113. Deoxy-nitrosugars

11th Communication[1])

Reactions of 1-*C*-Nitroglycosyl Halides and 1-*C*-Nitroglycosyl Sulfones with Dialkyl-Phosphite Anions: Nucleophilic Attack *vs.* Single-Electron Transfer

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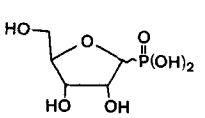
Treatment of the chloro-nitro-ribofuranose **7** with $KPO(OMe)_2$ gave the *O*-amino phosphate **8** (5%) and the nitrile **9** (62%). Compound **9** was also obtained by the reaction of **8** with $KPO(OMe)_2$, and its structure was established by X-ray analysis. Treatment of the chloro-nitro-mannofuranose **10**, the bromo-nitro-ribofuranose **14**, or the bromo-nitro-mannofuranose **16**, respectively, with the K or Na salt of $HPO(OMe)_2$ lead also to *O*-amino phosphates and nitriles. The (1-*C*-nitroglycosyl)phosphonate **22** was obtained (21%) together with the nitrile **21** (51%) from the chloro-nitro-mannofuranose **10** and $KPO(OEt)_2$. The reaction of the 1-*C*-nitroglycosyl sulfone **25** (NO_2-group *endo*) with $KPO(OEt)_2$ gave the (1-*C*-nitroglycosyl)phosphonate **22** (61%) and the nitrile **21** (11%), whilst the anomeric sulfone **26** (NO_2-group *exo*) gave **22** (15%) and **21** (58%). In the presence of [18]crown-6, a mixture of the anomers **25** and **26** gave the (1-*C*-nitroglycosyl)phosphonate **22** in 67% yield together with **21** (13%). These findings are rationalized as the result of a competition between a nucleophilic attack of the dialkyl-phosphite anions on the NO_2-group leading ultimately to the nitrile **21** and a single-electron transfer reaction leading to the (1-*C*-nitroglycosyl)phosphonate **22**.

Introduction. – Many phosphonate analogs of naturally occurring phosphates have been synthesized [2] [3]. Sugar-phosphonates possessing a phosphono group at C(2), C(3), C(4), C(5), or C(6) have been obtained either by a *Michaelis-Arbuzov* reaction [4] [5], by opening of an 1,6-anhydrohexopyranose with hypophosphoric acid [6], or by the addition of dialkyl-phosphite anions to carbonyl compounds [7] [8], to nitroolefins [7], or to unsaturated nitriles [9]. Compounds carrying a phosphono group at C(1) such as **1**, *i.e.* non-isosteric phosphonate analogs of naturally occuring aldose-1-phosphates have not been prepared[2]).



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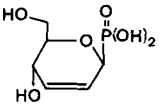

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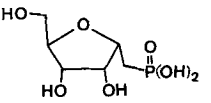

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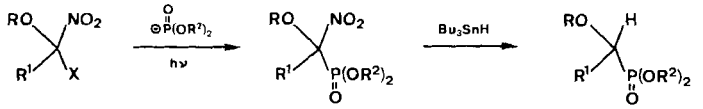
[1]) 10th Communication: [1].

[2]) *Paulsen* [10] has prepared some (2-hexenopyranosyl)- and (2-pentenopyranosyl)phosphonates such as **2** from peracetylated glycals and dimethyl phosphite in the presence of $BF_3 \cdot OEt_2$ followed by deprotection. Hydrogenation of the protected unsaturated phosphonate **2** gave a dimethyl 2,3-dideoxy phosphonate. Attempts to epoxydize the double bond failed.

Isosteric phosphonate analogs of aldose-1-phosphates, *i.e.* compounds carrying a phosphonomethyl group at the centre corresponding to the anomeric centre of aldose-1-phosphates such as **3** [11] are well-known [12–14].

Since non-isosteric phosphonate analogs of aldose-1-phosphates are α-alkoxyphosphonic acids, their second pK_a value, relevant in the 'physiological pH range', should be closer to the one of the natural phosphate monoesters than the second pK_a values of the less acidic isosteric phosphonate analogs [15–18]. This factor as well as the greater proximity of non-bonded electrons to the phosphono group in non-isosteric phosphonate analogs [15] [19] may well influence their biological activity and make their preparation a worthwhile target. Furthermore, α-alkoxyphosphonates may be preparatively useful in so far as they allow an inversion of polarization at the anomeric centre [20] [21].

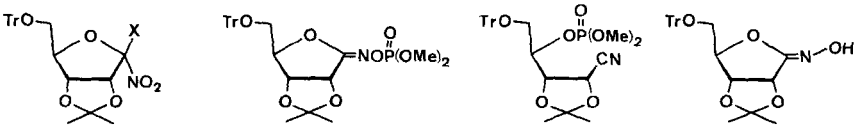
Scheme 1



4 X = Cl, Br, SO_2Ph **5** **6**

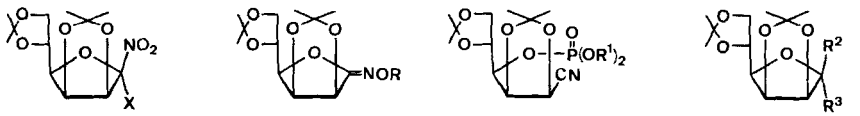
Our plan for the synthesis of glycosylphosphonates **6** *(Scheme 1)* was based on the expectation that the reaction of dialkyl-phosphite anions with geminal chloro- or arylsulfonyl-nitroalkanes reported by *Russell* and *Hershberger* [22] to give α-nitro-alkylphosphonates is applicable to the corresponding anomeric nitro-ether derivatives **4** of aldoses, which are readily available [23]. This expectation stems from the observation that the reaction reported in [22] follows a free-radical chain mechanism, which also seems to operate in the reaction of anomeric geminal chloronitro derivatives of aldoses with some weakly basic carbanions [24]. The reductive denitration of the tertiary nitro ethers **5** to **6** is expected to be straightforward [25].

Results and Discussion. – *Reaction of Halonitro Ethers with Dimethyl-Phosphite Anions.* Treatment of the chloronitroribofuranose **7** [23] with 3.0 equiv. of $KPO(OMe)_2$ in DMSO from −20°[3]) to r.t. under irradiation gave the *O*-glycosylideneamino phosphate **8**



7 X = Cl
14 X = Br

8 **9** **15**



10 X = Cl
16 X = Br

11 R = H
17 R = PO(OMe)$_2$

12 R^1 = Me
21 R^1 = Et

13 R^2 = H, R^3 = NO_2
22 R^2 = NO_2, R^3 = PO(OEt)$_2$

[3]) *No reaction occurred below this temperature.*

(5%) and the nitrile **9** (62%). Under similar conditions, but in the presence of 2.5 equiv. of $NaPO(OMe)_2$ the chloronitromannofuranose **10** gave the hydroximo-lactone **11** (21%) [26], the nitrile **12** (10%), the nitromannofuranose **13** (12%) [27], and starting material **10** (36%). No trace of a (1-*C*-nitroglycosyl)phosphonate was found. Compound **8** was also obtained from **7** by treatment with trimethyl phosphite (*cf.* [28]). The ^{1}H-NMR spectrum ($CDCl_3$) of **8** (foam) showed the presence of (*E*)- and (*Z*)-**8** (ratio 1:9, based on the integral of H–C(2)). The signal of H–C(2) appears at 5.34 ppm for the major diastereoisomer and at 5.56 ppm for the minor diastereoisomer. In the (*E*)-diastereoisomer, H–C(2) is closer to the *N*-phosphate group, and its signal is found at lower field than the one of H–C(2) of (*Z*)-**8** [29]. The structure of **9** was established by X-ray analysis (*Figure*)[4]).

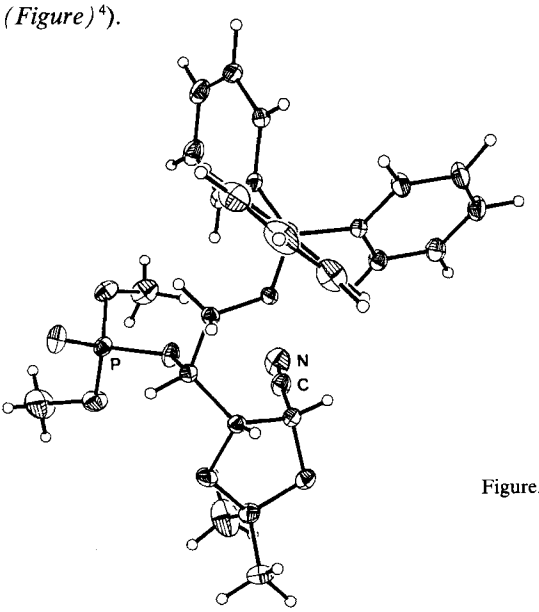
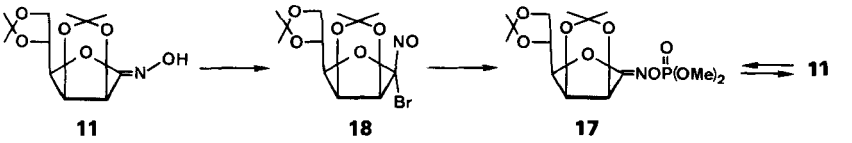


Figure. *ORTEP representation of* **9**

The undesired reactivity of the chloronitro ethers led us to examine the more reactive bromonitro ethers. The bromonitroribofuranose **14** [27] was treated with 3.0 equiv. of $KPO(OMe)_2$ in DMSO from −40° to r.t. under irradiation. A transient blue colour was observed between −40° and −30°. Two main products, the hydroximo-lactone **15** (11%) [26] and the *O*-amino phosphate **8** (65%) were isolated. The analogous treatment of the bromonitromannofuranose **16** [27] with 2.5 equiv. of $NaPO(OMe)_2$ gave mainly the *O*-amino phosphate **17** (45%). This phosphate was also obtained by treatment of **16** with trimethyl phosphite (88%), or by treatment of the hydroximo-lactone **11** with dimethyl phosphorochloridate (43%) [28]; **17** was readily transesterified with NaOEt to **11** (84%). In the presence of 4.0 equiv. of $NaPO(OMe)_2$, **16** gave predominantly the nitrile **12** (76%).

[4]) Crystallographic data have been deposited at the *Cambridge Crystallographic Data Center*. Orthorhombic space group $P2_12_12_1$: $a = 8.634(1)$, $b = 13.335(1)$, $c = 23.254(2)$ Å; $Z = 4$, D_x(cal.) = 1.33 g/cm^3. Intensity measurements at r.t. were made with a *Nicolet-R3* diffractometer (graphite monochromator, MoK_α, $\lambda = 0.7107$ Å). The structure was solved by direct methods and refined by full-matrix-least-squares calculation using 5826 reflections; SHELXTL [30]. H-atoms were located at an intermediate stage and included in the refinement with isotopic vibrational parameters (other atoms anisotropic). The final *R*-value was 0.042 ($R_w = 0.046$). A full paper will be published later [31].

Scheme 2

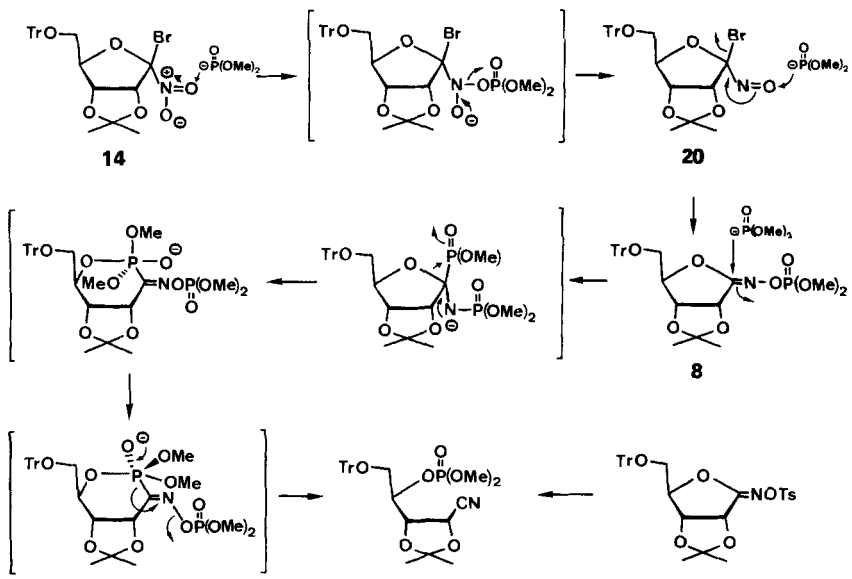


As for **8**, the ^{1}H-NMR spectrum ($CDCl_3$) of the *O*-amino phosphate **17** (m.p.: 129–130°) showed the presence of the (*E*)- and (*Z*)-diastereoisomers in a ratio of 1:9 as inferred from the integral of the H–C(2) signals appearing at 5.26 and at 5.46 ppm for the major and the minor diastereoisomer, respectively.

The appearence of a transient blue colour indicates an intermediate bromonitroso compound. The *O*-amino phosphate **17** was indeed obtained (48%) upon treatment of the 1-*C*-nitrosoglycosyl bromide **18**[5]) with $NaPO(OMe)_2$. The formation of **17** from the reaction of **16** with 2.5 equiv. of $NaPO(OMe)_2$ and the almost exclusive formation of the nitrile **12** in the presence of a large excess of the reagent suggest that **12** is formed from **16** via **17** and, by analogy, the nitrile **9** *via* the *O*-amino phosphate **8**. Treatment of **8** with $KPO(OMe)_2$ indeed gave the nitrile **9** (63%). The nitrile **9** was also obtained (72%) from the *O*-amino tosylate **19** [27] and $KPO(OMe)_2$ showing that the phosphono group of **9** derives from the dialkyl-phosphite anion *(Scheme 3)*. Oxygen or *m*-dinitrobenzene have no influence on the transformation of **8** to **9**.

These results are rationalized by assuming a nucleophilic attack of $(MeO)_2PO^-$ on the NO_2-group of the bromonitroribofuranose **14** (*cf.* [33] [34]), and the elimination of dimethyl phosphate to yield the 1-*C*-nitrosoglycosyl bromide **20** *(Scheme 3)*. A second nucleophilic attack of $(MeO)_2PO^-$ on the O-atom of the NO-group and elimination of bromide yields the *O*-amino phosphate **8**. This reaction is followed by the nucleophilic

Scheme 3



[5]) Prepared from the hydroximo-lactone **11** [27] and *N*-bromosuccinimide (cf. [32]) *(Scheme 2)*.

attack of $(MeO)_2PO^-$ at C(1) of **8**, migration of the C–O bond leading to a six-membered ring containing a pentavalent P-atom, pseudo-rotation, and elimination of dimethyl-phosphate anion to give the nitrile **9**. An analogous way holds for the transformation of **16** into **12** (**16**→**18**→**17**→**12**). The direct nucleophilic attack of $(MeO)_2PO^-$ on the O-atom of the furane ring in **8** while not excluded appears improbable.

Russell et al. [35] rationalized the formation of the dialkyl phosphate of acetone oxime (Me_2C=NOP(O)$(OR)_2$) obtained in the reaction of $Me_2C(NO_2)_2$ with $(RO)_2POK$ by a nucleophilic attack of $(RO)_2PO^-$ at one of the NO_2-groups[6]) leading to $(RO)_2P(O)NO_2$ and the 2-nitropropane anion (Me_2C=NO_2^-). Transfer of $(RO)_2P(O)$- to this anion should then give a *O*-phosphono-nitronic-acid derivative Me_2C=N(O)OP(O)$(OR)_2$, which is deoxygenated by a second equiv. of dialkyl-phosphite anion.

While in our case this mechanism does not account for the appearence of the blue colour in the reaction of the bromonitro compounds **14** and **16**, it explains the formation of the nitro compound **13** from the chloronitro ether **10** (X-philic attack of $(MeO)_2PO^-$ on the Cl-atom). Although in the reactions of dimethyl phosphite with the chloronitro ethers **7** and **10** a blue colour was not observed (the reaction started at a temperature where the blue colour observed during the reaction of the bromonitro ethers **14** and **16** had disappeared), we presume that the reaction of the chloronitro ethers leading to the nitriles **9** and **12**, respectively, also follows the mechanism indicated for the analogous transformation of the bromonitro ethers **14** and **16**.

*Reaction of Halonitro Ethers and 1-*C*-Nitroglycosyl Sulfones with Diethyl-Phosphite Anions.* Treatment of the chloronitromannofuranose **10** with 2.8 equiv. of $KPO(OEt)_2$ gave the nitrile **21** (51%) and the (1-*C*-nitroglycosyl)phosphonate **22** (21%, see above).

The P–C bond in **22** was evidenced by ^1J(P,C(1)) = 192.4 Hz (^{13}C-NMR) and δ(P) = +9.83 ppm (^{31}P-NMR). The assignment of the configuration at C(1) was based on a relation between $^3J(PCCH)$ and the corresponding dihedral angle deduced[7]) by *Tronchet* [37] in the form of $^3J(PCCH) = 24.8\cos^2\theta - 10\cos\theta$. The *A* values of the dimethyl phosphono group (*A* = 2 kcal/mol) [38] and of the NO_2-group (*A* = 0.78 kcal/mol) [39] and the values of the anomeric effect of the dimethylphosphono group (*AE* = 0.56 kcal/mol) [38] and of the NO_2-group (*AE* = 2.2–3.4 kcal/mol) [39] point to a pseudo-equatorial position of the diethylphosphono group in the (1-*C*-nitroglycosyl)phosphonate **22**. A *Dreiding* model of **22** (pseudo-equatorial position of the diethylphosphono group) shows a value of 30° to 45° for the dihedral angle, H–C(2)–C(1)–P, which agrees well with $^3J(HCCP)$ of 7.0 Hz.

The formation of the phosphonate **22** together with the nitrile **21** is interpreted as the result of an initial single-electron transfer competing with a nucleophilic attack[8]). This is consistent with the results reported in the *Table*. The dependence of the two pathways on the nature of the phosphite anions may be correlated with their relative bulk and with the sensitivity of nucleophilic attack to steric hindrance. The diethyl-phosphite anion may have an inherently greater ability to transfer one electron.

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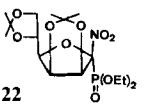
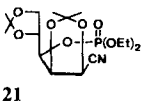
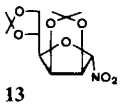
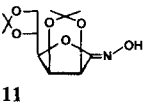
[6]) Attack at the N-atom of the NO_2-group is implied, leading to a substitution with a nitronate anion as the leaving group. This corresponds, at least formally, to an X-philic reaction as delineated by *Zefirov* and *Makhon'kov* [36]. In our case, attack at the O-atom of the NO_2-group is postulated, leading to an addition-elimination sequence. An addition-elimination could also operate in *Russell*s substitution; thus three possibilities (single-electron transfer, nucleophilic attack at N or O) have to be considered for an attack on the NO_2-group in this type of compounds.

[7]) From the study of 3-*C*-alkyl-3-*C*-phosphonopento- and hexofuranoses.

[8]) For other cases of a competition between nucleophilic attack and single-electron transfer, see [35] [40] [42].

Table. *Products and Yields of the Reaction of the Chloro-nitro Ether* **10** *with the Potassium Salt of Diethyl Phosphite under Different Reaction Conditions*

Conditions[a])	Products and yields [%]			
	 **22**	 **21**	 **13**	 **11**
a	21	51	–	–
b	18	52	9	–
c	16	45	14	4
d	< 3	54	16	5
e	4	50	14	4

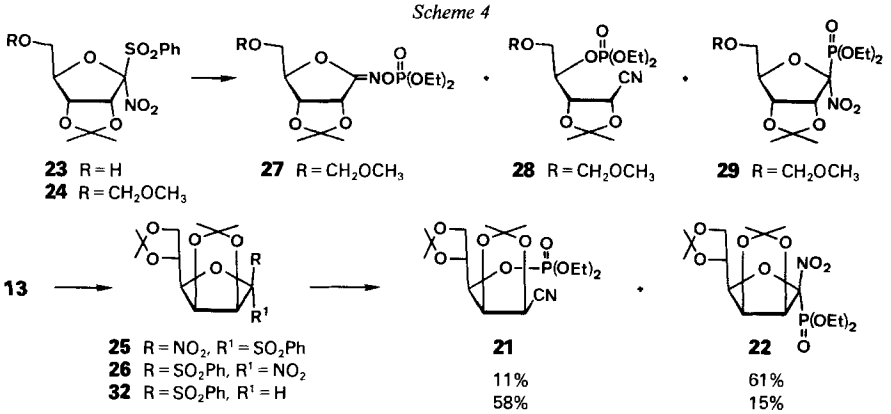
[a]) *a*) Irradiation, −60°, addition of **10** (see *Exper. Part*); *b*) reaction in the dark, −60°, addition as in *a*; *c*) reaction in the dark, −60°, slow inverse addition; *d*) reaction in the dark, −60°, slow inverse addition in the presence of O_2; *e*) as in *d* but with *m*-dinitrobenzene (0.2 mol-equiv. per mole **10**) instead of O_2.

Next we examined the reactions of 1-*C*-nitroglycosyl sulfones with diethyl-phosphite anions. Nitro sulfones, while less reactive towards nucleophilic substitution than nitro halides [41] [42], are still good single-electron acceptors [22] [43]. The 1-*C*-nitroglycosyl sulfone **23** was prepared (61%) from 1-deoxy-2,3-*O*-isopropylidene-1-nitro-β-D-ribofuranose [26] and sodium benzenesulfinate in the presence of $K_3Fe(CN)_6$ [44]. Reaction of **23** with formaldehyde dimethyl acetal in the presence of P_2O_5 gave the 1-*C*-nitroglycosyl-sulfone **24** (97%). The nitro sulfones **25** (38%) and **26** (41%) were obtained from the 1-deoxy-1-nitromannofuranose **13** by treatment first with LiOEt and I_2 and then with sodium benzenesulfinate [45] *(Scheme 4)*. The nitro sulfone **25** was also obtained (45%) from the nitronate anion of **13** with sodium benezenesulfinate in the presence of $K_3Fe(CN)_6$ [44].

The configuration at C(1) of **24**, **25**, and **26** was deduced from a comparison of the chemical shift values of H–C(2) (δ = 5.63 ppm for **24**, 5.64 ppm for **25**, and 5.44 ppm for **26**). The known shielding effect of the NO_2-group on a *cis*-H_{vic} [46] indicates such a configuration for **26**. The H–C(2) signals in the ^{1}H-NMR spectra of **24** and **25** have about the same chemical shift and denote the same configuration for these compounds.

Treatment of the 1-*C*-nitroglycosyl sulfone **24** with $KPO(OEt)_2$ gave three main products: the *O*-amino phosphate **27** (41%), the nitrile **28** (33%) and the (1-*C*-nitroglycosyl)phosphonate **29** (9%; *Scheme 4*).

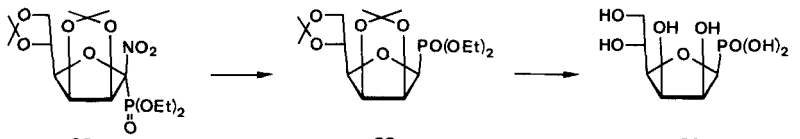
Scheme 4



The ^{1}H-NMR spectrum ($CDCl_3$) of the *O*-amino phosphate **27** again showed the presence of the (*E*)- and (*Z*)-diastereoisomers in a ratio of 1:9 based on the integral of the H–C(2) signals (δ = 5.21 and 5.43 ppm for the major and the minor diastereoisomers, respectively). The P–C bond in **29** was evidenced by ^1J(P,C(1)) = 196.2 Hz (^{13}C-NMR) and δ(P) = +19.19 ppm (^{31}P-NMR). The anomeric configuration of **29** was deduced from the value of $^3J(PCCH)$ (7.0 Hz), as discussed for **16**.

When treated with 3.0 equiv. of $KPO(OEt)_2$, the nitro sulfone **25** possessing an *endo*-NO_2-group gave 11% of the nitrile **21** and 61% of the nitro-phosphonate **22**, whilst under analogous conditions the nitro sulfone **26** possessing an *exo*-NO_2-group gave 58% of **21** and only 15% of **22**. The different ratio of the products **21** and **22** can be explained by the steric hindrance of the *endo*-NO_2-group in **25** which disfavours a single-electron transfer much less than a nucleophilic attack. From the preparative point of view, **25** and **26** being difficult to separate, it proved advantageous to start from a *ca.* 1:1 mixture of **25**/**26**. Using KH in the presence of [18]crown-6 [47] instead of *t*-BuOK, we obtained a 67% yield of **22**.

Scheme 5



22 **30** **31**

The reductive denitration [25] of the (1-*C*-nitroglycosyl)phosphonate **22** with Bu_3SnH in the presence of α,α'-azoisobutyronitrile (AIBN) gave the protected glycosylphosphonate **30** (78%; *Scheme 5*)[9]. In the ^{1}H-NMR spectrum of **30** the value of 3.8 Hz for J(1,2) is consistent with a (β-D-glycosyl)phosphonate. The value of 0 Hz for $^3J(PCCH)$ corresponds with a dihedral angle of 90° [37] and indicates a pseudo-equatorial position of the diethylphosphono group. The glycosylphosphonate **30** was deprotected by treatment with bromotrimethylsilane followed by hydrolysis at 50°. The free phosphonic acid **31** was purified as the barium salt (see *Exper. Part*).

We thank the *Swiss National Science Foundation* and *Sandoz*, Basle, for generous support, and Dr. *J. H. Bieri* and Dr. *R. Prewo* for the X-ray analysis.

Experimental Part

General. See [26]. DMSO was destilled from CaH_2. Bu_3SnH was prepared according to a procedure of *Kuivila* [48]. ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectra were recorded on a *Varian-FT-80A* (^{1}H(80 MHz), ^{13}C(20 MHz)), *Varian-HA-100* (^{13}C(25.2 MHz)), *Varian-XL-200* (^{1}H(200 MHz), ^{13}C(50 MHz), ^{31}P(80 MHz)), or *Bruker-AM-400* spectrometer (^{1}H(400 MHz), ^{13}C(100.6 MHz), ^{31}P(160 MHz)); $CDCl_3$ soln. unless otherwise specified. The chemical shifts are reported in ppm relative to TMS (for ^{1}H-NMR and ^{13}C-NMR) as internal standard or relative to H_3PO_4 (for ^{31}P-NMR) as internal reference (uncorrected). Mass spectra were recorded on a *Varian-711* spectrometer (FAB, bombardement with 8-keV Xe-atoms, glycerol matrix).

1. *(2,3-O-Isopropylidene-5-O-trityl-*D*-ribofuranosylidene)amino Dimethyl Phosphate* (**8**). – 1.1. *From* **14** *with KPO(OMe)$_2$.* A soln. of 228 µl (2.5 mmol) of dimethyl phosphite and 280 mg (2.5 mmol) of *t*-BuOK in 15 ml of THF was stirred under N_2 at r.t. for 15 min, cooled to −40°, and treated with a soln. of 450 mg (0.83 mmol) of **14** in 10 ml of THF. Under irradiation (60-W lamp), the intensive blue mixture was warmed to r.t. (2 h). At −30°, the blue colour disappeared. After evaporation of THF *in vacuo*, the residue was partitioned between AcOEt and brine.

[9]) Similarly, a 1:1 mixture **25**/**26** gave the β-D-glycosyl sulfone **32** (61%; J(1,2) = 3.8 Hz; *Scheme 4*).

Usual workup afforded an oil, which was purified by chromatography (50 g SiO_2, AcOEt/hexane 1:1) to give 40 mg (11%) of **15** and 299 mg (65%) of **8** as a foam, $[\alpha]_D^{25} = -44{,}6°$ (c = 1,13). IR: 3060*w*, 2995*m*, 2950*m*, 2870*w*, 2850*w*, 1675*m*, 1596*w*, 1488*m*, 1448*m*, 1383*m*, 1375*m*, 1355*m*, 1320*w*, 1275*s*, 1153*m*, 1094*s*, 1078*s*, 1044*s*, 1000*s*, 988*s*, 960*s*, 942*s*, 900*m*, 850*m*, 820*m*. ^{1}H-NMR (80 MHz): 7.42–7.07 (*m*, 15 arom. H); 5.56 (*d*, J = 5.8, 0.1H, H–C(2)); 5.34 (*d*, J = 5.8, 0.9H, H–C(2)); 4.78 (*t*, J = 1.7, H–C(4)); 4.65 (*d*, J = 5.8, 0.9H, H–C(3)); 4.55 (*d*, J = 5.8, 0.1H, H–C(3)); 3.83 (*d*, J(P, H) = 11.3, $POCH_3$); 3.72 (*d*, J(P, H) = 11.3, $POCH_3$); 3.80–3.65 (*m*, H–C(5)); 2.98 (*dd*, J = 10.8, 1.7, H–C(5)); 1.47 (*s*, CH_3); 1.33 (*s*, CH_3). ^{13}C-NMR (25.2 MHz): 164.39 (*sd*, J(P, C) = 11.4); 142.65 (*s*); 128.13 (*d*); 127.83 (*d*); 127.12 (*d*); 113.45 (*s*, 0.9 C); 112.95 (*s*, 0.1 C); 87.62 (*s*); 87.37 (*d*); 79.91 (*d*); 78.14 (*d*); 63.28 (*t*); 54.65 (*qd*, J(P, C) = 5.8); 26.65 (*q*); 25.50 (*q*). ^{31}P-NMR (160 MHz): 2.66 (0.23 P); 2.27 (0.77 P). Anal. calc. for $C_{29}H_{32}NO_8P$ (553.36): C 62.92, H 5.83, N 2.52, P 5.59; found: C 62.85, H 5.59, N 2.39, P 5.47.

1.2. *From* **7** *with* $P(OMe)_3$. A soln. of 1 g (2 mmol) of **7** and 0.707 ml (6 mmol) of trimethyl phosphite in 5 ml of CH_2Cl_2 was heated to 70° for 5 h. After concentration, the residue was purified by chromatography (100 g SiO_2, AcOEt/hexane 1:1) to give 1.07 g (96%) of **8**.

2. *2,3-O-Isopropylidene-4-O-dimethoxyphosphoryl-5-O-trityl-*D*-ribononitrile* (**9**). – 2.1. *From* **7** *with* $KPO(OMe)_2$. A soln. of 228 µl (2.5 mmol) of dimethyl phosphite and 280 mg (2.5 mmol) of *t*-BOK in 15 ml of THF was stirred under N_2 for 15 min, cooled to –40°, and treated with a soln. of 411 mg (0.83 mmol) of **7** in 10 ml of THF. Under irradiation (60-W lamp) the colourless mixture was warmed to r.t. (2 h). After concentration, the residue was partitioned between AcOEt and brine. Usual workup afforded an oil, which was purified by chromatography (50 g SiO_2, AcOEt/hexane 1:1) to give 23 mg (5%) of **8** and 276 mg (62%) of **9**, m.p. 124–125°, $[\alpha]_D^{25} = -39.6°$ (c = 1.22). IR: 3085*w*, 3060*w*, 2990*m*, 2950*m*, 2880*w*, 2850*w*, 1595*w*, 1485*w*, 1447*m*, 1383*m*, 1374*m*, 1275*s*, 1153*m*, 1110*m*, 1090*s*, 1057*s*, 1044*s*, 1009*s*, 960*m*, 900*m*, 859*s*. ^{1}H-NMR (200 MHz): 7.6–7.2 (*m*, 15 arom. H); 4.94 (*d*, J = 4.9, H–C(2)); 4.8–4.6 (*m*, H–C(4)); 4.54 (*dd*, J = 7.8, 4.9, H–C(3)); 3.73 (*d*, J(P, H) = 11.2, $POCH_3$); 3.70 (*d*, J(P, H) = 11.2, $POCH_3$); 3.73–3.65 (*m*, H–C(5)); 3.42 (*dd*, J = 10.4, 3.4, H–C(5)); 1.53 (*s*, CH_3); 1.39 (*s*, CH_3). ^{13}C-NMR (25.2 MHz): 143.15 (*s*); 128.56 (*d*); 127.65 (*d*); 127.04 (*d*); 116.39 (*s*); 112.28 (*s*); 86.86 (*s*); 75.94 (*d*); 75.71 (*d*); 75.64 (*d*); 66.95 (*d*); 62.86 (*td*, J(P, C) = 2.0); 54.56 (*qd*, J(P, C) = 5.8); 54.45 (*qd*, J(P, C) = 5.8); 26.77 (*q*); 25.90 (*q*). ^{31}P-NMR (160 MHz): 0.39. Anal. calc. for $C_{29}H_{32}NO_7P$ (537.54): C 64.79, H 6.00, N 2.60, P 5.76; found: C 64.80, H 5.99, N 2.51, P 5.59.

2.2. *From* **8** *with* $KPO(OMe)_2$. A soln. of 500 mg (0.9 mmol) of **8**, 166 µl (1.8 mmol) of dimethyl phosphite and 204 mg (1.8 mmol) of *t*-BuOK in 17 ml of THF was stirred at r.t. for 2 h. After concentration, the residue was partitioned between AcOEt and brine. Usual workup afforded an oil, which was purified by chromatography (50 g SiO_2, AcOEt/hexane 1:1) to give 304 mg (63%) of **9**.

2.3. *From* **19** [27] *with* $KPO(OMe)_2$. A soln. of 500 mg (0.83 mmol) of **19**, 152 µl (1.66 mmol) of dimethyl phosphite and 186 mg (1.66 mmol) of *t*-BuOK in 15 ml of THF was stirred at r.t. for 2 h. Workup as indicated above gave, after chromatography (50 g SiO_2, AcOEt/hexane 1:1), 321 mg (72%) of **9**.

3. *Reaction of* **10** *with the Sodium Salt of Dimethyl Phosphite.* A soln. of 686 µl (7.5 mmol) of dimethyl phosphite and 18 mg (7.5 mmol) of NaH in 17 ml of THF was stirred under N_2 at r.t. for 15 min, cooled to –40°, and treated with a soln. of 1 g (3 mmol) of **10** in 4 ml of THF. Under irradiation (60-W lamp), the colourless mixture was warmed to r.t. (2 h). Concentration, partitioning of the residue between AcOEt and brine, and usual workup afforded an oil, which gave, after chromatography (100 g SiO_2, AcOEt/hexane 1:1), 360 mg (36%) of starting material **10**, 172 mg (21%) of **11**, 109 mg (10%) of **12**, and 104 mg (12%) of **13**.

*2,3:5,6-Di-O-isopropylidene-4-O-dimethoxyphosphoryl-*D*-mannononitrile* (**12**). M.p. 106°, $[\alpha]_D^{25} = +43.5°$ (c = 1.02). IR: 2990*m*, 2960*m*, 2900*w*, 2860*w*, 1453*m*, 1386*s*, 1376*s*, 1275*s*, 1154*s*, 1083*s*, 1030 (br.), 902*m*, 850*s*. ^{1}H-NMR (200 MHz): 4.89 (*d*, J = 4.8, H–C(2)); 4.59 (*ddd*, J = 11.0, 9.0, 8.3, 1H); 4.35–4.00 (*m*, 4H); 3.82 (*d*, J(P, H) = 11.3, $POCH_3$); 3.80 (*d*, J(P, H) = 11.3, $POCH_3$); 1.61 (*s*, CH_3); 1.48 (*s*, CH_3); 1.40 (*s*, CH_3); 1.35 (*s*, CH_3). ^{13}C-NMR (25.2 MHz): 116.54 (*s*); 111.38 (*s*); 110.83 (*s*); 78.32 (*d*); 78.17 (*d*); 77.98 (*d*); 77.77 (*d*); 74.60 (*dd*, J(P, C) = 4.3); 67.79 (*t*); 66.30 (*d*); 54.56 (*qd*, J(P, C) = 6.2); 54.37 (*qd*, J(P, C) = 6.2); 26.85 (*q*); 25.94 (*q*); 25.45 (*q*); 25.24 (*q*). ^{31}P-NMR (80 MHz): 0.24. Anal. calc. for $C_{14}H_{24}NO_8P$ (365.31): C 46.03, H 6.62, N 3.83, P 8.47; found: C 45.99, H 6.85, N 3.59, P. 8.28.

4. *Reaction of* **16** *with the Sodium Salt of Dimethyl Phosphite.* – 4.1. *With 2.5 Equiv. of* $NaPO(OMe)_2$. A soln. of 778 µl (8.5 mmol) of dimethyl phosphite and 20 mg (8.5 mmol) of NaH in 20 ml of THF was stirred under N_2 at r.t. for 15 min, cooled to –40°, and treated with a soln. of 1.25 g (3.4 mmol) of **16** in 5 ml of THF. Under irradiation (60-W lamp), the light blue mixture was warmed to r.t. (2 h). At –30°, disappearance of the blue colour. After concentration the residue was partitioned between AcOEt and brine. Usual workup afforded an oil, which was

purified by chromatography (100 g SiO_2, AcOEt/hexane 1:1) to give 120 mg (13%) of **11**, 583 mg (45%) of **17**, and 74 mg (6%) of **12**.

(2,3:5,6-Di-O-isopropylidene-D-mannofuranosylidene)amino Dimethyl Phosphate (**17**). M.p. 129–130°, $[\alpha]_D^{25} = +82.0°$ ($c = 2.11$). IR: 2990*m*, 2955*m*, 2930*w*, 2890*w*, 2860*w*, 1675*m*, 1450*w*, 1383*m*, 1373*m*, 1275*s*, 1152*m*, 1120*m*, 1068*s*, 1045*s*, 1023*m*, 973*s*, 960*s*, 935*m*, 904*m*, 852*m*. ^{1}H-NMR (200 MHz): 5.46 (*d*, $J = 5.5$, 0.1H, H–C(2)); 5.26 (*d*, $J = 5.5$, 0.9H, H–C(2)); 4.88 (*dd*, $J = 5.5$, 3.2, H–C(3)); 4.44 (*dt*, $J = 8.0$, 4.5, H–C(5)); 4.36 (*dd*, $J = 8.0$, 3.2, H–C(4)); 4.15 (*dd*, $J = 9.2$, 4.5, H–C(6)); 4.09 (*dd*, $J = 9.2$, 4.5, H–C(6)); 3.82 (*d*, J(P, H) = 11.0, $POCH_3$); 3.81 (*d*, J(P, H) = 11.0, $POCH_3$); 1.45 (*s*, CH_3); 1.41 (*s*, CH_3); 1.36 (*s*, CH_3); 1.34 (*s*, CH_3). ^{13}C-NMR (25.2 MHz): 163.32 (*sd*, J(P, C) = 10.9); 114.56 (*s*); 109.72 (*s*); 83.61 (*d*, 0.9 C); 83.10 (*d*, 0.1 C); 77.97 (*d*); 77.41 (*d*); 72.46 (*d*); 66.30 (*t*); 55.02 (*qd*, J(P, C) = 5.7); 54.80 (*qd*, J(P, C) = 5.0); 26.89 (*q*); 26.78 (*q*); 25.84 (*q*); 25.14 (*q*). ^{31}P-NMR (80 MHz): 2.53 (0.83 P); 2.25 (0.17 P). Anal. calc. for $C_{14}H_{24}NO_9P$ (381.33): C 44.09, H 6.34, N 3.67, P 8.12; found: C 44.28, H 6.59, N 3.39, P 8.40.

4.2. *With 4.0 Equiv. of NaPO(OMe)$_2$.* Similarly, treatment of 1.24 ml (13.6 mmol) of dimethyl phosphite and 32 mg (13.6 mmol) of NaH in 20 ml of THF with a soln. of 1.25 g (3.4 mmol) of **16** in 5 ml of THF gave, after chromatography (100 g SiO_2, AcOEt/hexane 1:1), 944 mg (76%) of **12**.

5. *Preparation of* **17**. – 5.1. *From the Bromonitro Compound* **16** *with P(OMe)$_3$.* A soln. of 1 g (2.7 mmol) of **16** and 1 ml (8.4 mmol) of trimethyl phosphite in 5 ml of CH_2Cl_2 was heated to 70° for 3 h. After concentration, the residue was purified by chromatography (100 g SiO_2, AcOEt/hexane 1:1) to give 906 mg (88%) of **17**.

5.2. *From* **11** [27] *with CIPO(OMe)$_2$.* To a soln. of 274 mg (1 mmol) of **11** and 48 mg (1.2 mmol) of NaOH in 1 ml of H_2O was added dropwise at r.t. 144 mg (1 mmol) of dimethyl phosphorochloridate. The mixture was stirred for 2 h and extracted with AcOEt. Usual workup afforded a residue which was purified by chromatography (30 g SiO_2, AcOEt/hexane 1:1) to give 163 mg (43%) of **17**.

5.3. *From* **11** *with* N-*Bromosuccinimide and NaPO(OMe)$_2$.* A soln. of 200 mg (0.7 mmol) of **11** in 2 ml of Et_2O was added dropwise during 15 min to a stirred suspension at 5° of 195 mg (1.05 mmol) of *N*-bromosuccinimide and 82 mg (1 mmol) of NaOAc in 1.5 ml of H_2O. After 1 h, the mixture was extracted with AcOEt. After drying of the soln. and concentration, the blue-green residue was rapidly taken up in 1 ml of THF, cooled to –78° and treated with a soln. of 73 µl (0.8 mmol) of dimethyl phosphite and 18 mg (0.76 mmol) of NaH in 2 ml of THF. The colourless mixture was immediately warmed to r.t. and partitioned between AcOEt and brine. Usual workup afforded an oil, which was purified by chromatography (20 g SiO_2, AcOEt/hexane 1:1) to give 135 mg (48%) of **17**.

6. *Transesterification of* **17**. A soln. of 100 mg (0.26 mmol) of **17** and 36 mg (0.52 mmol) of NaOEt in 2 ml of EtOH was stirred at r.t. for 1 h. After concentration, the residue was partitioned between AcOEt and brine. Usual workup followed by chromatography (10 g SiO_2, AcOEt/hexane 1:1) gave 60 mg (84%) of **11**.

7. *Reaction of* **10** *with the Potassium Salt of Diethyl Phosphite.* A soln. of 3.09 ml (24 mmol) of diethyl phosphite and 2.6 g (23 mmol) of *t*-BuOK in 5 ml of THF was stirred under N_2 at r.t. for 15 min. After cooling to –60°, the mixture was treated under irradiation (60-W lamp) with a soln. of 2.62 g (8.1 mmol) of **10** in 10 ml of THF and warmed to r.t. (2 h). Concentration, partitioning of the residue between AcOEt and brine, normal workup, and chromatography (250 g SiO_2, AcOEt/hexane 1:1) gave 1.62 g (51%) of **21** and 0.714 g (21%) of **22**.

4-O-Diethoxyphosphoryl-2,3:5,6-di-O-isopropylidene-D-mannononitrile (**21**). M.p. 53–54°, $[\alpha]_D^{25} = +42.6°$ ($c = 1.12$). IR: 2985*s*, 2938*m*, 2900*m*, 1450*w*, 1444*w*, 1383*m*, 1373*s*, 1260*s*, 1150*s*, 1080*s*, 1025*s*, 980*s*, 890*m*, 852*m*, 840*m*. ^{1}H-NMR (200 MHz): 4.90 (*d*, $J = 5.0$, H–C(2)); 4.61 (*dt*, $J = 10.0$, 9.0, 1H); 4.45–4.00 (*m*, 8H); 1.60 (*s*, CH_3); 1.47 (*s*, CH_3); 1.39 (*s*, CH_3); 1.35 (*s*, CH_3); 1.34 (*t*, $J = 6.7$, 2 CH_3). ^{13}C-NMR (25.2 MHz): 116.58 (*s*); 111.24 (*s*); 110.71 (*s*); 78.32 (*dd*, J(P, C) = 3.6); 77.63 (*dd*, J(P, C) = 5.2); 74.71 (*dd*, J(P, C) = 4.2); 67.92 (*t*); 66.29 (*d*); 64.02 (*td*, J(P, C) = 6.2); 63.86 (*td*, J(P, C) = 6.2); 26.81 (*q*); 25.87 (*q*); 25.44 (*q*); 25.24 (*q*); 16.03 (*q*); 15.74 (*q*). ^{31}P-NMR (80 MHz): –2.10. Anal. calc. for $C_{16}H_{28}NO_8P$ (393.39): C 48.85, H 7.18, N 3.55, P 7.87; found: C 48.58, H 7.16, N 3.61, P 7.65.

Diethyl (2,3:5,6-Di-O-isopropylidene-1-nitro-α-D-mannofuranosyl)phosphonate (**22**). M.p. 141–142°, $[\alpha]_D^{25} = +47.5°$ ($c = 1.24$). IR: 2985*s*, 2938*m*, 2910*m*, 2890 (sh), 1573*s*, 1477*w*, 1452*w*, 1442*w*, 1380*s*, 1372*s*, 1350*m*, 1327*m*, 1255*s*, 1159*s*, 1148 (sh), 1123*m*, 1090*s*, 1068*s*, 1045*s*, 1023*s*, 970*m*, 952 (sh), 885*m*, 860*m*, 840*m*. ^{1}H-NMR (200 MHz): 5.27 (*dd*, J(P, H) = 7.0, $J = 5.8$, H–C(2)); 4.92 (*dd*, $J = 5.8$, 4.0, H–C(3)); 4.65 (*dt*, $J = 8.0$, 5.0, H–C(5)); 4.41 (*dd*, $J = 8.0$, 4.0, H–C(4)); 4.33 (*dq*, J(P, H) = 8.0, $J = 7.0$, $POCH_2$); 4.30 (*dq*, J(P, H) = 8.0, $J = 7.0$, $POCH_2$); 4.30–4.10 (*m*, 2H–C(6)); 1.46–1.33 (*m*, 6 CH_3). ^{13}C-NMR (25.2 MHz): 112.94 (*sd*, J(P, C) = 192.4); 115.37 (*s*); 109.48 (*s*); 83.85 (*d*); 83.73 (*d*); 83.62 (*d*); 83.51 (*d*); 79.17 (*d*); 72.69 (*dd*, J(P, C) = 1.4); 66.58 (*t*); 65.65 (*qd*, J(P, C) = 6.8); 64.98 (*qd*, J(P, C) = 7.3); 26.89 (*q*); 25.31 (*q*); 25.29 (*q*); 24.44 (*q*); 16.52 (*qd*, J(P, C) = 2.1); 16.30 (*qd*, J(P, C) = 1.4). ^{31}P-NMR (160 MHz): 9.83. Anal. calc. for $C_{16}H_{28}NO_{10}P$ (425.39): C 45.17, H 6.64, N 3.30, P 7.28; found: C 45.30, H 6.70, N 3.11, P 7.15.

8. *Phenyl (2,3-O-Isopropylidene-1-nitro-β-D-ribofuranosyl) Sulfone* (**23**). A soln. of 1 g (4.56 mmol) of 1-deoxy-2,3-*O*-isopropylidene-1-nitro-β-D-ribofuranose [26] and 270 mg (5.0 mmol) of NaOMe in 20 ml of EtOH was stirred at r.t. for 30 min. After concentration, the residue was taken up in 9 ml of H_2O and mixed with 3.3 g (20 mmol) of sodium benzenesulfinate and 60 ml of toluene. To the stirred mixture, a soln. of 4.28 g (13 mmol) of $K_3Fe(CN)_6$ in 12 ml of H_2O was added dropwise over 15 min. After an additional 20 min, the org. phase was isolated and the aq. phase extracted with AcOEt. Drying ($MgSO_4$) of the combined org. phases, concentration, and chromatography of the residue (100 g SiO_2, AcOEt/hexane/toluene 1:1:1) gave, after crystallisation from AcOEt/hexane 1 g (61%) of **23**. M.p. 153–154°, $[\alpha]_D^{25} = -48.4°$ ($c = 0.87$ in MeOH). IR: 3510 (br.), 2980*w*, 2940*w*, 2875*w*, 1597 (sh), 1578*s*, 1448*m*, 1384*m*, 1375*m*, 1330*m*, 1312 (sh), 1265*m*, 1210 (br.), 1172*s*, 1144*s*, 1090*s*, 1082*s*, 1000*m*, 923*m*, 852*m*. ^{1}H-NMR (80 MHz, $(CD_3)_2SO$): 8.0–7.5 (*m*, 5 arom. H); 5.52 (*d*, $J = 5.6$, H–C(2)); 5.02 (*t*, $J = 4.3$, HO–C(5)); 4.92 (*d*, $J = 5.6$, H–C(3)); 4.80 (*t*, $J = 2.8$, H–C(4)); 3.75–3.25 (*m*, 2H–C(5)); 1.47 (*s*, CH_3); 1.29 (*s*, CH_3). ^{13}C-NMR (20 MHz, $(CD_3)_2SO$): 135.22 (*d*); 134.50 (*s*); 130.51 (*d*); 129.03 (*d*); 125.69 (*s*); 113.93 (*s*); 91.40 (*d*); 86.90 (*d*); 81.45 (*d*); 61.22 (*t*); 24.47 (*q*); 23.96 (*q*). MS: 344 (11), 218 (20), 173 (5), 143 (5), 141 (11), 127 (5), 126 (11), 125 (100), 115 (7), 114 (5), 97 (9), 91 (12), 88 (9), 85 (26), 78 (11), 77 (56), 69 (12), 59 (46), 57 (22), 43 (99). Anal. calc. for $C_{14}H_{17}NO_8S$ (359.4): C 46.78, H 4.77, N 3.89, S 8.92; found: C 47.00, H 4.91, N 3.79, S 8.77.

9. *Phenyl (2,3-O-Isopropylidene-5-O-methoxymethyl-1-nitro-β-D-ribofuranosyl) Sulfone* (**24**). A stirred soln. of 200 mg (0.55 mmol) of **23** and 493 µl (5.5 mmol) of formaldehyde dimethyl acetal in 5 ml of CH_2Cl_2 was treated with 500 mg of P_2O_5 (50 mg every 10 min). After 1 h, 50 ml of CH_2Cl_2 was added, and the soln. was washed with sat. aq. $NaHCO_3$. Drying ($MgSO_4$), concentration, and chromatography of the residue (20 g SiO_2, AcOEt/hexane 1:2) gave 218 mg (97%) of **24**, which was crystallized from CH_2Cl_2/hexane. M.p. 113–114°, $[\alpha]_D^{25} = -29.7°$ ($c = 1.11$). IR: 2990*w*, 2940*w*, 2890*w*, 2825*w*, 1570*s*, 1449*w*, 1385*m*, 1353*s*, 1338 (sh), 1314*w*, 1270*w*, 1172*m*, 1150*s*, 1118*m*, 1082*s*, 1063*m*, 1020*s*, 970*w*, 918*w*, 860*m*. ^{1}H-NMR (80 MHz): 8.1–7.4 (*m*, 5 arom. H); 5.63 (*d*, $J = 5.7$, H–C(2)); 4.93 (*t*, $J = 2.4$, H–C(4)); 4.87 (*d*, $J = 5.7$, H–C(3)); 4.32 (*s*, 2H); 3.74 (*dd*, $J = 11.3$, 2.4, H–C(5)); 3.56 (*dd*, $J = 11.3$, 2.4, H–C(5)); 3.23 (*s*, CH_3O); 1.68 (*s*, CH_3); 1.40 (*s*, CH_3). ^{13}C-NMR (20 MHz): 134.82 (*d*); 134.36 (*s*); 130.61 (*d*); 128.59 (*d*); 125.35 (*s*); 114.99 (*s*); 96.37 (*t*); 89.26 (*d*); 87.36 (*d*); 81.52 (*d*); 67.90 (*t*); 55.63 (*q*); 24.62 (*q*); 24.07 (*q*). MS: 388 (4), 327 (3), 173 (1), 159 (1), 143 (2), 141 (2), 125 (19), 85 (7), 77 (10), 69 (4), 59 (11), 45 (100). Anal. calc. for $C_{16}H_{21}NO_9S$ (403.41): C 47.63, H 5.25, N 3.47, S 7.94; found: C 47.72, H 5.13, N 3.28, S 7.85.

10. *Reaction of* **24** *with the Potassium salt of Diethyl Phosphite.* A suspension of 297 mg (7.41 mmol) of KH, 953 µl (7.41 mmol) of diethyl phosphite and 1.95 g (7.41 mmol) of [18]crown-6 in 6 ml of THF was stirred under N_2 at r.t. for 30 min, cooled to –40°, and treated with a soln. of 1 g (2.47 mmol) of **24** in 4 ml of THF. Under irradiation (60-W lamp), the mixture was warmed to r.t. (2 h). After concentration, the residue was partitioned between AcOEt and brine. Usual workup afforded an oil, which was purified by chromatography (100 g SiO_2, CH_2Cl_2/hexane/CH_3CN 1:1:0.3) to give 388 mg (41%) of **27**, 299 mg (33%) of **28**, and 89 mg (9%) of **29**.

Diethyl (2,3-O-Isopropylidene-5-O-methoxymethyl-D-ribofuranosylidene)amino Phosphate (**27**). M.p. 69–70°, $[\alpha]_D^{25} = -104.6°$ ($c = 1.03$). IR: 2995*s*, 2940*m*, 2915*m*, 2895*w*, 2875*w*, 2830*w*, 1679 (br.), 1476*w*, 1453*m*, 1442*m*, 1384*m*, 1376*m*, 1358*m*, 1270*s*, 1153*s*, 1117*s*, 1100*s*, 1060 (br.), 1025 (br.), 988*s*, 965*s*, 940*s*, 919*s*, 870*m*. ^{1}H-NMR (200 MHz): 5.43 (*d*, $J = 5.6$, 0.1 H, H–C(2)); 5.21 (*d*, $J = 5.6$, 0.9 H, H–C(2)); 4.82 (*dd*, $J = 2.4$, 1.9, H–C(4)); 4.79 (*d*, $J = 5.6$, H–C(3)); 4.60, 4.55 (*AB*, $J = 6.5$, 2H); 4.26–4.17 (*m*, 4H); 3.81 (*dd*, $J = 11.1$, 2.4, H–C(5)); 3.70 (*dd*, $J = 11.1$, 1.9, H–C(5)); 3.33 (*s*, CH_3O); 1.48 (*s*, CH_3); 1.38 (*s*, CH_3); 1.35 (*t*, $J = 7.1$, 2 CH_3). ^{13}C-NMR (100.6 MHz): 164.16 (*sd*, J(P, C) = 11.2); 113.64 (*s*); 96.46 (*t*); 86.76 (*d*); 79.67 (*d*); 78.04 (*d*); 66.69 (*t*); 64.51 (*td*, J(P, C) = 6.0); 64.30 (*td*, J(P, C) = 6.0); 55.44 (*q*); 26.77 (*q*); 25.60 (*q*); 16.04 (*q*); 15.98 (*q*). ^{31}P-NMR (160 MHz): 0.53 (0.87 P); 0.05 (0.13 P). Anal. calc. for $C_{14}H_{26}NO_9P$ (383.33): C 43.86, H 6.83, N 3.65, P 8.08; found: C 43.57, H 6.89, N 3.40, P 8.20.

4-O-Diethoxyphosphoryl-2,3-O-isopropylidene-5-O-trityl-D-ribononitrile (**28**). M.p. 53–54° $[\alpha]_D^{25} = -41.4°$ ($c = 1.13$). IR: 2990*s*, 2940*m*, 2910*m*, 2890*m*, 2830*w*, 2790*w*, 1475*w*, 1452*m*, 1442*m*, 1385*s*, 1377*s*, 1340*w*, 1265 (br.), 1150*s*, 1120*s*, 1090*s*, 1030 (br.), 985*s*, 963 (sh), 919*m*, 860*m*, 820*m*. ^{1}H-NMR (200 MHz): 4.95 (*d*, $J = 5.0$, H–C(2)); 4.76–4.60 (*m*, H–C(4)); 4.68 (*s*, 2H); 4.41 (*dd*, $J = 8.2$, 5.0, H–C(3)); 4.24–4.10 (*m*, 4H); 4.04 (*dd*, $J = 11.5$, 2.6, H–C(5)); 3.85 (*dd*, $J = 11.5$, 3.3, H–C(5)); 3.38 (*s*, CH_3O); 1.58 (*s*, CH_3); 1.39 (*s*, CH_3); 1.35 (*t*, $J = 7.1$, 2 CH_3). ^{13}C-NMR (50.3 MHz): 116.42 (*s*); 112.50 (*s*); 96.53 (*t*); 75.69 (*dd*, J(P, C) = 9.3); 75.36 (*dd*, J(P, C) = 5.3); 67.04 (*d*); 66.48 (*t*); 64.25 (*td*, J(P, C) = 5.8); 64.17 (*td*, J(P, C) = 6.0); 55.28 (*q*); 26.75 (*q*); 25.86 (*q*); 16.03 (*q*); 15.90 (*q*). ^{31}P-NMR (80 MHz): –2.13. Anal. calc. for $C_{14}H_{26}NO_8P$ (367.33): C 45.77, H 7.13, N 3.81, P 8.43; found: C 45.48, H 7.40, N 3.55, P 8.20.

Diethyl (2,3-O-Isopropylidene-5-O-methoxymethyl-1-nitro-β-D-ribofuranosyl)phosphonate (**29**). $[\alpha]_D^{25} = -16.9°$ ($c = 0.95$). IR: 2995*s*, 2940*m*, 2895*m*, 2830*w*, 1570*s*, 1475*w*, 1453*m*, 1442*m*, 1386*s*, 1378*s*, 1330*m*, 1264*s*, 1150*s*, 1102*s*, 1082*s*, 1050 (br.), 1020 (br.), 980*s*, 950*s*, 917*m*, 890*m*, 860*s*. ^{1}H-NMR (200 MHz): 5.18 (*dd*, J(P, H) = 7.0,

J = 6.8, H–C(2)); 5.00 (*ddd*, J = 4.3, 4.2, 3.6, H–C(4)); 4.86 (*dd*, J = 6.8, 3.6, H–C(3)); 4.67 (*s*, 2H); 4.45–4.10 (*m*, 4H); 3.83 (*dd*, J = 11.0, 4.2, H–C(5)); 3.76 (*dd*, J = 11.0, 4.3, H–C(5)); 3.38 (*s*, CH_3O); 1.42 (*s*, CH_3); 1.36 (*t*, J = 7.1, 2 CH_3); 1.35 (*s*, CH_3). ^{13}C-NMR (50.3 MHz): 116.94 (*s*); 113.83 (*sd*, J(P, C) = 196.2); 96.89 (*t*); 87.21 (*dd*, J(P, C) = 8.4); 83.82 (*dd*, J(P, C) = 5.2); 80.96 (*dd*, J(P, C) = 4.8); 66.55 (*t*); 65.46 (*td*, J(P, C) = 6.5); 65.07 (*td*, J(P, C) = 6.5); 55.49 (*q*); 26.12 (*q*); 24.98 (*q*); 16.44 (*q*); 16.33 (*q*). ^{31}P-NMR (80 MHz): 19.19. Anal. calc. for $C_{14}H_{26}NO_{10}P$ (399.33): C 42.10, H 6.56, N 3.50, P 7.75; found: C 42.05, H 6.81, N 3.40, P 7.50.

11. *Phenyl (2,3:5,6-Di-O-isopropylidene-1-nitro-α- and β-*D*-mannofuranosyl) Sulfone* (**25** and **26**, resp.). – 11.1. In a stirred soln. of 4 g (13.8 mmol) of **13** in 15 ml of EtOH, 770 mg (14.8 mmol) of LiOEt were dissolved. The soln. was concentrated under reduced pressure and the resulting white solid again dissolved in 40 ml of H_2O and cooled (ice-bath). To this soln. a soln. of 3.8 g (13.8 mmol) of I_2 in 30 ml of Et_2O was rapidly added under stirring. The resulting colourless to pale yellow Et_2O phase was isolated, and the aq. phase was extracted with 2 × 30 ml of Et_2O. After drying of the Et_2O phase and concentration, the yellow residue was taken up in 20 ml of DMF and added rapidly under N_2 to a cooled (–20°) suspension of 4.6 g (28 mmol) of sodium benzenesulfinate in 40 ml of DMF. The mixture was stirred in the dark for 4 h. The resulting yellow mixture was concentrated and partitioned between AcOEt and brine. Normal workup followed by chromatography (400 g SiO_2, $CHCl_3$) gave 2.25 g (38%) of **25** and 2.42 g (41%) of **26**.

Data of **25**. M.p. 150.5–151.5°, $[\alpha]_D^{25}$ = +129.8° (c = 1.09). IR: 3060*w*, 3037*w*, 2990*m*, 2940*m*, 2900*w*, 1585*s*, 1580*s*, 1480*w*, 1450*m*, 1383*s*, 1375*s*, 1340*s*, 1335*s*, 1315*m*, 1260*m*, 1177*s*, 1160*s*, 1148*s*, 1121*s*, 1090*s*, 1070*s*, 1040*m*, 1023*m*, 1000*m*, 988*m*, 970*m*, 957*m*, 890*m*, 860*m*. ^{1}H-NMR (200 MHz): 7.93–7.55 (*m*, 5 arom. H); 5.64 (*d*, J = 5.7, H–C(2)); 5.04 (*dd*, J = 5.7, 4.0, H–C(3)); 4.70 (*dd*, J = 6.5, 4.0, H–C(4)); 4.53 (*dt*, J = 6.5, 5.0, H–C(5)); 4.14 (*d*, J = 5.0, 2H–C(6)); 1.43 (*s*, CH_3); 1.40 (*s*, CH_3); 1.37 (*s*, 2 CH_3). ^{13}C-NMR (20 MHz): 135.51 (*d*); 132.37 (*s*); 130.58 (*d*); 129.26 (*d*); 122.13 (*s*); 115.60 (*s*); 109.55 (*s*); 85.83 (*d*); 81.87 (*d*); 79.25 (*d*); 72.51 (*d*); 66.11 (*t*); 26.53 (*q*); 26.21 (*q*); 25.16 (*q*); 24.19 (*q*). MS: 414 (3), 244 (2), 243 (11), 185 (6), 157 (5), 149 (7), 143 (5), 125 (15), 101 (22), 88 (15), 85 (10), 77 (14), 69 (12), 57 (40), 43 (100). Anal. calc. for $C_{18}H_{23}NO_9S$ (429.45): C 50.34, H 5.40, N 3.25, S 7.46; found: C 50.15, H 5.27, N 3.19, S 7.39.

Data of **26**. M.p. 164–164°, $[\alpha]_D^{25}$ = +13.1° (c = 1.2). IR: 2985*m*, 2940*w*, 2890*w*, 1570*s*, 1449*m*, 1383*s*, 1375*s*, 1354*s*, 1340 (sh), 1315*m*, 1263*m*, 1180*s*, 1162*s*, 1118*m*, 1084*s*, 1070*s*, 999*m*, 972*m*, 963*m*, 953*m*, 862*m*, 840*m*. ^{1}H-NMR (200 MHz): 7.97–7.50 (*m*, 5 arom. H); 5.44 (*d*, J = 5.7, H–C(2)); 4.86 (*dd*, J = 5.7, 4.0, H–C(3)); 4.41 (*dt*, J = 6.4, 5.0, H–C(5)); 4.28 (*dd*, J = 6.4, 4.0, H–C(4)); 4.08 (*d*, J = 5.0, 2H–C(6)); 1.47 (*s*, CH_3); 1.44 (*s*, CH_3); 1.36 (*s*, CH_3); 1.34 (*s*, CH_3). ^{13}C-NMR (20 MHz): 135.08 (*s* and *d*); 131.12 (*d*); 128.62 (*d*); 123.60 (*s*); 115.49 (*s*); 109.24 (*s*); 86.74 (*d*); 85.62 (*d*); 78.96 (*d*); 72.27 (*d*); 65.92 (*t*); 26.57 (*q*); 24.93 (*q*); 24.49 (*q*); 23.84 (*q*). MS: 415 (2), 414 (7), 243 (1), 225 (7), 184 (2), 164 (2), 155 (3), 143 (2), 141 (4), 125 (39), 109 (9), 101 (27), 77 (14), 43 (100). Anal. calc. for $C_{18}H_{23}NO_9S$ (429.45): C 50.34, H 5.40, N 3.25, S 7.46; found: C 50.41, H 5.41, N 3.22, S 7.30.

11.2. A soln. of 1 g (3.45 mmol) of **13** in 4 ml of EtOH and 193 mg (3.7 mmol) of LiOEt was concentrated under reduced pressure. The resulting white solid was dissolved in 5 ml of H_2O and mixed with 2.29 g (14 mmol) of sodium benzenesulfinate and 20 ml of toluene. To this stirred mixture, a soln. of 2.88 g (8.7 mmol) of $K_3Fe(CN)_6$ in 5 ml of H_2O was added dropwise under N_2 at r.t. After an additional 20 min, workup with AcOEt followed by chromatography (100 g SiO_2, AcOEt/hexane 1:1) gave 666 mg (45%) of **25**.

12. *Reaction of* **25** *and* **26** *with the Potassium Salt of Diethyl-Phosphite.* – 12.1. To a stirred suspension of 449 µl (3.48 mmol) of diethyl phosphite and 390 mg (3.48 mmol) of *t*-BuOK in 3 ml of THF under N_2 at –40°, a soln. of 500 mg (1.16 mmol) of a *ca.* 1:1 mixture of **25**/**26** in 2 ml of THF was added. Under irradiation (60-W lamp), the mixture was warmed to r.t. (2 h). Concentration, partitioning of the residue between AcOEt and brine, usual workup, and chromatography (50 g SiO_2, AcOEt/hexane 1:1) gave 160 mg (35%) of **21** and 183 mg (37%) of **22**.

12.2. Similarly, treatment of 100 mg (0.23 mmol) of **25** in 0.4 ml of THF with 90 µl (0.7 mmol) of diethyl phosphite and 78 mg (0.7 mmol) of *t*-BuOK in 0.6 ml of THF gave after chromatography (10 g SiO_2, AcOEt/hexane 1:1) 10 mg (11%) of **21** and 60 mg (61%) of **22**.

12.3. Treatment as under *12.1* of 100 mg (0.23 mmol) of **26** in 0.4 ml of THF with 90 µl (0.7 mmol) of diethyl phosphite and 78 mg (0.7 mmol) of *t*-BuOK in 0.6 ml of THF gave, after chromatography (10 g SiO_2, AcOEt/hexane 1:1), 57 mg (58%) of **21** and 15 mg (15%) of **22**.

12.4. To a stirred suspension of 449 µl (3.48 mmol) of diethyl phosphite under N_2 at –40°, 140 mg (3.48 mmol) of KH, and 920 mg (3.48 mmol) of [18]crown-6 in 6 ml of THF, a soln. of 500 mg (1.16 mmol) of a *ca.* 1:1 mixture **25**/**26** in 2 ml of THF was added. Under irradiation (60-W lamp) the mixture was warmed to r.t. (2 h). After concentration, the residue was partitioned between AcOEt and brine. Usual workup followed by chromatography (50 g SiO_2, AcOEt/hexane 1:1) gave 60 mg (13%) of **21** and 330 mg (67%) of **22**.

13. *Phenyl (2,3:5,6-Di-O-isopropylidene-α-D-mannofuranosyl) Sulfone* (**32**). Freshly distilled Bu_3SnH (1.15 ml, 4.33 mmol) and 37.5 mg (0.23 mmol) of AIBN in 10 ml of toluene was added dropwise under Ar over 1 h to a boiling soln. of 500 mg (1.16 mmol) of a *ca.* 1:1 mixture **25**/**26** in 20 ml of toluene. After an additional 4 h, the mixture was cooled and concentrated. The residue was purified by chromatography (40 g SiO_2, AcOEt/hexane/toluene 1:1:1) to give 272 mg (61%) of **32**. M.p. 119.5–120.5°, $[\alpha]_D^{25} = +46.6°$ ($c = 0.98$). IR: 3030*w*, 2985*m*, 2940*w*, 2880*w*, 1584*w*, 1479*w*, 1448*m*, 1382*m*, 1372*m*, 1322*s*, 1310 (sh), 1250*m*, 1153*s*, 1145*s*, 1113*s*, 1083*m*, 1068*s*, 1050 (sh), 1016*w*, 997*w*, 971*w*, 946*w*, 882*m*, 858*m*, 837*m*. ^{1}H-NMR (80 MHz): 8.1–7.3 (*m*, 5 arom. H); 5.08 (*dd*, $J = 5.6$, 3.8, H–C(2)); 4.74 (*dd*, $J = 5.6$, 3.8, H–C(3)); 4.56 (*d*, $J = 3.8$, H–C(1)); 4.34 (*dt*, $J = 6.3$, 5.6, H–C(5)); 4.00 (*d*, $J = 5.6$, 2H–C(6)); 3.72 (*dd*, $J = 6.3$, 3.8, H–C(4)); 1.41 (*s*, CH_3); 1.35 (*s*, CH_3); 1.25 (*s*, CH_3); 1.04 (*s*, CH_3). ^{13}C-NMR (20 MHz): 140.40 (*s*); 135.17 (*d*); 131.18 (*d*); 129.85 (*d*); 115.55 (*s*); 110.60 (*s*); 95.70 (*d*); 84.12 (*d*); 81.50 (*d*); 81.22 (*d*); 74.23 (*d*); 67.70 (*t*); 28.18 (*q*); 26.66 (*q*); 25.86 (*q*); 25.40 (*q*). MS: 370 (5), 369 (24), 185 (28), 167 (10), 145 (10), 141 (10), 127 (15), 125 (49), 101 (53), 99 (12), 95 (7), 85 (23), 77 (26), 71 (10), 69 (12), 59 (22), 57 (10), 43 (100). Anal. calc. for $C_{18}H_{24}O_7S$ (384.46): C 56.23, H 6.30, S 8.34; found: C 56.44, H 6.59, S 8.51.

14. *Diethyl (2,3:5,6-Di-O-isopropylidene-β-D-mannofuranosyl)phosphonate* (**30**). Freshly distilled Bu_3SnH (1.5 ml, 5.65 mmol) and 40 mg of AIBN (0.24 mmol) in 12 ml of toluene was added dropwise under Ar over 3 h to a boiling soln. of 500 mg (1.17 mmol) of **22** in 30 ml of toluene. After an additional 3 h, the mixture was cooled and concentrated. The residue was purified by chromatography (40 g SiO_2, AcOEt) to give 350 mg (78%) of **30**. $[\alpha]_D^{25} = +7.0°$ ($c = 1.12$). IR: 2987*s*, 2930*m*, 2870*w*, 1452*w*, 1442*w*, 1382*m*, 1372*m*, 1253*m*, 1160*m*, 1109*m*, 1063*s*, 1048*s*, 1028*s*, 967*m*, 945*m*, 884*m*, 860*m*, 840*m*. ^{1}H-NMR (200 MHz): 4.98 (*dd*, $J = 6.0$, 3.8, H–C(2)); 4.78 (*dd*, $J = 6.0$, 3.7, H–C(3)); 4.44 (*dt*, $J = 8.0$, 5.0, H–C(5)); 4.45–4.10 (*m*, 6H); 3.80 (*dd*, J(P, H) = 10.0, $J = 3.8$, H–C(1)); 3.54 (*ddd*, J(P, H) = 0.8, $J = 8.0$, 3.7, H–C(4)); 1.52 (*s*, CH_3); 1.44 (*s*, CH_3); 1.37 (*s*, 2 CH_3); 1.34 (*t*, $J = 7.0$, 2 CH_3). ^{13}C-NMR (100.6 MHz): 113.17 (*s*); 109.17 (*s*); 84.17 (*dd*, J(P, C) = 16.5); 81.48 (*dd*, J(P, C) = 3.5); 80.26 (*dd*, J(P, C) = 9.3); 78.08 (*dd*, J(P, C) = 172.7); 72.90 (*d*); 66.85 (*t*); 62.93 (*td*, J(P, C) = 6.0); 62.37 (*td*, J(P, C) = 6.0); 26.89 (*q*); 25.53 (*q*); 25.26 (*q*); 24.25 (*q*); 16.47 (*qd*, J(P, C) = 5.1); 16.33 (*qd*, J(P, C) = 5.8). ^{31}P-NMR (160 MHz): 17.06. Anal. calc. for $C_{11}H_{29}O_8P$ (380.40): C 50.52, H 7.69, P 8.14; found: C 50.25, H 7.87, P 7.99.

Barium Salt of (β-D-Mannofuranosyl)phosphonic Acid (**31**). Bromotrimethylsilane (544 µl, 4.2 mmol) was added dropwise under N_2 over 15 min to a soln. of 400 mg (1.05 mmol) of **30** in 10 ml of CH_2Cl_2. The mixture was stirred at r.t. for 2 h. After concentration and drying under high vacuum (2 h), the residue was taken up in 10 ml of H_2O and heated to 50° for 4 h. The mixture was cooled and washed with 3 × 2 ml of Et_2O. The aq. phase was treated with 332 mg (1.05 mmol) of $Ba(OH)_2 \cdot 8H_2O$ and lyophilized. The resulting powder was dissolved in 5 ml of EtOH and 353 mg (88%) of the barium salt of **31** precipitated. M.p. > 250°, $[\alpha]_D^{25} = -4.0°$ ($c = 1.18$, H_2O/HCl). IR (KBr): 3600–2600*s*, 1640*w*, 1440*w*, 1385*w*, 1350*w*, 1258*w*, 1242*w*, 1210*w*, 1163*m*, 1138*m*, 1120*s*, 1100*s*, 1052*m*, 1032*m*, 980*s*, 952*m*, 912*w*, 885*w*, 845*w*, 800*m*. ^{1}H-NMR (200 MHz, DCl/D_2O): 4.77 (*ddd*, J(P, H) = 14.5, $J = 7.0$, 5.5, H–C(2)); 4.39 (*dd*, $J = 5.5$, 4.0, H–C(3)); 4.24 (*dd*, J(P, H) = 4.0, $J = 7.0$, H–C(1)); 4.03 (*ddd*, $J = 8.0$, 5.6, 3.0, H–C(5)); 3.90 (*dd*, $J = 8.0$, 4.0, H–C(4)); 3.82 (*dd*, $J = 12.0$, 3.0, H–C(6)); 3.67 (*dd*, $J = 12.0$, 5.6, H–C(6)). ^{13}C-NMR (50.3 MHz, DCl/D_2O): 81.82 (*d*); 81.76 (*d*); 77.16 (*dd*, J(P, C) = 164.2); 72.66 (*d*); 70.75 (*d*); 63.95 (*t*). ^{31}P-NMR (160 MHz, DCl/D_2O): 19.09. MS (FAB of the free phosphonic acid): 245 ($M + 1$), 267 ($M - 1 + Na$), 289 ($M - 2 + 2Na$). Anal. calc. for $C_6H_{11}BaO_8P$ (379.4): C 19.00, H 2.93, P 8.16; found: C 18.74, H 3.04, P 8.01.

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