98. 1,7-Dideaza-2′,3′-dideoxyadenosine: Syntheses of Pyrrolo[2,3-*b*]pyridine 2′,3′-Dideoxyribofuranosides and Participation of Purine N(1) during HIV-1 Reverse Transcriptase Inhibition

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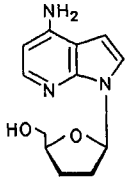
The syntheses of 1,7-dideaza-2′,3′-dideoxyadenosine (**1**) and related pyrrolo[2,3-*b*]pyridine 2′,3′-dideoxyribo- and 2′,3′-didehydro-2′,3′-dideoxyribonucleosides (see **2**–**5**) are described. As starting materials, 2′-deoxyribonucleosides **6** or **7** were used. The 3′-OH group was removed by *Barton* deoxygenation or *via* mesylation followed by elimination and catalytic hydrogenation. Compound **1** was also obtained from the direct glycosylation of 4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine (**17**) with the 2,3-dideoxyribofuranosyl chloride **18**. The triphosphate **25** of **1** showed only marginal activity against HIV-1 reverse transcriptase, indicating that purine N(1) is required for the inhibitory activity of the parent 2′,3′-dideoxyadenosine.

Introduction. – In a previous publication, we have shown that 7-deazapurine 2′,3′-dideoxynucleoside triphosphates are equally effective inhibitors of HIV reverse transcriptase as the parent purine compounds [1]. Moreover, a higher selectivity index of compounds related to 2′,3′-dideoxyadenosine ($A_{d_2^{2',3'}}$) or 2′,3′-dideoxyguanosine ($G_{d_2^{2',3'}}$) was observed between reverse transcriptase and DNA polymerases [2]. This demonstrates that HIV-1 reverse transcriptase binds 2′,3′-dideoxyribonucleosides into the active centre without using N(7) as an acceptor position. As it was unknown whether N(1) takes part in enzyme binding or its absence prevents *Watson-Crick* base pairing with the RNA template, we considered the preparation of 1,7-dideaza-2′,3′-dideoxyribonucleosides. In the following, we report on the syntheses of 1,7-dideazaadenosine (**1**) [3] and its deamino derivatives **2** and **4**. Moreover, the nitro-dideoxynucleosides **3** and **5** will be prepared which are useful intermediates for further transformation.

Three different approaches will be used for 1,7-dideazapurine 2′,3′-dideoxyribonucleoside syntheses: *i*) *Barton* deoxygenation of the 3′-OH group of a 2′-deoxyribo-



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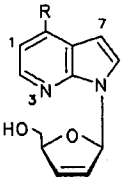
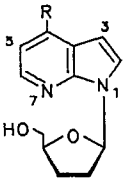


2 R = H [a])
3 R = NO_2



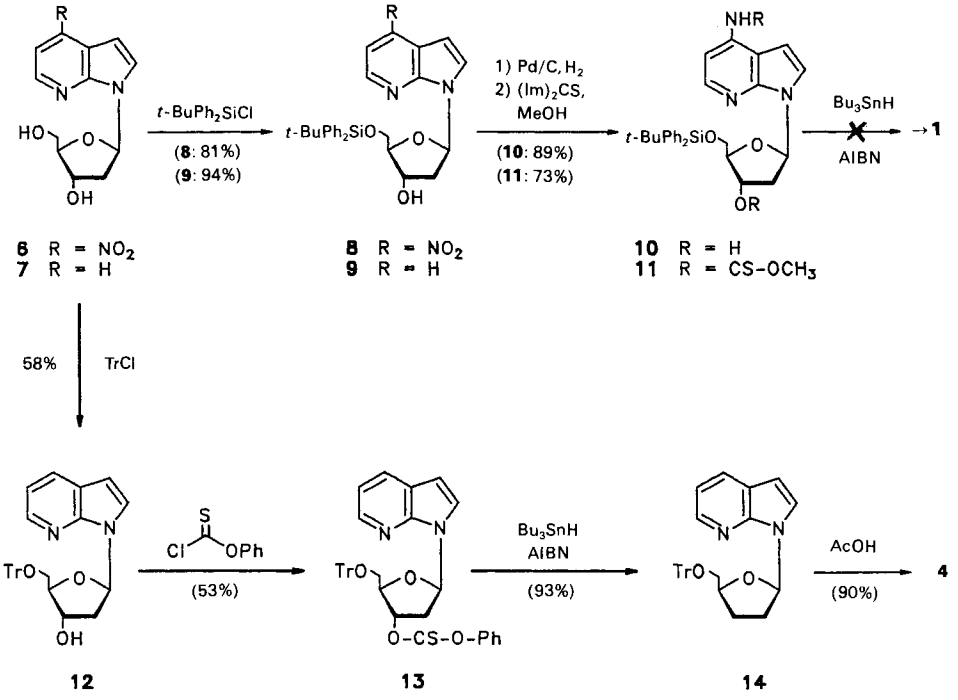
4 R = H [b])
5 R = NO_2

[a]) Purine numbering. [b]) Systematic numbering.

nucleoside [4], *ii*) elimination of the 3′-OH group followed by catalytic hydrogenation of 2′,3′-dideoxydidehydronucleosides [5], and *iii*) direct glycosylation using a nucleobase-anion precursor and the 2′,3′-dideoxysugar halide **18** [6]. Furthermore, triphosphates will be prepared from these nucleosides and their inhibitory activity against HIV-1 reverse transcriptase (RT) be compared with other base-modified purine 2′,3′-dideoxynucleotides.

Results and Discussion. – For the synthesis of 2′,3′-dideoxynucleoside **1**, the 2′-deoxynucleoside **6** was chosen as starting material (*Scheme 1*). The latter has been prepared recently in our laboratory [7]. Its 5′-OH group was protected selectively with the (1,1-dimethylethyl)diphenylsilyl residue to give compound **8**. Similarly, **9** was prepared from **7** [7] (^{1}H-NMR of **9**: no *t* for OH–C(5′); ^{13}C-NMR $\Delta\delta$ (**9**–**7**) = 2.3 ppm for C(5′); *Table 1*). As previous investigations have shown that *Barton* deoxygenation does not work in the presence of an aromatic NO_2 group [8], **8** was hydrogenated (Pd/C) to the amino derivative **10**.

Scheme 1



Earlier experiments with 5′-protected 2′-deoxyadenosine [9] or 2-amino-4-chloropyrrolo[2,3-*d*]pyrimidine β-D-2′-deoxyribofuranoside [10] have shown that *N*,*N*′-(thiocarbonyl)bis[imidazole] can be reacted selectively with a 3′-OH group without affecting the heterocyclic amino groups. Employing the same conditions for compound **10**, the bis[methoxy(thiocarbonyl)] derivative **11** was formed. Bis-acylation was confirmed by elemental analysis and ^{1}H-NMR spectroscopy. The positions of acylation was deduced

from the ^{13}C-NMR spectrum, exhibiting a 9-ppm upfield shift of C(4) as well as a downfield shift of C(3′) compared to **10** (*Table 1*). The increased reactivity of the 6-amino group of **10** compared to that of purines or pyrrolo[2,3-*d*]pyrimidines can be attributed to an increased nucleophilicity of the amino group of compound **1**. As expected, conversion of the bis[methoxy(thiocarbonyl)] compound **11** with Bu_3SnH in the presence of

Table 1. *^{13}C-NMR Chemical Shifts of 1,7-Dideazapurine Nucleosides in (D_6)DMSO at 23°*[a])

	C(2)	C(3)	C(3a)	C(4)	C(5)	C(6)	C(7a)
1	121.2	98.5	108.0	148.4	100.1	143.3	147.8
2	126.0	100.7	120.6	128.7	116.4	142.4	147.2
3	132.1	100.2	113.0	144.9	110.4	142.9	150.5
4	126.0	100.3	120.5	128.6	116.2	142.3	147.0
5	132.1	99.9	113.0	144.9	110.2	142.8	150.4
6 [7]	132.0	100.4	113.0	145.0	110.4	142.9	150.5
7 [7]	126.4	100.8	120.8	128.9	116.4	142.4	147.2
8	131.8	100.3	113.0	145.0	110.5	143.1	150.5
9	125.7	100.8	120.5	128.7	116.4	142.5	147.2
10	120.8	99.2	107.8	148.5	100.4	143.6	148.2
11	124.5	100.1	113.6[b])	137.8	109.8[b])	143.2	148.8
12	125.9	100.9	120.6	128.7	116.4	142.5	147.2
13	125.9	101.4	120.8	129.0	116.7	142.7	147.4
14	125.7	100.6	120.6	128.8	116.4	142.5	147.2
15	131.9	100.6	113.2	145.1	110.6	143.1	150.4
16	126.0	101.2	120.8	128.9	116.7	142.6	147.3
19	131.7	99.6	112.8	144.8	110.1	142.7	150.1
20	132.0	99.9	112.8	144.8	110.2	142.8	150.3
21	120.4	98.5	107.6	148.3	100.1	143.6	148.2
22	132.1	99.9	112.8	144.8	110.2	142.8	150.3
23	120.8	98.6	107.7	148.2	100.1	143.8	148.3
24	120.8	98.6	107.8	148.3	100.2	143.8	148.5

	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)
1	84.2	31.2	26.5	80.1	63.7
2	87.5[c])	126.2	133.8	87.1[c])	63.5
3	88.0[c])	125.7	134.5	87.6[c])	63.0
4	83.4	31.5	26.4	80.5	63.4
5	84.3	32.1	26.0	81.4	63.0
6 [7]	83.3	DMSO	71.0	87.6	61.7
7 [7]	83.0	DMSO	71.2	87.2	62.2
8	83.3	DMSO	70.3	86.7	64.2
9	82.4	DMSO	70.5	86.2	64.3
10	82.4	DMSO	70.6	86.1	64.5
11	82.9[b])	36.1	82.9[b])	83.2[b])	64.0
12	82.4	DMSO	70.8	86.0	64.5
13	83.1	DMSO	84.7	86.3	64.2
14	83.3	31.3	28.8	78.7	64.9
15	83.3	DMSO	80.2	83.8	63.2
16	82.7	38.0	80.6	83.3	63.3
19	84.1	32.0	25.5	80.9	64.4
20	84.6	31.5	25.7	80.8	65.1
21	83.1	31.6	26.1	79.7	64.9
22	84.5	31.3	26.5	80.8	63.4
23	83.4	31.1	26.9	79.9	63.7
24	83.6	31.3	26.8	79.5	65.6

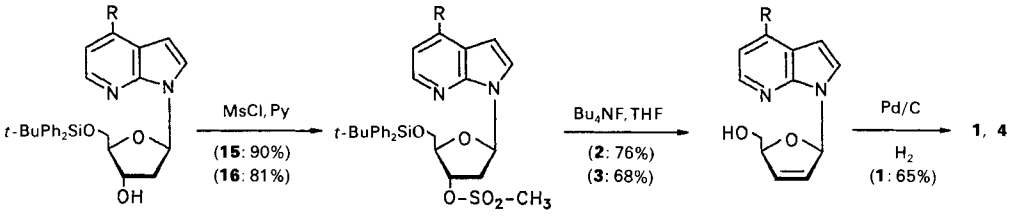
[a]) Systematic numbering. [b]) Tentative. [c]) From ^{1}H,^{13}C correlation spectra.

azoisobutyronitrile (AIBN) [11] did not result in the formation of the 5′-silylated derivative of **1**. Several unidentified reaction products were formed. Therefore, another route was chosen to convert **6** to 2′,3′-dideoxynucleoside **1** (see below).

Contrary to the amino-deoxynucleoside, the deamino compound **7** was converted into the corresponding 2′,3′-dideoxynucleoside **4**. In this case, the trityl group was introduced to protect the 5′-OH position yielding **12**. The latter was reacted with *O*-phenyl carbonochloridothioate (= phenoxy(thiocarbonyl)chloride) [12] to give **13**. Deoxygenation of **13** by tributylstannane in toluene in the presence of AIBN yielded, after chromatographic workup, **14** from which the trityl group was removed with AcOH resulting in the dideoxynucleoside **4**.

As *Barton* deoxygenation failed in the case of **6**, we tried to remove the 3′-OH group by elimination: Treatment of mesyl derivative **15** (obtained from **6** *via* **8**) with Bu_4NF [5] provided 1-(2,3-dideoxy-β-D-*glycero*-pent-2-enofuranosyl)-4-nitro-1*H*-pyrrolo[2,3-*b*]-pyridine (**3**; *Scheme 2*). Catalytic hydrogenation gave 1,7-dideaza-2′,3′-dideoxyadenosine (**1**) which was isolated as colourless crystals. Similarly, **7** gave, *via* **9** and the fully protected **16**, the target compounds **2** and **4**.

Scheme 2



8 R = NO_2
9 R = H

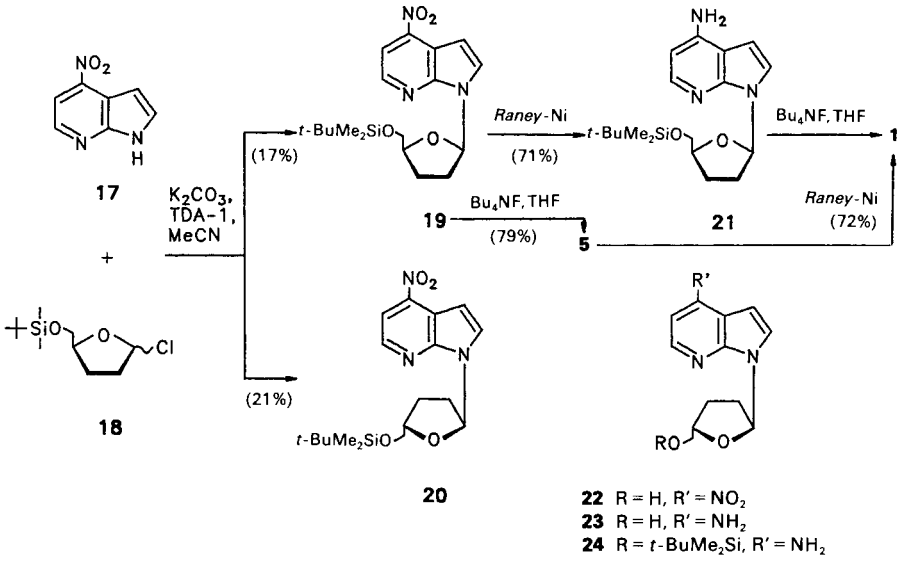
15 R = NO_2
16 R = H

3 R = NO_2
2 R = H

The overall yield of the reaction route starting with base **17** [13] [14], using the 2′-deoxyribonucleoside **6** as intermediate, and ending with **1** was 17%. As this protocol was time-consuming, we decided to synthesize **1** by direct glycosylation. Thus, nitro compound **17** and 2′,3′-dideoxysugar halide **18** [6] were used as starting materials. Compound **18** has already been employed during the syntheses of 3-deazapurine [15] as well as 7-deazapurine 2′,3′-dideoxyribonucleosides [2] and was obtained from the corresponding lactol [16] by *Appel* chlorination [17]. The N-anion of **17** was generated under solid-liquid phase-transfer conditions [18] with K_2CO_3 and cryptand TDA-1 (tris[2-(2-methoxyethoxy)ethyl]amine) in MeCN, and the cold THF solution of **18** was added portionwise. The use of K_2CO_3 instead of KOH minimized coloured side products which were formed in the presence of powdered KOH, and the total glycosylation yield of **19** and **20** was 38% (β/α-D ratio 0.8:1). Deprotection of **19** or **20** with 1M Bu_4NF afforded **5** and **22**, respectively. On the other hand, reduction with *Raney*-Ni catalyst afforded **21** and **24**, respectively. Finally, the latter were desilylated to **1** and **23**. The overall yield for the target compound **1** was 10% in this three-step reaction sequence.

Anomeric configurations were assigned on the basis of ^{1}H-NMR NOE difference spectroscopy [19]. In the case of the β-D-anomer **5**, saturation at the H–C(1′) signal gave a NOE of 2.1% on H–C(4′), clearly indicating β-D-configuration [20]. In the case of

Scheme 3



α-D-anomer **22**, this NOE was not observed. The anomeric configuration of **1** was proved by comparison with the reaction product obtained by reduction of **3** (see *Scheme 2*). *Table 1* summarizes the ^{13}C-NMR chemical shifts of 1,7-dideazapurine nucleosides. The nucleobases were assigned in analogy to corresponding 2′-deoxyribonucleosides [7]; assignment of the glycosyl moieties are based on data reported earlier [5] [6] [10] or were accomplished by 2D ^{1}H,^{13}C-correlation spectroscopy.

Compared to $A_{d_2^{2',3'}}$ or $c^3A_{d_2^{2',3'}}$ [15] containing an imidazole moiety, the pyrrolo dideoxyribonucleosides $c^7A_{d_2^{2',3'}}$ [2], $c_2^{1,7}A_{d_2^{2',3'}}$ (**1**), $c_2^{3,7}A_{d_2^{2',3'}}$ [6] and $c_3^{1,3,7}A_{d_2^{2',3'}}$ [8] have a much more stable N-glycosylic bond. The latter compounds are also not deaminated by adenosine deaminase. The lipophilicity of these nucleosides is determined by the number of N-atoms. This can be shown from the HPLC pattern on a reversed-phase resin using an aq. (Et_3NH)OAc/MeCN gradient (*Fig. 1*). According to that, $A_{d_2^{2',3'}}$ is the most hydrophilic and the indole 2′,3′-dideoxynucleoside $c_2^{1,3,7}A_{d_2^{2',3'}}$ [8] the most lipophilic compound. Indepedently from the N-pattern, the monodeaza compounds as well as the dideaza compounds form groups of comparable retention times.

In an earlier publication, we reported on the inhibitory activity of 7-deazapurine 2′,3′-dideoxyribonucleoside triphosphates on HIV-1 reverse transcriptase [2]. From these experiments, it became apparent that the purine N(7) atom is not recognized by the active centre of the enzyme. As compound **1** additionally lacks N(1), it can be used to prove the participation of this N-atom during the binding of purine 2′,3′-dideoxynucleosides into the active centre of HIV-1 reverse transcriptase. As 2′,3′-dideoxyribonucleoside triphosphates are the actual inhibitors of the enzyme, the triphosphates **25**–**28** were prepared from **1** and **3**–**5**, respectively, and compared with the related $p_3c_3^{1,3,7}A_{d_2^{2',3'}}$ (**29**), $p_3c^7A_{d_2^{2',3'}}$ (**30**), and $p_3A_{d_2^{2',3'}}$ (= ddATP; **31**).

The synthesis of the 2′,3′-dideoxyribonucleoside triphosphates **25**–**28** was carried out in a one-pot reaction following a protocol originally developed for phosphorylation of

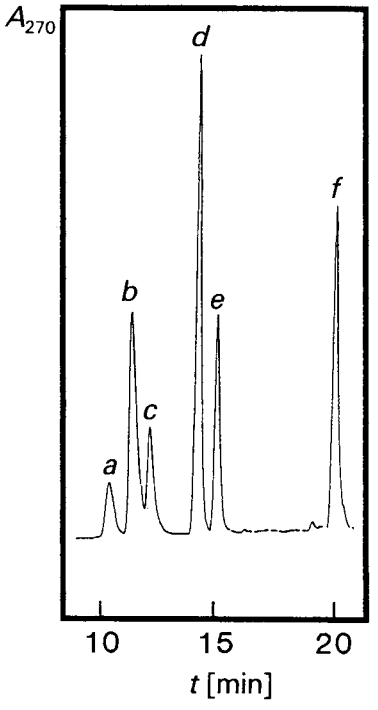


Fig. 1. *HPLC profile of 2′,3′-dideoxyribonucleosides.* *a*) $A_{d_2^{2',3'}}$; *b*) $c^3A_{d_2^{2',3'}}$; *c*) $c^7A_{d_2^{2',3'}}$; *d*) $c_2^{3,7}A_{d_2^{2',3'}}$; *e*) $c_2^{1,7}A_{d_2^{2',3'}}$ (**1**); *f*) $c_3^{1,3,7}A_{d_2^{2',3'}}$. Column: 4 × 250 mm *RP-18 Lichrosorb* (*Merck*); solvent system: *A*, 0.1M $(Et_3NH)OAc$ (pH 7.0)/MeCN 95:5; *B*, MeCN; gradient: 25 min 0–50% *B* in *A*.

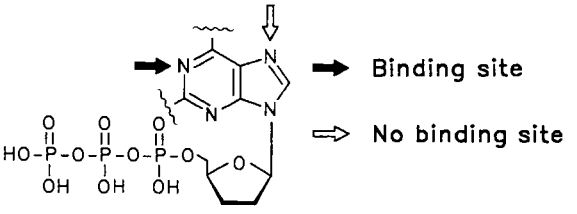
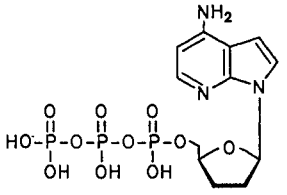


Fig. 2. *Binding sites of HIV-1 reverse transcriptase*

purine and pyrimidine 2′-deoxynucleosides [21]. The reaction was carried out in $PO(OMe)_3$ with $POCl_3$ followed by condensation with tetrakis(tributylammonium) diphosphate ($(Bu_3NH)_4P_2O_7$). The products were purified on a *DEAE* cellulose ion exchanger and isolated as colourless amorphous Et_3NH^+ salts. ^{31}P-NMR spectroscopy was used for characterization resulting in the pattern of the triphosphate moiety (*Table 2*).



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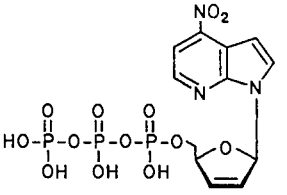

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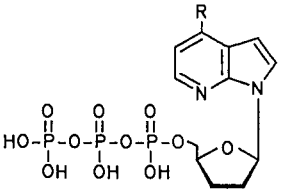
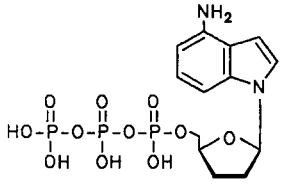


27 R = H
28 R = NO_2



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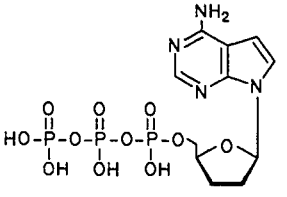

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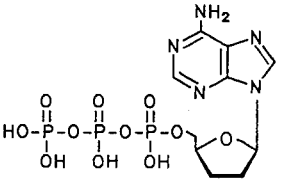

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Table 2. *Yields and ^{31}P-NMR Chemical Shifts of 2′,3′-Dideoxynucleoside 5′-O-Triphosphates* **25–29**

Product	Yield $OD\lambda_{max}$ (%)	UV (H_2O) λ_{max}	^{31}P-NMR[a])		
			δ(P(α))	δ(P(β))	δ(P(γ))
25	187 (22)	271	−10.27 (J = 19)	−21.44 (J = 19)	−6.61 (J = 19)
26	180 (36)	358	−10.52 (J = 20)	−21.75 (J = 20)	−6.18 (J = 20)
27	368 (49)	288	−10.32 (J = 19)	−22.04 (J = 19)	−7.46 (J = 19)
28	106 (21)	358	−10.12 (J = 19)	−21.45 (J = 19)	−6.74 (J = 19)
29	134 (17)	271	−10.08 (J = 19)	−21.40 (J = 19)	−6.84 (J = 19)

[a]) Measured in D_2O/0.1M *Tris*-HCl buffer (pH 8.0) 1:1, containing 100 mM Na_4EDTA. δ(P) in ppm rel. to 85% H_3PO_4 soln. as external standard, J in Hz.

Table 3. *Inhibitory Data of 2′,3′-Dideoxyribonucleoside Triphosphates on HIV-1 Reverse Transcriptase* (RT)[a])

	IC_{50} [μM]		IC_{50} [μM]		IC_{50} [μM]		IC_{50} [μM]
25	> 1000	**27**	3400	ddATP (**31**)[b])	0.45	**29**	23.7
26	4120	**28**	> 1000	$c^7A_{dd}TP$ (**30**)[b])	0.39	AZTTP[b])	0.5

[a]) The RT inhibitory tests were performed in the laboratories of the *Boehringer Mannheim GmbH*.

[b]) ddATP = $p_3A_{d_2^{2',3'}}$ = 2′,3′-dideoxyadenosine 5′-triphosphate; $c^7A_{dd}TP$ = $p_3c^7A_{d_2^{2',3'}}$ = 7-deaza-2′,3′-dideoxyadenosine 5′-triphosphate; AZTTP = $p_3T_{d_2^{2',3'}az^{3'}}$ = 3′-azido-3′-deoxythymidine 5′-triphosphate.

Next, the inhibitory data of the triphosphates were determined against HIV-1 reverse transcriptase and compared with purine and 7-deazapurine 2′,3′-dideoxyribonucleotides. As this polymerase is a template-directed enzyme, the four regular 2′-deoxyribonucleosides triphosphates have to be present for chain elongation. *Table 3* summarizes the values of 50% inhibition of HIV reverse transcriptase by the 1,7-dideazapurine 2′,3′-dideoxyribonucleoside triphosphates **25–28** and for comparison of the related $p_3c^7A_{d_2^{2',3'}}$ (**30**) and $p_3A_{d_2^{2',3'}}$ (**31**; for details, see [2]). The 1,7-dideazapurine compounds show only marginal activity as compared to **31** or **30**. From this, it is concluded that the N(1) atom of ddATP is required for the active site directed binding of purine 2′,3′-dideoxyribonucleosides on HIV-1 reverse transcriptase. This finding can be explained by the phenomenon that the likelihood of binding and making a phosphodiester bond is very low unless the incoming nucleotide forms a *Watson-Crick* base pair with the opposing nucleotide on the template. In this way, the enzyme behaves similar as DNA-polymerases. The purine N(7) atom does not participate in this process. Therefore, HIV-1 reverse transcriptase as well as DNA-polymerases incorporate 7-deazapurine 2′-deoxyribo- [22] and 2′,3′-dideoxyribonucleoside triphosphates [23].

Triphosphate **29** was synthesized [24] from the already reported 4-aminoindole 2′,3′-dideoxy-β-D-ribofuranoside [8] and included in the HIV-1 reverse transcriptase inhibition assay. Surprisingly, 1,3,7-trideaza compound **29** shows a much better inhibitory activity than 1,7-dideazapurine derivative **25** (*Table 3*). On the other hand, it contains no ring N-atom as potential proton-acceptor sites. This indicates, that a H-bond N(1) and the enzyme and/or the template can be substituted in part by hydrophobic forces. This is underlined by the fact that the indole moiety is the most hydrophobic nucleobase within the series of base-modified purine 2′,3′-dideoxyribonucleosides (see *f*) in *Fig. 1*). However, other parameters such as the dipole moment of the aglycone can play an important role during 2′,3′-dideoxyribonucleoside binding on the HIV reverse transcriptase/RNA template complex.

We thank Mrs. *A. Röling* for the preparation of the triphosphates **25**–**28** and Dr. *W. Mertens* and Dr. *B. König* from the *Boehringer Mannheim GmbH* for the inhibitory tests on HIV-1 reverse transcriptase. We also thank Dr. *H. Rosemeyer* for the NMR spectra. Financial support of the *Bundesminister für Forschung und Technologie* is gratefully acknowledged.

Experimental Part

General. See [2]. M.p.: *Büchi-SMR-20* apparatus (*Büchi*, Switzerland).

*1-{2-Deoxy-5-O-[(1,1-dimethylethyl)diphenylsilyl]-β-*D-erythro-*pentofuranosyl}-1H-pyrrolo[2,3-b]pyridine* (**9**). By co-evaporation with pyridine (2 × 20 ml), 1-(2-deoxy-β-D-*erythro*-pentofuranosyl)-1*H*-pyrrolo[2,3-*b*]-pyridine (**7**; 1.0 g, 4.27 mmol) [7] was dried and then dissolved in pyridine (30 ml). *t*-$BuPh_2SiCl$ (1.3 ml, 5 mmol) was added at 0° and stirring continued for 8 h. The mixture was evaporated and co-evaporated with toluene (2 × 20 ml) and the residue separated by FC (silica gel, column 10 × 5 cm, CH_2Cl_2/MeOH 95:5:): colorless foam (1.9 g, 94%). TLC (CH_2Cl_2/MeOH 95:5): R_f 0.2. UV (MeOH): 288 (8300). ^{1}H-NMR ((D$_6$)DMSO): 1.01 (*s*, *t*-Bu); 2.28 (*m*, H_α–C(2′)); 2.56 (*m*, H_β–C(2′)); 3.80 (*m*, 2 H–C(5′)); 3.90 (*m*, H–C(4)); 4.50 (*m*, H–C(3′)); 5.37 (*d*, *J* = 4.3, OH–C(3′)); 6.48 (*d*, *J* = 3.6, H–C(3)); 6.76 ('*t*', *J* = 6.5, H–C(1′)); 7.12 (*dd*, *J* = 4.7, 7.8, H–C(5)); 7.97 (*d*, *J* = 7.8, H–C(4)); 8.24 (*d*, *J* = 4.7, H–C(6)); arom. H. Anal. calc. for $C_{28}H_{32}N_2O_3Si$ (472.7): C 71.15, H 6.82, N 5.93; found: C 71.33, H 6.89, N 6.11.

*1-{2-Deoxy-5-O-[(1,1-dimethylethyl)diphenylsilyl]-3-O-mesyl-β-*D-erythro-*pentofuranosyl}-1H-pyrrolo-[2,3-b]pyridine* (**16**). A soln. of **9** (1.5 g, 3.17 mmol) in CH_2Cl_2 (50 ml) containing methanesulfonyl chloride (MsCl; 1 ml, 13 mmol) and pyridine (15 ml) was stirred for 12 h at r.t. After addition of MeOH (30 ml) and stirring for another 15 min, the soln. was diluted with $CHCl_3$ (200 ml) and washed with 0.1N HCl (2 × 40 ml) and H_2O (2 × 50 ml). After drying (Na_2SO_4) and evaporation of the org. phase, the residue was submitted to FC (column 8 × 3 cm, CH_2Cl_2/AcOEt 95:5): colorless foam (1.40 g, 80%). TLC (CH_2Cl_2/AcOEt 9:1): R_f 0.8. UV (MeOH): 288 (8100). ^{1}H-NMR ((D$_6$)DMSO): 1.03 (*s*, *t*-Bu); 2.70 (*m*, H_α–C(2′)); 3.07 (*m*, H_β–C(2′)); 3.89 (*m*, 2 H–C(5′)); 4.31 (*m*, H–C(4′)); 5.54 (*m*, H–C(3′)); 6.53 (*d*, *J* = 3.7, H–C(3)); 6.76 (*dd*, *J* = 5.9, 8.5, H–C(1′)); 7.16 (*dd*, *J* = 4.7, 7.8, H–C(5)); 8.00 (*dd*, *J* = 1.4, 7.8, H–C(4)); 8.24 (*dd*, *J* = 1.5, 4.7, H–C(6)); arom. H.

*1-(2,3-Dideoxy-β-*D-glycero-*pent-2-enofuranosyl)-1H-pyrrolo[2,3-b]pyridine* (**2**). To a soln. of **16** (500 mg, 0.91 mmol) in dry THF (20 ml), Bu_4NF (1M in THF, 10 ml) was added. After 4 h stirring at 80° under Ar, the solvent was evaporated and the residue applied to FC (column 4 × 25 cm, CH_2Cl_2/aceton 9:1): colorless crystals (150 mg, 76%) from acetone. TLC (CH_2Cl_2/AcOEt 9:1): R_f 0.35. M.p. 108°. UV (MeOH): 288 (8300). ^{1}H-NMR ((D$_6$)DMSO): 3.57 (*m*, 2 H–C(5′)); 4.85 (*m*, H–C(4′)); 4.96 (*s*, OH); 6.10 (*m*, H–C(2′)); 6.49 (*m*, H–C(3′)); 6.55 (*d*, *J* = 3.7, H–C(3)); 7.16 (*dd*, *J* = 4.7, 7.8, H–C(5)); 7.38 (*m*, H–C(1′)); 7.57 (*d*, *J* = 3.7, H–C(2)); 8.01 (*dd*, *J* = 1.5, 7.8, H–C(4)); 8.29 (*dd*, *J* = 1.5, 4.7, H–C(6)). Anal. calc. for $C_{12}H_{12}N_2O_2$ (216.24): C 66.65, H 5.59, N 12.96; found: C 66.63, H 5.71, N 12.99.

*1-[2-Deoxy-5-O-(triphenylmethyl)-β-*D-erythro-*pentofuranosyl]-1H-pyrrolo[2,3-b]pyridine* (**12**). Compound **7** (1.48 g, 6.32 mmol) was co-evaporated with anh. pyridine (2 × 30 ml) and then dissolved in anh. pyridine (40 ml). (i-Pr)$_2$EtN (3.3 ml, 19 mmol) and triphenylmethyl chloride (3.55 g, 12.6 mmol) were added. The soln. was stirred at r.t. for 4 h, then 5% aq. $NaHCO_3$ soln. (200 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 150 ml). The combined org. layers were dried ($NaSO_4$) and evaporated. FC (column 7 × 4.5 cm, CH_2Cl_2/acetone 8:2) gave a colorless foam (1.75 g, 58%). TLC (CH_2Cl_2/acetone 8:2): R_f 0.8. UV (MeOH): 288 (7600). ^{1}H-NMR ((D$_6$)DMSO): 2.28 (*m*, H_α–C(2′)); 2.61 (*m*, H_β–C(2′)); 3.17 (*d*, *J* = 4.8, 2 H–C(5′)); 3.97 (*m*, H–C(4′)); 4.39 (*m*, H–C(3′)); 5.38 (*d*, *J* = 4.7, OH–C(3′)); 6.53 (*d*, *J* = 3.6, H–C(3)); 6.76 ('*t*', *J* = 4.0, H–C(1′)); 7.13 (*dd*, *J* = 4.7, 7.8, H–C(5)); 7.59 (*d*, *J* = 3.7, H–C(2)); 7.97 (*dd*, *J* = 1.5, 7.8, H–C(4)); 8.24 (*dd*, *J* = 1.5, 4.7, H–C(6)). Anal. calc. for $C_{31}H_{28}N_2O_3$ (476.58): C 78.13, H 5.92, N 5.88; found: C 78.06, H 6.04, N 5.79.

*1-{2-Deoxy-3-O-[phenoxy(thiocarbonyl)]-5-O-(triphenylmethyl)-β-*D-erythro-*pentofuranosyl}-1H-pyrrolo-[2,3-b]pyridine* (**13**). To a stirred soln. of **12** (1.75 g, 3.67 mmol) in anh. MeCN (50 ml) under Ar, 4-(dimethylamino)pyridine (1.12 g, 9.2 mmol) and phenoxy(thiocarbonyl)chloride (1.0 ml, 7.4 mmol) were added through a septum. After 48 h stirring, the solvent was evaporated and the residue applied to FC (column 10 × 4 cm, CH_2Cl_2, R_f 0.6). From the main zone, **13** was obtained as colorless foam (1.2 g, 53%). UV (MeOH): 285 (8600). ^{1}H-NMR ((D$_6$)DMSO): 2.77 (*m*, H_α–C(2′)); 3.18 (*m*, H_β–C(2′)); 3.38 (*m*, 2 H–C(5′)); 4.42 (*m*, H–C(4′)); 5.93 (*m*, H–C(3′)); 6.62 (*d*, *J* = 3.7, H–C(3)); 6.81 (*dd*, *J* = 5.5, 9.1, H–C(1′)); 7.18 (*dd*, *J* = 4.7, 7.8, H–C(5)); 7.67 (*d*, *J* = 3.7, H–C(2)); 8.03 (*dd*, *J* = 1.4, 7.8, H–C(4)); 8.24 (*dd*, *J* = 1.4, 4.7, H–C(6)); arom. H. Anal. calc. for $C_{38}H_{32}N_2O_4S$ (612.74): C 74.49, H 5.26, N 4.57; found: C 74.65, H 5.41, N 4.35.

*1-[2,3-Dideoxy-5-O-(triphenylmethyl)-β-*D-glycero-*pentofuranosyl]-1H-pyrrolo[2,3-b]pyridine* (**14**). A soln. of **13** (1.2 g, 1.96 mmol) in anh. toluene (60 ml) was stirred with AIBN (90 mg, 0.6 mmol) and Bu_3SnH (1.1 ml, 4

mmol) for 5 h at 80° under Ar. The solvent was evaporated and the residue applied to FC (column 8 × 3 cm, solvent CH_2Cl_2): colorless needles (0.8 g, 93%). TLC (CH_2Cl_2/acetone 95:5): R_f 0.83. M.p. 115° (i-PrOH). UV (MeOH): 289 (8100). ^{1}H-NMR ((D$_6$)DMSO): 2.08 (*m*, 2 H–C(3′)); 2.37 (*m*, 2 H–C(2′)); 3.12 (*m*, 2 H–C(5′)); 4.24 (*m*, H–C(4′)); 6.48 (*d*, *J* = 3.7, H–C(3)); 6.63 (*dd*, *J* = 4.0, 6.9, H–C(1′)); 7.13 (*dd*, *J* = 4.7, 7.8, H–C(5)); 7.61 (*d*, *J* = 3.7, H–C(2)); 7.97 (*dd*, *J* = 1.5, 7.8, H–C(4)); 8.26 (*dd*, *J* = 1.4, 4.7, H–C(6)); arom. H. Anal. calc. for $C_{31}H_{28}N_2O_2$ (460.58): C 80.84, H 6.13, N 6.08; found: C 80.79, H 6.16, N 6.14.

*1-(2,3-Dideoxy-β-*D*-*glycero*-pentofuranosyl)-1*H*-pyrrolo[2,3-*b*]pyridine* (**4**). A soln. of **14** (240 mg, 0.52 mmol) in 80% aq. AcOH (30 ml) was stirred for 3 h at r.t. The mixture was evaporated, and traces of AcOH were removed by repeated co-evaporation with H_2O. The residue was applied to FC (column 8 × 3 cm, CH_2Cl_2/acetone 95:5): colorless crystals (102 mg, 90%). TLC (CH_2Cl_2/MeOH 95:5): R_f 0.24. M.p. 124–125° (H_2O). UV (MeOH): 288 (7500). ^{1}H-NMR ((D$_6$)DMSO): 2.08 (*m*, 2 H–C(3′)); 2.31 (*m*, 2 H–C(2′)); 3.56 (*m*, 2 H–C(5′)); 4.08 (*m*, H–C(4′)); 4.98 (*t*, *J* = 5.5, OH–C(5′)); 6.54 (*d*, *J* = 3.2, H–C(3)); 6.59 ('*t*', *J* = 5.4, H–C(1′)); 7.13 (*dd*, *J* = 4.7, 7.7, H–C(5)); 7.77 (*d*, *J* = 3.2, H–C(2)); 7.98 (*d*, *J* = 7.7, H–C(4)); 8.25 (*d*, *J* = 4.8, H–C(6)). Anal. calc. for $C_{12}H_{14}N_2O_2$ (218.26): C 66.04, H 6.47, N 12.83; found: C 66.09, H 6.57, N 12.84.

*1-{2-Deoxy-5-*O*-[(1,1-dimethylethyl)diphenylsilyl]-β-*D*-*erythro*-pentofuranosyl}-4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine* (**8**). Compound **6** (1.0 g, 3.58 mmol) was co-evaporated with anh. pyridine (2 × 30 ml) and then dissolved in anh. pyridine (50 ml). The soln. was cooled to 0° and *t*-BuPh_2SiCl (1.18 ml, 4.6 mmol) added dropwise while stirring under Ar. Stirring was continued for 8 h at r.t. The solvent was evaporated, the residue diluted with $CHCl_3$ (200 ml) and extracted with 0.1N HCl (2 × 40 ml) and H_2O, and the org. layer dried (Na_2SO_4) and evaporated. FC (column 10 × 3 cm, CH_2Cl_2/acetone 95:5) gave a yellow foam (1.5 g, 81%). TLC (CH_2Cl_2/acetone 9:1): R_f 0.66. UV (MeOH): 357.0 (4442), 338.0 (4350). ^{1}H-NMR ((D$_6$)DMSO): 0.99 (*s*, *t*-Bu); 2.38 (*m*, H$_\beta$–C(2′)); 2.63 (*m*, H$_\alpha$–C(2′)); 3.75 (*dd*, *J* = 4.8, 10.9, 1 H–C(5′)); 3.87 (*dd*, *J* = 4.8, 10.9, 1 H–C(5′)); 3.96 (*m*, H–C(4′)); 4.53 (*m*, H–C(3′)); 5.46 (*d*, *J* = 4.4, OH–C(3′)); 6.79 ('*t*', *J* = 6.6, H–C(1′)); 6.98 (*d*, *J* = 3.6, H–C(3)); 7.97 (*d*, *J* = 5.3, H–C(5)); 8.07 (*d*, *J* = 3.6, H–C(2)); 8.53 (*d*, *J* = 5.3, H–C(6)); arom. H. Anal. calc. for $C_{28}H_{31}N_3O_5Si$ (517.66): C 64.97, H 6.04, N 8.12; found: C 65.00, H 6.24, N 8.01.

*4-Amino-1-{2-deoxy-5-*O*-[(1,1-dimethylethyl)diphenylsilyl]-β-*D*-*erythro*-pentofuranosyl}-1*H*-pyrrolo[2,3-*b*]pyridine* (**10**). Compound **8** (1.3 g, 2.5 mmol) in MeOH (100 ml) was hydrogenated in the presence of 10% Pd/C (200 mg) for 2 h (normal pressure, r.t.). The catalyst was filtered off, the filtrat evaporated, and the residue applied to FC (column 15 × 5 cm, AcOEt): **10** (1.1 g, 89%) as colorless foam. TLC (CH_2Cl_2/MeOH 9:1): R_f 0.67. UV (MeOH): 291.6 (10839), 270.8 (9728). ^{1}H-NMR ((D$_6$)DMSO): 1.01 (*s*, *t*-Bu); 2.20 (*m*, 2 H–C(2′)); 3.74 (*m*, 2 H–C(5′)); 3.85 (*m*, H–C(4′)); 4.43 (*m*, H–C(3′)); 5.34 (*d*, *J* = 4.2, OH–C(3′)); 6.20 (*d*, *J* = 5.4, H–C(5)); 6.29 (*s*, NH_2–C(4)); 6.54 (*d*, *J* = 3.7, H–C(3)); 6.63 (*m*, H–C(1′)); 7.22 (*d*, *J* = 3.7, H–C(2)); 7.41 (*d*, *J* = 5.4, H–C(6)); arom. H. Anal. calc. for $C_{28}H_{33}N_3O_3Si$ (487.67): C 68.96, H 6.82, N 8.62; found: C 69.03, H 6.77, N 8.71.

*4-Amino-1-{2-deoxy-5-*O*-[(1,1-dimethyl)diphenylsilyl]-3-*O*-[methoxy(thiocarbonyl)]-β-*D*-*erythro*-pentofuranosyl}-1*H*-pyrrolo[2,3-*b*]pyridine* (**11**). A soln. of **10** (800 mg, 1.6 mmol) in dry 1,2-dichloroethane (50 ml) containing 1,1′-(thiocarbonyl)bis[imidazole] (1.17 g, 6.56 mmol) was stirred for 8 h at r.t. The solvent was evaporated and the residue stirred with MeOH (100 ml) for additional 12 h at 60°. After evaporation, the residue was applied to FC (column 15 × 5 cm, $CHCl_2$): **11** (760 mg, 73%) as colorless foam. TLC (CH_2Cl_2): R_f 0.52. UV (MeOH): 308.4 (18417), 264.6 (6585). ^{1}H-NMR ((D$_6$DMSO): 1.03 (*s*, *t*-Bu); 2.62 (*m*, H$_\beta$–C(2′)); 2.99 (*m*, H$_\alpha$–C(2′)); 3.90 (*m*, 2 H–C(5′)); 4.04, 4.07 (2*s*, 2 MeO); 4.26 (*m*, H–C(4′)); 5.96 (*m*, H–C(3′)); 6.54 (*d*, *J* = 3.7, H–C(3)); 6.70 (*m*, H–C(1′), H–C(3)); 7.55 (*d*, *J* = 3.7, H–C(2)); 8.17 (*d*, *J* = 5.3, H–C(6)); 11.42 (*s*, NH–C(4)); arom. H. Anal. calc. for $C_{32}H_{37}N_3O_5S_2Si$ (635.87): C 60.45, H 5.87, N 6.61; found: C 60.31, H 5.80, N 6.50.

*1-{2-Deoxy-5-*O*-[(1,1-dimethyl)diphenylsilyl]-3-*O*-mesyl-β-*D*-*erythro*-pentofuranosyl}-4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine* (**15**). To a soln. of **8** (1.0 g, 1.93 mmol) in CH_2Cl_2 (50 ml) containing pyridine (15 ml), MsCl (1 ml, 13 mmol) was added and the resulting mixture stirring at r.t. for 12 h. After addition of MeOH (20 ml) and stirring for another 15 min, the solvent was evaporated and the residue diluted with $CHCl_3$ (200 ml). The org. soln. was extracted with 0.1N HCl and H_2O, dried (Na_2SO_4), and evaporated and the residue applied to FC (column 8 × 3 cm, CH_2Cl_2): **15** as a yellow foam (1.04 g, 90%). TLC (CH_2Cl_2): R_f 0.33. UV (MeOH): 352.2 (4400), 337.8 (4700). ^{1}H-NMR ((D$_6$)DMSO): 0.99 (*s*, *t*-Bu); 2.80 (*m*, H$_\alpha$–C(2′)); 3.11 (*m*, H$_\beta$–C(2′)); 3.90 (*m*, 2 H–C(5′)); 4.32 (*m*, H–C(4′)); 5.54 (*m*, H–C(3′)); 6.28 ('*t*', *J* = 6.3, H–C(1′)); 7.02 (*d*, *J* = 4.9, H–C(3)); 7.98 (*d*, *J* = 5.3, H–C(5)); 8.09 (*d*, *J* = 3.6, H–C(2)); 8.52 (*d*, *J* = 5.3, H–C(6)); arom. H. Anal. calc. for $C_{29}H_{33}N_3O_7SSi$ (595.74): C 58.47, H 5.58, N 7.05; found: C 58.69, H 5.65, N 7.03.

*1-(2,3-Dideoxy-β-*D*-*glycero*-pent-2-enofuranosyl)-4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine* (**3**). To a soln. of **15** (400 mg, 0.67 mmol) in THF (10 ml), Bu_4NF (1M in THF, 5 ml) was added. After 4 h stirring at 70°, the solvent was evaporated and the residue applied to FC (column 10 × 3 cm, CH_2Cl_2/MeOH 95:5): yellow gum (120 mg, 68%) which crystallized from i-PrOH. M.p. 154°. TLC (CH_2Cl_2/MeOH 9:1): R_f 0.63. UV (MeOH): 358 (5000), 338

(4700). ^{1}H-NMR ((D$_6$)DMSO): 3.57 (*m*, 2 H–C(5′)); 4.87 (*m*, H–C(4′)); 4.96 (*t*, *J* = 5.4, OH–C(5′)); 6.14 (*m*, H–C(2′)); 6.52 (*m*, H–C(3′)); 7.05 (*d*, *J* = 3.6, H–C(3)); 7.40 (*m*, H–C(1′)); 7.99 (*d*, *J* = 5.3, H–C(5)); 8.03 (*d*, *J* = 3.6, H–C(2)); 8.58 (*d*, *J* = 5.3, H–C(6)). Anal. calc. for $C_{12}H_{11}N_3O_4$ (261.24): C 55.17, H 4.24, N 16.09; found: C 55.27, H 4.38, N 16.03.

*2,3-Dideoxy-5-*O*-[(1,1-dimethylethyl)dimethylsilyl]-*D-glycero-*pentofuranosyl Chloride* (**18**). To a soln. of (2*RS*,5*S*)-5-{{[(1,1-dimethylethyl)dimethylsilyl]oxy}methyl}tetrahydrofuran-2-ol [16] (1.50 g, 6.5 mmol) in anh. THF (26 ml) containing CCl_4 (0.97 ml) at −78° under Ar, tris(dimethylamino)phosphane (1.55 ml) was added dropwise. After 2 h stirring at −78°, the *in situ* generated halogenose **18** was used without further purification.

*1-{2,3-Dideoxy-5-*O*-[(1,1-dimethylethyl)dimethylsilyl]-β-*D-glycero-*pentofuranosyl}-4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine* (**19**). K_2CO_3 (5.0 g) and tris[2-(2-methoxyethoxy)ethyl]amine (80 µl, 0.27 mmol) were added to a soln. of 4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine (**17**; 500 mg, 3.07 mmol) [13] in MeCN (100 ml) under Ar. The mixture was stirred for 50 min, then **18** (see above) added in 3 portions, and stirring continued for another 60 min. Insoluble material was filtered off and the filtrate added to sat. aq. $NaHCO_3$ soln. (200 ml). The resulting mixture was extracted with $CHCl_3$ (3 × 200 ml), the combined org. layer dried (Na_2SO_4) and evaporated, and the residue applied to FC (column 20 × 5 cm, light petroleum ether/AcOEt 95:5). From the zone with R_f 0.15, **19** (200 mg, 17%) was isolated. Yellow oil. UV (MeOH): 359 (4400), 228 (13600). ^{1}H-NMR ((D$_6$)DMSO): 0.01 (2*s*, Me_2Si); 0.85 (*s*, *t*-Bu); 2.00 (*m*, 2 H–C(3′)); 2.27 (*m*, 2 H–C(2′)); 3.76 (*m*, 2 H–C(5′)); 4.14 (*m*, H–C(4′)); 6.63 (*dd*, *J* = 3.4, 6.8, H–C(1′)); 7.01 (*d*, *J* = 3.6, H–C(3)); 7.95 (*d*, *J* = 5.3, H–C(5)); 8.21 (*d*, *J* = 3.6, H–C(2)); 8.54 (*d*, *J* = 5.3, H–C(6)). Anal. calc. for $C_{18}H_{27}N_3O_4Si$ (377.52): C 57.27, H 7.21, N 11.13; found: C 57.45, H 7.28, N 11.20.

*1-{2,3-Dideoxy-5-*O*-[(1,1-dimethylethyl)dimethylsilyl]-α-*D-glycero-*pentofuranosyl}-4-nitro-1*H-*pyrrolo[2,3-*b*]pyridine* (**20**). The zone with R_f 0.33 (see FC above) yielded **20** (240 mg, 21%). Yellow oil. UV (MeOH): 358 (4300), 226 (13800). ^{1}H-NMR ((D$_6$)DMSO): 0.03 (*s*, Me_2Si); 0.86 (*s*, *t*-Bu); 1.85 (*m*, 2 H–C(3′)); 2.33 (*m*, 2 H–C(2′)); 3.65 (*m*, 2 H–C(5′)); 4.43 (*m*, H–C(4′)); 6.69 (*dd*, *J* = 4.1, 6.7, H–C(1′)); 7.05 (*d*, *J* = 3.7, H–C(3)); 7.96 (*d*, *J* = 5.4, H–C(5)); 8.15 (*d*, *J* = 3.7, H–C(2)); 8.56 (*d*, *J* = 5.4, H–C(6)). Anal. calc. for $C_{18}H_{27}N_3O_4Si$ (377.52): C 57.27, H 7.21, N 11.13; found: C 57.32, H 7.26, N 11.10.

*1-(2,3-Dideoxy-β-*D-glycero-*pentofuranosyl)-4-nitro-1*H-*pyrrolo[2,3-*b*]pyridine* (**5**). A soln. of **19** (20 mg, 0.53 mmol) in THF (50 ml) containing Bu_4NF (2 mmol) was stirred for 2 h at r.t. After evaporation, the residue was applied to FC (column 20 × 2 cm, CH_2Cl_2/acetone 95:5): **5** as yellow crystals (110 mg, 79%) from i-PrOH. M.p. 205°. TLC (CH_2Cl_2/acetone 8:2): R_f 0.55. UV (MeOH): 360 (4200), 228 (12900). ^{1}H-NMR ((D$_6$)DMSO): 2.09 (*m*, 2 H–C(3′)); 2.30 (*m*, 2 H–C(2′)); 3.57 (*m*, 2 H–C(5′)); 4.14 (*m*, H–C(4′)); 4.96 (*t*, *J* = 5.5, OH–C(5′)); 6.65 (*dd*, *J* = 3.9, 6.9, H–C(1′)); 7.07 (*d*, *J* = 3.6, H–C(3)); 7.97 (*d*, *J* = 5.3, H–C(5)); 8.27 (*d*, *J* = 3.6, H–C(2)); 8.56 (*d*, *J* = 5.3, H–C(6)). Anal. calc. for $C_{12}H_{13}N_3O_4$ (263.25): C 54.75, H 4.98, N 15.96; found: C 54.91, H 5.26, N 15.41.

*1-(2,3-Dideoxy-α-*D-glycero-*pentofuranosyl)-4-nitro-1*H-*pyrrolo[2,3-*b*]pyridine* (**22**). As described for **5** from **20**: yellow foam (105 mg, 75%). TLC (CH_2Cl_2/acetone 8:2): R_f 0.55. UV (MeOH): 358 (4100), 227 (13100). ^{1}H-NMR ((D$_6$)DMSO): 1.88 (*m*, 2 H–C(3′)); 2.27 (*m*, 2 H–C(2′)); 3.40 (*m*, 2 H–C(5′)); 4.34 (*m*, H–C(4′)); 4.78 (br., OH–C(5′)); 6.66 (*dd*, *J* = 4.4, 6.6, H–C(1′)); 7.01 (*d*, *J* = 3.6, H–C(3)); 7.93 (*d*, *J* = 5.3, H–C(5)); 8.11 (*d*, *J* = 3.6, H–C(2)); 8.52 (*d*, *J* = 5.3, H–C(6)). Anal. calc. for $C_{12}H_{13}N_3O_4$ (263.25): C 54.75, H 4.98, N 15.96; found: C 54.84, H 5.06, N 15.75.

*4-Amino-1-{2,3-dideoxy-5-*O*-[(1,1-dimethylethyl)dimethylsilyl]-β-*D-glycero-*pentofuranosyl}-1*H-*pyrrolo[2,3-*b*]pyridine* (**21**). A soln. of **19** (100 mg, 0.26 mmol) in dioxane (10 ml) was added dropwise to a suspension of *Raney*-Ni catalyst (1.0 g) in MeOH (50 ml) at r.t. After the mixture became colorless, the catalyst was filtered off and the filtrate evaporated. The residue was applied to FC (column 15 × 2 cm, CH_2Cl_2): colorless foam (66 mg, 72%). TLC ($CHCl_2$/acetone 95:5): R_f 0.71. UV (MeOH): 292 (11800), 271 (10200), 228 (33000). ^{1}H-NMR ((D$_6$)DMSO): 0.04 (*s*, Me_2Si); 0.88 (*s*, *t*-Bu); 2.06 (*m*, 2 H–C(3′)); 2.30 (*m*, 2 H–C(2′)); 3.72 (*m*, 2 H–C(5′)); 4.05 (*m*, H–C(4′)); 6.18 (*d*, *J* = 5.4, H–C(5)); 6.21 (*s*, NH_2); 6.45 (*dd*, *J* = 4.5, 6.6, H–C(1′)); 6.55 (*d*, *J* = 3.7, H–C(3)); 7.31 (*d*, *J* = 3.7, H–C(2)); 7.72 (*d*, *J* = 5.4, H–C(6)). Anal. calc. for $C_{18}H_{29}N_3O_2Si$ (347.53): C 62.21, H 8.41, N 12.09; found: C 62.16, H 8.49, N 12.14.

*4-Amino-1-{2,3-dideoxy-5-*O*-[(1,1-dimethylethyl)dimethylsilyl]-α-*D-glycero-*pentofuranosyl}-1*H-*pyrrolo[2,3-*b*-]pyridine* (**24**). As described for **21** from **20**. Colorless foam (63 mg, 68%). TLC (CH_2Cl_2/acetone 95:5): R_f 0.80. UV (MeOH): 292 (14200), 271 (11700). ^{1}H-NMR ((D$_6$)DMSO): 0.05 (*s*, Me_2Si); 0.88 (*s*, *t*-Bu); 1.65 (*m*, 2 H–C(3′)); 2.23 (*m*, 2 H–C(2′)); 3.61 (*m*, 2 H–C(5′)); 4.31 (*m*, H–C(4′)); 6.18 (*d*, *J* = 5.4, H–C(5)); 6.19 (*s* NH_2); 6.50 (*dd*, *J* = 4.3, 6.4, H–C(1′)); 6.56 (*d*, *J* = 3.7, H–C(3)); 7.23 (*d*, *J* = 3.7, H–C(2)); 7.73 (*d*, *J* = 5.4, H–C(6)). Anal. calc. for $C_{18}H_{29}N_3O_2Si$ (347.53): C 62.21, H 8.41, N 12.09; found: C 62.20, H 8.37, N 12.06.

*4-Amino-1-(2,3-dideoxy-β-*D-glycero-*pentofuranosyl)-1*H-*pyrrolo[2,3-*b*]pyridine* (**1**). From **5** (80 mg, 0.3 mmol) as described for **21**. After FC (column 15 × 2 cm, CH_2Cl_2/MeOH 9:1), colorless solid (51 mg, 72%).

From **3**: A soln. of **3** (50 mg, 0.19 mmol) in MeOH (25 ml) was hydrogenated in the presence of 10% Pd/C (5 mg) for 2 h (normal pressure, r.t.). The catalyst was filtered off, the filtrate evaporated, and the residue applied to FC (column 15 × 2 cm, CH_2Cl_2/MeOH 95:5): colorless solid (29 mg, 65%).

From **21**: A soln. of **21** (37 mg, 0.11 mmol) in THF (20 ml) containing Bu_4NF (1 mmol) was stirred for 2 h at r.t. After evaporation, the residue was applied to FC (column 20 × 2 cm, CH_2Cl_2/MeOH 95:5): colorless solid (21 mg, 85%). M.p. 133° (i-PrOH). TLC (CH_2Cl_2/MeOH 9:1): R_f 0.56. UV (MeOH): 292 (10100), 271 (8500), 228 (27000). ^{1}H-NMR ((D$_6$)DMSO): 2.01 (*m*, 2 H–C(3′)); 2.26 (*m*, 2 H–C(2′)); 3.50 (*m*, 2 H–C(5′)); 4.02 (*m*, H–C(4′)); 6.17 (*d*, J = 5.4, H–C(5)); 6.25 (*s*, NH_2); 6.34 ('*t*', J = 6.0, H–C(1′)); 6.53 (*d*, J = 3.7, H–C(3)); 7.27 (*d*, J = 3.7, H–C(2)); 7.70 (*d*, J = 5.4, H–C(6)). Anal. calc. for $C_{12}H_{15}N_3O_2$ (233.27): C 61.79, H 6.48, N 18.01; found: C 61.95, H 6.52, N 17.88.

*4-Amino-1-(2,3-dideoxy-α-*D*-glycero-pentofuranosyl)-1*H*-pyrrolo[2,3-b]pyridine* (**23**). As described for **21** from **22** (70 mg, 0.27 mmol). FC (CH_2Cl_2/MeOH 9:1) yielded a colorless solid (40 mg, 65%). TLC (CH_2Cl_2/MeOH 9:1): R_f 0.37. UV (MeOH): 292 (13800), 272 (11200). ^{1}H-NMR ((D$_6$)DMSO): 1.71 (*m*, 2 H–C(3′)); 2.12 (*m*, 2 H–C(2′)); 3.27 (*m*, 2 H–C(5′)); 4.11 (*m*, H–C(4′)); 4.62 (br. OH–C(5′)); 6.03 (*d*, J = 5.3, H–C(5)); 6.05 (*s*, NH_2); 6.36 ('*t*,' J = 6.6, H–C(1′)); 6.41 (*d*, J = 3.6, H–C(3)); 7.09 (*d*, J = 3.6, H–C(2)); 7.59 (*d*, J = 5.4, H–C(6)). Anal. calc. for $C_{12}H_{15}N_3O_2$ (233.27): C 61.79, H 6.48, N 18.01; found: C 61.92, H 6.56, N 17.82.

1,7-Dideaza- and 1,3,7-Trideaza-2′,3′-dideoxyribonucleoside Triethylammonium 5′-Triphosphates **25–29**: *General Procedure.* The dideoxyribonucleoside (0.1 mmol of **1**, **3–5**, or $c_3^{1,3,7}A_{d2'3'}$ was dissolved in $PO(OMe)_3$ (0.5 ml), cooled to 0° (ice-bath), and treated with $POCl_3$ (20 µl, 0.21 mmol). The mixture was stored at 4° for 3 h (refrigerator). $(Bu_3NH)_4P_2O_7$ in anh. DMF (0.5M, 1 ml) and Bu_3N (100 µl, 0.42 mmol) were added. After stirring for 1 min at 0°, 1M aq. $(Et_3NH)HCO_3$ (pH 7–8; 10 ml) was poured into the soln., and the solvent evaporated. The residue was dissolved in H_2O (100 ml), applied to an ion-exchange column (*DEAE-Sephadex*, HCO_3^- form, column 32 cm × 2 cm), and chromatographed using a linear gradient of $(Et_3NH)HCO_3$ 0.1M (1.0 l) to 0.7M (1.0 l). The 5′-triphosphates were eluted at 0.5M. The phosphate-containing fractions were lyophilized: colorless oils.

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