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Synthesis, structure, and transformations of 1,2,4-phosphites of α-D-xylopyranose

Eduard E. Nifant'ev*, Michail P. Koroteev, Victor A. Sychev, Anna R. Bekker, Larissa K. Vasyanina, and Nikolay N. Nevskii
Department of Chemistry, V. I. Lenin Moscow Pedagogical State University, Moscow (U.S.S.R.)

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ABSTRACT

The reaction of D-xylose with tris(3,5-dimethylpyrazolyl) phosphite gave the 1,2,4-phosphite, which was oxidised to the 1,2,4-phosphate and also converted into the 1,2,4-thio- and -seleno-phosphates. These compounds were hydrolysed readily to give, first, the 1,4-phosphates and then the 4-phosphates. The direction of hydrolysis of the 1,2,4-phosphates is discussed on the basis of X-ray data on the starting compounds.

INTRODUCTION

Bicyclophosphites of carbohydrates[1] have potential application in the synthesis of bioregulators[2] and were obtained first by phosphorylation of partially substituted carbohydrates. We now report on the conversion of D-xylopyranose into a 1,2,4-phosphite.

RESULTS AND DISCUSSION

The reaction of α,β-D-xylopyranose (α,β-ratio 1:1; ^{13}C-n.m.r. data) in dry dioxane–pyridine with tris(3,5-dimethylpyrazolyl) phosphite[4] gave, after chromatography on silica gel, 40% of the syrupy 1,2,4-triphosphite **1** (*cf.* ref. 3). The use of triamidophosphites or phosphorus trichloride gave lower yields of **1**.

The structure of **1** was established on the basis of ^{31}P-, ^{1}H-, and ^{13}C-n.m.r. data (Tables I and II). Thus, there was a single ^{31}P resonance (s) at 111.2 p.p.m., which corresponded to those of other bicyclophosphites[1]; H-1,2,4 were involved in $^{3}J_{H,P}$ couplings; and the resonances for C-1,2,3,4 were doublets due to coupling with P, whereas that for C-5 was a singlet.

On storage, **1** underwent partial intermolecular alcoholysis due to the free hydroxyl group, but the acetate (**2**), benzoate (**3**), and phenylcarbamate (**4**) were stable derivatives. The structures of **2–4** were confirmed by the n.m.r. data. The ^{31}P-n.m.r. spectra of **1–4** were similar, but the signals for H-3 of **2–4** were shifted upfield compared to that of H-3 in **1** and indicated the substituents to be at position 3.

* To whom correspondence should be addressed.

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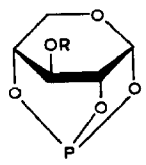
TABLE I

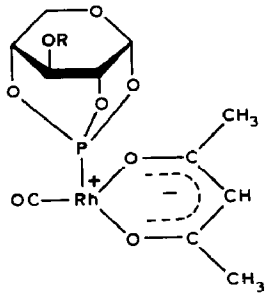
^{1}H- and ^{31}P-n.m.r. data[a] (δ in p.p.m, J in Hz)

Compound	*H-1* $J_{1,2}$ $J_{1,P}$	*H-2* $J_{2,3}$ $J_{2,P}$	*H-3* $J_{3,4}$	*H-4* $J_{4,5a}$ $J_{4,P}$	*H-5a* $J_{5a,5b}$	*H-5b* $J_{4,5b}$	^{31}P
1	6.22 (5.2) (5.9)	4.75 (4.4) (8.1)	4.47 (5.2)	4.70 (3.7) (9.6)	4.53 (12.5)	4.26 (0)	111.2
2	5.88 (5.2) (6.6)	4.47 (2.9) (8.1)	5.13 (2.2)	4.52 (4.4) (8.8)	4.15 (12.5)	4.07 (<1)	111.5
3	6.21 (5.1) (5.4)	4.88 (1.9) (10.1)	5.54 (4.4)	4.84 (4.8) (9.5)	4.29 (12.0)	4.15 (<1)	111.5
4	5.92 (5.1) (6.0)	4.54 (3.0) (8.2)	5.18 (4.2)	4.62 (4.5) (9.6)	4.28 (12.2)	4.16 (<1)	111.3
9	6.01 (5.5) (17.1)	4.82 (3.1) (19.5)	5.30 (4.5)	4.78 (4.3) (24.7)	4.43 (13.0)	4.24 (0)	6.6
10	6.00 (5.3) (17.0)	4.75 (3.0) (19.1)	4.48 (4.5)	4.68 (4.2) (24.0)	4.40 (12.6)	4.20 (<1)	6.6
15	6.04 (5.5) (16.8)	4.72 (4.6) (17.6)	5.34 (2.2)	4.82 (4.6) (30.1)	4.43 (13.1)	4.20 (0)	74.0 ($J_{P,Se}$ 1100)
16	6.11 (5.4) (16.6)	4.85 (2.3) (19.5)	5.62 (2.0)	4.95 (4.4) (25.9)	4.50 (12.7)	4.30 (<1)	74.0 ($J_{P,Se}$ 1100)
17	6.03 (5.04) (17.0)	4.75 (1.9) (19.0)	5.32 (4.8)	4.81 (4.4) (23.9)	4.44 (12.7)	4.20 (0)	70.7
18	6.10 (5.9) (16.9)	4.85 (1.5) (18.4)	5.60 (4.4)	4.91 (4.4) (21.3)	4.52 (12.5)	4.31 (<1)	70.9
19	6.07 (5.5) (17.0)	4.82 (1.8) (19.5)	5.40 (4.5)	4.92 (4.5) (22.5)	4.49 (13.0)	4.26 (0)	70.9
20	5.46 (3.6) (27.9)	4.06 (3.7)	6.56 (1.5)	4.45 (<1) (27.9)	4.29 (11.8)	4.07 (<1)	35.8 ($J_{P,Se}$ 800)
21	5.48 (3.4) (24.9)	4.10 (3.9)	6.44 (1.4)	4.45 (<1) (27.3)	4.27 (12.2)	4.11 (<1)	48.6
23α	5.2 (3.4)	4.50 (<1) (21.5)	6.33 (2.2)	4.65 (2.9) (21.9)	4.49 (12.7)	4.21 (<1)	−0.8
23β	6.03 (4.9)	4.43 (<1) (8.8)	5.95 (3.7)	4.61 (2.2) (11.2)	4.38 (12.7)	3.90 (2.20)	−0.6

[a] The ^{1}H resonances of the protecting groups are not recorded.



1 R = H
2 R = Ac
3 R = Bz
4 R = PhNHCO



5 R = Ac
6 R = Bz

TABLE II

^{13}C Chemical shift data[a] (δ in p.p.m., $J_{P,C}$ values in Hz)

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*
1	98.9	73.1	64.9	77.4	65.9
	(5.4)	(2.4)	(4.9)	(3.8)	
2	98.5	70.4	65.5	73.7	65.7
	(5.3)	(2.6)	(6.0)	(3.3)	
3	98.7	70.4	65.8	73.6	66.0
	(5.6)	(2.7)	(6.1)	(3.5)	
4	98.4	70.7	65.4	74.1	65.7
	(5.3)	(2.1)	(6.1)	(3.2)	
5	97.2	71.2	64.9	74.4	65.1
	(8.8)	(5.6)	(4.1)	(10.9)	
6	97.1	71.2	65.0	74.4	64.8
	(8.8)	(5.7)	(3.2)	(11.1)	
15	97.8	73.2	64.2	75.5	64.9
	(5.6)	(4.6)	(2.7)	(12.2)	
16	97.8	73.3	64.2	75.5	65.0
	(5.9)	(4.5)	(2.7)	(12.1)	
17	96.9	72.9	64.2	74.6	64.7
	(3.5)	(2.7)	(2.3)	(11.1)	
18	96.9	73.1	64.3	74.7	64.9
	(3.5)	(3.4)	(2.4)	(10.7)	
19	96.8	73.2	64.5	74.8	64.7
	(3.4)	(2.8)	(2.5)	(10.9)	
20	96.7	73.6	72.4	71.7	64.2
	(12.1)	(2.0)		(9.8)	
21	96.5	73.6	72.9	71.4	64.4
	(11.1)			(9.2)	
23α	87.5	71.1	63.0	72.2	60.4
		(8.6)	(5.3)	(8.5)	
23β	88.1	70.0	60.8	71.5	61.2
		(7.6)	(5.0)	(7.9)	

[a] The ^{13}C resonances of the protecting groups are not recorded.

TABLE III

Interatomic distances (Å) and bond angles (°) for **3** and **16**

	3	**16**		**3**	**16**
P–O-1	1.620(9)	1.594(9)	O-1–P–O-2	92.72(39)	95.47(45)
P–O-2	1.618(8)	1.619(9)	O-1–P–O-4	101.44(43)	106.66(42)
P–O-4	1.636(8)	1.596(7)	O-2–P–O-4	100.18(36)	103.50(46)
O-1–C-1	1.421(10)	1.481(13)	P–O-1–C-1	111.29(66)	107.08(69)
O-2–C-2	1.438(11)	1.459(12)	P–O-2–C-2	106.92(68)	100.94(67)
O-4–C-4	1.459(10)	1.394(11)	P–O-4–C-4	122.11(66)	116.60(63)

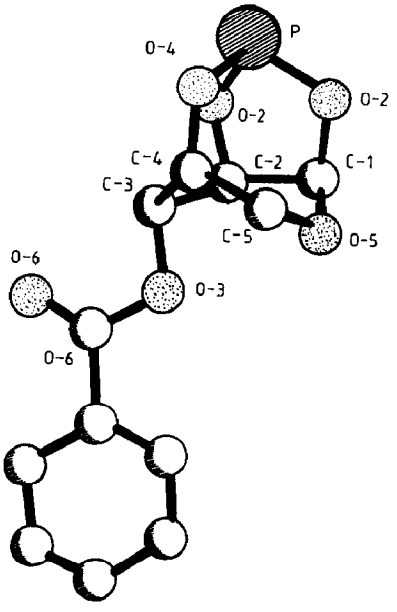


Fig. 1. Projection of the 3-*O*-benzoyl-α-D-xylopyranose 1,2,4-phosphite (**3**) molecule.

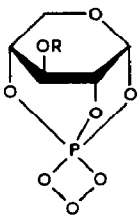
X-Ray analysis of the benzoate **3** (Fig. 1 and Table III) revealed that (*a*) the carbohydrate moiety had a $B_{3,O}$ conformation; (*b*) the phosphorinane ring had a $^2C_4$ conformation with C-4 and C-2 deviating from the plane of the other four atoms by 0.570 and 0.845 Å, respectively; and (*c*) the phospholane ring had an E_2 conformation with O-2 0.673 Å out of the plane. The constraints on the O–P–O angles result in a significant increase of the *s*-character of the lone pair of electrons on the phosphorus, which should decrease its basicity and nucleophilicity[1].

Reaction of the acetate **2** and the benzoate **3** with rhodium(I) dicarbonyl acetylacetonate gave the chiral rhodium complexes **5** and **6**, respectively, which, on treatment with triaminophosphites, regenerated **2** and **3**. The n.m.r. spectra of **5** and **6** contained doublets for ^{31}P at 135.0 p.p.m. with a $^1J_{P,Rh}$ value of 290.0 Hz; in the ^{13}C-n.m.r. spectra (Table II) signals of C-1,2,3,4 in **5** and **6** have $^3J_{C,P}$, the value of which differ from those in

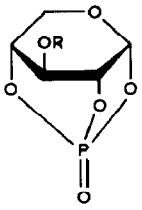
2 and 3 and indicated a change in the geometry of the 1,2,4-phosphite upon complexation.

Treatment of 2 and 3 with ozone in dichloromethane at −70° afforded ozonides (7 and 8, respectively) with pentacoordinate phosphorus, detected by ^{31}P-n.m.r. spectroscopy (^{31}P at 32 p.p.m.), which lost oxygen at 20° to form the 1,2,4-phosphates[5] 9 and 10, respectively.

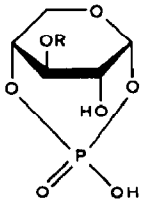
The structures of 9 and 10 were established by the ^{31}P- and ^{1}H-n.m.r. data (Table I). There was a ^{31}P resonance at 6.6 p.p.m. and the ^{1}H resonances, in general, were similar to those of 2 and 3. However, the $J_{H,P}$ values were increased significantly (6→17 Hz for H-1, 8→19 Hz for H-2, and 9→24 Hz for H-4). Compounds 9 and 10 polymerised readily on storage.



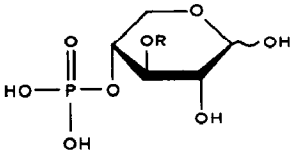
7 R = Ac
8 R = Bz



9 R = Ac
10 R = Bz



11 R = Ac
12 R = Bz



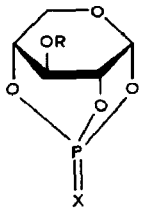
13 αβ R = Ac
14 αβ R = Bz

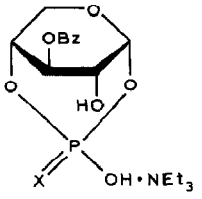
Oxidation of 1,2-*O*-alkylidene-D-glucofuranose 3,5,6-phosphites with aqueous 30% hydrogen peroxide gave the 3,5,6-phosphates that could be hydrolysed selectively to afford the stable 3,5-phosphates[6]. Similar treatment of 2 and 3 with hydrogen peroxide gave, first, the 1,2,4-triphosphates 9 and 10, respectively, which were then hydrolysed to give the 1,4-phosphates (11 and 12) that were converted into the 4-phosphates 13 and 14, respectively.

The ^{13}C-n.m.r. spectra of 13 and 14 contained signals for the α and β anomers, and the signals for C-1,2 in each anomer were now singlets.

The 1,2,4-phosphites 2–4 reacted variously with selenium and sulfur in dry dioxane at 100° to give 15–19 with a consequent upfield shift of the ^{31}P resonances due to the four-coordinate phosphorus. There were also increases in the $J_{H,P}$ and $J_{C,P}$ values. The structure of the seleno derivative 16 was confirmed by the X-ray analysis data (Fig. 2 and Table III). The phosphorinane ring has a $^{4}C_{2}$ conformation with O-4 and O-2 being 0.613 and 0.865 Å, respectively, out of the plane; the phospholane ring has an E_{2} conformation, the deviation of O-2 being 0.722 Å; and the carbohydrate moiety has the $B_{3,O}$ conformation. Compared to those in 2–4, the O–P–O angles are increased by 3–5° and the P–O–C angles are decreased by 4–6°. There are also changes in the P–O and O–C bond lengths. Thus, the P–O-2 bond is the shortest in 3 and the longest in 16. These changes, also observed in previous work[7], cause an increase in the strain energy.

The seleno derivatives 15 and 16 were reactive compounds. Thus, with hexaethylphosphoric triamide at room temperature, 15 was re-converted into 2.





15 X = Se, R = Ac
16 X = Se, R = Bz
17 X = S, R = Ac
18 X = S, R = Bz
19 X = S, R = CONHPh

20 R = Se
21 R = S

The strain in the 1,2,4-phosphate molecules can be relieved by conversion into the 1,4-phosphates. Similar to the 1,2,4-phosphates **9** and **10**, the 1,2,4-thio- and 1,2,4-seleno-phosphates reacted with aqueous triethylamine to give **20** and **21**. Each hydrolysis involved the P–O-2 bond, which is the longest (1.619 Å, *cf.* 1.594 Å for the P–O-1 bond and 1.596 Å for the P–O-4 bond: see Table III).

The structures of **20** and **21** were established by the ^{31}P-, ^{1}H-, and ^{13}C-n.m.r. data. The ^{31}P resonance of **20** was shifted to higher field (35.8 p.p.m.) and there was no

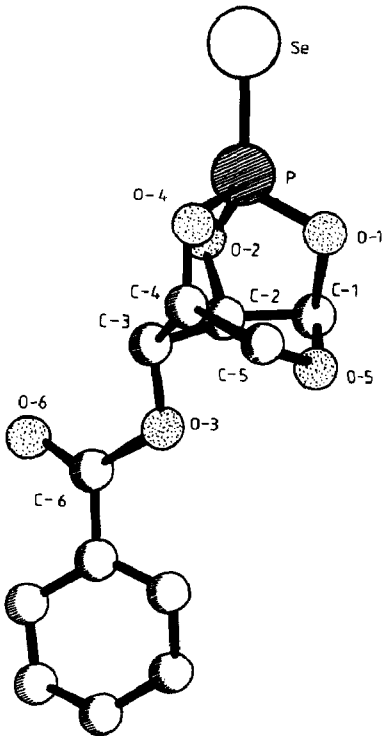
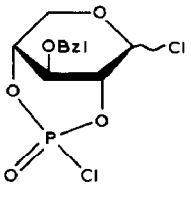


Fig. 2. Projection of the 3-*O*-benzoyl-α-D-xylopyranose 1,2,4-selenophosphate (**16**) molecule.

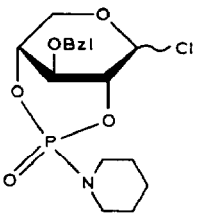
coupling between P and H-2, as expected after cleavage of the P–O-2 bond[6]. The signal of C-2 was no longer a doublet and was shifted to higher field. Large $J_{C,P}$ values were observed for C-1 and C-4. Similar results were obtained for the thio derivative **21**.

Thus, the regio- and stereo-specific opening of the condensed phospholane–phosphorinane system in aqueous triethylamine, to afford the 1,4-phosphates, is similar to that of the furanose analogues[6].

Reaction of **3** with chlorine under homolytic conditions[8] gave the glycosyl chloride **22**$\alpha\beta$, which was highly reactive but could be stabilised by reaction with piperidine to give **23**$\alpha\beta$. The α and β anomers of **23** were isolated by chromatography on silica gel and their structures were established by the ^{31}P-, ^{1}H-, and ^{13}C-n.m.r. data. Each anomer gave two ^{31}P signals with similar chemical shifts (δ −0.8 and −0.6 p.p.m.) indicative[8] of the absence of geometrical isomerism at phosphorus. The $J_{H\text{-}1,H\text{-}2}$ values were 3.4 and 4.9 Hz. That the P–O-1 bond in **3** had been cleaved was indicated by the C-1 signals that were now singlets and the absence of coupling between H-1 and P. The upfield shift of the signals for C-1 is characteristic of pyranosyl chlorides[9].



22$\alpha\beta$



23$\alpha\beta$

EXPERIMENTAL

Experiments with trivalent phosphorus derivatives were carried out under dry nitrogen. T.l.c. was performed on Silufol-254 and column chromatography on silica gel L 40–100, using benzene–1,4-dioxane, 3:1 (*A*) and 1:1 (*B*); hexane–1,4-dioxane, 3:1 (*C*) and 1:1 (*D*); and *E*, 19:1 chloroform–methanol. ^{31}P- (32.4 MHz; external aqueous 85% H_3PO_4), ^{13}C- (75.4 MHz), and ^{1}H-n.m.r. spectra (400.1 MHz; external Me_4Si) were obtained with Bruker WP-80, WM-300, and AM-400 spectrometers, respectively. Optical rotations were determined with a DIP-360 polarimeter. X-Ray analysis was performed with a CAD-4 Enraf–Nonius diffractometer and the detailed results will be published elsewhere.

α-D-*Xylopyranose 1,2,4-phosphite* (**1**) *and some derivatives.* — To a stirred solution of D-xylose (1.50 g) in 1,4-dioxane (50 mL) and pyridine (20 mL) was added a solution of tris(3,5-dimethylpyrazolyl) phosphite (1.58 g, 0.5 mol) in 1,4-dioxane. The mixture was stirred for 0.5 h at room temperature and more phosphite (0.79, 0.40, and 0.40 g) was added every 0.5 h. After a further 0.5 h, the mixture was filtered, and the solvent was evaporated *in vacuo*. Column chromatography (solvent *A*) of the residue gave **1** (0.71 g, 40%), isolated as a syrup, $[\alpha]_D^{20}$ +50° (*c* 0.5, dioxane), R_F 0.60 (solvent *A*), 0.70 (solvent *B*) (Found: C, 33.51; H, 3.72; P, 17.53. $C_5H_7O_5P$ calc.: C, 33.72; H, 3.96; P, 17.39%).

Conventional acetylation of **1** (0.35 g) with acetic anhydride (0.28 mL) and pyridine (15 mL), with column chromatography (solvent *A*) of the product, gave the 3-acetate **2**, isolated as a syrup (0.38 g, 88%), $[\alpha]_D^{20}$ +8° (*c* 1.2, chloroform), R_F 0.82 (Found: C, 38.00; H, 3.98; P, 14.22. $C_7H_9O_6P$ calc.: C, 38.20; H, 4.12; P, 14.07%).

Conventional benzoylation of **1** (0.35 g) with triethylamine (0.28 mL), pyridine (5 mL), and benzoyl chloride (0.24 mL), with column chromatography (solvent *C*) of the product, gave the 3-benzoate **3** (0.40 g, 73%), m.p. 74–75° (from benzene), $[\alpha]_D^{20}$ +36° (*c* 2.7, chloroform), R_F 0.49 (Found: C, 50.92; H, 3.80; P, 11.10. $C_{12}H_{11}O_6P$ calc.: C, 51.08; H, 3.93; P, 10.98%).

Conventional reaction of **1** (0.35 g) in pyridine (5 mL) with phenyl isocyanate (0.22 mL), followed by column chromatography (solvent *A*) of the product, gave the 3-phenylcarbamate **4** (0.41 g, 71%), isolated as a syrup, $[\alpha]_D^{20}$ +32° (*c* 2.0, chloroform), R_F 0.74 (Found: C, 48.35; H, 3.95; N, 4.50; P, 10.52. $C_{12}H_{12}NO_6P$ calc.: C, 48.50; H, 4.07; N, 4.71; P, 10.42%).

To rhodium(I) dicarbonyl acetylacetonate (0.26 g) was added a solution of **2** (0.22 g) in benzene (5 mL) with stirring at room temperature. Part of the solvent was evaporated and the (acetylacetonato)carbonylrhodium complex **5** (0.34 g, 75%) was precipitated with hexane as a syrup, $[\alpha]_D^{20}$ +36° (*c* 0.8, benzene), R_F 0.71 (solvent *A*) (Found: C, 34.41; H, 3.40; P, 7.02. $C_{13}H_{16}O_9PRh$ calc.: C, 34.69; H, 3.58; P, 6.88%).

The (acetylacetonato)carbonylrhodium complex **6** (0.41 g, 80%), prepared from **3** (0.28 g) as described for **5**, had m.p. 75–80° (dec.) (from hexane), $[\alpha]_D^{20}$ +34.5° (*c* 2.3, benzene), R_F 0.88 (solvent *A*) (Found: C, 42.10; H, 3.36; P, 5.90. $C_{18}H_{18}O_9PRh$ calc.: C, 42.21; H, 3.54; P, 6.05%).

3-O-Acetyl-α-D-xylopyranose 1,2,4-phosphate (**9**). — Through a solution of **2** (0.44 g) in dichloromethane (10 mL) at −70° was passed a stream of ozone (2% by vol.) at 5 L/h until the solution turned blue. ^{31}P-N.m.r. spectroscopy revealed the quantitaive formation of the ozonide **7** (^{31}P, δ −32) which, on raising the temperature to 20–25°, polymerised almost completely. The mixture was filtered and the solvent was evaporated to leave **9** as a syrup, $[\alpha]_D^{20}$ +23° (*c* 0.7, chloroform), R_F 0.43 (solvent *A*), 0.54 (solvent *B*) (Found: C, 35.42; H, 3.70; P, 13.24. $C_7H_9O_7P$ calc.: C, 35.61; H, 3.84; P, 13.12%).

3-O-Benzoyl-α-D-xylopyranose 1,2,4-phosphate (**10**). — Following the procedure for **9**, a stream of ozone was bubbled through a solution of **3** (0.28 g) in dichloromethane (10 mL) at −70°. The temperature of the mixture was raised to 20–25°, the mixture was filtered, and the solvent was evaporated to leave **10** as a syrup, $[\alpha]_D^{20}$ +18° (*c* 0.8, chloroform), R_F 0.50 (solvent *A*) (Found: C, 48.12; H, 3.65; P, 10.50. $C_{12}H_{11}O_7P$ calc.: C, 48.34; H, 3.72; P, 10.39%).

3-O-Acetyl-D-xylopyranose 4-phosphate (**13**). — To a solution of **2** (0.44 g) in 1,4-dioxane (5 mL) was added aqueous 30% hydrogen peroxide (0.34 mL), and the mixture was stored for 0.5 h. ^{31}P-N.m.r. spectroscopy revealed the quantitative formation of the 1,4-phosphate **11** (^{31}P, δ −4.5), which was hydrolysed to give **13**$\alpha\beta$ (^{31}P, δ −1.0). The solvent was evaporated *in vacuo* and the residue was washed with hexane to yield **13**$\alpha\beta$ (0.49 g, 90%), as a syrup, R_F 0.20 (solvent *E*) (Found: C, 30.65; H, 4.75; P, 11.58. $C_7H_{13}O_9P$ calc.: C, 30.89; H, 4.82; P, 11.38%).

3-O-Benzoyl-D-xylopyranose 4-phosphate (**14**). — To a solution of **3** (0.28 g) in 1,4-dioxane (5 mL) was added aqueous 30% hydrogen peroxide (0.17 mL). The mixture was stored for 0.5 h. ^{31}P-N.m.r. spectroscopy revealed the quantitative formation of **10**, which was hydrolysed to give **14**$\alpha\beta$ (^{31}P, δ − 0.6). The solvent was evaporated *in vacuo* and the residue was washed with hexane to yield **14**$\alpha\beta$ (0.29 g, 88%), as a syrup, R_F 0.20 (solvent *E*) (Found: C, 42.95; H, 4.35; P, 9.38. $C_{12}H_{15}O_9P$ calc.: C, 43.12; H, 4.52; P, 9.27%).

3-O-Acetyl-α-D-xylopyranose 1,2,4-selenophosphate (**15**). — To a solution of **2** (0.44 g) in 1,4-dioxane (5 mL) was added powdered selenium (0.16 g), the mixture was stirred for 8 h at 100°, then filtered, and the solvent was evaporated *in vacuo*. Column chromatography (solvent *C*, then solvent *D*) of the residue gave **15** (0.43 g, 72%), isolated as a syrup, $[\alpha]_D^{20}$ +11° (*c* 2.5, chloroform), R_F 0.18 (solvent *C*), 0.73 (solvent *D*) (Found: C, 28.05; H, 2.91; P, 10.11. $C_7H_9O_6PSe$ calc.: C, 28.11; H, 3.03; P, 10.36%).

3-O-Benzoyl-α-D-xylopyranose 1,2,4-selenophosphate (**16**). — Following the procedure for **15**, **3** (0.56 g) was treated with selenium (0.16 g) in 1,4-dioxane. Column chromatography (solvent *C*) of the product gave **16** (0.49 g, 68%), m.p. 157–158° (from benzene), $[\alpha]_D^{20}$ +30° (*c* 1.8, chloroform), R_F 0.25 (solvent *C*), 0.71 (solvent *D*) (Found: C, 39.72; H, 2.92; P, 8.72. $C_{12}H_{11}O_6PSe$ calc.: 39.11; H, 3.07; P, 8.58%).

3-O-Acetyl-α-D-xylopyranose 1,2,4-thiophosphate (**17**). — A mixture of **2** (0.44 g) and sulfur (0.10 g) in 1,4-dioxane was stirred for 12 h at 100°, then filtered, and the solvent was evaporated *in vacuo*. Column chromatography (solvent *C*) of the residue gave **17** (0.30 g, 60%), isolated as a syrup, $[\alpha]_D^{20}$ +18° (*c* 0.3, chloroform), R_F 0.40 (Found: C, 33.25; H, 3.52; P, 12.35; S, 12.60. $C_7H_9O_6PS$ calc.: C, 33.34; H, 3.60; P, 12.28; S, 12.72%.

3-O-Benzoyl-α-D-xylopyranose 1,2,4-thiophosphate (**18**). — Following the procedure for **17**, **3** (0.28 g) was treated with sulfur (0.60 g) in 1,4-dioxane. Column chromatography (solvent *C*) of the product gave **18** (0.19 g, 60%), m.p. 140–142° (from benzene), $[\alpha]_D^{20}$ +14° (*c* 1.3, chloroform), R_F 0.25 (solvent *C*), 0.72 (solvent *D*) (Found: C, 45.72; H, 3.39; P, 10.04; S, 9.95. $C_{12}H_{11}O_6PS$ calc.: C, 45.84; H, 3.53; P, 9.86; S, 10.21%).

3-O-Phenylcarbamoyl-α-D-xylopyranose 1,2,4-thiophosphate (**19**). — Following the procedure for **17**, **4** (0.30 g) was treated with sulfur (0.60 g) in 1,4-dioxane. Column chromatography (solvent *D*) of the product gave **19** (0.21 g, 63%), isolated as a syrup, $[\alpha]_D^{20}$ +22° (*c* 1.6, chloroform), R_F 0.64 (Found: C, 43.61; H, 3.49; N, 4.02; P, 9.58; S, 9.60. $C_{12}H_{12}NO_6PS$ calc.: C, 43.77; H, 3.67; N, 4.25; P, 9.41; S, 9.74%).

Triethylammonium 3-O-benzoyl-α-D-xylopyranose 1,4-selenophosphate (**20**). — To a solution of **16** (0.72 g) in 1,4-dioxane (5 mL) were added water (0.06 mL) and triethylamine (0.28 mL). The mixture was stirred for 4 h at 20° and the solvents were then evaporated *in vacuo* to leave **20** as a syrup, $[\alpha]_D^{20}$ − 2.5° (*c* 0.8, chloroform), R_F 0.33 (solvent *E*) (Found: C, 44.85; H, 5.70; N, 2.72; P, 6.60. $C_{18}H_{28}NO_7PSe$ calc.: C, 45.01; H, 5.88; N, 2.92; P, 6.45%).

Triethylammonium 3-O-benzoyl-α-D-xylopyranose 1,4-thiophosphate (**21**). — To a solution of **18** (0.63 g) in 1,4-dioxane (5 mL) were added water (0.06 mL) and triethylamine (0.28 mL). The mixture was stored at 20° for 6 h and the solvents were then

evaporated *in vacuo* to leave **21** as a syrup, $[\alpha]_D^{20}$ +9° (*c* 0.57, pyridine), R_F 0.31 (solvent *E*) (Found: C, 49.62; H, 5.60; P, 3.28; S, 7.28. $C_{18}H_{28}NO_7PS$ calc.: C, 49.88; H, 6.51; N, 3.23; P, 7.15%).

3-O-Benzoyl-α-D-xylopyranosyl chloride 2,4-phosphoropiperididate (**23**). — Dry chlorine was bubbled through a solution of **3** (0.28 g) in dichloromethane (10 mL) at −10 to −15° until it turned green. The excess of chlorine was removed by evaporating the solvent *in vacuo*. To a stirred solution of the residue in dichloromethane at 0° was added piperidine (0.21 mL). The mixture was stored for 2 h at 20°, then filtered, and the solvent was evaporated. Column chromatography (solvent *A*) of the residue gave **23β** (0.09 g, 22.5%), isolated as a syrup, R_F 0.60, $[\alpha]_D^{20}$ −33° (*c* 0.9, chloroform). Eluted second was **23α** (0.09 g, 22.5%), R_F 0.40, m.p. 83–84° (from benzene), $[\alpha]_D^{20}$ −50° (*c* 1.3, chloroform) (Found: C, 50.65; H, 5.05; N, 3.25; P, 7.92. $C_{17}H_{21}ClNO_6P$ calc.: C, 50.82; H, 5.27; N, 3.49; P, 7.71%).

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