Carbohydrate Research, 145 (1985) 25–35
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF 1,2,3,5-TETRA-*O*-ACETYL-4-DEOXY-4-*C*-[(*S*)-ETHYLPHOSPHINYL]-α-D-RIBOFURANOSE, AND CONFORMATIONS OF ALDOPENTOFURANOSE ANALOGS HAVING PHOSPHORUS IN THE HEMIACETAL RING

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

HIROSHI YAMAMOTO*, AND SABURO INOKAWA
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700 (Japan)

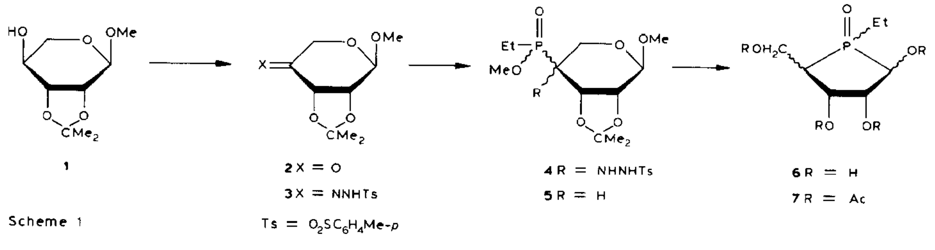
(Received February 8th, 1985; accepted for publication, June 12th, 1985)

ABSTRACT

X-Ray crystallographic analysis was performed on the compound to which had been assigned the structure 1,2,3,5-tetra-*O*-acetyl-4-deoxy-4-*C*-[(*S*)-ethylphosphinyl]-α-D-ribofuranose. The results showed that the compound has the proposed configuration, the five-membered ring is in the $^3T_2$ conformation with a tendency towards the E_2 form, the substituents on C-1, C-4, and P-5 are linked bisectionally, and the acetoxyl groups on C-2 and C-3 are respectively attached axially and equatorially. Based on the X-ray crystallographic and ^{1}H-n.m.r.-spectral data, favored conformations of P-in-ring analogs of aldopentofuranose peracetates in solution are discussed.

INTRODUCTION

We previously reported[1] the preparation of the six kinds of 1,2,3,5-tetra-*O*-acetyl-4-deoxy-4-*C*-(ethylphosphinyl)pentofuranoses (**7**), starting from methyl 2,3-*O*-isopropylidene-α-L-lyxopyranoside (**1**) by the sequence **1**→**2**→**3**→**4**→**5**→**6**→**7** (see Scheme 1). The structures of the 4-*C*-[(*R*,*S*)-ethylphosphinyl]-D-*ribo*- and -L-

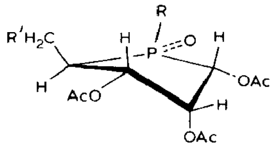


Scheme 1. Preparation of 4-deoxy-4-*C*-(ethylphosphinyl)pentofuranose tetraacetates.

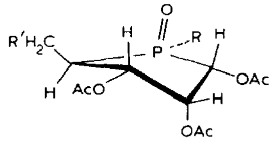
---

*To whom correspondence may be addressed.

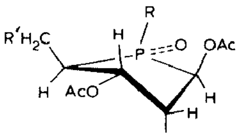
0008-6215/85/$ 03.30



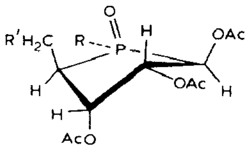
8a,b



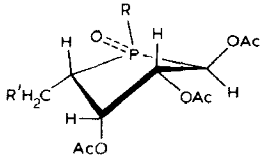
9a,b



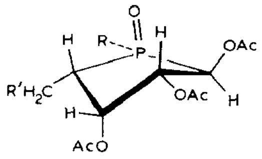
10a,b



11a,b

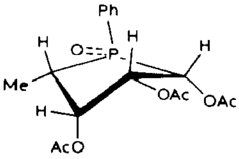


12a,b



13a,b

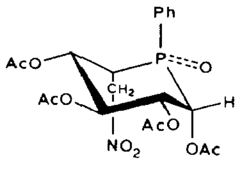
a R = Et, R′ = OAc
b R = Ph, R′ = H



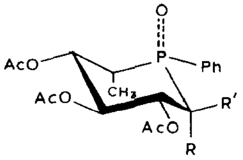
14

lyxo-furanoses **8–13a**, together with their plausible conformations in solution, were assigned to the final products by analysis of the 400-MHz, ^{1}H-n.m.r. spectra. Among these peracetates **8–13a**, compound **8a** was the only crystalline product (m.p. 145–146°), and it was proposed[1] that it had the structure 4-*C*-[(*S*)-ethylphosphinyl]-α-D-ribofuranose, which was likely to exist in the E_2 conformation in solution. This tentative assignment necessitated conducting a precise, X-ray crystallographic analysis of **8a**, which, in turn, was considered to justify, unambiguously, the validity of the assignments, made by the use of ^{1}H-n.m.r.-spectral analysis[1], of the configurations and conformations of the rest of these pentofuranoses (and similar analogs).

Moreover, such an X-ray analysis would be of value from the viewpoint of comparative, X-ray crystallographic study of pentofuranose and hexopyranose



15



16 R = H, R′ = OAc
17 R = OAc, R′ = H
18 R = H, R′ = H

TABLE I

CRYSTAL DATA FOR **8a** (E S D VALUES IN PARENTHESES)

Formula	$C_{15}H_{23}O_9P$
Lattice constants (nm, degrees)	$a = 1.1806(5)$ $b = 1.5432(8)$ $c = 0.5330(2)$ $\beta = 92.04(3)$
Cell volume (nm^3)	$V = 0.9704$
Formula units per cell	$Z = 2$
X-Ray density ($Mg \cdot m^{-3}$)	$\rho_x = 1.287$
Space group	$P2_1$
Total number of reflections ($\theta < 27°$)	2182
Unobserved ($I < 2\sigma$)	495
Linear absorption coefficient (MoKα, cm^{-1})	$\mu = 1.90$
R value[a,b]	0.057

[a]The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$. [b]$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

analogs having phosphorus in the hemiacetal ring [the L-lyxofuranose **12b** (ref. 2) and the D-idopyranoses **15** (ref. 3), **16, 17** (ref. 4), and **18** (ref. 5)], as well as from that of molecular biology[6].

EXPERIMENTAL

Colorless, prismatic crystals of the title compound **8a** (grown from ethyl acetate–hexane) were available, and a specimen having a size of ~0.35 × 0.25 × 0.40 mm was used for the X-ray measurements. Precise lattice-constants and the intensity data for two octands (h, k, l, and $\bar{h}$, k, l) were measured on a DEC Micro PDP 11 controlled Stoe, four-circle diffractometer with MoKα radiation (graphite monochromator, $\lambda = 71.068$ pm). A summary of the crystallographic data is given in Table I.

Phase determination was made by direct methods (MULTAN[7]). The refinement, with least-squares techniques, was executed with the corresponding programs of the X-RAY 76 program[8] system. The intensity data were corrected for the anomalous scattering of phosphorus. An absorption correction was not applied. Except for those in the acetoxyl groups on C-2 and C-3, all hydrogen atoms were located unambiguously from difference syntheses. For the methyl hydrogen atoms on C-21 and C-31 a distribution of maxima was found; this could be explained by a double occupancy of this group in such positions that the hydrogen atoms became staggered, partly to the carbonyl oxygen atom and partly to the ether oxygen atom. This situation had previously been observed in several acetylated sugars[9,10]. The heavy atoms were refined with anisotropic temperature-factors, and the hydrogen positions were refined with isotropic, thermal parameters, except for the hydrogen atoms of the disordered methyl groups. Their positional parameters and isotropic temperature-factors (taken from the corresponding C atom) were kept invariant.

TABLE II

ATOMIC PARAMETERS (E.S.D. VALUES IN PARENTHESES; U_{eq} AND U VALUES IN $Å^2$ (× 100))

Atom	*x*	*y*	*z*	U_{eq}, *U*
C-1	0.6867(6)	1.0803(5)	0.898(1)	4.8(2)
O-1	0.6580(5)	1.1493(4)	0.727(1)	6.4(2)
C-10	0.5987(8)	1.2143(6)	0.810(2)	7.1(3)
C-11	0.587(1)	1.2852(7)	0.618(2)	7.9(4)
O-11	0.564(1)	1.2159(6)	1.007(2)	18.6(6)
C-2	0.8125(7)	1.0807(5)	0.970(1)	5.2(2)
O-2	0.8779(5)	1.0997(3)	0.756(1)	5.8(2)
C-20	0.9350(8)	1.1752(5)	0.752(2)	6.7(3)
C-21	1.0091(9)	1.1808(7)	0.534(2)	8.5(4)
O-21	0.9236(9)	1.2295(5)	0.909(1)	12.2(4)
C-3	0.8430(5)	0.9878(5)	1.058(1)	4.9(2)
O-3	0.9631(4)	0.9836(5)	1.069(1)	6.9(2)
C-30	1.0141(7)	0.9391(6)	1.255(2)	6.9(3)
C-31	1.1401(9)	0.9407(8)	1.235(3)	13.5(7)
O-31	0.9629(6)	0.9016(5)	1.411(1)	9.0(3)
C-4	0.7906(6)	0.9244(5)	0.866(1)	5.0(2)
C-5	0.7824(9)	0.8332(5)	0.975(2)	6.1(3)
O-5	0.7285(5)	0.7807(4)	0.778(1)	6.2(2)
C-50	0.7217(8)	0.6953(6)	0.825(2)	6.8(3)
C-51	0.661(1)	0.6483(8)	0.614(2)	8.1(4)
O-51	0.7630(8)	0.6630(5)	1.011(1)	11.1(4)
P-5	0.6586(1)	0.9737(–)	0.7458(3)	4.54(4)
O-50	0.6438(4)	0.9768(4)	0.4690(8)	6.0(2)
C-501	0.5408(7)	0.9290(5)	0.905(1)	5.3(2)
C-502	0.4293(8)	0.9722(8)	0.831(2)	7.5(3)
H-1	0.638(5)	1.084(4)	1.05(1)	4.(2)
H-111	0.506(8)	1.297(6)	0.61(2)	11.(3)
H-112	0.609(9)	1.329(8)	0.67(2)	10.(4)
H-113	0.63(1)	1.277(8)	0.46(2)	16.(5)
H-2	0.827(4)	1.125(4)	1.10(1)	2.(1)
H-211	1.067(–)	1.132(–)	0.543(–)	8.50(–)
H-212	0.964(–)	1.175(–)	0.372(–)	8.50(–)
H-213	1.053(–)	1.237(–)	0.527(–)	8.50(–)
H-214	0.986(–)	1.234(–)	0.437(–)	8.50(–)
H-215	1.088(–)	1.190(–)	0.607(–)	8.50(–)
H-216	1.021(–)	1.136(–)	0.398(–)	8.50(–)
H-3	0.814(5)	0.975(5)	1.23(1)	5.0(2)
H-311	1.174(–)	0.965(–)	1.397(–)	12.90(–)
H-312	1.166(–)	0.879(–)	1.218(–)	12.90(–)
H-313	1.187(–)	0.972(–)	1.102(–)	12.90(–)
H-314	1.164(–)	0.915(–)	1.069(–)	12.90(–)
H-315	1.170(–)	1.003(–)	1.240(–)	12.90(–)
H-316	1.178(–)	0.912(–)	1.408(–)	12.90(–)
H-4	0.836(6)	0.923(5)	0.73(1)	6.(2)
H-51	0.857(6)	0.814(5)	1.02(1)	4.(2)
H-52	0.740(9)	0.836(7)	1.16(2)	12.(4)
H-511	0.72(1)	0.616(8)	0.53(2)	15.(5)
H-512	0.59(1)	0.625(9)	0.66(2)	17.(5)
H-513	0.639(9)	0.681(7)	0.47(2)	12.(4)
H-5011	0.560(6)	0.936(5)	1.10(1)	6.(2)
H-5012	0.525(6)	0.871(5)	0.88(1)	5.(2)
H-5021	0.428(7)	1.023(6)	0.89(2)	7.(3)
H-5022	0.417(7)	0.965(7)	0.64(2)	9.(3)
H-5023	0.354(9)	0.939(7)	0.92(2)	14.(4)

The distribution of ΔF was found to be almost independent of $|F|$, and we therefore decided to use unit weights. After convergence of all parameters, a final R value of 5.7% was obtained. The final atomic coordinates are given in Table II*; the U_{eq} values were calculated as described by Hamilton[11].

RESULTS AND DISCUSSION

The atomic-numbering scheme and bond lengths are given in Fig. 1. A SCHAKAL[12] representation of the molecular structure of **8a** is shown in Fig. 2. Bond angles and a choice of torsion angles are listed in Tables III and IV.

The five-membered ring has the $^{3}T_{2}$ conformation, with a tendency towards the E_2 form. The Cremer–Pople puckering parameters are $q_2 = 41.4(8)$ pm and $\phi_2 = 263.4(9)°$ (refs. 13 and 14). The asymmetry parameters, after Duax and coworkers[15], are $\Delta c_2 = 6.3°$ for the $^{3}T_{2}$ conformation and $\Delta c_s = 13.0°$ for the E_2 conformation. In a previous investigation[2], the situation for **12b** was found to be almost the opposite, and the favored conformation of its five-membered ring was the E_3 form, with a tendency towards the $^{2}T_{3}$ form, although, in both cases, the hybrid character of the conformation of the five-membered ring, between an envelope and a twist form, was obvious (see later for a discussion of the conformational analysis in solution).

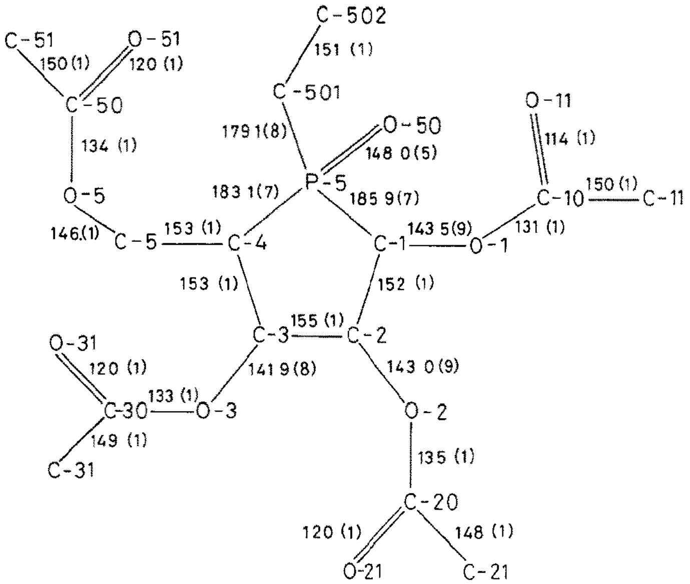


Fig. 1. Atom-numbering scheme and bond lengths in pm (e.s.d. values in parentheses) for **8a**.

---

*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 Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/324/*Carbohydr. Res.*, 145 (1985) 25–35.

TABLE III

BOND ANGLES IN **8a** (E S D VALUES IN PARENTHESES)

Bond	*Angle (degrees)*
O-1–C-1–C-2	111 2(6)
O-1–C-1–P-5	110.2(5)
C-2–C-1–P-5	105.7(5)
C-1–O-1–C-10	118.2(6)
O-1–C-10–C-11	111.5(8)
O-1–C-10–O-11	122.7(9)
C-11–C-10–O-11	126 (1)
C-1–C-2–O-2	110.6(6)
C-1–C-2–C-3	106 6(6)
O-2–C-2–C-3	107 7(6)
C-2–O-2–C-20	118.3(6)
O-2–C-20–C-21	111.8(7)
O-2–C-20–O-21	121.8(9)
C-21–C-20–O-21	126.4(9)
C-2–C-3–O-3	106.1(6)
C-2–C-3–C-4	107.9(6)
O-3–C-3–C-4	112.3(6)
C-3–O-3–C-30	118.7(6)
O-3–C-30–C-31	111 3(9)
O-3–C-30–O-31	122.8(8)
C-31–C-30–O-31	126 (1)
C-3–C-4–C-5	111.5(6)
C-3–C-4–P-5	106.7(5)
C-5–C-4–P-5	116.8(6)
C-4–C-5–O-5	105 7(6)
C-5–O-5–C-50	115 9(6)
O-5–C-50–C-51	111.4(8)
O-5–C-50–O-51	122.6(8)
C-51–C-50–O-51	126.0(9)
C-1–P-5–C-4	94.4(3)
C-1–P-5–O-50	114.9(3)
C-1–P-5–C-501	105.3(3)
C-4–P-5–O-50	115 6(3)
C-4–P-5–C-501	109 8(3)
O-50–P-5–C-501	114 7(3)
P-5–C-501–C-502	113.0(6)

The substituent diagram illustrated in Fig. 3 shows the positions of the exocyclic bonds relative to the five-membered ring. As required for a ring of the conformation found, the substituents on P-5 are in bisectional positions. Because this also holds for the substituents O-1 and C-5 of the neighboring ring-atoms (see Fig. 3), the side groups along the C-4–P-5 and P-5–C-1 bonds are in almost eclipsed arrangements. The acetoxyl groups on C-2 and C-3 are respectively attached axially and (almost) equatorially. These groups, as well as that on C-1, are in the usual, *syn*-parallel arrangement of the C=O bond with the C–H bond of the adjacent, corresponding ring-atom, as their torsion angles C-i0–O-i–C-i–H-i (i = 1, 2, 3) are all close to zero.

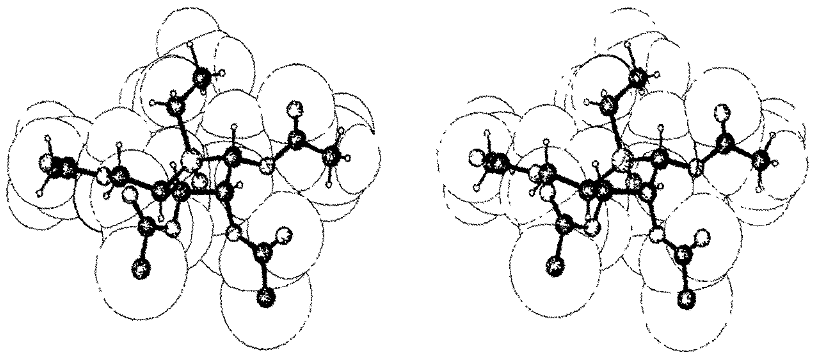


Fig. 2. Stereoview of the molecular model of **8a**, generated with SCHAKAL[12]. Open circles indicate the space filling model. The doubly occupied methyl hydrogen atoms on C-21 and C-31 have been omitted for clarity.

TABLE IV

A CHOICE OF TORSION ANGLES FOR **8a** (E S D VALUES IN PARENTHESES)

Sequence	*Angle (degrees)*
C-1–C-2–C-3–C-4	46.6(7)
C-2–C-3–C-4–P-5	−32.8(6)
C-3–C-4–P-5–C-1	9.3(5)
C-4–P-5–C-1–C-2	16.7(5)
P-5–C-1–C-2–C-3	−37.8(6)
C-501–P-5–C-1–C-2	128.6(5)
O-50–P-5–C-1–C-2	−104.2(5)
O-1–C-1–C-2–C-3	−157.3(5)
O-2–C-2–C-3–C-4	−72.2(7)
O-3–C-3–C-4–P-5	−149.3(5)
C-5–C-4–P-5–C-1	134.8(6)
O-5–C-5–C-4–C-3	178.4(6)
O-5–C-5–C-4–P-5	55.3(8)
O-11–C-10–O-1–C-1	−4.(1)
O-21–C-20–O-2–C-2	−7.(1)
O-31–C-30–O-3–C-3	1.(1)
O-51–C-50–O-5–C-5	−4.(1)
C-50–O-5–C-5–C-4	174.3(7)
C-502–C-501–P-5–C-1	74.4(7)
C-502–C-501–P-5–C-4	175.0(6)
C-502–C-501–P-5–O-50	−52.8(8)
C-10–O-1–C-1–H-1	15.(4)
C-20–O-2–C-2–H-2	−7.(3)
C-30–O-3–C-3–H-3	22.(5)

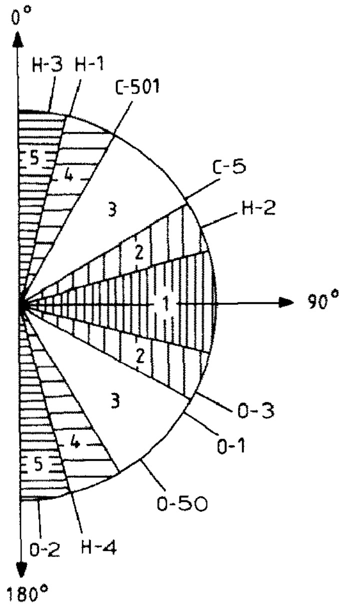


Fig. 3. Illustration of the bond types of the five-membered-ring substituents For each substituent, the angle between its exocyclic bond and the normal of the five-membered ring is plotted. The exocyclic bond attachments are 1 = equatorial, 2 = *quasi*-equatorial, 3 = bisectional, 4 = *quasi*-axial, and 5 = axial

The bond lengths around the hetero-atom are in close agreement with those observed in a previous investigation[2] of **12b**. Moreover, the present results confirm the previous findings[5] that the lengths of the endocyclic bonds P-5–C-4 and P-5–C-1 are longer when the alkyl or aryl substituent on the ring-phosphorus atom is linked axially (or *quasi*-axially) (as in **8a**, **12b**, and **15**), rather than equatorially (as in **16–18**). The lengths of the exocyclic bonds P-5–O-5 (148.0 pm) and P-5–C-501 (179.1 pm) agree well with the bond lengths previously determined[2–5] for other P-in-ring sugars.

*Conformational analysis of per-O-acetyl-4-deoxy-4-C-phosphinyl-*D-ribo- *and* -L-lyxo-*furanoses.* — It is significant that, in the large number of X-ray crystallographic studies carried out on furanose derivatives, including many nucleosides and nucleotides, only puckering at C-2 or C-3 has been observed[16]. It is also known that the conformation that occurs in a crystal is, in most cases, similar to the one that is favored in solution[17]. Indeed, although the conformations of furanose derivatives are not so readily established as those of pyranoses, monocyclic furanoid derivatives are regarded as existing as rapidly interconverting conformers in solution, favoring puckering in the C-2–C-3 region of the furanoid ring[17,18]. This appears to be mainly because 1,2-*cis*, non-bonded interactions are the most significant, and these are minimized through displacement of C-2 and C-3 away from a plane defined by the remaining atoms of the ring.

As the precise structure, as well as the conformation in the solid state, of the

TABLE V

CHARACTERISTIC FEATURES OF THE δ AND J VALUES FOR 4-(ETHYL- AND -PHENYL-PHOSPHINYL)-D-*ribo*- AND -L-*lyxo*-FURANOSES AND THEIR PREPONDERANT CONFORMATIONS[a]

Ring protons	*Values*	$^3T_2$ (E_2)			$^3T_2 \rightleftharpoons {}^2T_3$	$^2T_3$ (E_3)		
		8a (8b)[b]	**9a (9b)**[b]	**10a (10b)**[b]	**11a (11b)**[b]	**12a**[a] **(12b)**[b]	**14**	**13a**[a] **(13b)**[a,b]
H-1	δ	5.0 (5.25)	5.45	5.4	5.0	5.72 (5.5)	5.3	4.98 (5.3)
	$J_{1,P}$	2.5 (1)	12	8	2	12.5	6	1.0 (1.0)
	$J_{1,2}$	5	5	3.5	6	9.8	3	10.0 (9.0)
H-2	δ	5.75 (5.9)	5.8	5.4 (5.6)	5.7	5.07 (5.4)	5.4	5.50 (5.70)
	$J_{2,P}$	25 (27)	27	16	11	1.0	5	3.5 (3.5)
	$J_{2,3}$	3	3	4	4	3.5	3	0.5 (0.5)
H-3	δ	5.0	5.4	5.2	5.5	5.69	5.6	5.72 (5.75)
	$J_{3,P}$	1	1	6	13.5	24.5 (28)	23	28 (27.0)
	$J_{3,4}$	12	11	10	6	4.3	6	4.0 (4.0)
H-4	δ	3.1	2.6	2.9	2.65	2.54	2.6	2.88 (2.75)
	$J_{4,P}$	22 (24)	9	21 (23)	6	6.0	6	21.0 (21.5)

[a] Values (400 MHz, ^{1}H-n.m.r.) are from refs. 1 and 19, except for those of **12a**, **13a**, and **13b**, which were later obtained by simulation analysis using an NEC PC9801 personal computer (ref. 25). [b] Parameters for the 4-(phenylphosphinyl) compounds are almost identical to those for the corresponding 4-(ethylphosphinyl) derivatives, except for those shown in parentheses.

P-in-ring D-ribofuranose analog **8a** has been established, a reliable structural analysis can now be made more systematically for the rest of the D-*ribo* and L-*lyxo* analogs[1] **9–13a** and also for the 4,5-dideoxy-4-*C*-(phenylphosphinyl) analogs[19] **8–13b** and **14**. General trends of the parameters for these P sugars are summarized* in Table V. Some features of these spectral data, important and valuable for the structural and conformational analysis, are as follows.

(1) When the H-4 signal appears at relatively low field (δ 3.1–2.9) and the $J_{4,P}$ values are large (21–24 Hz), H-4 apparently lies close to the oxygen atom on the ring-phosphorus atom (namely, the *cis* or *gauche* relationship between these two groups), whereas a smaller δ value (2.6–2.5) with a medium $J_{4,P}$ value (~6 Hz) indicates that the two groups are remote (namely, in an almost *trans* relationship), inferred by analogy with the n.m.r. data for non-sugar, phosphorus compounds[20]. Similarly, relatively large values of δ (5.7–5.3) and $J_{1,P}$ (10–12 Hz) for the H-1 signal indicate the *cis* (or *gauche*) relationship of the H-1 and P=O groups, whereas small values of δ (5.3–5.0) and $J_{1,P}$ (0.8–2.5 Hz) suggest a *trans* relationship. Then, a relatively large magnitude of $J_{3,4}$ (10–12 Hz) suggests an almost *trans* relationship between H-3 and H-4 (thus indicating the D-ribofuranose form), whereas smaller values (4–6 Hz) suggest the L-lyxofuranose structure in most cases. Combination of these results readily permits establishment of the configurations of C-1, C-4, and

---

*Examination of the ^{1}H-n.m.r. parameters of the extremely minor L-*lyxo* products **12a** and **13a,b** by computer analysis has clarified those reported to be uncertain[19], or has led to a slight revision of a few of the reported values[1], as recorded in Table V.

P-5; for these features, an exception lies in the parameters for compounds **11a,b**, having an intermediate magnitude of $J_{3,4}$ (6–7 Hz); see later for a discussion.

(2) The significant difference in the magnitudes of $J_{2,P}$ and $J_{3,P}$, combined with those of the δ values of H-2 and H-3, is indicative of an unsymmetrical conformation with respect to the hydrogen atoms on C-2 and C-3. When these 4-*C*-phosphinylpentofuranoses have a large $J_{2,P}$ value (25–28 Hz) and a small $J_{3,P}$ value ($\sim$1 Hz), as for **8a,b** and **9a,b**, the compounds exist preponderantly in the E_2 (or readily variable $^3T_2$) conformation, wherein the approximate dihedral angles of P–C-1–C-2–H and P–C-4–C-3–H are 150 and 90°, respectively. It should be noted that the concurrent differences in the δ values of H-2 (5.8–5.9) and H-3 (5.0–5.4) are in conformity with their respective *quasi*-equatorial and *quasi*-axial orientation. Compounds **10a,b** are presumed to be in the $^3T_2$ conformation also, but with a slight tendency towards the rapidly interconverting $^2T_3$ form, judging from the magnitudes of the corresponding δ and J values (see later). On the other hand, reversed magnitudes of $J_{2,P}$ and $J_{3,P}$, together with the δ values for H-2 and H-3, as with compounds **12–14**, support the E_3 (or $^2T_3$) conformation for these compounds; the E_3 conformation of **12b** was confirmed by X-ray crystallographic analysis[2]. These shapes would allow minimization of the significant 1,2-*cis*, as well as 1,3-*syn*, non-bonded interactions among the alkyl or aryl group on the ring-phosphorus atom and the substituents on the adjacent ring-atoms, taking into consideration the longer C-1–P-5 and C-4–P-5 bonds (183–186 nm) that would to some extent relieve the eclipsed congestion among the substituents on these ring atoms. Some examples of similar, angular dependence of ^{31}P–C–C–^{1}H vicinal coupling-constants upon the dihedral angles in the case of phosphonate compounds[21] and P(V)-heterocyclic systems[22,23] have been reported.

(3) When the magnitudes of $J_{2,P}$ and $J_{3,P}$ and the δ values of H-2 and H-3 are almost the same, as for **11a,b**, this suggests an averaging between the E_2 and E_3 [or $^3T_2$ (^3E) and $^2T_3$ (^2E)] conformations. As molecule **11** possesses a near-C_2 symmetry, and the energy barrier between the E_2 and E_3 forms is considered to be relatively low (13–21 kJ; 3–5 kcal)[16,17,24], rapidly interconverting conformations would be expected to exist for **11** (and **10**) in solution. The assignment of the D-ribofuranose structure to **11** was made by considering the chemical shifts of H-2 and H-3 at relatively low field, which suggested that the P=O group and the hydrogen atoms on C-2 and C-3 all lie on the same side of the plane of the five-membered ring. Thus, combination of these data with the configurations of C-1, C-4, and P-5 (determined according to the characteristic features already described) led to the 4-[(*R*)-ethylphosphinyl]-β-D-*ribo* structure for **11a,b**.

These findings, for the first time, establish the precise structure of a D-ribofuranose having phosphorus in the hemiacetal ring, and also demonstrate that 400-MHz, ^{1}H-n.m.r. spectroscopy is an extremely effective tool for structural and conformational analysis of the aldopentofuranose analogs.

REFERENCES

1 H. YAMAMOTO, Y. NAKAMURA, S. INOKAWA, M. YAMASHITA, M.-A. ARMOUR, AND T. T. NAKASHIMA, *J. Org. Chem.*, 49 (1984) 1364–1370.
2 P. LUGER, H. YAMAMOTO, AND S. INOKAWA, *Carbohydr. Res.*, 110 (1982) 187–194.
3 P. LUGER, M. YAMASHITA, AND S. INOKAWA, *Carbohydr. Res.*, 84 (1980) 25–33.
4 S. INOKAWA, K. YAMAMOTO, H. KAWAMOTO, H. YAMAMOTO, M. YAMASHITA, AND P. LUGER, *Carbohydr. Res.*, 106 (1982) 31–42.
5 H. YAMAMOTO, K. YAMAMOTO, S. INOKAWA, AND P. LUGER, *Carbohydr. Res.*, 113 (1983) 31–43.
6 H. YAMAMOTO AND S. INOKAWA, *Adv. Carbohydr. Chem. Biochem.*, 42 (1984) 131–195.
7 P. MAIN, M. WOOLFSON, AND G. GERMAIN, *MULTAN, A Computer Program for the Automatic Solution of Crystal Structures*, University of York, Gt. Britain, 1975.
8 J. M. STEWART, *The X-Ray System, Version 1976*, Technical Report TR-446, University of Maryland, College Park, MD, U.S.A., 1976.
9 G. KOTHE, P. LUGER, AND H. PAULSEN, *Acta Crystallogr., Sect. B*, 35 (1979) 2079–2087.
10 P. LUGER AND H. PAULSEN, *Chem. Ber.*, 107 (1974) 1579–1589.
11 W. C. HAMILTON, *Acta Crystallogr.*, 12 (1968) 321–324.
12 E. KELLER, *Chem. Unserer Zeit.*, 14 (1980) 56.
13 D. CREMER AND J. A. POPLE, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
14 P. LUGER AND R. BULOW, *J. Appl. Crystallogr.*, 16 (1983) 431–432.
15 W. L. DUAX, C. M. WEEKS, AND D. C. ROHRER, *Top. Stereochem.*, 9 (1976) 271–383.
16 M. SUNDARALINGAM, *J. Am. Chem. Soc.*, 87 (1965) 599–606.
17 J. F. STODDART, *Stereochemistry of Carbohydrates*, Wiley, New York, 1971.
18 S. J. ANGYAL, *Carbohydr. Res.*, 77 (1979) 37–50.
19 H. YAMAMOTO, Y. NAKAMURA, H. KAWAMOTO, S. INOKAWA, M. YAMASHITA, M.-A. ARMOUR, AND T. T. NAKASHIMA, *Carbohydr. Res.*, 102 (1982) 185–196.
20 L. D. QUIN, *The Heterocyclic Chemistry of Phosphorus*, Wiley, New York, 1981, pp. 319–359.
21 L. EVELYN, L. D HALL, L. LYNN, P. R. STEINER, AND D. H. STOKES, *Carbohydr. Res.*, 27 (1973) 21–27.
22 O. AWERBOUCH AND Y. KASHMAN, *Tetrahedron*, 31 (1975) 33–43.
23 T. C. CHAN AND K. T. NWE, *Tetrahedron*, 31 (1975) 2537–2542.
24 L. D. HALL, P. R. STEINER, AND C. PEDERSEN, *Can. J. Chem.*, 48 (1970) 1155–1165, and references cited therein.
25 K. SATAKE, Y. HARA, H. MURATA, AND H. YAMAMOTO, *Kagaku*, 39 (3) (1984) A1–A8.