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X-ray crystal structures of 1,2,4-tri-*O*-acetyl-5-deoxy-3-*O*-methyl-5-[(*S*)-phenylphosphinyl]-α-D-xylopyranose and its 5-[(*S*)-phenylphosphinothioyl] derivative, and conformations of D-xylopyranose analogs having a $C_6H_5P(=R)$ group in the hemiacetal ring

Thomas Richter, Peter Luger*,
Institut für Kristallographie der Freien Universität Berlin, D-1000 Berlin 33 (Germany)
Tadashi Hanaya, and Hiroshi Yamamoto*
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700 (Japan)

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ABSTRACT

X-ray crystallographic analyses are reported for the two title compounds (**8** and **9**), of which the former crystallized in two modifications (**8a** and **8b**). In all three structures, the pyranose rings have the $^4C_1$ (D) conformation and the substituents at C-1 are axial and those at C-2–C-4 are equatorial. The phenyl rings are oriented equatorially with their planes nearly parallel to the axial $P=R$ bond ($R = O, S$). The favored conformations of various $PhP(=R)$-in-ring D-xylopyranose acetates ($R = O, S$, lone-pair; **8**–**19**) in solution are discussed. The inclination of the equatorial *P*-phenyl group of the α- and β-D-xylopyranose analogs **8**–**13** is similar to that observed in the solid, whereas the inclination of the axial phenyl ring of the P-5 epimers **14**–**19** is near 90° with respect to the equatorial $P=R$ bond.

INTRODUCTION

We recently reported[1] that 5-deoxy-5-[(ethoxy)phenylphosphinothioyl]-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylofuranose (**2**) gave a moderate yield of 5-deoxy-3-*O*-methyl-5-(phenylphosphinothioyl)-D-xylopyranoses (**4**). The products were characterized as four separable triacetates (**6**), *i.e.*, 1,2,4-tri-*O*-acetyl-5-deoxy-3-*O*-methyl-5-[(*S*)-phenylphosphinothioyl]-α- (**9**) and -β-D-xylopyranose (**12**), and their 5-[(*R*)-phenylphosphinothioyl] epimers (**15** and **18**). The triacetates (**6**) were later found[2] to be more efficiently prepared by sulfurization of the corresponding 5-phenylphosphino compounds (**7**) derived from the respective 5-phenylphosphinyl compounds **5** (refs. 1 and 3) by deoxygenation. As a consequence, compounds **6** have become available more easily by the sequence of **1** → **3** → **5** → **7** → **6**.

The sugar analogs **4** having a ring-phosphinothioyl group are expected to be of interest from the viewpoint of the physicochemical properties and biological activity[4].

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* To whom correspondence should be addressed.

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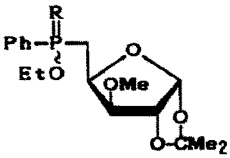
In particular, the P = S functional group is known to be effective in permeating the skin of insects and through slow oxidative desulfurization generating the active P = O form by the action of a microsomal oxidase *in vivo*[5].

Athough the approximate conformations of the four diastereoisomers of **5** and **6** [in (^{2}H)chloroform] were derived from the n.m.r. spectral data, there remained some ambiguity in the assignments of the anomalous values of the ^{1}H-n.m.r. parameters, particularly for H-1, AcO-1, and two H-5 signals[1]. X-ray crystallographic analysis of the key diastereoisomers **8** (m.p. 202–203°) and **9** (m.p. 177–178°) could verify the validity of the assignments of the configurations and conformations (including the inclination of the *P*-phenyl ring) of the remaining triacetates.

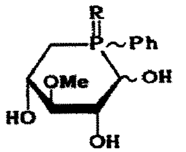
EXPERIMENTAL

Colorless crystals of **8** and **9** were grown from ethyl acetate–hexane. Two crystals with different habits were found for **8**: **8a** (plate-shaped) was orthorhombic, $P2_12_12_1$, and **8b** (needles) was monoclinic, $P2_1$. The space group of **9** (needles) was orthorhombic, $P2_12_12_1$. Precise lattice constants and the intensity data for one octant (**8a** and **9**) and two octants (**8b**) were measured on a Stoe four-circle diffractometer with the ω–2θ–scan technique with Ni-filtered Cu-K_α radiation.

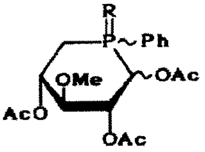
The crystal structures were solved with the SHELXS[6] and subsequent least-squares refinements were done with the XTAL program system[7]. Anomalous scattering coefficients of phosphorus, sulfur, and oxygen atoms were included in the structure factor calculation during refinement. The heavy atoms were refined with anisotropic temperature factors. For **8b**, most of the hydrogen atoms could be located from difference syntheses, and the remainder were fixed at calculated positions 100 pm apart



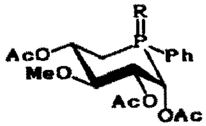
1 R = O
2 R = S

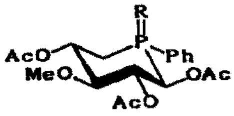


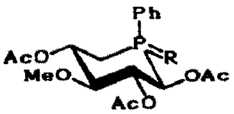
3 R = O
4 R = S

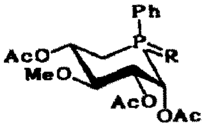


5 R = O
6 R = S
7 R = lone pair









8 R = O
9 R = S
10 R = lone pair

11 R = O
12 R = S
13 R = lone pair

14 R = O
15 R = S
16 R = lone pair

17 R = O
18 R = S
19 R = lone pair

from the respective parent atom. For **8a** and **9**, all hydrogen atom positions were calculated. Because the hydrogen atom positions in the acetyl-methyl groups could be staggered with respect to the carbonyl oxygen atom or the ether oxygen atom, both possible positions, with half occupancy, were used. This type of disorder had previously been observed in several acetylated sugars[8,9]. The isotropic temperature factors for the calculated hydrogen atoms were set at a value higher than the one of the corresponding parent atom. A summary of crystallographic and refinement data is given in Table I. The final atomic coordinates of **8a**, **8b**, and **9** are given in Tables II–IV*, respectively.

RESULTS AND DISCUSSION

The three molecular structures are very similar, as can be seen from their SCHAKAL[10] representations in Fig. 1, which also shows the atomic numbering scheme. A summary of the bond lengths and selected dihedral angles are listed in Tables V and VI, respectively. These values indicated that major differences exist only in the orientation of OAc-4, the torsion along the O-3–C-3 bond, and the inclination of the phenyl ring.

TABLE I

Crystallographic and refinement data for compounds **8a**, **8b**, and **9**

Data	**8a**[a]	**8b**[a]	**9**[a]
Formula	$C_{18}H_{23}O_8P$	$C_{18}H_{23}O_8P$	$C_{18}H_{23}O_7PS$
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
Lattice constants			
a (nm)	1.7097(4)	1.0472(2)	1.6962(5)
b (nm)	1.2964(4)	1.7254(4)	1.2684(4)
c (nm)	0.9235(3)	0.5812(1)	0.9701(4)
β (degree)		98.91(2)	
Cell volume (nm^3)	2.0470	1.0374	2.0871
Crystal size (nm)	0.25 × 0.2 × 0.1	0.65 × 0.07 × 0.07	0.325 × 0.1 × 0.05
$\rho\chi$ ($g \cdot cm^{-3}$)	1.293	1.275	1.319
μ ($Cu\text{-}K_\alpha, cm^{-1}$)	15.47	15.26	23.67
Reflections	1941	1963	1844
after merging	1941	1776	1844
unobserved ($I < 2\sigma$)	194	86	607
R_F	5.1%	3.2%	6.9%
wR_F	4.5%	2.7%	
S	3.15	2.32	
Function minimized	$\sum h[1/\sigma F(\lvert F\rvert o - \lvert F\rvert c)^2]$	$\sum h[1/\sigma F(\lvert F\rvert o - \lvert F\rvert c)^2]$	$\sum h(\lvert F\rvert o - \lvert F\rvert c)^2$

[a] Numbers in parentheses are e.s.d. values.

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* A complete atom list, with the hydrogen atom parameters, all the temperature parameters included, a list of valence angles, 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/480/*Carbohydr. Res.*, 222 (1991) 11–21.

TABLE II

Atomic parameters, and U_{eq} and U values for **8a**

Atom	x^a	y^a	z^a	U_{eq},U(*Å*^{2})
P-5	0.07043(9)	0.5793(1)	0.1783(2)	4.14(5) × 10^{-2}
O-5	0.0023(2)	0.5743(3)	0.2755(4)	5.4(1)
C-51	0.1354(4)	0.6862(5)	0.2118(7)	4.5(2)
C-52	0.1980(4)	0.7109(5)	0.1225(7)	5.4(2)
C-53	0.2456(4)	0.7953(6)	0.1564(9)	7.0(3)
C-54	0.2310(4)	0.8503(6)	0.282(1)	7.7(3)
C-55	0.1699(4)	0.8264(6)	0.3709(9)	7.0(3)
C-56	0.1214(4)	0.7429(5)	0.3372(8)	5.6(2)
C-1	0.1264(3)	0.4610(5)	0.1967(6)	4.0(2)
O-1	0.1993(2)	0.4706(3)	0.1154(4)	4.2(1)
C-11	0.2666(4)	0.4455(6)	0.1840(7)	5.8(3)
O-11	0.2681(3)	0.4182(5)	0.3065(5)	9.7(2)
C-12	0.3351(4)	0.4642(7)	0.0900(7)	8.1(3)
C-2	0.0794(3)	0.3702(5)	0.1356(6)	3.9(2)
O-2	0.1247(2)	0.2765(3)	0.1469(4)	4.6(1)
C-21	0.1268(4)	0.2318(5)	0.2801(8)	5.5(3)
O-21	0.0945(3)	0.2646(4)	0.3841(5)	6.5(2)
C-22	0.1761(4)	0.1357(5)	0.2723(9)	7.2(3)
C-3	0.0608(3)	0.3814(5)	−0.0271(6)	3.9(2)
O-3	0.0171(2)	0.2959(3)	−0.0716(5)	5.1(2)
C-31	0.0554(5)	0.2299(6)	−0.169(1)	9.2(4)
C-4	0.0103(3)	0.4769(5)	−0.0552(6)	4.1(2)
O-4	0.0012(2)	0.4778(3)	−0.2131(4)	4.6(1)
C-41	−0.0707(4)	0.4584(6)	−0.2672(7)	6.2(3)
O-41	−0.1281(3)	0.4592(5)	−0.1947(6)	9.3(2)
C-42	−0.0663(5)	0.4428(7)	−0.4270(8)	8.3(3)

[a] Numbers in parentheses are e.s.d. values.

As indicated by the ring-torsion angles (Table VI) and the Cremer–Pople puckering parameters[11–13] (Table VII), the pyranose rings of all three structures have $^4C_1$ (D) conformations. In all molecules, OAc-1 is in axial position and OAc-2, OAc-4, and OMe-3 group are in equatorial position. OAc-1, -2, and -4 have the usual *syn*-parallel arrangement of the C–O bond with the C–H bond of the adjacent ring-atom (see the dihedral angles C-il–O-i–C-i–H-i,i = 1,2, or 4).

The phosphinyl oxygen atom O-5 in **8a** and **8b**, and phosphinothioyl sulfur atom S-5 in **9** are in axial and the phenyl groups on P in equatorial position. The bond lengths around the phosphorus atom (180–183 pm for P-5–C-1, P-5–C-5, and P-5–C-51, and 147–148 pm for P-5–O-5) agree well with those previously observed investigations of P(=O)-containing hexopyranose analogs **20–25** (refs. 14–17) and pentofuranose analogs[18,19]. The length of the P=S bond (195.3 pm), measured for the first time in the series of P-in-ring sugars, is also within the normal range (186–195 pm) observed for various aliphatic and alicyclic phosphinothioyl-containing compounds[20–22].

The inclination of the phenyl ring for the three compounds and for the comparable pyranose analogs **20–22** (refs. 14, 15) is illustrated in Fig. 2A. With respect to the

TABLE III

Atomic parameters, and U_{eq} and U values for **8b**

Atom	x^a	y^a	z^a	U_{eq},U(Å^2)
P-5	0.62306(8)	0.22050(−)	0.3619(1)	4.80(2) × 10^{-2}
O-5	0.5633(2)	0.2378(2)	0.5713(4)	6.7(1)
C-51	0.7591(3)	0.2820(2)	0.3361(6)	5.6(1)
C-52	0.8296(4)	0.2778(2)	0.1539(8)	6.6(1)
C-53	0.9342(4)	0.3279(3)	0.154(1)	8.4(2)
C-54	0.9641(5)	0.3812(3)	0.326(1)	9.5(2)
C-55	0.8916(7)	0.3862(4)	0.502(1)	10.8(3)
C-56	0.7904(6)	0.3364(3)	0.5091(8)	8.2(2)
C-1	0.6771(3)	0.1196(2)	0.3709(5)	4.9(1)
O-1	0.7490(2)	0.1069(2)	0.1818(3)	5.08(7)
C-11	0.8619(4)	0.0670(2)	0.2317(7)	6.3(1)
O-11	0.9013(3)	0.0427(2)	0.4210(5)	9.0(1)
C-12	0.9281(4)	0.0623(3)	0.0238(8)	9.1(2)
C-2	0.5605(4)	0.0661(2)	0.3478(6)	5.5(1)
O-2	0.6030(3)	−0.0130(2)	0.3388(4)	6.54(9)
C-21	0.6396(4)	−0.0493(3)	0.5443(8)	7.3(2)
O-21	0.6417(4)	−0.0186(2)	0.7251(6)	10.7(2)
C-22	0.6795(5)	−0.1319(3)	0.5020(9)	9.3(2)
C-3	0.4649(4)	0.0773(2)	0.1229(6)	6.0(1)
O-3	0.3587(3)	0.0266(2)	0.1352(5)	8.7(1)
C-31	0.3433(6)	−0.0332(4)	−0.032(1)	13.7(3)
C-4	0.4112(4)	0.1585(3)	0.0938(6)	5.5(1)
O-4	0.3288(2)	0.1580(2)	−0.1309(4)	6.9(1)
C-41	0.2187(4)	0.1968(3)	−0.1547(8)	7.7(2)
O-41	0.1872(4)	0.2354(3)	−0.0043(6)	14.9(2)
C-42	0.1417(6)	0.1847(5)	−0.394(1)	9.8(2)
C-5	0.5128(3)	0.2213(3)	0.0921(5)	5.3(1)

[a] Numbers in parentheses are e.s.d. values.

P = O or P = S bond, the inclination angles are 9.3, −0.2, and 6°, respectively, for **8a**, **8b**, and **9**, all of which have an axial OAc-1, but have no bulky, axial substituent at C-5. Because **22**, which has an axial methyl group at C-5 but no axial substituent at C-1, has[15] the angle of − 13.6°, the angles of the opposite inclination of the *P*-phenyl ring of **8a** and **9** are reasonable. It has been shown in all of these cases that the phenyl ring tends to align so as to avoid close contact primarily with the equatorial hydrogen atoms (or substituents) at C-1 and C-5 and, supplementarily, with axial substituent group(s) at C-1 or C-5 (or both).

*Conformational analysis of tri-O-acetyl-5-deoxy-3-O-methyl-5-phenylphosphinyl-, -phenylphosphinothioyl-, and -phenylphosphino-*D*-xylopyranoses.* — With the precise structures of **8** and **9** in the solid state known, the structural analysis of these compounds and their analogs in solution could be made more systematically. Thus, the assignments of all signals, previously made[1,2] for the key diastereoisomers **8** and **9** by the analysis of the δ and J values in the n.m.r. spectra, have been proved to be correct. This, in turn, verified the assignments of the analogs **11**, **14**, **17**, and **12**, **15**, **18**,; as well as

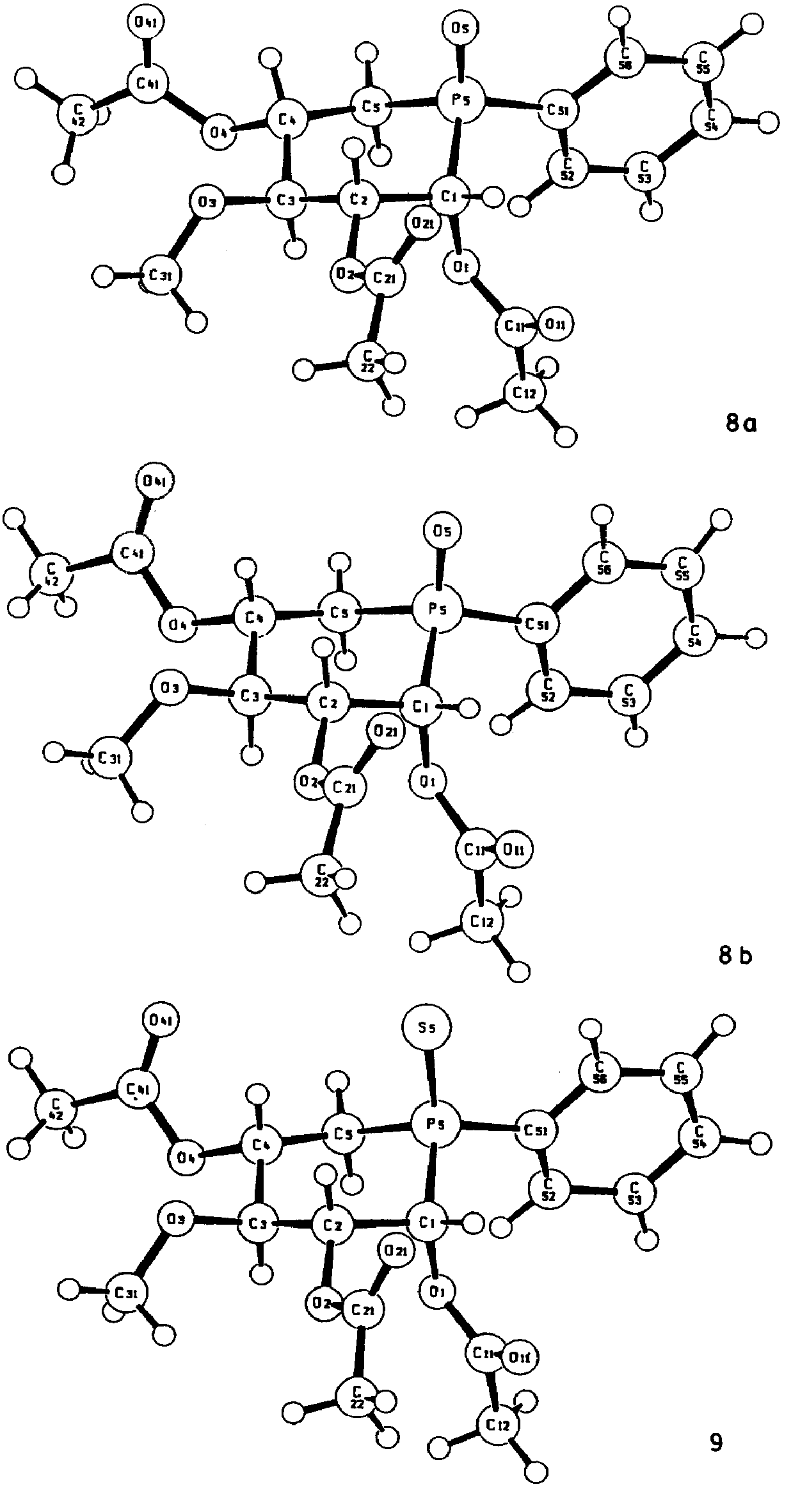


Fig. 1. SCHAKAL representations of the molecular structures of **8a**, **8b**, and **9**.

TABLE IV

Atomic parameters, and U_{eq} and U values for **9**

Atom	x^a	y^a	z^a	$U_{eq}, U(Å^2)$
C-1	0.5511(7)	0.6103(9)	0.281(1)	5.6(4) × 10^{-2}
O-1	0.5704(4)	0.6861(6)	0.3858(7)	5.3(3)
C-11	0.6060(8)	0.647(1)	0.499(1)	6.9(5)
O-11	0.6247(6)	0.5584(8)	0.518(1)	9.4(4)
C-12	0.620(1)	0.735(1)	0.601(2)	10.0(7)
C-2	0.6098(6)	0.619(1)	0.165(1)	5.4(4)
O-2	0.6886(4)	0.6055(5)	0.2190(9)	5.4(3)
C-21	0.7127(8)	0.504(1)	0.243(1)	6.9(5)
O-21	0.6751(5)	0.4297(7)	0.211(1)	7.9(4)
C-22	0.7901(8)	0.504(1)	0.313(1)	6.9(5)
C-3	0.6113(7)	0.7259(9)	0.093(1)	5.0(4)
O-3	0.6629(5)	0.7212(7)	−0.023(1)	6.7(3)
C-31	0.7368(9)	0.765(1)	−0.010(2)	10.7(7)
C-4	0.5307(7)	0.7569(9)	0.040(1)	5.1(4)
O-4	0.5428(5)	0.8625(7)	−0.0184(8)	7.0(3)
C-41	0.5062(8)	0.885(1)	−0.138(1)	7.3(6)
O-41	0.4590(7)	0.8270(9)	−0.187(1)	12.3(5)
C-42	0.533(1)	0.989(1)	−0.194(2)	10.0(7)
C-5	0.4649(7)	0.762(1)	0.144(1)	6.7(5)
P-5	0.4521(2)	0.6333(3)	0.2178(4)	5.7(1)
S-5	0.4236(2)	0.5246(3)	0.0842(4)	9.0(2)
C-51	0.3867(7)	0.643(1)	0.364(1)	6.0(4)
C-52	0.3926(8)	0.723(1)	0.462(2)	7.2(5)
C-53	0.344(1)	0.720(1)	0.575(2)	9.2(7)
C-54	0.2862(9)	0.647(2)	0.584(2)	10.8(8)
C-55	0.2774(9)	0.569(1)	0.487(2)	10.5(8)
C-56	0.3285(9)	0.569(1)	0.377(2)	8.9(6)

[a] Numbers in parentheses are e.s.d. values.

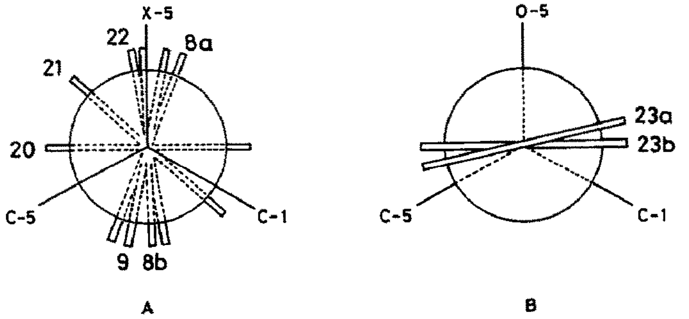


Fig. 2. "Newman" projection down the P–C(phenyl) bond in the equatorial (A) and axial (B) case, illustrating the inclination of the phenyl ring. The digits mark the phenyl rings for compounds **8a** (8a), **8b** (8b), **9** (9), **20** (20), **21** (21), **22** (22), and **23** (23a, 23b).

TABLE V

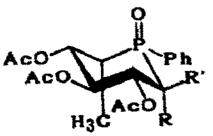
Bond lengths for **8a**, **8b**, and **9**

Bond	*Length*[a] *(pm)*		
	8a	**8b**	**9**
P-5–O-5	147.2(4)	148.3(3)	
P-5–S-5			195.3(5)
P-5–C-51	180.3(6)	180.1(4)	181(1)
P-5–C-1	181.6(6)	182.9(3)	181(1)
P-5–C-5	180.8(6)	179.7(3)	180(1)
C-51–C-52	138.9(9)	138.3(6)	139(2)
C-51–C-56	139.2(9)	137.8(6)	137(2)
C-52–C-53	140(1)	139.5(7)	137(2)
C-53–C-54	138(1)	135.9(8)	136(2)
C-54–C-55	137(1)	137(1)	137(3)
C-55–C-56	140(1)	137.0(9)	137(3)
C-1–O-1	146.0(7)	144.2(4)	143(1)
C-1–C-2	153.3(8)	151.9(5)	151(2)
O-1–C-11	135.3(7)	136.0(5)	135(2)
C-11–O-11	118.5(8)	119.0(5)	118(2)
C-11–C-12	147.9(9)	148.6(6)	151(2)
C-2–O-2	144.4(7)	143.9(5)	145(1)
C-2–C-3	154.2(8)	153.1(5)	153(2)
O-2–C-21	136.1(8)	135.1(5)	136(2)
C-21–O-21	118.7(9)	117.4(6)	118(2)
C-21–C-22	150(1)	151.6(7)	148(2)
C-3–O-3	139.9(7)	142.6(5)	142(1)
C-3–C-4	153.1(9)	151.0(6)	151(2)
O-3–C-31	140(1)	141.1(7)	138(2)
C-4–O-4	146.7(7)	145.0(4)	147(1)
C-4–C-5	153.2(9)	151.9(6)	151(2)
O-4–C-41	135.1(8)	132.2(5)	135(2)
C-41–O-41	118.8(9)	118.6(7)	119(2)
C-41–C-42	149(1)	150.9(8)	150(2)

[a] Numbers in parentheses are e.s.d. values.

5-phenylphosphino analogs **10**, **13**, **16**, and **19**. For comparative, conformational study, selected ^{1}H-n.m.r. parameters for these P sugars, together with those for the corresponding diastereoisomers of P-ethyl congeners **26**–**37** (ref. 2), are summarized in Table VIII. Characteristic features newly obtained are as follows.

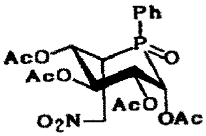
(a) Anomalous downfield shifts (0.7–0.55 p.p.m.) and the concomitant upfield shifts (0.4–0.2 p.p.m.) were observed for H-5*a* and AcO-1, respectively, signals of **8**, **9**, and **10**, when compared with the δ values of the corresponding proton signals of P-ethyl congeners **26**, **27**, and **28** (ref. 2), the values of which can be regarded as inherent ones in this type of sugar analogs (excluding the anisotropic effect by the phenyl ring). These characteristic data and the above-described X-ray results led to the conclusion that the conformation of the *P*-phenyl group of **8**–**10** in (^{2}H)chloroform would be similar to those for the solid state (see Fig. 2A); this conformation accounts for the unusual δ



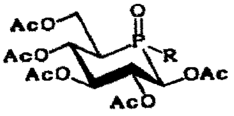
20 R = OAc R' = H

21 R = H R' = OAc

22 R = H R' = H

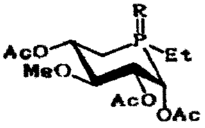


23



24 R = Et

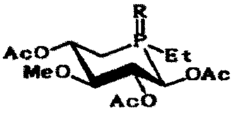
25 R = OMe



26 R = O

27 R = S

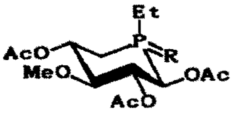
28 R = lone pair



29 R = O

30 R = S

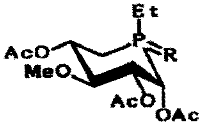
31 R = lone pair



32 R = O

33 R = S

34 R = lone pair



35 R = O

36 R = S

37 R = lone pair

TABLE VI

Selected dihedral angles for **8a**, **8b**, and **9**

Sequence	*Angle*[a] *(degrees)*		
	8a	**8b**	**9**
C-1–C-2–C-3–C-4	−61.9(6)	−58.7(4)	−55(1)
C-2–C-3–C-4–C-5	61.9(6)	58.8(4)	57(1)
C-3–C-4–C-5–P-5	−60.9(5)	−60.2(4)	−62(1)
C-4–C-5–P-5–C-1	53.9(4)	55.0(3)	56.5(9)
C-5–P-5–C-1–C-2	−54.7(4)	−54.8(2)	−57.1(9)
P-5–C-1–C-2–C-3	61.5(5)	59.2(3)	60(1)
O-5–P-5–C-5–C-4	−63.8(5)	−62.6(3)	
S-5–P-5–C-5–C-4			−60.7(9)
O-5–P-5–C-1–C-2	68.1(4)	66.5(2)	
S-5–P-5–C-1–C-2			63.2(8)
C-51–P-5–C-1–C-2	−166.9(4)	−169.7(2)	−170.7(8)
C-56–C-51–P-5–O-5	9.3(6)	−0.2(5)	
C-56–C-51–P-5–S-5			6(1)
O-1–C-1–P-5–C-5	64.6(4)	65.8(2)	63.3(9)
O-2–C-2–C-3–C-4	178.3(4)	−178.1(3)	−175.4(9)
O-3–C-3–C-4–C-5	−179.7(6)	176.5(3)	177.5(9)
O-4–C-4–C-5–P-5	−174.9(4)	−176.8(2)	−178.6(7)
C-51–P-5–C-5–C-4	166.9(4)	169.2(3)	169.7(8)
O-11–C-11–O-1–C-1	−1(1)	0.4(7)	3(2)
O-21–C-21–O-2–C-2	0(1)	−2.4(6)	7(2)
O-41–C-41–O-4–C-4	14(1)	4.1(7)	8(2)
C-11–O-1–C-1–H-1	10.5(7)	20(2)	18(1)
C-21–O-2–C-2–H-2	−39.0(7)	−36(2)	−42(1)
C-31–O-3–C-3–H-3	6.6(8)	6(2)	18(2)
C-41–O-4–C-4–H-4	−33.0(7)	27(2)	25(1)

[a] Numbers in parentheses are e.s.d. values.

TABLE VII

Cremer–Pople puckering parameters

Parameters	*Compounds examined*			*Ideal* $^4C_1$ (D) *conformation*
	8a[a]	**8b**[a]	**9**[a]	
q_2,q_3(pm)	5.1(5),64.7(6)	8.8(3),63.0(4)	13(1),63(1)	0, Q
ϕ(degree)	8(7)	1(3)	−3(5)	free
Q(pm)	64.9(6)	63.6(4)	64(1)	$\sqrt{1/6}$ × bond length
θ(degree)	4.5(5)	8.0(3)	11(1)	0

[a] Numbers in parentheses are e.s.d. values.

TABLE VIII

Characteristic ^{1}H-n.m.r. parameters (δ) for 5-deoxy-5-phosphinyl-, -phosphinothioyl-, and -phosphino-D-xylopyranoses[a]

Compound	*H-1*	*H-5*a	*H-5*e	*AcO-1*
8(26)		2.49(1.95)		1.98(2.17)
9(27)		2.91(2.22)		1.94(2.20)
10(28)		2.52(1.88)		1.77(2.18)
11(29)	5.60(5.21)	2.05(1.70)		1.93(2.15)
12(30)	5.79(5.35)	2.44(2.00)		1.91(2.14)
13(31)	5.58(5.26)	2.03(1.55)		1.92(2.08)
14(32)			3.01(2.61)	
15(33)			3.23(2.67)	
16(34)			2.70(2.10)	
17(35)	6.10(5.68)		3.00(2.49)	
18(36)	6.11(5.61)		3.16(2.55)	
19(37)	6.07(5.59)		2.54(2.05)	

[a] Values (500-MHz ^{1}H-n.m.r., $CDCl_3$) from refs. 1 and 2. For parameters not listed in this Table (including those for other ring protons), the differences between the δ values of the corresponding *P*-phenyl and *P*-ethyl compounds is, in almost all cases, within ±0.2 p.p.m.

values of H-5*a* and AcO-1 of these compounds, as well as for those of 5-phenylphosphino derivative **10**. The *P*-phenyl ring of **8** in solution may possess an average inclination between the **8a** and **8b** forms.

(b) A similar tendency was observed (but a slightly less extent) for the δ values of H-5*a* and AcO-1 signals of the β-D anomers **11**, **12**, and **13**, as compared with those of the corresponding compounds **29**, **30**, and **31** (see Table VIII). A downfield shift of almost the same extent (0.4–0.3 p.p.m.) could also be noticed for the H-1*a* signals of these *P*-phenyl compounds. Because of the absence of a bulky, axial substituent at C-1, the inclination of the *P*-phenyl group of **11**, **12**, and **13** with respect to P=O or P=S bond, thus, is considered to be even smaller than that observed in the case of **8**–**10**.

(c) For the ring-phosphorus epimers **14**–**16** and **17**–**19**, in which the phenyl ring is linked axially, significant downfield shifts (0.6–0.4 p.p.m.) were observed for H-5*e* and

H-1 (particularly for the α-D anomers **17–19**), as compared with the *δ* values of the corresponding *P*-ethyl congeners **32–34** and **35–37** (see Table VIII). This tendency for an anisotropic effect can be explained by assuming that the inclination of the phenyl ring in solution is similar to that observed for the L-idopyranose analog **23** (which crystallized in two modifications[16], **23a** and **23b**) in the solid state; namely, the inclination of the phenyl ring with respect to the P=O or P=S bond is near 90° (see Fig. 2B). This conformation is most likely to minimize the steric repulsion between the *P*-phenyl ring and the ring protons (particularly H-2 and H-4 at the 1,3-diaxial positions).

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