass spectrum. The precise structure of 2,3,4-tri-*O*-acetyl-1,5-anhydro-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-L-iditol (**6**) was derived by X-ray crystallographic analysis.

In the formation of **4**–**8**, it was observed that only phosphinyl sugars of the *ido* type were isolated on treatment of the precursors **1a** or **1b** (or **2a,b**) with SDMA, followed by the successive action of mineral acid, and acetic anhydride–pyridine. No per-*O*-acetyl derivatives of 5,6-dideoxy-5-*C*-([*RS*)-phenylphosphinyl]-D-glucopyranoses (**10**) appeared to be present among the reaction products. Such a predominant formation of the L-*ido* type of P sugars is in striking contrast to the result of the similar ring enlargement of (5*RS*)-5-deoxy-5-*C*-[(*RS*)-*O*-ethylphosphinate]-1,2-*O*-isopropylidene-6-*O*-(triphenylmethyl)-α-D-*xylo*-hexofuranoses (**13**) solely to the 5-deoxy-5-*C*-(ethylphosphinyl)-D-glucopyranoses (**14**)[5,6].



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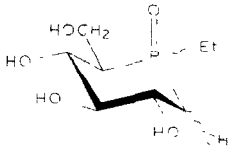

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A possible explanation for these results is that there is a thermodynamically controlled, more favorable production of the (5*S*)-epimer **3b** after an equilibration caused by the strongly basic SDMA during reduction, because there apparently exists less steric congestion between the bulky *P*-phenyl and the 3-hydroxyl (or protected hydroxyl) group in **3**, as illustrated in Scheme 1. This (5*S*)-epimer **3b**, in turn, readily affords, after acetylation, **4**, **5**, **7**, and **8**, despite the presence of a slightly less favorable steric requirement for the intermediate **9b** compared with the counterpart **9a**.

On the other hand, the formation of a small proportion of **6** from **1a,b** can be explained in terms of the further reduction of **3b**, by an excess of SDMA, to the phosphine **11**, which subsequently leads to **6**, *via* intermediate **12**, through the transfer of oxygen from C-1 to the phosphorus atom (see Scheme 1), as in the following, frequently observed example[7].

$$RR'C{=}O + PH_3 \xrightarrow{H^+} RR'CH\text{-}P(H_2){=}O$$

Although it was not isolated, the 5-*C*-[(*R*)-phenylphosphinyl] epimer of **6** could actually have been produced, and it may have been included among the large amount of polar substances that remained uneluted by the t.l.c. separation.

The ratio of the combined yields of the (*S*) to the (*R*) isomer of the ring-phosphorus atom (**4**, **5**, **6** to **7**, **8**) is ~1:1.1 (from **1a**,**b**) and 1:1.6 (from **2a**,**b**). These figures suggest that hemiacetal formation from **9b** (and **12**) to **4**, **5**, **7**, and **8** (and **6**) proceeds almost equally, or slightly more readily, for the 5-*C*-[(*R*)-phenylphosphinyl]-L-idopyranoses.

X-Ray structural analysis. — Very thin crystals of compound **6**, having the form of hexagonal prisms, were available by recrystallization from ethyl acetate–hexane. A specimen with a size of ~0.15 × 0.6 mm was selected for the X-ray measurements. Precise lattice constants, and the intensity data for an independent set of reflections, were measured on a DEC PDP 15/40, controlled, four-circle diffractometer with Ni-filtered CuKα radiation (λ = 154.18 pm). A summary of the crystallographic data is given in Table II.

Phase determination was made by direct methods (MULTAN[8]). The refinement with least-squares techniques was executed with the corresponding programs of the XRAY 76 program system[9]. The intensity data were corrected for the anomalous scattering of phosphorus; because of the small crystal size, an absorption correction was not applied. 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 thermal parameters for the hydrogen atoms, a weighting scheme was applied that made wΔF independent from |F|. After convergence of all

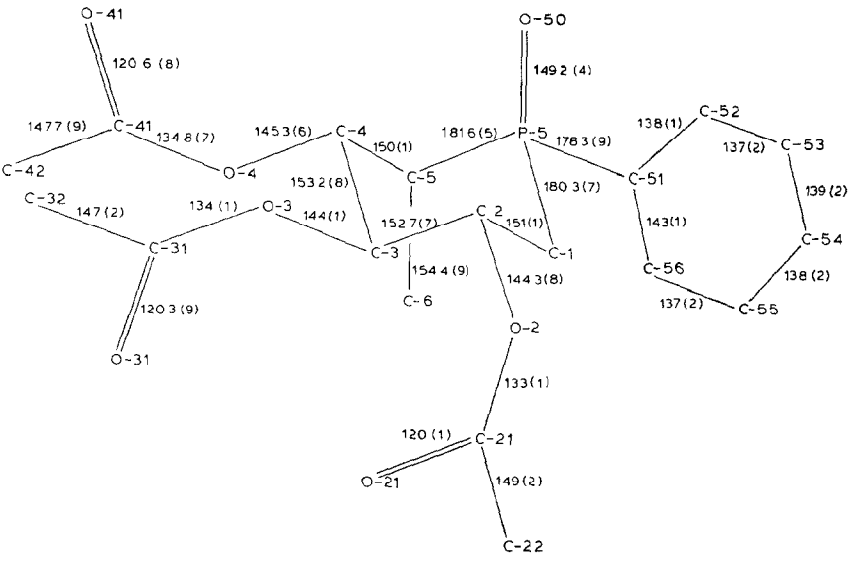


Fig. 1. Atom-numbering scheme, and bond lengths (pm), for 2,3,4-tri-*O*-acetyl-1,5-anhydro-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-L-iditol (**6**) (e.s.d. values in parentheses).

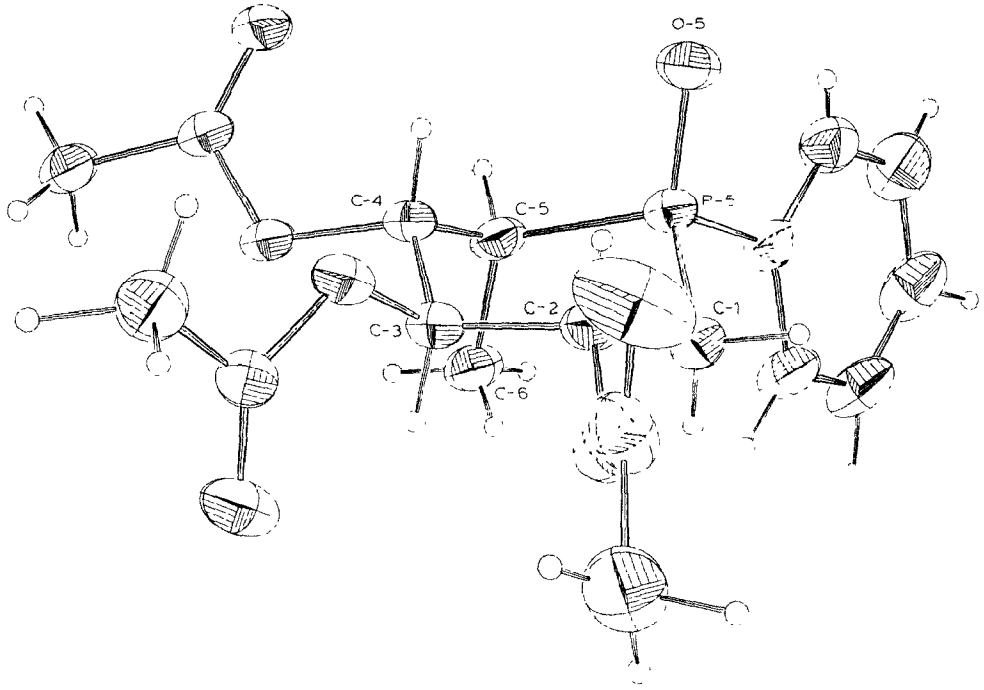


Fig. 2. ORTEP[10] representation of a molecular model of **6**. Thermal ellipsoids are plotted at a 20% probability level.

TABLE II

CRYSTAL DATA FOR 2,3,4-TRI-*O*-ACETYL-1,5-ANHYDRO-5,6-DIDEOXY-5-*C*-[(*S*)-PHENYLPHOSPHINYL]-L-IDITOL (**6**) (E.S.D. VALUES IN PARENTHESES)

Formula	$C_{18}H_{23}O_7P$
Lattice constants (nm)	a = 1.8387(5)
	c = 1.1534(4)
Cell volume (nm^3)	V = 3.3770
Formula units/cell	Z = 6
Space group	hexagonal $P6_5$
X-Ray density ($Mg.m^{-3}$)	ρ_X = 1.1209
Linear absorption coefficient (CuKα, cm^{-1})	μ = 13.53
Total number of reflections (θ < 64°)	1970
Unobserved ($I < 2\sigma$)	334

The function minimized was $\Sigma w(F_o - F_c)^2$, with $w = x \cdot y$, and $x = 1$ for $\sin\theta < a$, $x = \sin\theta/a$ otherwise; $y = 1$ for $|F_o| < b$, $y = b/|F_o|$ otherwise.

a	0.85
b	8.0
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	4.4%
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	5.8%

TABLE III

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

Atom	*x*	*y*	*z*
C-1	.4296(4)	.0344(4)	.2042(5)
C-2	.3956(4)	.0235(4)	.2315(5)
O-2	.3472(3)	.0235(3)	.1330(4)
C-21	.2696(5)	.0091(4)	.1493(9)
O-21	.2352(4)	−.0086(7)	.2416(9)
C-22	.2323(8)	.0191(8)	.041(1)
C-3	.4622(4)	.1151(3)	.2525(5)
O-3	.4191(3)	.1560(3)	.2979(3)
C-31	.4123(5)	.2129(4)	.2334(6)
O-31	.4403(5)	.2320(4)	.1369(5)
C-32	.3657(7)	.2459(6)	.2966(9)
C-4	.5276(3)	.1268(3)	.3440(4)
O-4	.5842(3)	.2170(2)	.3486(3)
C-41	.6244(4)	.2489(4)	.4497(5)
O-41	.6136(4)	.2050(3)	.5330(4)
C-42	.6816(6)	.3406(5)	.4414(6)
C-5	.5752(3)	.0814(3)	.3213(5)
C-6	.6329(5)	.1139(5)	.2139(6)
P-5	.49767(9)	−.02973(8)	.3200(—)
C-51	.5462(4)	−.0890(4)	.2789(5)
C-52	.5566(6)	−.1375(5)	.3614(8)
C-53	.5941(7)	−.1837(6)	.335(1)
C-54	.6220(7)	−.1815(7)	.222(1)
C-55	.6125(7)	−.1338(7)	.1381(9)
C-56	.5757(5)	−.0870(5)	.1636(7)
O-50	.4552(3)	−.0553(3)	.4351(4)
H-11	.459(4)	−.023(4)	.138(8)
H-12	.381(4)	−.094(4)	.198(6)
H-2	.365(3)	.009(3)	.297(6)
H-221	.185(8)	−.037(8)	.01(1)
H-222	.23(1)	.05(1)	.07(2)
H-223	.266(8)	.021(8)	−.02(1)
H-3	.491(4)	.138(4)	.179(6)
H-321	.386(7)	.311(8)	.30(1)
H-322	.316(5)	.238(4)	.253(7)
H-323	.346(5)	.218(5)	.365(9)
H-4	.498(3)	.109(3)	.416(6)
H-421	.727(5)	.351(5)	.384(8)
H-422	.655(6)	.367(6)	.408(9)
H-423	.722(7)	.363(6)	.50(1)
H-5	.610(4)	.087(4)	.387(7)
H-61	.664(3)	.084(3)	.203(5)
H-62	.673(4)	.168(4)	.221(6)
H-63	.605(4)	.105(4)	.160(8)
H-52	.537(8)	−.142(8)	.42(1)
H-53	.609(5)	−.212(5)	.387(9)
H-54	.647(5)	−.221(6)	.200(8)
H-55	.638(4)	−.121(4)	.058(8)
H-56	.570(5)	−.051(5)	.105(9)

TABLE IV

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

Bond	*Angle (degrees)*	*Bond*	*Angle (degrees)*
C-2–C-1–P-5	109.5(4)	C-1–C-2–O-2	107.9(5)
C-1–C-2–C-3	115.1(5)	O-2–C-2–C-3	106.2(5)
C-2–O-2–C-21	119.3(6)	O-2–C-21–O-21	123.3(9)
O-2–C-21–C-22	111.8(9)	O-21–C-21–C-22	125(1)
C-2–C-3–O-3	106.7(5)	C-2–C-3–C-4	113.9(5)
O-3–C-3–C-4	105.9(4)	C-3–O-3–C-31	119.8(5)
O-3–C-31–O-31	123.3(9)	O-3–C-31–C-32	110.4(7)
O-31–C-31–C-32	126.3(9)	C-3–C-4–O-4	104.4(5)
C-3–C-4–C-5	115.9(5)	O-4–C-4–C-5	110.9(5)
C-4–O-4–C-41	116.9(4)	O-4–C-41–O-41	121.8(5)
O-4–C-41–C-42	111.3(5)	O-41–C-41–C-42	126.9(6)
C-4–C-5–C-6	113.8(6)	C-4–C-5–P-5	106.2(3)
C-6–C-5–P-5	115.5(4)	C-1–P-5–C-5	101.3(3)
C-1–P-5–C-51	108.7(3)	C-1–P-5–O-50	113.7(3)
C-5–P-5–C-51	109.8(3)	C-5–P-5–O-50	109.9(2)
C-51–P-5–O-50	112.8(3)	P-5–C-51–C-52	119.0(6)
P-5–C-51–C-56	122.0(7)	C-52–C-51–C-56	119.0(9)
C-51–C-52–C-53	121.6(9)	C-52–C-53–C-54	119(1)
C-53–C-54–C-55	121(1)	C-54–C-55–C-56	121(1)
C-51–C-56–C-55	119.0(9)		

parameters, a final R-value of 4.4% was obtained. The final atomic coordinates are given in Table III*.

The atom-numbering scheme for **6** and the average bond lengths thereof are given in Fig. 1. An ORTEP[10] representation of the molecular structure of **6** is shown in Fig. 2. Bond angles and a choice of torsion angles are listed in Tables IV and V.

As Figs. 1 and 2 show, compound **6** is 2,3,4-tri-*O*-acetyl-1,5-anhydro-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-L-iditol. This pyranoid compound has an almost perfect $^4C_1$(L) conformation (see ring-torsion angles in Table V), although the Cremer–Pople[11,12] puckering parameters (Q = 65.3 pm, θ = 13.68°, ϕ = 347.31°) indicate a small tendency towards the sofa form having the phosphorus atom as the out-of-plane atom. The acetoxyl groups on C-2, C-3, and C-4 are in equatorial positions, and the methyl group on C-5 is linked axially. Of the two exocyclic bonds at the phosphorus atom, the P=O bond is axial, and the phenyl group on P is equatorial.

The inclination of the phenyl ring for the comparable derivatives[1] **4**, **5**, and **6**,

*A complete atom list, with the temperature parameters included, and the 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/237/*Carbohydr. Res.*, 113 (1983) 31–43.

TABLE V

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

Sequence	*Angle (degrees)*
C-1–C-2–C-3–C-4	−52.8(7)
C-2–C-3–C-4–C-5	57.1(6)
C-3–C-4–C-5–P-5	−62.1(5)
C-4–C-5–P-5–C-1	59.2(4)
C-5–P-5–C-1–C-2	−57.9(4)
P-5–C-1–C-2–C-3	56.9(5)
C-6–C-5–C-4–C-3	66.0(5)
C-6–C-5–P-5–C-1	−67.9(6)
O-50–P-5–C-5–C-4	−61.3(4)
O-50–P-5–C-1–C-2	59.9(4)
C-51–P-5–C-1–C-2	−173.6(3)
C-52–C-51–P-5–O-50	−13.6(6)
O-2–C-2–C-3–C-4	−172.2(5)
O-3–C-3–C-4–C-5	174.0(4)
O-4–C-4–C-5–P-5	179.2(3)
C-51–P-5–C-5–C-4	174.1(4)
O-21–C-21–O-2–C-2	−4(1)
O-31–C-31–O-3–C-3	1(1)
O-41–C-41–O-4–C-4	−1(1)
C-21–O-2–C-2–H-2	5(4)
C-31–O-3–C-3–H-3	8(4)
C-41–O-4–C-4–H-4	40(5)

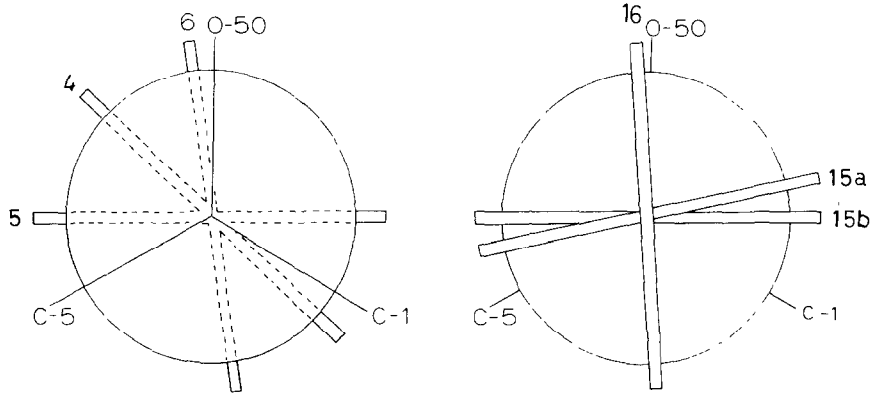


Fig. 3. "Newman" projection down the P–C(phenyl) bond in the equatorial (left) and axial (right) case, illustrating the inclination of the phenyl ring. The digits mark the phenyl rings for compounds **4** (4); **5** (5); **6** (6); **15**, mols. 1 and 2 (15a and b); and **16** (16).

TABLE VI

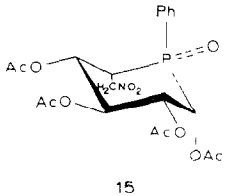
SUMMARY AND AVERAGES OF P–C AND P=O BOND-LENGTHS (pm) FOR VARIOUS PHOSPHORUS SUGARS (E.S.D. VALUES IN PARENTHESES)

Compound	*Config. of P*	*P–C–5*	*P–C–1*	*P–O–50*	*P–C–51*
4	(*S*)	181.5(3)	183.8(3)	148.3(2)	180.0(3)
5	(*S*)	181.3(4)	183.2(4)	148.7(3)	180.1(4)
6	(*S*)	181.6(5)	180.3(7)	149.2(4)	178.3(9)
15 (Mol. 1)	(*R*)	182.5(4)	184.1(4)	147.9(3)	179.8(4)
(Mol. 2)	(*R*)	183.7(5)	185.0(5)	148.2(3)	179.9(4)
16	(*R*)	182.6(6)[a]	186.1(5)	148.5(4)	179.5(5)
Average (total)		182.2(8)	183.8(21)	148.5(4)	179.6( )
Average [only (*S*) config.]		181.5(1)	182.4(15)	148.7(4)	179.5(8)
Average [only (*R*) config.]		182.9(5)	185.1(8)	148.2(2)	179.7(2)

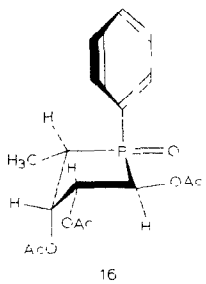
[a] In the furanoid ring of **16**, this bond is P–C-4.

for which the phenyl ring is always equatorial, is illustrated in Fig. 3. Interestingly, this inclination is totally different in the three cases. With respect to the P=O bond, the inclination angle is smallest for **6**, where no bulky substituent is present on C-1. The angle has a medium size for **4**, where an equatorial acetoxyl group is present on C-1, and reaches a value of almost 90° for **5**, which has an axial acetoxyl group on C-1. Thus, this angle of inclination is largely affected by the steric situation at C-1.

If the phenyl ring is linked axially, as in 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-6-*C*-nitro-5-*C*-[(*R*)-phenylphosphinyl]-β-L-idopyranose[13] (**15**) and 1,2,3-tri-*O*-acetyl-4,5-dideoxy-4-*C*-[(*R*)-phenylphosphinyl]-α-L-lyxofuranose[14,15] (**16**), a similar variety of inclination of the phenyl ring is observed: for **16**, it is almost zero, whereas for two independent molecules of **15**, it is near 90° (see Fig. 3), although these two compounds have only slightly different steric situations at the neighboring ring-atoms.



15



16

The distribution of bond lengths around the phosphorus atom of these P sugars (**4**, **5**, **6**, **15**, and **16**) is tabulated for comparison (see Table VI). There is some evidence that, for the (*R*) configuration, the endocyclic, P–C bonds are longer than

for the (*S*) configuration, although the differences between the (*R*) and (*S*) averages are in the range of three to five times the standard deviations of the single-bond lengths. For the exocyclic, P=O and P–C bonds, all bond lengths agree well.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto MP-S3 instrument and are uncorrected. Silica gel B-5F (Wako) was used for preparative t.l.c. All reactions were monitored by t.l.c. on plates precoated with silica gel 60F (0.25 mm, Merck), and the products were detected with sulfuric acid–ethanol, or cobalt(II) chloride–acetone as the indicator. ^{1}H-N.m.r. spectra were recorded with a Hitachi–Perkin–Elmer R-20A (60 MHz) or a Bruker WH-400 cryospectrometer (400 MHz) at 27°. Compounds stated to be identical were compared by means of t.l.c. (silica gel, using ethyl acetate as the eluant) and their ^{1}H-n.m.r. spectra.

Materials. — (5*R*)- and (5*S*)-5,6-Dideoxy-5-*C*-[(*RS*)-(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**1a** and **1b**, or *vice versa*) were prepared from 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-α-D-*xylo*-hexofuranos-5-ulose in three steps, according to the procedure described previously[1,4,16], and were used without purification.

2,3,4-Tri-O-*acetyl-1,5-anhydro-5,6-dideoxy-5*-C-[(S)-*phenylphosphinyl*]-L-*iditol* (**6**). — *Method A.* A solution of **1a,b** (1 : 1 mixture) (309 mg) in dry toluene (20 mL) was degassed, and bubbled with argon. To this was slowly added, at −20°, under argon, SDMA (70%, in toluene; 1.0 mL, ~5 mol. equiv.) that had been further diluted with dry toluene (7 mL), followed by stirring at −20°, and then at 0°, until the **1a,b** had almost disappeared in t.l.c. (~2 h). A small volume of water was added at 0°, to decompose the excess of SDMA, and then the usual processing[1] afforded (5RS)-*5,6-dideoxy-1,2*-O-*isopropylidene-5*-C-[(RS)-*phenylphosphinyl*]-α-D-xylo-*hexofuranose* (**3**) as a colorless syrup; R_F 0.70 in ethyl acetate. (This crude product was contaminated by a small amount of a byproduct that contained no phosphorus atom; R_F 0.55 in EtOAc).

Product **3** was immediately dissolved in ethanol (2 mL), and treated with oxygen-free, 0.5M hydrochloric acid (20 mL) as already described[1], giving (5RS)-*5,6-dideoxy-5*-C-[(RS)-*phenylphosphinyl*]-D-xylo-*hexopyranose* (205 mg) as a pale-yellow syrup; R_F 0.05 in EtOAc. This product was treated with acetic anhydride (0.6 mL) in pyridine (1 mL) in the usual way, giving a mixture of crude tetraacetates **4**, **5**, **7**, and **8**, and triacetate **6** as a pale-yellow syrup. By preparative t.l.c. using ethyl acetate as the eluant, this mixture was separated into four fractions, namely, A, B, C, and D (according to R_F values), and each fraction was eluted with ethanol.

Fraction A (R_F 0.50 in EtOAc) gave colorless crystals, found by n.m.r. spectroscopy to be a mixture of **4** (22 mg, 5.8%) and **5** (22 mg, 5.8%); these were separable by fractional recrystallization[1].

Fraction B (R_F 0.35) afforded **7** as colorless needles (31 mg, 8.1%), m.p. 138° (lit.[1] m.p. 138°).

Fraction C (R_F 0.25) gave **6** as colorless needles (16 mg, 4.9%), m.p. 158 (from ethyl acetate); lit.[1] m.p. 158°; high-resolution, e.i. mass spectrum*, *m/z* (relative intensity): 383 (7; M + 1⁺), 340 (5), 281 (82), 239 (100), 238 (81), and 162 (41); exact mass, Calc. for $C_{18}H_{24}O_7P$ (M + 1): 383.1206, Found: 383.1202.

Anal. Calc. for $C_{18}H_{23}O_7P$: C, 56.54, H, 6.03. Found: C, 56.35; H, 6.18.

Fraction D (R_F 0.20) gave **8** as colorless needles (40 mg, 10.5%), m.p. 168 (lit.[1] m.p. 168°).

Besides these compounds obtained from Fractions A–D, other products were present in considerable amount, these were detected on t.l.c. plates, particularly at R_F 0.8–0.9 (phosphorus-free compounds) and at R_F 0–0.05 (phosphorus-containing products). However, isolation of these products was not sought.

Method B. Similar treatment of the (5*R* or *S*)-epimer **1a** (540 mg) with SDMA (1.5 mL, ~4 mol. equiv.) for 3 h at 0°, followed by processing as already described, afforded **4** (29 mg, 4.3%), **5** (29 mg, 4.3%), **7** (31 mg, 4.6%), **6** (21 mg, 3.6%), and **8** (53 mg, 7.9%).

Method C. Similarly, the other epimer **1b** (409 mg) was treated with SDMA (0.96 mL, 3.5 mol. equiv.) for 4 h at 0°, thus giving **4** (24 mg, 4.5%), **5** (24 mg, 4.5%), **7** (29 mg, 5.7%), **8** (42 mg, 8.5%), and **6** (17 mg, 3.9%).

Method D. (5*RS*)-5,6-Dideoxy-5-C-[(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-3-*O*-(tetrahydropyran-2-yl)-α-D-*xylo*-hexofuranose[2] (**2**) (807 mg) was treated with SDMA (0.85 mL, 2 mol. equiv.) at 0° until evolution of hydrogen ceased (1 h); almost no elimination product was detected by t.l.c. After processing as already described, **4** (81 mg, 10%), **5** (81 mg, 10%), **7** (100 mg, 12%), and **8** (178 mg, 22%) were obtained. By repeating the preparation, it was confirmed that almost no triacetate **6** was formed, and the elimination reaction was considerably suppressed when **2a,b** was used as the starting material.

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*We thank Dr. M.-A. Armour of the University of Alberta, Canada, for the high-resolution, e.i. mass spectrum.

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