150. Deoxy-nitrosugars

17th Communication[1])[2])

Synthesis of Ketose-Derived Nucleosides from 1-Deoxy-1-nitroribose

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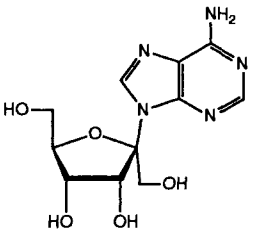
(16.VIII.91)

A new approach to ketose-derived nucleosides is described. It is based upon a chain elongation of 1-deoxy-1-nitroaldoses, followed by activation of the nitro group as a leaving group, and introduction of a pyrimidine or purine base. Thus, the nitroaldose **7** was prepared from **3** by pivaloylation (→**4**), synthesis of the anomeric nitrones **5**/**6**, and ozonolysis of **6** (*Scheme 1*). Partial hydrolysis of **4** yielded **8**/**9**, which were characterized as the acetates **10**/**11** and transformed into the nitrones **12**/**13**. Ozonolysis of **12**/**13** gave **14**/**15**, which were acetylated to **16**/**17**. *Henry* reaction of **7** lead to **19** and **20**, which were acetylated to **21** and **22** (*Scheme 2*). *Michael* addition of **7** to acrylonitrile and to methyl propynoate yielded the anomers **23**/**24** and **25**/**26**, respectively. Similar reactions of **16**/**17** were prevented by a facile β-elimination. Therefore, the nitrodiol **15** was transformed into the orthoesters **27** and then, by *Henry* reaction, partial hydrolysis, and acetylation, into **28** and **29** (*Scheme 2*). The structure of **19** was established by X-ray analysis. It was the major product of the kinetically controlled *Henry* reaction of **7**. Similarly, the β-D-configurated nitroaldoses **23** and **25** were the major products of the *Michael* addition. This indicates a preferred '*endo*'-attack on the nitronate anion derived from **7**. AM1 calculations for this anion indicate a strong pyramidalization at C(1), in agreement with an '*endo*'-attack. Nucleosidation of **21** by **31** afforded **32** and **33**. Yields depended strongly upon the nature and the amount of the promoter and reached 77% for **33**, which was transformed into **34**, **35**, and the known 'psicouridine' (**36**; *Scheme 3*). To probe the mechanism, the trityl-protected **30** was nucleosidated yielding **37**, or **37** and **38**, depending upon the amount of $FeCl_3$. Nucleosidation of the nitroacetate **28** was more difficult, required $SnCl_2$ as a promoter, and yielded **39** and **40**. The β-D-anomer **40** was transformed into **36**. Nucleosidation of **23** ($SnCl_4$) yielded the anomers **41** and **42**, which were transformed into **43** and **44**, and hence into **45** and **46** (*Scheme 4*). Similarly, nucleosidation of **25** yielded **47** and **48**, which were deprotected to **49** and **50**, respectively. The nucleoside **49** was saponified to **51**. Nucleosidation of **21** by **52** ($SnCl_2$) afforded the adenine nucleosides **53** and **54** (*Scheme 5*). The adenine nucleoside **53** was deprotected (→**55**→**56**) to 'psicofuranine' (**1**), which was also obtained from **58**, formed along with **57** by nucleosidation of **28**. The structure and particularly the conformation of the nitroaldoses, nitroketoses, and nucleosides are examined.

Introduction. – 'Psicofuranine' (**1**) and 'decoyinine' (**2**) (= 'angustmycine C and A'), hexulose nucleosides elaborated by *Streptomyces hygroscopicus* [2] [3], show antibacterial and antitumor activity [3]. Their biological activity has elicited interest in these compounds and, more generally, in analogues derived from chain-elongated ketoses. 'Psicofuranine' (**1**) has been synthesized by *Schroeder* and *Hoeksema* [2], *Farkas* and *Sorm* [4], *Alexandrova* and *Lichtenthaler* [5], and *Grouiller* and *Chattopadhyaya* [6]. 'Decoyinine' (**2**) has been synthesized by *McCarthy et al.* [7] and *Moffatt* and coworkers [8]. The

[1]) 16th Communication [1].

[2]) Presented, in part, at the '197th ACS National Meeting', Dallas, Texas, 9th–14th April 1989, Abstr. Carb. 9, and at the 'Fifth European Symposium on Carbohydrates', *Eurocarb V*, Prague, Czechoslovakia, 21st–25th Aug. 1989, poster no. A–112.



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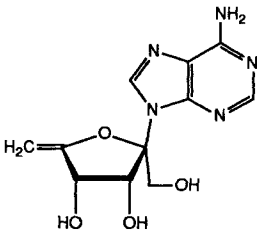

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nucleobase was introduced by *N*-glycosidation of *O*-acylpsicofuranosyl halides, or of psicofuranosyl pentabenzoate, which were prepared either from diisopropylidene fructose or from 2,3,4,5-tetra-*O*-acetylribonoyl chloride [8].

Longer-chain ketoses are accessible from 1-deoxy-1-nitroaldoses by a *Henry* reaction or by a *Michael* addition leading to tertiary nitroethers. Substitution of the NO_2 group[3]), presumably in a S_N1-type process, by an OH group yields chain-elongated ketoses [9]. In a similar way, these tertiary nitroethers could react with suitably derivatized nucleobases and yield nucleoside analogues.

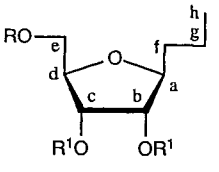
We have examined this *N*-glycosidation and the extent to which it is influenced by the nature of the protecting groups, as these are known to strongly modulate the reactivity of glycosyl donors [11].

Results and Discussion. – *Synthesis of the Chain-Elongated Ketoses.* The 2,3-*O*-alkyl- and the 2,3-*O*-acyl-protected 1-deoxy-1-nitroribofuranoses **7** and **17** (*Scheme 1*), required for the preparation of the chain-elongated nitroketoses, were prepared from 2,3-*O*-isopropylidene-5-*O*-pivaloyl-D-ribofuranose (**4**), which was obtained in 97% yield (α-D/β-D = 1:2.3) from 2,3-*O*-isopropylidene-D-ribofuranose [12] (**3**). Treatment of **4** with hydroxylamine hydrochloride in pyridine [13] yielded the corresponding oximes (95%; (*E*)/(*Z*) = 1:2 [14]). Without purification, this mixture was treated with 4-nitrobenzaldehyde under previously established conditions [15]. The resulting nitrones **5** and **6** (77%; α-D/β-D = 1:2.5) were separated on silica gel. The major nitrone **6** was ozonized [15] to **7** (88%). The anomer of **7** was not isolated.

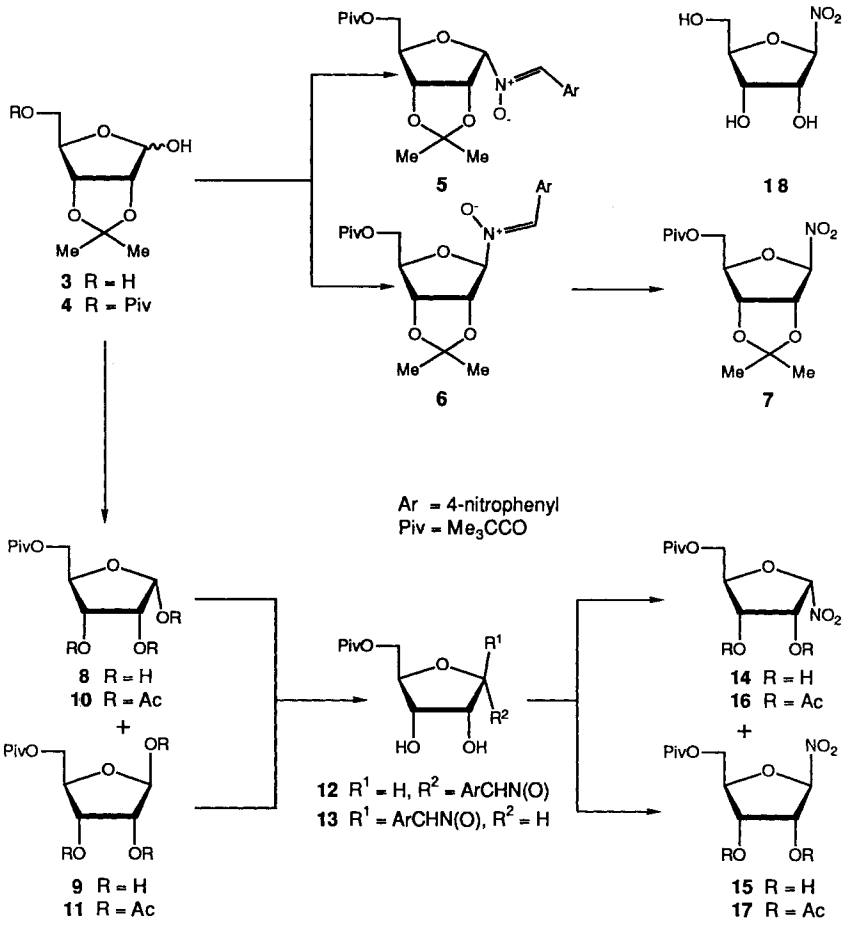
The structures of **4**–**7** are in agreement with the spectroscopic data. The ^{1}H-NMR spectrum of crude **5**/**6** shows two signals for ArC*H*, indicating the formation of two nitrones [15]. The absence of signals for aromatic protons in the ^{1}H-NMR spectrum of **7**, the presence of a strong band at 1570 cm^{-1} in its IR spectrum (NO_2 group), and the presence of a base peak for $[M - 46]^+$ (loss of NO_2) in the CI-MS of **7** indicate the formation of a nitroribofuranose. J(a,b)[4]) $\leq$ 1.2 Hz for β-D-**4**, **6**, and **7**, J(a,b) > 3.0 Hz for α-D-**4** and **5** (*Table 1*), and positive $\Delta\delta(\beta - \alpha)$ values for C(a) in **4** (5.52 ppm) and in **5**/**6** (5.26 ppm) [16] (*Table 2*) support the assigned configuration. Moreover, the

[3]) The use of an NO_2 group as a leaving group in cationic process has been reviewed in [10].

[4]) In the *General Part* and in the *Tables*, the C-atoms of the glycosyl moiety are marked a–e and f–h as shown below



Scheme 1



$\Delta\delta$ values for the isopropylidene Me groups in **5** (0.02 ppm) and **6** (0.19 ppm) and in the nitro-ribofuranose **7** (0.16 ppm) follow *Imbach*'s criterion[5]) for the assignment of the anomeric configuration of ribonucleosides.

Selective hydrolysis of the acetal function of **7** should lead to the diol **15**. Unfortunately, this direct approach failed. Given a large supply of **4**, we hydrolyzed this intermediate to a mixture **8**/**9** (3:1; 99%). Acetylation (Ac_2O, pyridine) of **8**/**9** and chromatography on silica gel gave the triacetates **10** (21%) and **11** (63%). Similarly as described above, the mixture **8**/**9** was converted into a 1:2 mixture of the nitrones **12** and **13** (69% from (**8**/**9**). Whereas pure **13** was obtained by crystallization from AcOEt/hex-

[5]) *Imbach* and *Kam* [17] have correlated the $\Delta\delta$ values of isopropylidene Me groups of 2,3-*O*-isopropylidene-ribonucleosides with the anomeric configuration. The phenomenon was explained on the basis of anisotropic effects of the nucleobase. The assumption that the proximity of an unsaturated substituent at C(a) and the '*endo*'-Me group leads to an upfield shift of its signal and to small $\Delta\delta$ values, as observed for **5**, is corroborated by the large and smilar $\Delta\delta$ values for both anomers of **4** (0.18 ppm for α-D-**4** and 0.16 ppm for β-D-**4**, *Table 1*).

Table 1. *Selected ^{1}H-NMR* (200 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the Aldoses* **4**–**11**, **13**, *and* **16**–**18**[4])

	α-D-**4**	**5**[a])	**8**[b])	**10**[a])	**16**	β-D-**4**	**6**[a])	**7**[a])	**9**[b])	**11**	**13**	**17**	**18**[c])
H–C(a)	5.40	5.60	5.38	6.38	5.89	5.46	5.55	5.64	5.32	6.17	5.39	5.71	5.81
H–C(b)	[d])	5.17	[d])	5.26–5.23	5.53	[d])	5.25	5.17	[d])	5.39–5.34	4.66	5.75	4.63
H–C(c)	[d])	4.80	[d])	5.26–5.23	5.32	[d])	4.78	4.74	[d])	5.39–5.34	4.23	5.35	4.20
H–C(d)	[d])	4.77	[d])	4.44	4.98	[d])	4.69	4.77	[d])	4.40–4.36	4.52–4.36	4.65–4.58	4.35
H–C(e)	[d])	4.27	[d])	4.26	4.41	[d])	4.41	4.31	[d])	4.23	4.52–4.36	4.46	3.97
H′–C(e)	[d])	4.22	[d])	4.19	4.27	[d])	4.36	4.26	[d])	4.23	4.52–4.36	4.36	3.79
Me_2C	1.57, 1.39	1.33, 1.31				1.49, 1.33	1.58, 1.39	1.53, 1.37					
J(a,b)	3.4	4.8	4.2	[d])	6.2	[d])	*ca.* 1.2	*ca.* 1.0	1.3	[d])	2.0	2.0	1.5
J(b,c)	[d])	5.8	[d])	[d])	6.3	[d])	6.0	5.8	[d])	[d])	5.0	5.0	4.5
J(c,d)	[d])	*ca.* 1.0	[d])	[d])	2.4	[d])	2.0	*ca.* 1.0	[d])	[d])	5.0	6.0	6.0
J(d,e)	[d])	3.2	[d])	3.2	3.0	[d])	4.5	4.6	[d])	4.4	[d])	3.5	4.0
J(d,e′)	[d])	3.2	[d])	3.3	3.2	[d])	5.7	4.4	[d])	4.4	[d])	5.1	6.0
J(e,e′)	[d])	12.2	[d])	12.2	12.4	[d])	12.1	12.3	[d])	[d])	[d])	12.4	12.8

[a]) 400 MHz. [b]) 300 MHz. [c]) In D_2O [20]. [d]) Not determined.

Table 2. *^{13}C-NMR* (50.6 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *of the Aldoses* **4**–**17** *and* **18**[4])

	α-D-**4**	**5**	**8**	**10**	**12**	**14**	**16**	β-D-**4**	**6**	**7**	**9**	**11**	**13**	**15**	**17**	**18**[a])[b])
C(a)	97.49	99.48	96.48	93.71	99.31	107.38	103.21	103.01	104.74	112.17	101.60	98.07	101.97	110.67	107.99	110.90
C(b)[c])	79.17	80.89	71.36	69.70	75.28	71.29	70.10	84.80	84.60	85.99	75.32	74.14	75.21	75.65	74.27	76.10
C(c)[c])	78.48	80.62	71.12	69.58	72.35	69.92	69.31	81.81	81.41	81.27	71.54	70.33	70.74	70.49	70.29	70.30
C(d)	81.43	82.73	81.14	81.55	86.57	84.82	84.64	85.85	87.38	87.66	80.59	79.20	83.97	84.17	82.70	87.40
C(e)	65.47	65.00	63.82	62.99	63.72	62.93	62.83	65.25	64.19	64.23	64.99	63.19	63.65	63.93	63.09	61.90
Me_2C	113.94	113.96						112.55	113.80	114.18						
	26.09	25.81						26.42	26.82	26.58						
	24.71	24.22						24.92	25.05	24.98						
Me_3CCO	178.75	177.66	178.61	177.43	178.27	178.70	177.57	178.53	177.86	177.69	179.16	177.86	178.37	179.26	177.87	
	39.00	38.63	38.76	38.44	38.77	38.81	38.73	38.80	38.71	38.64	38.82	38.75	38.80	38.81	38.70	
	27.10	27.13	27.05	26.80	27.09	26.90	27.06	27.10	27.01	26.98	27.05	27.02	27.05	26.90	26.95	
Ac				169.73			169.79					169.50			169.18	
				169.32			168.96					169.30			168.76	
				168.98			20.31					168.96			20.24	
				20.65			20.13					20.95			20.18	
				20.24								20.95				
				19.90								20.39				
ArCHN(O)		148.00			148.56				148.04				148.26			
		135.04			134.22				135.17				134.64			
		129.57			130.27				129.85				130.42			
		129.40			130.05				129.30				129.88			
		123.72			124.18				123.76				123.72			

[a]) 25.2 MHz. [b]) In D_2O [20]. [c]) The assignments in the α-D-series may be interchanged.

ane, pure **12** could be obtained neither by crystallization nor by chromatography on silica gel. Ozonolysis of **12/13** afforded a 1:2 mixture of the nitrodiols **14** and **15** (85%), which gave the diacetates **16** (28%) and **17** (57%), respectively.

The absence of bands above 3200 cm^{-1} in the IR spectra of **10** and **11** and the appearance of 3*s* (at *ca.* 2 ppm) in their ^{1}H-NMR spectra show the formation of the triacetates **10** and **11** (*Table 1*). The *β*-D-configuration of **11** was assigned on the basis of the broad *s* for H–C(a); H–C(a) of **10** shows 'virtual' coupling [18] between H–C(a) and H–C(c). The molecular rotations of **10** (+234) and of **11** (−68), and the positive $\Delta\delta$ values for C(a) in the ^{13}C-NMR spectra of **8/9** (5.12 ppm) and of **10/11** (4.36 ppm; *Table 2*) ascertain the assigned configuration [16] [19]. The presence of the ArH signals in the ^{1}H-NMR spectrum of **12/13** indicates the formation of nitrones. The mixture of the nitrodiols **14** and **15** is characterized by broad IR bands for the OH groups (3670, 3600 cm^{-1}) and a strong absorption for the NO_2 group (1565 cm^{-1}). The nitro diacetates **16** and **17** are characterized by strong IR bands at *ca.* 1575 cm^{-1}, the base peak for $[M-46]^+$ at *m/z* 301 in their Cl-MS, and the appearance of 2*s* (at *ca.* 2 ppm) in their ^{1}H-NMR spectra. The small J(a,b) (= 2.0 Hz; *Table 1*) for **13** and for the nitroribofuranose **17** indicate the *β*-D-configuration, and the large J(a,b) (= 6.2 Hz) for **16** indicates the *α*-D-configuration. The positive values for $\Delta\delta(\beta-\alpha)$ of C(a) in the ^{13}C-NMR spectra [16] of **12/13** (2.66 ppm), **14/15** (3.29 ppm), and **16/17** (4.78 ppm; *Table 2*) confirm the configurational assignments for compounds **12–17**. The molecular rotations of **16**, **7**, and **17**, and of **5**, **6**, and **13** (see *Exper. Part*) show that *Hudson*'s rule of isorotation [19] is valid for 1-deoxy-1-nitroaldofuranoses, but not for the corresponding nitrones [20].

According to X-ray analysis, 1-deoxy-1-nitro-*β*-D-ribofuranose [20] (**18**, *Scheme 1*) crystallizes in a northern conformation [21] ($^3T_2$ and E_2[6])), with NO_2–C(a) and OH–C(b) in a pseudoaxial and OH–C(c) in a pseudoequatorial position. The dihedral angle OC(d)–C(a)–N–O is relatively large (40.7°) [20]. The pseudoequatorial CH_2OH group prefers a *gt* conformation. The vicinal coupling constants in the ^{1}H-NMR spectrum of **18** (*Table 1*) indicate a similar ring conformation ($^3T_2$) in aqueous solution as in the solid state and the presence of an equilibrium of the *gt*- and *gg*-rotamers[7]). The vicinal couplings of the monocyclic *β*-D-anomers **13** and **17** are similar to the ones of **18**, indicating only a weak influence of the substituents (NO_2 *vs.* ArCHN(O), OH *vs.* AcO) upon the conformational equilibrium. The bicyclic *β*-D-anomers **6** and **7** show small J(a,b) and J(c,d) values (< 2 Hz), which are compatible with an equilibrium between the ^1E- and ^4E-conformers. The monocyclic and the bicyclic *β*-D-anomers (**6**, **7**, **13**, and **17**) exhibit a similar population of rotamers with respect to the C(d)–C(e) bond in soln. ($gg \geqslant gt \approx tg$). The monocyclic *α*-D-anomer **16** possesses a southern conformation ($^2T_3$), as evidenced by J(a,b) = 6.2 and J(c,d) = 2.4 Hz, whereas the bicyclic *α*-D-nitrone **5** shows vicinal couplings which are similar to those of the bicyclic *β*-D-nitrone **6**, and may be present as an equilibrium of the ^4E- and E_0-conformers. The monocyclic *α*-D-nitroether **16** and the bicyclic *α*-D-nitrone **5** are exclusively present as *gg*-rotamers.

Henry reaction of the nitroaldose **7** with paraformaldehyde gave the nitroketoses **19** (86%) and **20** (4%; corresponding acetates, **21** and **22**; *Scheme 2*). *Michael* addition to

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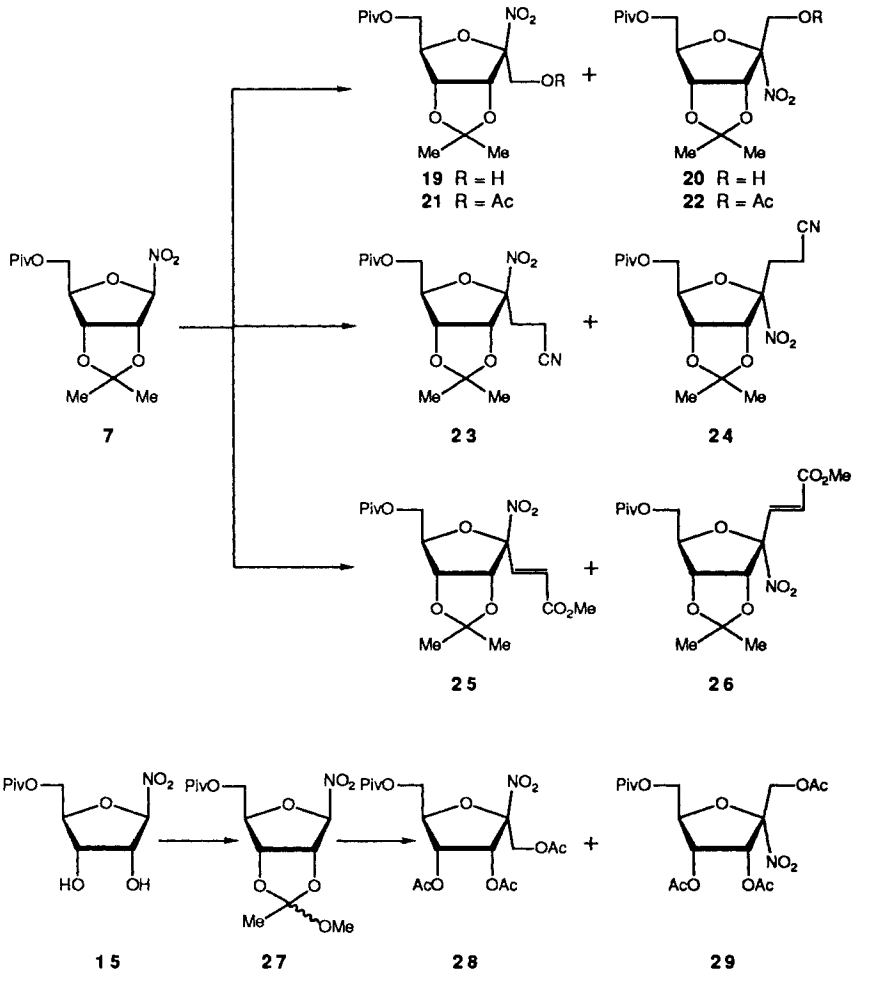
[6]) *Altona* and *Sundaralingam*'s notations [21] are used for the conformational analysis of the furanose ring.

[7]) The rotamer populations may be deduced from J(d,e) and J(d,e'). According to *Gerlt* and *Youngblood* [22], the methylene proton which resonates at a lower field is assigned to the *pro-S* H-atom. This assignment, which is applied to all furanoses in this paper, was confirmed by *Serianni* and *Kline* [23], *Perkins et al.* [24], and *Ohrui* and coworkers [25] by using selectively deuterated compounds. For the calculation of the rotamer populations in furanoses and pyranoses, *Manor et al.* [26] and *Sarma et al.* [27] developed two sets of equations. Both predict similar populations of the rotamers, but the equations of *Manor et al.* favor the *gg*-rotamers at the expense of the *gt*-rotamers. Qualitatively, small J(d,e) and J(d,e') values (⩽ 3 Hz) indicate the nearly exclusive presence of *gg*-rotamers. Increasing values for J(d,e') and J(d,e) indicate an increasing population of *gt*- and *tg*-conformers, respectively.

Scheme 2



acrylonitrile and to methyl propynoate, according to our procedures for the chain elongation of the 6-*O*-trityl-2,3-*O*-isopropylidene-D-ribofuranose [9], converted **7** to **23** (69%) and **24** (5%), and to **25** (48%) and **26** (24%), respectively. The anomers were separated on silica gel. A facile β-elimination [20] prohibited the chain elongation of the nitrodiacetate **17**. This difficulty was circumvented by transforming **15** into the orthoesters **27** (2:3 mixture of isomers) using trimethyl orthoacetate in the presence of a catalytic amount of TsOH [28]. The crude mixture was subjected, in sequence, to the action of paraformaldehyde and K_2CO_3, Ac_2O/pyridine, 80% aq. AcOH, and again Ac_2O/pyridine. Chromatography on silica gel yielded the fully acylated nitropsicofuranoses **28** (59%) and **29** (8%). The same yields and ratios of **28** and **29** were obtained using **15** or mixtures of **14** and **15** as starting material. According to TLC, the treatment of **14**/**15** with trimethyl orthoacetate led to a mixture of four products, of which two correspond to the isomers **27** obtained from **15**.

The absence of broad bands above 3200 cm^{-1} in the IR spectrum of **27**, the base peak for $[M - 46]^+$ in the CI-MS, 2*s* each for *Me*C (1.67 and 1.62 ppm) and *Me*O (3.35 and 3.30 ppm) in the ^{1}H-NMR spectrum, and 2*s* for Me(MeO)*C* (129.80 and 129.70 ppm) in the ^{13}C-NMR spectrum indicate the presence of diastereoisomeric nitro orthoesters. The 2*s* for H–C(a) (5.79 and 5.65 ppm) and the 2*d* for C(a) at 111.49 and 112.05 ppm confirm the β-D-configuration for both isomers of **27**. The small *J*(a,b) and the large *J*(b,c) (= 5.5 Hz)[8]) reveal the same conformation of the furanose ring for **27** and for **7**. The base peaks for $[M - 46]^+$, arising from the loss of the NO_2 group, in the CI-MS of the ketoses **19**–**22**, **24**–**26**, **28**, and **29**, and the strong bands at 1565–1575 cm^{-1} in the IR spectra of **19**–**26**, **28**, and **29** confirm the presence of an NO_2 group. The anomeric configurations of **21** and **22** are established by NOE difference spectroscopy: irradiation of the more shielded (= '*exo*') Me group of the isopropylidene moiety of **21** and **22** results in NOE's at H–C(b) and H–C(c), whereas irradiation of the more deshielded Me group gives NOE's at H–C(d). An additional NOE between the '*endo*'-Me group and H–C(f) at 4.49 ppm is only observed for **21**. This indicates a β-D-configuration for **21** and an α-D-configuration for **22**. Indeed, irradiation at H–C(f) of **22** at 4.55 ppm leads to an NOE for H–C(b) and H–C(c).

The assignment of the configuration at the anomeric center of **21** is corroborated by the X-ray analysis of the alcohol **19** (*Fig. 1*, *Table 3*, and *Exper. Part*). The remarkable features of the structure include a southern conformation, between ^4E and $^4T_3$, with all the substituents of the furanose ring in a pseudoaxial position, except for the CH_2OH group at C(2)[9]). The free OH group at C(1) is involved in an intermolecular H-bond with the

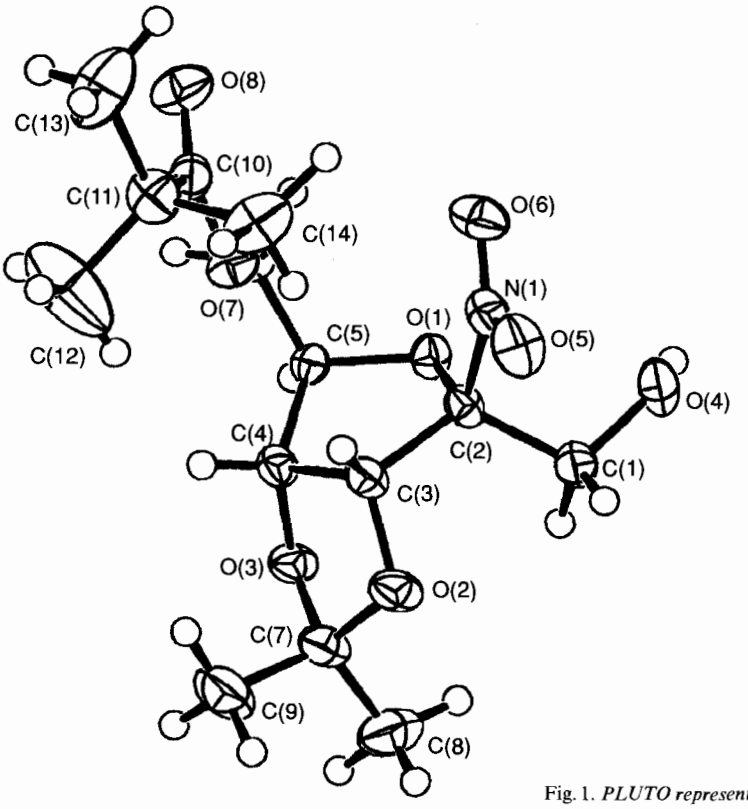


Fig. 1. *PLUTO representation for* **19**

[8]) The overlapping signals of H–C(c) and H–C(d) prevent the determination of *J*(c,d).

[9]) In the discussion of X-ray structure, numbering of the atoms refers to *Fig. 1*.

Table 3. *Selected Torsion Angles* [degrees] *and Bond Lengths* [pm] *for* **19**. E.s.d.'s in parentheses

Torsion angles			
C(2)–O(1)–C(5)–C(4)	–25.7(3)	N(1)–C(2)–C(3)–O(2)	–126.8(2)
C(2)–O(1)–C(5)–C(6)	98.2(3)	N(1)–C(2)–C(3)–C(4)	119.8(2)
C(5)–O(1)–C(2)–N(1)	–102.2(2)	C(1)–C(2)–C(3)–O(2)	–7.6(3)
C(5)–O(1)–C(2)–C(1)	142.8(2)	C(1)–C(2)–C(3)–C(4)	–121.0(2)
C(5)–O(1)–C(2)–C(3)	14.4(3)	O(2)–C(3)–C(4)–O(3)	–19.2(3)
O(5)–N(1)–C(2)–O(1)	178.9(2)	O(2)–C(3)–C(4)–C(5)	–134.8(2)
O(5)–N(1)–C(2)–C(1)	–63.8(3)	C(2)–C(3)–C(4)–O(3)	97.8(2)
O(5)–N(1)–C(2)–C(3)	62.2(3)	C(2)–C(3)–C(4)–C(5)	–17.8(3)
O(6)–N(1)–C(2)–O(1)	–3.2(3)	O(3)–C(4)–C(5)–O(1)	–83.6(2)
O(6)–N(1)–C(2)–C(1)	114.0(3)	O(3)–C(4)–C(5)–C(6)	154.0(2)
O(6)–N(1)–C(2)–C(3)	–119.9(3)	C(3)–C(4)–C(5)–O(1)	26.2(3)
O(1)–C(2)–C(3)–O(2)	116.2(2)	C(3)–C(4)–C(5)–C(6)	–96.3(3)
O(1)–C(2)–C(3)–C(4)	2.9(3)		
Bond lengths			
O(1)–C(2)	138.3(3)	O(4)–C(1)	141.2(4)
O(1)–C(5)	145.7(3)	O(5)–N(1)	123.3(4)
C(1)–C(2)	152.0(5)	O(6)–N(1)	122.4(4)
C(2)–C(3)	155.1(5)	N(1)–C(2)	155.8(4)

carbonyl group. The N–O bonds of the NO_2 group are nearly periplanar to the C(2)–O(1) bond (dihedral angles O–N–C(2)–O(1), 3 and 181°, see *Table 3*). The C(2)–O(1) bond length (1.383 Å) is typical for the anomeric effect, associated with the NO_2 group [29] (*Table 3*). The CH_2OH group prefers a *gt*, and the $AcOCH_2$ group a *gg*-conformation.

The '*endo*'-Me group in the β-D-anomers **19**, **21**, and **23** resonates at 1.56–1.57 ppm (*Table 4*); in α-D-anomers **20**, **22**, and **24**, its signal is shifted upfield ($\leq$ 1.45 ppm) due to the anisotropy effect of the NO_2 group. According to the molecular rotations (see *Exper. Part*), the α-D-anomers **20**, **22**, and **24** are more dextrorotatory than the β-D-anomers **19**, **21**, and **23**. Hence, *Hudson*'s rule of isorotation [19] is valid for nitroketoses and allows to assign the anomeric configuration of the octenulosonates **25** and **26**, and the psicose triacetates **28** and **29**. The signal of the '*endo*'-Me group is shifted upfield in both anomers of the octenulosonates **25** and **26** (1.42 and 1.45 ppm, resp.), due to the presence of an additional anisotropic functionality (α,β-unsaturated ester) at C(a).

The vicinal coupling constants in the ^{1}H-NMR spectrum of the bicyclic β-D-anomers **19**, **21**, **23**, and **25** are similar to each other (*Table 4*) and indicate a ring conformation (^4E to E_3) which is similar to the one of **19** in the solid state, and similar preferences for the *gg*-rotamers around the C(d)–C(e) bond. J(c,d) = 5.0 Hz reveals a $^3T_2$- to E_4-conformation for the monocyclic β-D-nitroulose **28**. The J(c,d) values for the monocyclic and bicyclic α-D-nitrouloses **20**, **22**, **24**, **26**, and **29** are in the range of 3.0 to 3.4 Hz (*Table 4*), indicating a northern ring conformation, close to $^3T_2$. The *gg*-rotamers (around C(d)–C(e) bond) in the chain-elongated ketoses **19–26**, **28**, and **29** are favored irrespective of the anomeric configuration and of the presence or absence of the dioxolane ring. Only small differences in ^{13}C-NMR chemical shifts of the nitroketose anomers are observed (*Table 5*).

The configurations of the nitroketoses **19–26**, **28**, and **29** are opposite to an earlier, tentative proposal for the configurations of analogous compounds [9], which was based mainly upon the chemical shift of H–C(b). According to the values in *Table 4*, H–C(b) of the β-D-anomers of the nitroketoses is more deshielded than H–C(b) of the corresponding α-D-anomers ($\Delta\delta$ = 0.34–0.62 ppm). This relation is also valid for the anomeric nitroaldofuranoses **16** and **17**, but not for the 1-deoxy-2,3-*O*-isopropylidene-1-nitro-5-*O*-trityl-D-ribofuranoses [9], illustrating the weakness of this criterion. The X-ray analysis of **19**, and the comparison of the ^{1}H-NMR spectra of the nitroketoses and of the molecular rotations show that the assignments in [9] have to be reversed. The chain

Table 4. *Selected ^{1}H-NMR* (400 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the Nitroketoses* **19–26**, **28**, *and* **29**[4])

	20	**22**	**24**[a])	**26**	**29**[a])	**19**	**21**	**23**[a])	**25**	**28**
H–C(b)	5.04	4.75	4.75	4.76	5.53	5.38	5.30	5.23	5.38	6.03
H–C(c)	4.75	4.79	4.83	4.80	5.31	4.80	4.79	4.77	4.78	5.43
H–C(d)	5.06–5.04	5.05	5.07	5.11	4.96	4.73	4.76	4.73–4.68	4.81	4.62–4.59
H–C(e)	4.42	4.33	4.41	4.47	4.34	4.29	4.29	4.30	4.34	4.37
H′–C(e)	4.30	4.29	4.33	4.32	4.34	4.20	4.23	4.18	4.27	4.29
Me_2C	1.43, 1.34	1.44, 1.34	1.45, 1.36	1.45, 1.33		1.56, 1.37	1.56, 1.36	1.57, 1.37	1.42, 1.34	
J(b,c)	6.8	6.8	6.8	6.7	6.4	5.9	5.8	6.0	5.6	5.0
J(c,d)	3.4	3.1	3.4	3.3	3.0	1.2	~ 1.0	1.4	1.0	5.0
J(d,e)	4.8	3.7	3.3	3.0	3.0	4.5	4.3	4.0	4.2	3.0
J(d,e′)	3.0	3.8	3.7	3.1	3.0	4.0	3.9	4.0	3.7	3.7
J(e,e′)	12.4	12.4	12.5	12.4	[b])	12.4	12.5	12.4	12.5	12.7

[a]) 200 MHz. [b]) Not determined.

Table 5. *^{13}C-NMR* (50.6 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *for the Nitroketoses* **19**, **21–26**, **28**, *and* **29**[4])

	22	**24**	**26**	**29**	**19**	**21**	**23**	**25**	**28**
C(a)	117.15	117.29[a])	117.14	112.56	119.71	117.65	117.96[a])	118.83	114.06
C(b)	82.66	85.10[b])	85.35[a])	70.67[b])	84.97[b])	85.43[b])	85.49[b])	85.46[a])	74.06[b])
C(c)	80.95	80.86	80.65	69.82[b])	81.67	81.20	81.39	81.46	70.74[b])
C(d)	85.04	85.24[b])	86.03[a])	84.27	85.92[b])	85.98[b])	85.95[b])	86.85[a])	82.91
C(e)	63.11[a])	62.93	62.98	62.81[a])	64.10[a])	64.35[a])	63.92	64.15	62.75[a])
C(f)	64.23[a])	32.37	138.82	63.88[a])	64.83[a])	63.82[a])	30.84	138.31	63.04[a])
C(g)		11.85	124.73				11.76	125.14	
C(h)		117.71[a])	165.10				119.60[a])	165.17	
Me_2C	115.46	116.81	115.20		114.18	114.14	114.33	114.56	
	25.99	25.88	25.97		25.94	25.77	26.04	25.93	
	24.84	24.78	24.84		24.39	24.24	24.40	24.85	
Me_3CCO	177.73	177.61	177.66	177.53	177.77	177.37	177.55	177.60	177.78
	38.88	38.80	38.79	38.78	38.63	38.38	38.55	38.57	38.68
	27.18	27.13	27.09	27.12	26.94	26.71	26.87	26.90	26.92
AcO or MeO	169.69		52.10	169.61, 169.34, 168,68,		169.45		52.00	169.65, 169.10, 168.29,
	20.51			20.35, 20.25, 20.11		20.30			20.43, 20.34, 20.16

[a]) [b]) Assignments may be interchanged.

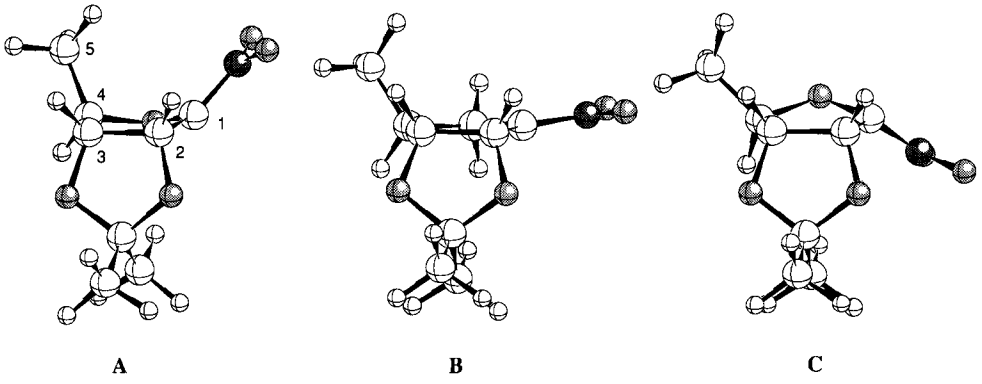


Fig. 2. *AM1 calculations: the most stable conformers* **A** *and* **C** *of the nitronate anions derived from 1,5-dideoxy-2,3-O-isopropylidene-1-nitro-*D*-ribofuranose and conformer* **B** *of its carbocyclic* (oxolane O-atom replaced by CH_2) *analogue*

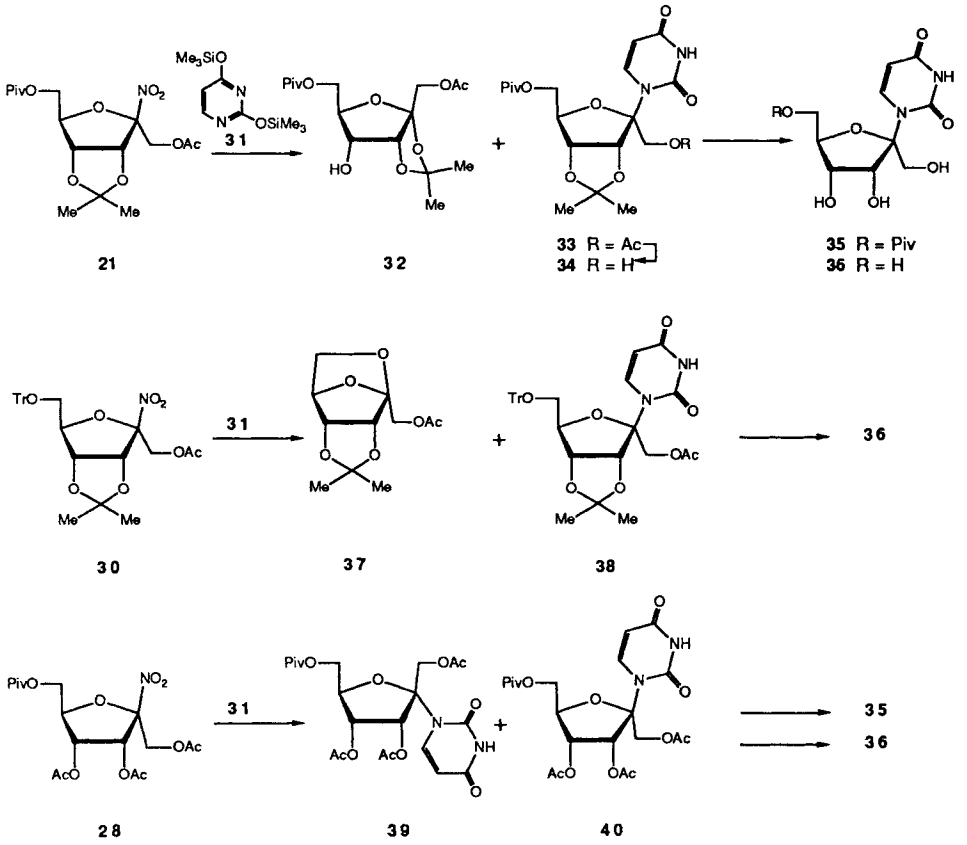
elongation of **7** and **27** yielded mostly the β-D-anomers, with β/α ratios of 24:1 for **19**/**20**, 14:1 for **23**/**24**, 2:1 for **25**/**26**, and 7:1 for **28**/**29** which implies that an *'endo'*-attack on the nitronate anion of **7** and **27** is favored. Under the conditions of chain elongation, only the formation of secondary products (solvolysis of the nitro-ether function), but no isomerization of pure samples of **19** or **20** was observed, showing that the addition of electrophiles to the nitronate anion of **7** and **27** is kinetically controlled. AM1 calculations [30] for the nitronate anion of the 5-deoxy analogue of **7** predict that the most stable conformer possesses a ^1E-conformation of the furanose ring (**A** in *Fig. 2*) with the NO_2 substituent displaced from the plane defined by O–C(4)[10]), C(1), and C(2). The degree of pyramidalization at C(1) of the ^1E-conformer, as expressed by the distance of C(1) from the plane, defined by O–C(4), N, and C(2), amounts to 0.28 Å, as compared to 0.51 Å for 1-deoxy-1-nitro-β-D-nitroribofuranose [20]. The E_1-conformer **C** (*Fig. 2*), which also exhibits a pyramidalized C(1), is less stable by 3.4 kcal/mol. The conformer with a sp^2-hybridized C(1) and a flat oxolane ring is not a minimum, in contrast to the analogous nitrocyclopentane anion (oxolane O-atom replaced by CH_2), for which only the conformation **B** (*Fig. 2*) is a minimum. Thus, the calculated structure of a 1-alkoxy-nitronate anion looks like a hybrid between a planar nitronate anion with completely delocalized charge and a C(1) carbanion in a conformation which is determined by the anomeric effect of the NO_2 group and steric interaction between the NO_2 group and the C(2) substituent. In the ^1E-conformer, the *'endo'*-attack is electronically favored. Thus, the AM1 calculations agree well with the observed selectivity of the electrophilic additions to **7** and **27**.

Synthesis of the Pyrimidine Nucleosides. Treatment of the nitropsicofuranose **21** with 2,4-bis[(trimethylsilyl)oxy]pyrimidine [31] (**31**; *Scheme 3*) under *Hilbert-Johnson* conditions ($SnCl_4$, MeCN) [32] gave 66% of the psicofuranose **32** and only 15% of the desired nucleoside **33**. Under optimized conditions (3.0 equiv. $FeCl_3$ in MeCN at 80°), we obtained a mixture of two nucleosides (77%) in a ratio of 4.7:1[11]), with **33** as the major

[10]) The numbering for AM1 calculations refers to *Fig. 2*.

[11]) Determined by ^{1}H-NMR spectroscopy.

Scheme 3



product. The minor product decomposed partially during chromatography and was not obtained pure[12]). The major product was partially deprotected with NaOMe in MeOH to yield 90% of **34**, and with aq. H_2SO_4 in MeOH to give 80% of **35**. It was completely deprotected by treatment with Bu_4NOH and then with *Dowex 50 W X 8* (H^+ form) to yield 76% of 'psicouridine' (= 1-(β-D-psicofuranosyl)uracil; **36**) [6].

The low diastereoselectivity and the retention of configuration in the *N*-gylcosidation of **21** are compatible with an S_N1-type process. To probe the mechanism of this reaction, we treated the 5-*O*-trityl-nitropsicofuranose **30** [9] with **31** in the presence of $FeCl_3$. We anticipated that the facile formation of 2,6-anhydrohexulofuranoses [33] under conditions which generate the corresponding glycosyl cation and the easy cleavage of trityl ethers upon exposure to electrophiles would lead to anhydropsicofuranose **37**, if the nucleoside is formed *via* a glycosyl cation. We obtained the anhydro sugar **37** and the nucleoside **38** in ratios which depended upon the relative amount of $FeCl_3$ (*Table 6*). The maximum yield of **37** (> 90%) was realized in the presence of 3 equiv. of $FeCl_3$, while the

[12]) The minor component is assumed to be the α-D-anomer of **33** ($\Delta\delta$ = 0.05 ppm for the isopropylidene Me groups, as observed in the ^{1}H-NMR spectrum of the mixture).

Table 6. *Selected Conditions for the Nucleosidation of* **30**: *Products and Yields of Isolated Compounds*

Promoting agent [equiv.]	Solvent	Products [%]	Promoting agent [equiv.]	Solvent	Products [%]
$SnCl_4$ (3.0)	CH_2Cl_2	**37** (> 90)	$FeCl_3$ (1.0)	MeCN	**38** (68)[a]), **37** (23)
$TiCl_4$ (3.0)	CH_2Cl_2	**37** (> 90)	$FeCl_3$ (2.0)	MeCN	**38** (45)[a]), **37** (50)
			$FeCl_3$ (3.0)	MeCN	**37**(> 90)

[a]) Contains some α-D-anomer.

maximum yield of the nucleoside **38** (68%) was realized in the presence of 1 equiv. of $FeCl_3$, showing that the transition states leading to the two products depend upon the stoichiometry of the promoter. It cannot be excluded that **30** is detritylated in the presence of excess $FeCl_3$ before ring closure to **37**. Treatment of **38** with 1N H_2SO_4 in MeOH gave again **36** (70%), confirming the β-D-configuration of **38**.

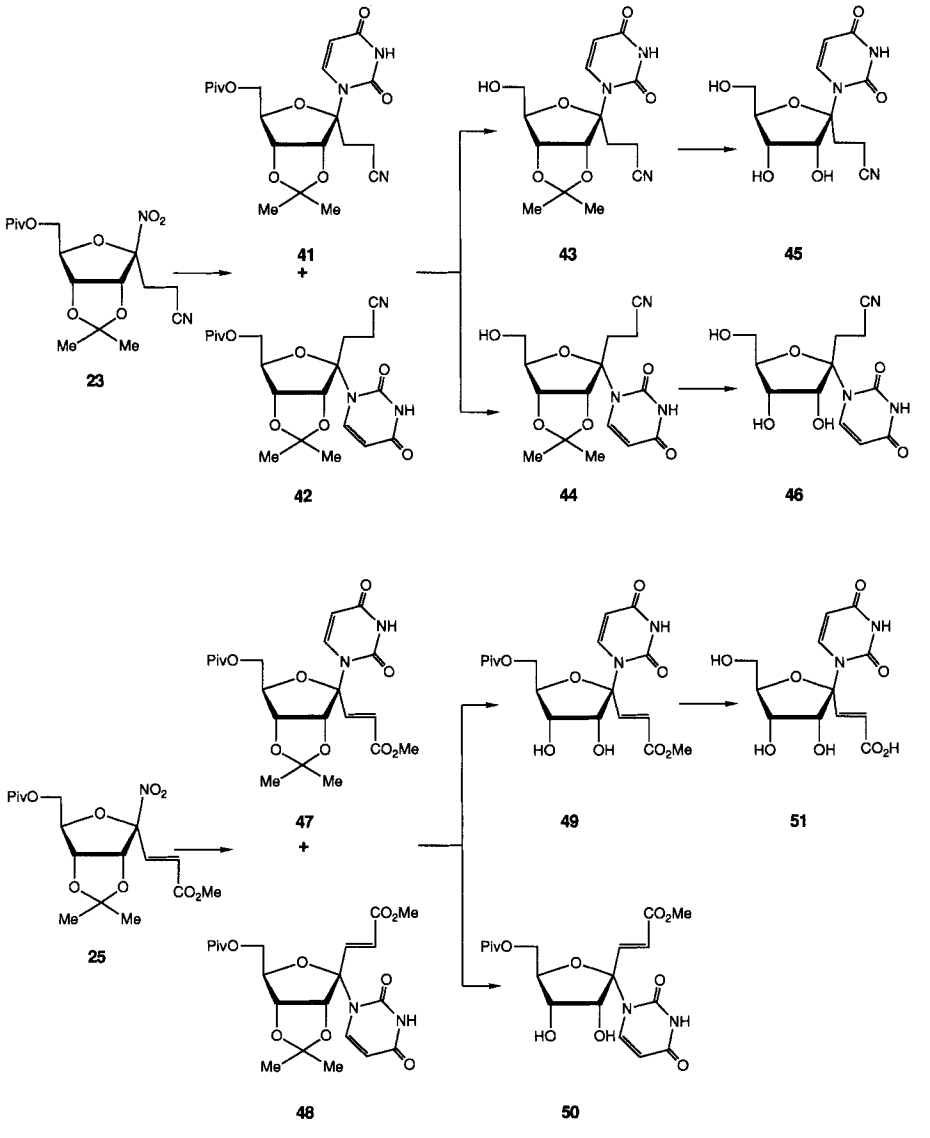
The reactivity of a glycosyl donor depends upon the protecting groups, stronger σ-acceptor leading to lower reactivity [11]. Hence, **28** should be a poorer glycosyl donor than **21** and **30** and allow a closer evaluation of the leaving-group ability of the NO_2 substituent. When the triacetate **28** was subjected to nucleosidation conditions (3 equiv. of $FeCl_3$ in MeCN at 80°), the expected decrease of reactivity was indeed observed, and the nucleosides **39** and **40** (1:4) were obtained in only 10% yield. Optimized conditions (3 equiv. of $SnCl_2$ in MeCN at 60° for 30 min) yielded 12% of **39** and 48% of **40** (*Scheme 3*). Deacetylation of **40** with NaOMe in MeOH gave the pivaloate **35** (83%), and complete deacylation with Bu_4NOH gave **36** (51%).

Nucleosidation of the nitrooctulose **23** (*Scheme 4*) worked best in the presence of *ca.* 2.6 equiv. of $SnCl_4$ at −30° and yielded 40% of a 3:2 mixture of the anomers **41** and **42**, while the nitrooctulose **25** yielded 30% of a 1.2:1 mixture of the anomers **47** and **48**. The mixture **41**/**42** was depivaloylated with 25% aq. NH_3 in MeOH. Chromatography yielded 57% of **43** and 38% of **44**, which were completely deprotected in 80% aq. CF_3COOH to **45** (94%) and to **46** (94%), respectively. Treatment of the mixture **47**/**48** with 30% aq. H_2SO_4 in MeOH 1:1 gave the diols **49** (38%) and **50** (25%). Saponification of the β-D-anomer **49** with Bu_4NOH in dioxane gave **51** (70%), while the analogous reaction of the α-D-anomer **50** failed.

The absence of bands for an NO_2 and for the uracil group in the IR spectra of **32** and **37**, and the absence of a signal for an anomeric H-atom in their ^{1}H-NMR spectra evidence that the NO_2 group is replaced by another group than the nucleobase. According to the ^{1}H-NMR spectrum, **32** contains an isopropylidene, an acetyl, a pivaloyl, and a secondary OH group. D_2O exchange and selective decoupling at H–C(b)[4]) and H–C(d) (see *Exper. Part*) prove that the OH group is bound at C(c). J(b,c) = 5 and J(c,d) = 9 Hz are compatible with an E_o-conformation and agree well with data of related compounds [34]. In the ^{1}H-NMR spectrum of **37**, the downfield shift of the signal of H–C(d) (4.71 ppm), which couples only with H_{exo}–C(e) (3.8 Hz), and the small geminal J(e,e′) = 7.2 Hz reveal the dioxabicyclo[2.2.1]heptane structure of **37**. The spectral data of **37** agree well with those of a related dioxabicycloheptane [35].

The IR spectra of **33**, **38** and **34**–**51** are characterized by the absence of nitro bands and by the presence of bands at *ca.* 3390 (NH) and *ca.* 1690 cm^{-1} (carbonly groups of the uracil moiety). A characteristic loss of the uracil moiety ($[M - 111]^+$) leading to the base peak is observed in their MS. The UV maxima at *ca.* 262 nm (*ca.* 10000), and the absence of a bathochromic shift in 0.01N methanolic KOH indicate glycosidation at N^1 [31] [36]. The configuration at the anomeric centre of **39**, **40**, **43**, **44**, **49**, and **50** was established by NOE difference spectroscopy. NOE's between H–C(b) or H–C(c) and H–C(f) establish the α-D-configuration for **39**, **44**, and **50**. As expected, no NOE between H–C(c) or H–C(b) and H–C(f) of **40**, **43**, and **49** is observed, but NOE's between H–C(6) and

Scheme 4



H–C(b) of **40**, and between H–C(6) and OH–C(e) of **43** ascertain the β-D-configuration. In addition, NOE's between the more shielded *O*-isopropylidene Me group and H–C(b) or H–C(c) of **43** are in keeping with *Imbach*'s rule, according to which also the '*endo*'-Me group of the β-D-anomers **33**, **38**, **34**, and **41** resonates at lower field (1.58–1.60 ppm) than the '*exo*'-Me group (1.34–1.38 ppm, $\Delta\delta \approx 0.23$ ppm; *Table 7*). In DMSO solution, both Me signals of **43** are shifted upfield, but the shift difference is maintained ($\Delta\delta = 0.2$ ppm). Small $\Delta\delta$ values are found for the α-D-nucleosides **42** and **44**. The assignment of the anomeric configuration is corroborated by the ^{13}C-NMR spectra (*Table 8*), where C(a) of the β-D-anomers resonates at lower field than the corresponding α-D-anomers ($\Delta\delta = 0.3$–2.1 ppm) [37]. The C(f) signals of **41** and **43** are shifted upfield by *ca.* 2 ppm in comparison with the C(f) signals of **42** and **44** due to a γ-effect with O–C(b) [43].

Table 7. *Selected ^{1}H-NMR* (400 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Pyrimidine Nucleosides* **33–36**, **38–46**, *and* **49–51**[4])

	33	**38**	**34**	**35**[a])	**36**[a])	**40**	**41**	**43**[a])
H–C(b)	5.28	5.32	5.32	4.70	4.59	6.05	5.10	5.03
H–C(c)	4.70	4.55	4.72–4.68	3.90–3.87	3.85–3.81	5.36	4.68	4.67
H–C(d)	4.67	4.69–4.61	4.72–4.68	4.23–4.13	3.93–3.90	4.57–4.53	4.65–4.62	4.32
H–C(e)	4.25	3.34	4.24	4.23–4.13	3.70–3.61	4.26	4.34–4.18	3.50–3.40
H′–C(e)	4.16	3.26	4.16	4.23–4.13	3.48–3.43	4.26	4.34–4.18	3.50–3.40
Me_2C	1.60, 1.36	1.59, 1.34	1.58, 1.37				1.61, 1.38	1.47, 1.27
Pyrimidine moiety	7.64, 5.66	7.63, 5.47	7.72, 5.63	7.71, 5.48	7.97, 5.43	7.74, 5.69	7.69, 5.72	7.79, 5.51
J(b,c)	6.3	6.2	6.1	4.6	4.8	5.6	6.2	6.1
J(c,d)	1.7	1.2	[c])	5.6	7.5	4.4	2.2	1.4
J(d,e)	3.1	3.7	3.1	[c])	2.8	3.0	[c])	[c])
J(d,e′)	4.4	4.8	4.7	[c])	4.7	3.0	[c])	[c])
J(e,e′)	12.6	10.9	12.5	[c])	12.7	[c])	[c])	[c])
	45[a])	**49**	**51**[b])	**39**	**42**	**44**[a])	**46**[a])	**50**
H–C(b)	4.41	4.67	*ca.* 4.82	5.89	4.94	4.83–4.78	4.13	4.76
H–C(c)	3.93–3.83	4.36	4.10	5.43	4.76	4.83–4.78	4.05–4.01	4.17–4.11
H–C(d)	3.93–3.83	4.66–4.64	4.17–4.13	4.38–4.15	4.44	4.24	3.83–3.80	4.22
H–C(e)	3.71	4.29	3.88	4.38–4.15	4.34–4.18	3.60–3.50	3.70	4.52
H′–C(e)	3.50	4.15	3.68	4.38–4.15	4.34–4.18	3.60–3.50	3.44	4.35
Me_2C					1.33, 1.38	1.23, 1.23		
Pyrimidine moiety	8.05, 5.50	7.69, 5.76	8.17, 5.62	7.68, 5.77	7.62, 5.76	7.71, 5.56	7.63, 5.52	7.73, 5.76
J(b,c)	4.5	5.1	4.6	4.8	5.8	[c])	4.1	4.7
J(c,d)	8.4	*ca.* 1.1	7.4	9.1	4.4	[c])	[c])	9.2
J(d,e)	2.3	3.3	2.6	[c])	4.1	[c])	[c])	2.1
J(d,e′)	4.4	3.8	4.1	[c])	4.1	[c])	4.1	4.0
J(e,e′)	12.4	12.5	12.5	[c])	[c])	[c])	12.3	12.8

[a]) In (D_6)DMSO. [b]) In CD_3OD. [c]) Not determined.

Table 8. *^{13}C-NMR* (50.6 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *of the Pyrimidine Nucleosides* **33–36**, **38–46**, *and* **49–51**[4])

	33	**34**	**38**	**35**[a])	**36**[a])	**40**	**41**	**43**
C(a)	99.01	100.42	99.30	99.51	99.05	96.11	100.42	100.91
C(b)	83.40[b])	83.08[b])	85.08[b])	74.47	74.34	75.15	83.40[b])	86.43[b])
C(c)	80.97	81.25	81.71	69.77	68.99	70.89	80.70	81.44
C(d)	86.26[b])	85.66[b])	86.27[b])	80.60	83.43	81.11	86.76[b])	87.00[b])
C(e)	63.98[c])	63.94[c])	64.66[c])	63.05[b])	59.79[b])	62.39[b])	63.52	62.19
C(f)	63.73[c])	63.46[c])	63.53[c])	61.44[b])	61.30[b])	63.25[b])	30.38	30.88
C(g)							11.22	11.29
C(h)							118.65	119.15
Pyrimidine moiety	163.61	165.15	163.60	163.94	163.96	163.54	163.41	164.71
	150.11	150.30	150.10	150.90	150.69	150.20	150.12	150.19
	140.60	142.31	142.89	142.18	142.84	140.11	139.34	141.34
	101.00	101.25	100.79	100.01	99.13	101.28	101.93	100.47
Me_2C	114.05	113.51	113.46				114.10	113.21
	25.83	25.72	25.84				26.01	25.97
	24.28	24.26	24.40				24.41	24.42
Me_3CCO or trityl	117.67	177.77	87.74	177.52		177.61	177.64	
	38.65	38.64	143.35–139.75	[d])		38.60	38.69	
	26.92	26.94	128.81–127.12	27.01		26.82	26.95	

Table 8 (cont.)

	33	**34**	**38**	**35**[a])	**36**[a])	**40**	**41**	**43**
AcO or MeO	169.91		169.92			169.86		
	20.56		20.63			169.18		
						168.41		
						20.44		
						20.30		
						20.10		

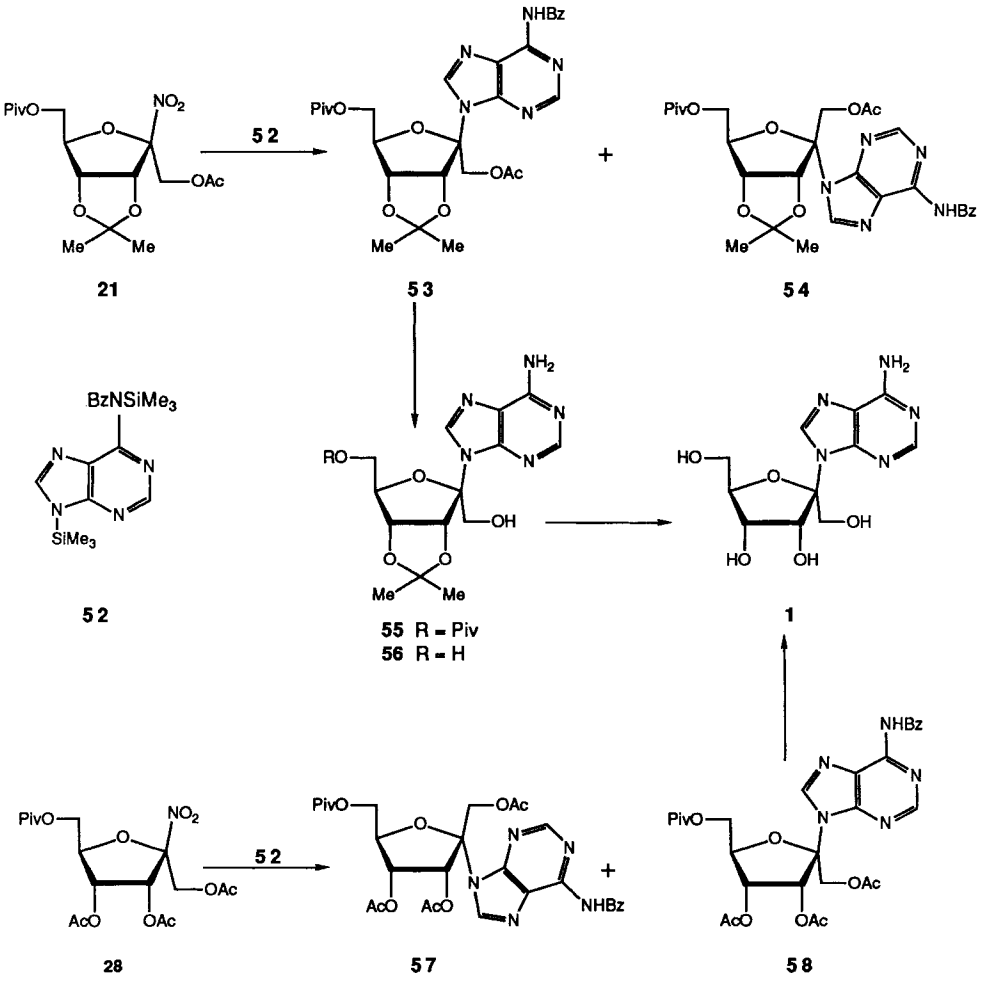
	45	**49**	**51**[a])	**39**	**42**	**44**	**46**[a])	**50**
C(a)	98.17	98.46	97.77	95.81	98.37	99.27	97.55	96.68
C(b)	74.93	78.29	74.96	72.13	83.23[b])	85.32[b])	74.39	74.86
C(c)	68.49	72.61	68.92	69.70	80.22	80.44	69.27	69.43
C(d)	83.67	84.43	83.94	77.97	84.95[b])	86.18[b])	82.77	80.64
C(e)	59.18	63.50	59.64	62.18[b])	63.20	62.17	59.98	61.97
C(f)	28.67	139.69[b])	136.99	64.86[b])	32.84	32.21	31.76	139.88[b])
C(g)	10.05	122.99	129.43		11.08	11.35	10.35	123.66
C(h)	120.23	165.99[c])	170.99		118.31	119.72	120.45	165.92[c])
Pyrimidine moiety	163.65	163.56[c])	163.78	163.64	163.10	164.00	164.10	164.92[c])
	150.59	151.64	150.53	149.72	150.12	150.10	150.57	151.05
	140.76	141.33[b])	140.96	139.20	139.34	140.19	141.00	142.37[b])
	100.32	102.75	100.12	101.53	101.51	101.14	99.94	101.71
Me_2C					114.47	113.87		
					25.22	26.71		
					25.22	25.12		
Me_3CCO or trityl		177.85		177.83	177.50			178.26
		38.74		38.78	38.60			38.93
		27.04		27.02	27.14			27.15
AcO or MeO		52.00		169.53				51.99
				168.98				
				168.23				
				20.57				
				20.23				
				20.15				

[a]) In (D_6)DMSO. [b]) [c]) Assignments may be interchanged. [d]) Hidden by the signals of solvent.

The pronounced β-D-selectivity in the nucleosidation of **21**, **28**, and **30** and the moderate β-D-selectivity in the nucleosidation of **23** and **25** suggest a neighboring-group participation of AcO–C(f) (or AcO–C(b)). A strong dependence of the nucleosidations upon the promoter is observed, requiring a careful optimization of the conditions for each reaction. Thus, $FeCl_3$ was the best promoter for the nucleosidation of **21** and **30**, $SnCl_2$ was the best one for **23**, and $SnCl_4$ for **25**.

Synthesis of the Purine Nucleosides. Treatment of **21** with N^6-benzoyl-N^6,9-bis(trimethylsilyl)-9*H*-adenine [38] (**52**) in the presence of $SnCl_2$ in MeCN gave a 10:1 mixture **53**/**54** (50%; *Scheme 5*). The major nucleoside **53** was treated with a soln. of 25% aq. NH_3 in MeOH for 7 days at r.t., yielding **55** (38%) and **56** (48%). Similarly, nucleosidation of **28** with **52** in the presence of $SnCl_2$ gave a 2:3 mixture of **57** and **58** (44%). Both **56** and **58** were deprotected to yield 'psicofuranine' (= 9-(β-D-psicofuranosyl)adenine; **1**). The melting point and the spectroscopic data of **1**, obtained from either **56** or **58**, are identical and agree well with the published values [2] [6].

Scheme 5



The UV absorption of the benzamidopurines **54**, **53**, **57**, and **58** at 279 nm ($\varepsilon \approx 20000$) and of the aminopurines **55**, **56**, and **1** at 260 nm, ($\varepsilon \approx 13000$) are characteristic for N^9-gylcosylated purines [31] [39]. The anomeric configuration of the isopropylidene derivatives **54**–**56** is confirmed by the deshielded '*endo*'-Me group for the β-D-anomers **53**, **55** (1.66–1.65 ppm), and **56** (1.48 ppm, in (D_6)DMSO; *Table 9*). The anisotropy effect of the purine base in **54** is so strong that the '*endo*'-Me group resonates at 0.78 ppm. Similarly, two of the three AcO signals of the triacetate **57** are shifted upfield (2.03, 1.89, and 1.75 ppm; compare **58**: 2.26, 2.12, and 1.91 ppm). In contrast to this, the *t*-Bu group of the *O*-pivaloylated β-D-purine nucleosides resonates at higher field (1.00–1.06 ppm) than the one of the corresponding α-D-anomers (1.28–1.29 ppm). The ^{13}C-NMR spectra (especially the chemical shift of C(a); *Table 10*), the optical rotations, and the CD spectra agree very well with the assigned configurations.

Comparison of the vicinal coupling constants of the pyrimidine and purine nucleosides with those of the corresponding nitroketoses shows that the ring conformations of the isopropylidenated β-D-nucleosides deviate strongly from those of the corresponding

Table 9. *Selected ^{1}H-NMR* (400 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the Purine Nucleosides* **1**, *and* **53**–**58**[4])

	53	**55**	**56**[a])	**58**	**1**[a])	**54**	**57**
H–C(b)	5.90	5.85	5.72	6.45	4.88	5.09	6.01
H–C(c)	4.81	4.81	4.77	5.41	3.86–3.83	4.84–4.79	5.47
H–C(d)	4.76–4.73	4.70–4.67	4.32–4.29	4.65–4.61	4.00–3.97	4.84–4.79	4.72
H–C(e)	4.20	4.21	3.36–3.26	4.35	3.73	4.35	4.34–4.33
H′–C(e)	4.15	4.15	3.36–3.26	4.35	3.49	4.27	4.34–4.33
Me_2C	1.66, 1.45	1.65, 1.43	1.48, 1.31			0.78, 1.23	
Me_3CCO	1.00	1.03		1.06		1.28	1.29
Purine moiety	8.87, 8.23	8.29, 8.07	8.12, 8.10	8.76, 8.29	8.24, 8.09	8.82, 8.23	8.73, 8.24
J(b,c)	6.1	6.2	6.1	5.3	4.7	5.6	5.2
J(c,d)	2.0	2.2	1.5	5.3	4.4	[b])	4.1
J(d,e)	4.0	5.6	6.2	3.3	2.5	4.7	[b])
J(d,e)	5.5	5.6	5.6	3.3	4.2	4.5	[b])
J(e,e′)	12.4	12.3	11.7	[b])	12.3	12.0	[b])

[a]) In (D_6)DMSO. [b]) Not determined.

Table 10. *^{13}C-NMR* (50.6 MHz, $CDCl_3$) *Data: Chemical Shifts* [ppm] *for the Purine Nucleosides* **1** *and* **53**–**58**[4])

	53	**55**	**56**[a])	**58**	**1**[a])	**54**	**57**
C(a)	98.23	99.92	99.54	95.33	98.09	97.73	95.16
C(b)	84.08[b])	83.76[b])	84.49[b])	74.40	74.36	82.58[b])	71.49[b])
C(c)	81.64	81.79	81.90	70.50	69.40	82.22[b])	71.30[b])
C(d)	84.96[b])	85.06[b])	86.63[b])	81.04	83.88	82.58[b])	81.38
C(e)	64.58[c])	63.85[c])	61.45[c])	62.66[b])	60.48[b])	64.90[c])	62.98[c])
C(f)	63.61[c])	64.26[c])	62.94[c])	63.30[b])	62.23[b])	64.04[c])	64.38[c])
Purine moiety	152.66	155.10	156.16	152.57	156.20	152.66	152.22
	150.90	152.65	152.18	150.58	151.89	151.11	151.28
	149.54	148.69	148.90	149.63	148.28	149.49	149.64
	141.84	139.88	140.56	141.21	140.76	141.02	141.28
	123.82	119.91	120.11	123.66	120.14	123.62	123.64
Me_2C	114.59	114.08	112.38			114.75	
	26.05	26.13	26.21			25.40	
	24.63	24.69	24.88			24.78	
Me_3CCO	177.54	177.73		177.76		177.83	177.84
	38.52	38.54		38.64		38.79	38.83
	26.76	26.77		26.85		27.14	27.12
AcO	169.59			169.83		169.72	169.56
	20.35			169.21		20.55	169.15
				168.65			168.71
				20.40			20.51
							20.27
							20.19
PhCO	164.45			164.52		164.58	164.67
	133.53			133.58		133.70	133.51
	132.66			132.70		132.65	132.79
	128.73			128.77		128.76	128.80
	127.74			127.80		127.76	127.23

[a]) In (D_6)DMSO. [b]) [c]) Assignments may be interchanged.

β-D-nitroketoses (^4E to E_3). The deprotected or acylated β-D-nucleosides exhibit different conformations. Whereas the tetraacylated **40** and **58** (in $CDCl_3$), triol **35** (in (D_6)DMSO), and tetrol **1** (in (D_6)DMSO) adopt similar conformations as the peracylated nitroketose **28** ($^3T_2$ to E_4), the triols **45** (in (D_6)DMSO) and **51** (in CD_3OD) and the tetrol **36** (in (D_6)DMSO) exhibit similar conformations (E_4 to ^3E) as 1-(β-D-psicofuranosyl)cytosine in the solid state (^3E [40]). The diol **49** (in $CDCl_3$ or (D_6)DMSO) exhibits a southern conformation (^4E to E_3), as evidenced by J(c,d) of *ca.* 1.1 Hz (*Table 7*). Thus, the ring conformations depend strongly upon the substituents. The α-D-nucleosides prefer a northern conformation ($3T_2$ to E_4 for **42** and **57**, ^4E to E_3 for **39** and **50**). The rotamer distribution around the C(d)–C(e) bond in all nucleosides is dominated by the *gg*-conformation. In the pyrimidine series, only the *gt*-conformation contributes to the equilibrium. The purine series shows an inconsistent behaviour, with **8** possessing nearly exclusively a *gg*-conformation, while **1** is a mixture of the *gg*(major)- and the *gt*(minor)-conformers, and **54**–**56** are *ca.* 1:1:1 mixtures of the *gg*-, *gt*-, and *tg*-conformers[7]).

The completely protected β-D-nucleosides **33**, **38**, and **40** show negative *Cotton* effects, and the primary alcohols **34**–**36** exhibit positive *Cotton* effects. This implies that the χ angle [41] is $0 \pm 90°$ for **33**, **38**, and **40** (*'syn'*-conformations), and $180 \pm 90°$ for **34**–**36** (*'anti'*-conformations). These results indicate an intramolecular H-bond between the primary OH group and the carbonyl group in **34**–**36**. In $CDCl_3$, **40** shows an NOE of 6% between H–C(6) and H–C(c), requiring an *'anti'*-conformation. The apparent contradiction with the interpretation of the CD spectra may reflect the strong influence of the solvents upon the χ angle. Weak positive *Cotton* effects for **43** ($\Delta\varepsilon = 0.51$) and **45** ($\Delta\varepsilon = 0.27$) indicate a weak preference only for the *'anti'*-conformation. This presumably means that there is a weak intramolecular H-bond between OH–C(e) and the C(2) carbonyl group. The α-D-nucleosides **39**, **44**, and **46** exhibit negative *Cotton* effects (*'anti'*-conformation). The additional chromophore in **49**–**51** complicates the interpretation of their CD spectra. As shown by the molecular rotation of **43**–**46** (see *Exper. Part*), the pyrimidine nucleosides do not follow *Hudson*'s rule of isorotation [19].

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basle, for generous support, and Dr. *A. Linden* for the X-ray analysis.

Experimental Part

General: See [42]. MeCN was distilled over CaH_2. Nucleosidations were conducted under dried Ar (BTS catalyst (*Fluka*) and silica gel with moisture indicator). Usual workup implies washing of the org. layer with aq. sat. $NaHCO_3$ soln., H_2O, and brine, drying ($MgSO_4$), and evaporating the solvent at or below 40°. Column chromatography (CC): silica gel. M.p.: not corrected. Optical rotations: at 25°; solns. in MeOH. UV (λ_{max} in nm (ε)) and CD spectra (λ in nm ($\Delta\varepsilon$)): solns. in MeOH. ^{1}H- and ^{13}C-NMR spectra: unless otherwise stated, at 400 and 50 MHz resp.; solns. in $CDCl_3$. CI-MS (M^+ (% intensity)): isobutane as carrier gas.

1. Chain-Elongated Uloses. *2,3-O-Isopropylidene-5-O-pivaloyl-D-ribofuranose* (**4**). At −10°, 3.55 ml (28.6 mmol) of pivaloyl chloride were slowly added to a soln. of 5.0 g (26.0 mmol) of 2,3-*O*-isopropylidene-D-ribofuranose [12] in pyridine (25 ml). After 2 h, 7.5 ml of MeOH were added, and the soln. was allowed to warm to r.t. Usual workup gave 7.0 g (97%) of **4**. An anal. sample was obtained by CC (Et_2O/hexane 1:3). R_f (Et_2O/hexane 1:1) 0.44. IR: 3600*w*, 3520–3380*w*, 3035*w* (sh), 2980*m*, 2957*m*, 2940*m*, 2910*w*, 2876*w*, 1725*s*, 1480*m*, 1460*m*, 1400*m*, 1385*m*, 1375*m*, 1280*s*, 1235*m* (sh), 1155*s* (br.), 1075*s* (br.), 1035*s*, 1000*m*, 970*m*, 942*w*, 920*w*, 870*s*. ^{1}H-NMR (200 MHz; α-D/β-D 1:2.3): 5.46 (*d*, J = 3.0, addn. of $D_2O \rightarrow$ *s*, 0.7 H); 5.40 (*dd*, J = 10.8, 3.4, addn. of $D_2O \rightarrow$ *d*, J = 3.0, 0.3 H,

H–C(1)); 4.72–4.03 (*m*, 5 H); 4.00 (*d*, *J* = 10.8, 0.3 H); 3.69 (*d*, *J* = 3.0, 0.7 H, exchangeable with D_2O, OH–C(1)); 1.57 (*s*, 0.9 H); 1.49 (*s*, 2.1 H, Me); 1.39 (*s*, 0.9 H); 1.33 (*s*, 2.1 H, Me); 1.22 (br. *s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 259 (14, $[M-15]^+$), 257 (100, $[M-17]^+$), 217 (5), 126 (2), 114 (2), 85 (4), 69 (5), 68 (2). Anal. calc. for $C_{13}H_{22}O_6$ (274.32): C 56.92, H 8.08; found: C 56.65, H 8.11.

N-*(4-Nitrobenzylidene)-2,3-*O-*isopropylidene-5-*O-*pivaloyl-α- and β-*D-*ribofuranosylamine* N-*Oxide* (**5** and **6**, resp.). At r.t., 2.92 g (41.4 mmol) of $NH_2OH \cdot HCl$ were added to a soln. of 6.5 g (23.7 mmol) of **4** in 15 ml of pyridine. The mixture was stirred for 4 h. Usual workup gave 6.6 g (95%) of *2,3-*O-*isopropylidene-5-*O-*pivaloyl-*D-*ribose oxime* ((*E*/*Z*) 1:2), which was used for the next step without further purification. A mixture of 6.5 g (22.4 mmol) of the oxime, 50 ml of CH_2Cl_2, 3.39 g (22.4 mmol) of 4-nitrobenzaldehyde, 2 ml of AcOH, and 2 g of anh. $CaCl_2$ was stirred at r.t. for 8 h, worked up as usual, and purified by CC (Et_2O/hexane 1:3): 7.3 g (77%) of **5**/**6**, ratio 1:2.5. Pure samples of **5** and **6** were obtained by CC (AcOEt/hexane 1:3).

Data of **5**: R_f (AcOEt/hexane 1:1) 0.36. M.p. 117°. $[\alpha]_D = -94$ (*c* = 0.19). UV: 337 (10931), 248 (7435). IR: 3038*w* (sh), 2980*m*, 2940*m*, 2910*w*, 2875*w*, 1735*s*, 1600*m*, 1580*m*, 1520*s*, 1480*m*, 1460*m* (br.), 1422*m*, 1400*w*, 1385*m*, 1375*m*, 1345*s*, 1315*w*, 1305*w*, 1280*m*, 1230–1200*m*, 1155*s*, 1120*s*, 1108*s*, 1090*s*, 1070*m*, 1030*m*, 1012*m*, 1005*m*, 970*m*, 940*w*, 920*w*, 895*m*, 865*s*, 850*m*, 688*w*, 660*w*. ^{1}H-NMR: 8.48 (*d*, *J* = 9.0, 2 arom. H); 8.27 (*d*, *J* = 9.0, 2 arom. H); 7.91 (*s*, ArC*H*); 5.60 (*d*, *J* = 4.8, H–C(1)); 5.17 (*dd*, *J* = 5.8, 4.8, H–C(2)); 4.80 (*dd*, *J* = 5.8, *ca.* 1.0, H–C(3)); 4.77 (*m*, H–C(4)); 4.27 (*dd*, *J* = 12.2, 3.2, H–C(5)); 4.22 (*dd*, *J* = 12.2, 3.2, H–C(5)); 1.33 (*s*, Me); 1.31 (*s*, Me); 1.25 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 423 (100, $[M+1]^+$), 407 (58, $[M-15]^+$), 257 (22). Anal. calc. for $C_{20}H_{26}N_2O_8$ (422.44): C 56.86, H 6.20, N 6.63; found: C 56.69, H 6.28, N 6.59.

Data of **6**: R_f (Et_2O/hexane 1:1) 0.34. M.p. 41–45°. $[\alpha]_D = -50$ (*c* = 0.11). UV: 340 (15706), 249 (9447). IR: 2980*m*, 2940*w*, 2915*w* (sh), 2878*w*, 1730*s*, 1600*s*, 1570*w*, 1520*w*, 1482*m*, 1460*w* (br.), 1420*w*, 1400*w*, 1388*m*, 1378*m*, 1348*s*, 1280*m*, 1240–1200*m*, 1150*s*, 1140*s* (sh), 1110*s*, 1080*s*, 1035*m*, 865*s*. ^{1}H-NMR: 8.44 (*d*, *J* = 8.5, 2 arom. H); 8.28 (*d*, *J* = 8.5, 2 arom. H); 7.89 (*s*, ArC*H*); 5.55 (br. *s*, H–C(1)); 5.25 (*dd*, *J* = 6.0, *ca.* 1.2, H–C(2)); 4.78 (*dd*, *J* = 6.0, 2.0, H–C(3)); 4.69 (*m*, H–C(4)), 4.41 (*dd*, *J* = 12.1, 4.5, H–C(5)); 4.36 (*dd*, *J* = 12.1, 5.7, H–C(5)); 1.58 (*s*, Me); 1.39 (*s*, Me); 1.12 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 423 (100, $[M+1]^+$), 407 (17, $[M-15]^+$), 258 (5), 257 (42), 57 (27). Anal. calc. for $C_{20}H_{26}N_2O_8$ (422.44): C 56.86, H 6.20, N 6.63; found: C 56.88, H 6.25, N 6.46.

*1-Deoxy-2,3-*O-*isopropylidene-1-nitro-5-*O-*pivaloyl-β-*D-*ribofuranose* (**7**). A soln. of 5 g (11.8 mmol) of **6** in CH_2Cl_2 (200 ml) was treated with $NaHCO_3$ (600 mg) and cooled to −78°. O_3 was passed through the soln., until the deep blue color persisted for 0.5 h, then O_2 (20 min) and N_2 (20 min) were passed through the soln. After the addition of 2 ml of Me_2S, the mixture was allowed to warm to r.t. Usual workup and CC (Et_2O/hexane 1:3) gave 3.15 g (88%) of **7**. Yellow viscous oil. R_f (AcOEt/hexane 1:3) 0.58. $[\alpha]_D = -68$ (*c* = 0.97). IR: 3040*w* (sh), 2980*m*, 2940*m*, 2915*w*, 2880*w*, 1732*s*, 1570*s*, 1482*m*, 1460*w* (br.), 1400*w*, 1380*s*, 1345*w*, 1280*m*, 1240–1200*m*, 1160*s*, 1140*s*, 1100*s*, 1070*s*, 1035*m*, 995*w*, 970*w*, 938*w*, 915*w*, 868*m*, 850*m* (sh). ^{1}H-NMR: 5.64 (br. *s*, H–C(1)); 5.17 (*dd*, *J* = 5.8, *ca.* 1.0, H–C(2)); 4.77 (br. *t*, *J* ≈ 4.5, H–C(4)); 4.74 (*dd*, *J* = 5.8, *ca.* 1, H–C(3)); 4.31 (*dd*, *J* = 12.3, 4.6, H–C(5)); 4.26 (*dd*, *J* = 12.3, 4.4, H–C(5)); 1.53 (*s*, Me); 1.37 (*s*, Me); 1.17 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 288 (15, $[M-15]^+$), 272 (8), 258 (26), 257 (100, $[M-46]^+$), 201 (6), 189 (5), 183 (7), 125 (8), 114 (7), 113 (6), 98 (6), 97 (9), 85 (15). Anal. calc. for $C_{13}H_{21}NO_7$ (303.31): C 51.48, H 6.98, N 4.62; found: C 51.72, H 6.83, N 4.41.

*5-*O-*Pivaloyl-α- and -β-*D-*ribofuranose* (**8** and **9**, resp.) *and 1,2,3-Tri-*O-*acetyl-5-*O-*pivaloyl-α- and -β-*D-*ribofuranose* (**10** and **11**, resp.). A soln. of 5.5 g (23.5 mmol) of **4** in 80 ml of HCO_2H (*ca.* 98%) was cooled to 0° and treated with 20 ml of H_2O. After 90 min, excess HCO_2H was evaporated and H_2O was removed by azeotropic distillation with toluene (4 × 50 ml). CC (AcOEt/hexane 1:1) of the residue gave 4.65 g (99%) of **8**/**9** (3:1). After acetylation of **8**/**9** in Ac_2O/pyridine 1:1 (10 ml, 24 h), CC (Et_2O/hexane 1:3) gave **10** (1.50 g, 21%) and **11** (4.50 g, 63%).

Data of **8**/**9**: IR: 3610*w*, 3440*m* (br.), 3040*w* (sh), 2980*m*, 2945*m*, 2915*m*, 2880*w*, 1730*s*, 1482*m*, 1460*m* (br.), 1400*m*, 1370*m*, 1287*s*, 1240–1200*m*, 1160*s* (br.), 1120*s* (br.), 1070*s* (br.), 1040*s*, 995*m*, 955*m* (br.), 920*w*, 890*m* (br.). ^{1}H-NMR (300 MHz): 5.38 (br. *t*, *J* ≈ 5.0, addn. of D_2O→*d*, *J* = 4.2, 0.75 H); 5.32 (br. *s*, addn. of D_2O→5.25, br. *d*, *J* = 1.3, 0.25, H, H–C(1)); 4.37–3.14 (8 H, addn. of D_2O→4.35–3.99, 5 H); 1.23 (*s*); 1.22 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 235 (13, $[M+1]^+$), 234 (100, M^+), 218 (6), 217 (64), 58 (8), 57 (6), 39 (6).

Data of **10**: R_f (Et_2O/hexane 1:1) 0.28. $[\alpha]_D = +65$ (*c* = 1.16). IR: 3035–3015*m*, 2980*m*, 2940*w*, 2880*w*, 1745*s* (br.), 1715*s* (sh), 1602*w*, 1480*m*, 1455*w* (br.), 1370*s*, 1280*m*, 1255–1200*s*, 1160*s*, 1140*s* (sh), 1115*s*, 1085*m*, 1050*s*, 1010*s*, 948*m*. ^{1}H-NMR: 6.39–6.38 (*m*, *X* of *ABX*, irrad. at 5.24→*s*, H–C(1)); 5.26–5.23 (*m*, *AB* of *ABX*, H–C(2), H–C(3)); 4.44–4.43 (*m*, irrad. at 5.24→*t*, *J* = 3.2, H–C(4)); 4.26 (*dd*, *J* = 12.2, 3.2, H–C(5)); 4.19 (*dd*, *J* = 12.2, 3.3, H–C(5)); 2.10 (*s*, AcO); 2.09 (*s*, AcO); 2.05 (*s*, AcO); 1.19 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 302 (18), 301 (100, $[M-59]^+$), 198 (2), 181 (2), 157 (4), 139 (9), 115 (2), 85 (2), 71 (2), 67 (2). Anal. calc. for $C_{16}H_{24}O_9$ (360.36): C 53.33, H 6.71; found: C 53.19, H 6.75.

Data of **11**: R_f (Et_2O/hexane 1:1) 0.38. $[\alpha]_D = -19$ ($c = 1.51$). IR: 3035–3015*m*, 2980*m*, 2940*w*, 2915*w*, 2878*w*, 1750*s* (br.), 1600*w*, 1480*m*, 1460*w*, 1430*w* (br.), 1400*m*, 1370*s*, 1285*m*, 1245–1200*s*, 1158*s* (br.), 1110*s*, 1070*s*, 1028*s*, 970*s*, 895*w* (br.). ^{1}H-NMR (200 MHz): 6.17 (br. *s*, H–C(1)); 5.39–5.34 (*m*, H–C(2), H–C(3)); 4.40–4.36 (*m*, H–C(4)); 4.23 (*d*, $J = 4.4$, 2 H–C(5)); 2.13 (*s*, AcO); 2.10 (*s*, AcO); 2.07 (*s*, AcO); 1.23 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 302 (14), 301 (100, $[M - 59]^+$), 287 (2), 277 (3), 259 (2), 181 (3), 170 (2), 157 (2), 156 (4), 140 (3), 139 (9), 112 (2), 103 (2), 97 (2), 85 (3), 83 (2), 67 (3). Anal. calc. for $C_{16}H_{24}O_9$ (360.36): C 53.33, H 6.71; found: C 53.31, H 6.90.

N-*(4-Nitrobenzylidene)-5*-O-*pivaloly-α- and -β*-D-*ribofuranosylamine* N-*Oxide* (**12** and **13**, resp.). Similarly as described for **5**/**6**, 5.0 g of **8**/**9** (3:1) was transformed into **12**/**13** (1:2; 5.65 g, 69%), light yellow crystals. Crystallization from AcOEt/hexane gave pure **13**.

Data of **12**/**13** (1:2): R_f (AcOEt) 0.47. IR: 3555–3520*w*, 3360–3200*w*, 2980*m*, 2940*m* (sh), 2915*w*, 2875*w*, 1730*s*, 1712*s*, 1603*m*, 1525*s*, 1482*m*, 1345*s*, 1320*m* (sh), 1280*m*, 1155*s*, 1150*s* (*sh*), 1120–1105*s*, 1035*m* (sh), 1015*w*, 865*m*, 850*m*. ^{13}C-NMR: *Table 2*. MS: 384 (20), 383 (100, $[M + 1]^+$), 368 (10) 367 (50, $[M - 15]^+$), 250 (10), 232 (7), 218 (8), 217 (72), 167 (8), 103 (6).

Data of **13**: R_f (AcOEt) 0.44. M.p. 116–118°. $[\alpha]_D = +19$ ($c = 0.06$). UV: 338 (13766), 251 (9589). UV (0.01N methanolic HCl): 289 (9132). IR: 3660*w*, 3540*w* (br.), 3440*w* (br.), 3030*w*, 2978*m*, 2938*w*, 2910*w*, 2878*w*, 1730*s*, 1600*m*, 1580*w* (*br.*), 1520*s*, 1480*m*, 1460*w*, 1400*m*, 1345*s*, 1320*m*, 1307*m*, 1280*m*, 1158–1105*s*, 1012*m*, 940*w* (br), 900*w*, 865*m*, 845*w*, 685*w*, 660*w* (br.). ^{1}H-NMR (200 MHz): 8.45 (*d*, $J = 9.2$, 2 arom. H); 8.27 (*d*, $J = 9.2$, 2 arom. H); 8.10 (*s*, ArC*H*); 5.39 (*d*, $J = 2.0$, H–C(1)); 5.00–3.50 (2 br. *s*, exchangeable with D_2O, 2 OH); 4.66 (*dd*, $J = 5.0$, 2.0, H–C(2)); 4.52–4.26 (*m*, H–C(4), 2 H–C(5)); 4.23 (br. *t*, $J = 5.0$, H–C(3)); 1.16 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 383 (100, $[M + 1]^+$), 367 (21), 305 (10), 250 (8), 233 (7), 217 (40). Anal. calc. for $C_{17}H_{22}N_2O_8$ (382.38): C 53.40, H 5.80, N 7.33; found: C 53.50, H 6.08, N 7.53.

Ozonolysis of **12**/**13**. Ozone (70%) was passed through a soln. of 1.2 g (3.13 mmol) of **12**/**13** (1:2) in CH_2Cl_2 (100 ml) containing $NaHCO_3$ (160 mg) at r.t., until the blue color persisted for 10 min. Usual workup and CC (AcOEt/hexane 1:3) gave **14**/**15** (1:2; 710 mg, 85%) which, upon acetylation (Ac_2O/pyridine 1:1, 2 h) and CC (AcOEt/hexane 1:3), gave **16** (267 mg, 28%) and **17** (533 mg, 57%).

1-Deoxy-1-nitro-5-O-*pivaloyl-α- and -β*-D-*ribofuranose* (**14** and **15**, resp.): IR: 3670*w* (br.), 3600*w*, 3540–3350*m* (br.), 3020*w* (br.), 2978*m*, 2938*m*, 2910*w*, 2878*w*, 1725*s*, 1565*s*, 1480*m*, 1460*m*, 1400*m*, 1365*m*, 1350*m*, 1285*s*, 1160*s* (sh), 1135*s* (br.), 1108*s*, 1035*m*, 988*m*, 940*w*, 890*w* (br.), 690–660*w*. ^{1}H-NMR (**15**): 5.67 (*d*, $J = 1.0$, H–C(1)); 4.53–4.28 (3*m*, 5 H); 3.20 (*d*, $J = 3.2$, OH); 2.88 (*d*, $J = 5.7$, OH); 1.24 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 246 (5, $[M - 17]^+$), 219 (1), 218 (11), 217 (100, $[M - 46]^+$).

2,3-Di-O-*acetyl-1-deoxy-1-nitro-5*-O-*pivaloyl-α*-D-*ribofuranose* (**16**): R_f (AcOEt/hexane 1:2) 0.53. $[\alpha]_D = +95$ ($c = 4.15$). IR: 3040–3020*w* (br.), 2980*m*, 2940*w*, 2915*w*, 2880*w*, 1750*s* (br.), 1575*s*, 1480*m*, 1465–1455*m*, 1400*m*, 1370*s*, 1280*m*, 1240–1200*s*, 1145*s*, 1070*m*, 1050–1040*m*, 1005*m*, 975*m*, 905*m*. ^{1}H-NMR (200 MHz): 5.89 (*d*, $J = 6.2$, H–C(1)); 5.53 (br. *t*, $J = 6.3$, H–C(2)); 5.32 (*dd*, $J = 6.4$, 2.4, H–C(3)); 4.98 (br. *q*, $J \approx 3.0$, H–C(4)); 4.41 (*dd*, $J = 12.4$, 3.0, H–C(5)); 4.27 (*dd*, $J = 12.4$, 3.2, H–C(5)); 2.13 (*s*, AcO); 2.08 (*s*, AcO); 1.24 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 302 (9), 301 (100, $[M - 46]^+$), 228 (4), 217 (6), 186 (5), 181 (9), 157 (10), 143 (8), 140 (5), 139 (29), 127 (4), 126 (18), 103 (7), 98 (7), 97 (14), 91 (4), 85 (18), 81 (5), 69 (4). Anal. calc. for $C_{14}H_{21}NO_9$ (347.32): C 48.40, H 6.05, N 4.03; found: C 48.45, H 6.28, N 3.82.

2,3-Di-O-*acetyl-1-deoxy-1-nitro-5*-O-*pivaloyl-β*-D-*ribofuranose* (**17**): R_f (AcOEt/hexane 1:2) 0.42. $[\alpha]_D = -25$ ($c = 8.8$). IR: 3040–3020*w*, 2980*m*, 2940*w*, 2918*w*, 2880*w*, 1760*s* (br.), 1732*s* (sh), 1572*s*, 1480*m*, 1462–1452*w*, 1400*w*, 1370*s*, 1282*m*, 1240–1200*s*, 1135*s*, 1098*s*, 1070*s*, 1010*m*, 900*m*, 870*w*. ^{1}H-NMR (200 MHz): 5.75 (*dd*, $J = 5.0$, 2.0, H–C(2)); 5.71 (*d*, $J = 2.0$, H–C(1)); 5.35 (*dd*, $J = 6.0$, 5.0, H–C(3)); 4.65–4.58 (*m*, H–C(4)); 4.46 (*dd*, $J = 12.4$, 3.5, H–C(5)); 4.36 (*dd*, $J = 12.4$, 5.1, H–C(5)); 2.17 (*s*, AcO); 2.10 (*s*, AcO); 1.22 (*s*, *t*-Bu). ^{13}C-NMR: *Table 2*. MS: 302 (100), 259 (4), 257 (5), 246 (6), 245 (5), 217 (5), 199 (12), 181 (15), 157 (13), 140 (7), 139 (83), 126 (4), 112 (4), 97 (12), 85 (4). Anal. calc. for $C_{14}H_{21}NO_9$ (347.32): C 48.40, H 6.05, N 4.03; found: C 48.44, H 6.04, N 4.25.

2-Deoxy-3,4-O-*isopropylidene-2-nitro-6*-O-*pivaloyl-β- and -α*-D-*psicofuranose* (**19** and **20**, resp.). At r.t., 774 mg (25.8 mmol) of paraformaldehyde and 36 mg (0.26 mmol) of K_2CO_3 were added to a soln. of 784 mg (2.58 mmol) of **7** in 20 ml of MeOH and stirred for 1 h. Usual workup and CC (Et_2O/hexane 1:2) gave 744 mg (86%) of **19** and 31 mg (4%) of **20**. An anal. sample of **19** was obtained by crystallization from Et_2O/hexane. For X-ray analysis, the single crystal of **19** was obtained from MeOH at r.t.

Data of **19**: R_f (Et_2O/hexane 1:1) 0.31. M.p. 93–94°. $[\alpha]_D = -81$ ($c = 0.13$). IR: 3595*w*, 3500–3320*w*, 3040*w* (sh), 2980*m*, 2940*m*, 2910*w*, 2880*w*, 1730*s*, 1562*s*, 1480*m*, 1450*m*, 1400*m* (sh), 1388*m*, 1378*m*, 1350*m*, 1330*w*, 1280*m*, 1250–1190*m*, 1145*s* (br.), 1085*s*, 1035*m*, 1015*m*, 970*w*, 942–925*w*, 895*w*, 870*m*. ^{1}H-NMR: 5.38 (*d*, $J = 5.9$, H–C(3)); 4.80 (*dd*, $J = 5.9$, 1.2, H–C(4)); 4.73 (*ddd*, $J = 4.5$, 4.0, *ca.* 1.0, H–C(5)); 4.29 (*dd*, $J = 12.4$, 4.5, H–C(6)); 4.20 (*dd*, $J = 12.4$, 4.0, H–C(6)); 4.15 (*d*, $J = 12.5$, H–C(1)); 4.03 (*d*, $J = 12.5$, H–C(1)); 2.13 (br. *s*,

exchangeable with D_2O, OH–C(1)); 1.56 (*s*, Me); 1.37 (*s*, Me); 1.17 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 316 (5, $[M-17]^+$), 288 (13), 287 (100, $[M-46]^+$), 273 (3), 257 (12), 247 (3), 229 (14), 211 (3), 185 (4), 127 (4), 109 (13), 85 (3), 69 (4), 57 (30), 43 (13). Anal. calc. for $C_{14}H_{23}NO_8$ (333.34): C 50.45, H 6.95, N 4.20; found: C 50.51, H 6.99, N 4.09.

X-Ray Analysis of **19**. Data collection on a *Nicolet-R3* diffractometer with graphite-monochromated MoK_α radiation. Crystal size 0.18 × 0.18 × 0.44 mm, temp. −60°; $2\theta_{max} = 55°$; total data measured 2833; total data merged 2419. The refinement was performed using the SHELXS 86 package. $R = 0.0431$. Crystal data: monoclinic $P2_1$; $a = 9.701(2)$, $b = 6.9514(8)$, $c = 12.886(2)$ Å; $\beta = 102.95(1)$; $D = 1.307$ g cm^{-3}, $Z = 2$.

Data of **20**: R_f (Et_2O/hexane 3:1) 0.42. $[\alpha]_D = +2$ ($c = 0.20$). ^{1}H-NMR: 5.06–5.04 (*m*, H–C(5)); 5.04 (*d*, $J = 6.8$, H–C(3)); 4.75 (*dd*, $J = 6.9$, 3.4, H–C(4)); 4.42 (*dd*, $J = 12.4$, 4.8, H–C(6)); 4.30 (*dd*, $J = 12.4$, 3.0, H–C(6)); 4.25 (*dd*, $J = 12.5$, 8.5, addn. of $D_2O \rightarrow d$, $J = 12.5$, H–C(1)); 3.94 (*dd*, $J = 12.5$, 6.4, addn. of $D_2O \rightarrow d$, $J = 12.5$, H–C(1)); 2.67 (*dd*, $J = 8.5$, 6.5, exchangeable with D_2O, OH); 1.43 (*s*, Me); 1.34 (*s*, Me); 1.23 (*s*, *t*-Bu).

*1-O-Acetyl-2-deoxy-3,4-O-isopropylidene-2-nitro-6-O-pivaloyl-β- and -α-*D*-psicofuranose* (**21** and **22**, resp.). Acetylation of 1.0 g (3.0 mmol) of **19**/**20** (24:1) in Ac_2O/pyridine 1:1 for 2 h, followed by usual workup and CC (Et_2O/hexane 1:3) gave **21** (1.03 g, 91%) and **22** (43 mg, 4%).

Data of **21**: R_f (AcOEt/hexane 1:3) 0.40. $[\alpha]_D = -67$ ($c = 0.43$). IR: 3040*w* (sh), 2980*m*, 2940*w*, 2915*w*, 2878*w*, 1755*s*, 1735*s* (br.), 1567*s*, 1480*m*, 1450*m*, 1385*m*, 1370*m*, 1352*w*, 1335*w*, 1280*m*, 1245–1195*s*, 1145*s*, 1087*s*, 1052*m*, 1035*m*, 1018*m*, 970*w*, 955*w*, 945*w*, 895*w*, 870*m*. ^{1}H-NMR: 5.30 (*d*, $J = 5.8$, irrad. at 1.56→NOE of 0.2%, irrad. at 1.36→NOE of 1.2%, H–C(3)); 4.79 (*dd*, $J = 5.8$, *ca.* 1.0, irrad. at 1.56→NOE of 0.1%, irrad. at 1.36→NOE of 2.3%, H–C(4)); 4.76 (br. *t*, $J = 4.3$, 3.9, irrad. at 1.56→NOE of 0.4%, H–C(5)); 4.65 (*d*, $J = 12.3$, H–C(1)); 4.49 (*d*, $J = 12.3$, irrad. at 1.56→NOE of 1%, H–C(1)); 4.29 (*dd*, $J = 12.5$, 4.3, H–C(6)); 4.23 (*dd*, $J = 12.5$, 3.9, H–C(6)); 2.05 (*s*, AcO); 1.56 (*s*, irrad. at 1.36→NOE of 2.1%, Me); 1.36 (*s*, irrad. at 1.56→NOE of 1.9%, Me); 1.16 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 330 (9), 329 (100, $[M-46]^+$), 300 (12), 273 (12), 271 (13) 253 (8), 245 (17), 229 (10), 189 (9), 169 (9), 136 (10), 126 (9), 111 (9), 109 (15), 103 (18), 101 (9), 98 (16), 97 (14), 91 (10), 87 (15), 86 (11), 85 (19), 79 (20), 72 (11), 71 (34), 70 (14), 69 (40), 68 (10), 67 (31), 66 (9). Anal. calc. for $C_{16}H_{25}NO_9$ (375.38): C 51.20, H 6.71, N 3.73; found: C 51.36, H 6.57, N 3.85.

Data of **22**: R_f (AcOEt/hexane 1:3) 0.42. $[\alpha]_D = +4$ ($c = 0.14$). IR: 3035*w* (sh), 2980*m*, 2940*w*, 2910*w*, 2878*w*, 1735*s*, 1568*s*, 1480*m*, 1455*w* (br.), 1400*w*, 1387*m*, 1378*m*, 1370*m*, 1330*w*, 1278*m*, 1240–1195*s*, 1145*s*, 1110*s*, 1085*s*, 1040*w* (br.), 1015*s*, 955*m* (br.), 895*w* (br.), 869*m*. ^{1}H-NMR: 5.05 (br. *q*, $J = 3.5$, irrad. at 1.44→NOE of 0.6%, H–C(5)); 4.84 (*d*, $J = 12.0$, irrad. at 4.55→NOE of 37%, H–C(1)); 4.79 (*dd*, $J = 6.8$, 3.1, irrad. at 4.55→collective NOE of 7.7%, irrad. at 1.34→collective NOE of 3.5%, H–C(4)); 4.75 (*d*, $J = 6.8$, irrad. at 4.55→collective NOE of 7.7%, irrad. at 1.34→collective NOE of 3.5%, H–C(3)); 4.55 (*d*, $J = 12.0$, irrad. at 4.84→NOE of 33%, H–C(1)); 4.33 (*dd*, $J = 12.4$, 3.7, H–C(6)); 4.29 (*dd*, $J = 12.4$, 3.8, H–C(6)); 2.09 (*s*, AcO); 1.44 (*s*, irrad. at 1.34→NOE of 1.2%, Me); 1.34 (*s*, irrad. at 1.44→NOE of 1.7%, Me); 1.24 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 330 (17), 329 (100, $[M-46]^+$), 315 (7), 300 (5), 299 (23), 241 (6), 109 (20), 85 (7), 83 (8). Anal. calc. for $C_{16}H_{25}NO_9$ (375.38): C 51.20, H 6.71, N 3.73; found: C 51.40, H 6.86, N 3.82.

*2,3,4-Trideoxy-5,6-O-isopropylidene-4-nitro-8-O-pivaloyl-β- and -α-*D*-oct-4-ulofuranosononitrile* (**23** and **24**, resp.). A soln. of 0.23 ml (3.49 mmol) of acrylonitrile in 5 ml of CH_2Cl_2 was slowly added at 0° to a soln. of 845 mg (2.79 mmol) of **7** and 440 mg (1.4 mmol) of $Bu_4NF \cdot 3\,H_2O$ in 10 ml of CH_2Cl_2. After stirring for 1 h, the solvent was evaporated and the residue purified by CC (Et_2O/hexane 1:3) yielding 688 mg (69%) of **23** and 50 mg (5%) of **24**. An anal. sample of **23** was obtained by crystallization from Et_2O/hexane.

Data of **23**: R_f (Et_2O/hexane 1:1) 0.40. M.p. 61–62°. $[\alpha]_D = -63$ ($c = 0.27$). IR: 3040*w* (sh), 2980*m*, 2940*w*, 2915*w*, 2880*w*, 2260*w*, 1735*s*, 1562*s*, 1480*m*, 1460*w* (br.), 1440*w*, 1400*w*, 1385*m*, 1375*m*, 1280*m*, 1145*s*, 1085*s*, 1035*m*, 970*w*, 960*w* (br.), 870*m*. ^{1}H-NMR (200 MHz): 5.23 (*d*, $J = 6.0$, H–C(5)); 4.77 (*dd*, $J = 6.0$, 1.4, H–C(6)); 4.73–4.68 (*m*, H–C(7)); 4.30 (*dd*, $J = 12.4$, 4.0, H–C(8)); 4.18 (*dd*, $J = 12.4$, 4.0, H–C(8)); 2.58–2.26 (*m*, 4 H); 1.57 (*s*, Me); 1.37 (*s*, Me); 1.17 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 311 (7), 310 (43, $[M-46]^+$), 299 (5), 273 (20), 272 (16), 271 (100), 270 (6), 213 (8). Anal. calc. for $C_{16}H_{24}N_2O_7$ (356.38): C 53.93, H 6.79, N 7.86; found: C 53.96, H 6.92, N 7.61.

Data of **24**: R_f Et_2O/hexane 1:1) 0.35. $[\alpha]_D = -1.4$ ($c = 0.21$). IR: 3038*w* (sh), 2982*m*, 2940*m*, 2880*w*, 2260*w*, 1735*s*, 1565*s*, 1480*m*, 1460*w* (br.), 1440*w*, 1400*w*, 1388*m*, 1378*m*, 1330*w*, 1282*m*, 1255*m*, 1240–1200*m*, 1182*m*, 1150*s* (br.), 1090*s*, 1038*m*, 990*w*, 970*w*, 945*w*, 910*w* (br.), 862*m*. ^{1}H-NMR (200 MHz): 5.07 (*m*, H–C(7)); 4.83 (*dd*, $J = 6.8$, 3.4, H–C(6)); 4.75 (*d*, $J = 6.8$, H–C(5)); 4.41 (*dd*, $J = 12.5$, 3.3, H–C(8)); 4.33 (*dd*, $J = 12.5$, 3.7, H–C(8)); 3.15–3.02 (*m*, 1 H); 2.65–2.20 (*m*, 3 H); 1.45 (*s*, Me); 1.36 (*s*, Me); 1.27 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 311 (18), 310 (100, $[M-46]^+$), 299 (6), 273 (28), 254 (5), 252 (5), 227 (6), 226 (46), 215 (6), 203 (6). Anal. calc. for $C_{16}H_{24}N_2O_7$ (356.38): C 53.93, H 6.79, N 7.86; found: C 54.05, H 6.76, N 7.75.

Methyl (E)-2,3,5-Trideoxy-5,6-O-isopropylidene-4-nitro-8-O-pivaloyl-β- and -α-D-oct-2-en-4-ulofuranosonate (**25** and **26**, resp.). A soln. of 6.0 g (19.78 mmol) of **7** in 20 ml of CH_2Cl_2 was treated at −30° with 8.28 ml (59.4 mmol) of Et_3N. A soln. of 1.82 ml (21.78 mmol) of methyl propynoate in 20 ml CH_2Cl_2 was added dropwise during 30 min. The soln. was stirred for 30 min at −30°, then allowed to warm to r.t. and worked up. Purification of the crude by CC (Et_2O/hexane 1:3) gave 3.67 g (48%) of **25** and 1.83 g (24%) of **26**. The latter was crystallized from Et_2O/hexane.

Data of **25**: R_f (Et_2O/hexane 1:1) 0.46. $[\alpha]_D = -128$ ($c = 0.1$). IR: 3035*w* (sh), 2980*m*, 2960*m*, 2940*m*, 2915*w*, 2880*w*, 1775*w*, 1730*s*, 1665*w*, 1568*s*, 1480*m*, 1455*w* (br.), 1440*m*, 1400*w*, 1385*m*, 1377*m*, 1358*m*, 1310, 1280*s*, 1250*m*, 1240–1195*m*, 1150*s*, 1088*s*, 1035*w*, 1010*w* (br.), 980*w*, 940*w*, 865*m* (br.), 780–720*w*, 655*w*, 640*w*. ^{1}H-NMR: 7.10 (*d*, $J = 15.7$, H–C(3)); 6.39 (*d*, $J = 15.7$, H–C(2)); 5.38 (*d*, $J = 5.6$, H–C(5)); 4.81 (br. *t*, $J = 4.4, 3.8$, H–C(7)); 4.78 (*dd*, $J = 5.6, 1.0$, H–C(6)); 4.34 (*dd*, $J = 12.5, 4.2$, H–C(8)); 4.27 (*dd*, $J = 12.5, 3.7$, H–C(8)); 3.78 (*s*, MeO); 1.42 (*s*, Me); 1.34 (*s*, Me); 1.17 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 343 (7), 342 (19), 341 (100, $[M - 46]^+$), 327 (20), 243 (6), 107 (7). Anal. calc. for $C_{17}H_{25}NO_9$ (387.39): C 52.71, H 6.50, N 3.62; found: C 52.80, H 6.83, N 3.58.

Data of **26**: R_f (Et_2O/hexane 1:1) 0.39. M.p. 69–70°. $[\alpha]_D = -33$ ($c = 0.63$). UV: 206 (14270). IR: 3040*w* (sh), 2980*m*, 2940*m*, 2915*w*, 2880*w*, 1730*s*, 1665*w*, 1570*s*, 1480*m*, 1460*m* (br.), 1440*m*, 1390*m*, 1380*m*, 1360*m*, 1312*s*, 1280*s*, 1260*s*, 1240–1195*m*, 1155*s*, 1090*s*, 1035*m*, 1012*m*, 982*m*, 945*w*, 861*m*. ^{1}H-NMR: 7.51 (*d*, $J = 15.5$, H–C(3)); 6.29 (*d*, $J = 15.5$, H–C(2)); 5.11 (*q*, $J = 3.1$, H–C(7)); 4.80 (*dd*, $J = 6.7, 3.3$, H–C(6)); 4.76 (*d*, $J = 6.7$, H–C(5)); 4.47 (*dd*, $J = 12.4, 3.0$, H–C(8)); 4.32 (*dd*, $J = 12.4, 3.1$, H–C(8)); 3.78 (*s*, MeO); 1.45 (*s*, Me); 1.33 (*s*, Me); 1.20 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 342 (23), 341 (100), 273 (60), 257 (6), 215 (5), 203 (6). Anal. calc. for $C_{17}H_{25}NO_9$ (387.39): C 52.71, H 6.50, N 3.62; found: C 52.89, H 6.59, N 3.40.

1-Deoxy-2,3,-O-(1-methoxyethylidene)-5-O-pivaloyl-β-D-ribofuranose (**27**). At r.t., 78 mg (0.41 mmol) of $TsOH \cdot H_2O$ were added to a soln. of 2.17 g (8.25 mmol) of **15** in 25 ml of trimethyl orthoacetate. The reaction was complete within 5 min. The excess of trimethyl orthoacetate was evaporated: 2.63 g (quant.) of **27** (2:3 mixture of isomers) which was used for the next step without further purification. R_f (Et_2O/hexane 1:1) 0.47, 0.14. IR: 3040*w* (sh), 2980*m*, 2915*w*, 2880*w*, 2840*w*, 1735*s*, 1570*s*, 1480*m*, 1460*w* (br.), 1435*w*, 1390*m*, 1370*m*, 1345*w* (sh), 1280*s*, 1158*s*, 1140*s*, 1095*m*, 1050*s*, 1035*s*, 1000*w* (sh), 940*w* (sh), 900*m* (br.). ^{1}H-NMR (300 MHz; 1:1.5 mixture of two isomers): 5.79 (*s*, 0.4 H), 5.65 (*s*, 0.6 H, H–C(1)); 5.31 (*d*, $J = 5.9$, 0.6 H); 5.24 (*d*, $J = 5.5$, 0.4 H, H–C(2)); 4.87 (br. *d*, $J = 6.1$, H–C(3)); 4.79 (*m*, H–C(4)); 4.36–4.25 (*m*, H–C(5)); 3.35 (*s*, 0.4 H), 3.30 (*s*, 0.6 H, MeO); 1.67 (*s*, 0.6 H); 1.62 (*s*, 0.4 H, Me); 1.18 (*s*, *t*-Bu). ^{13}C-NMR: major isomer: 177.50 (*s*); 129.80 (*s*); 111.49 (*d*); 87.42 (*d*); 85.87 (*d*); 81.44 (*d*); 64.02 (*t*); 50.42 (*q*); 38.58 (*s*); 26.91 (3*q*); 21,24 (*q*); minor isomer: 177.60 (*s*); 129.70 (*s*); 112.05 (*d*); 87.75 (*d*); 85.71 (*d*); 81.19 (*d*); 64.19 (*t*); 50.55 (*q*); 38.58 (*s*); 27.03 (3*q*); 20.64 (*q*). MS: 288 (12, $[M - 31]^+$), 274 (13), 273 (100, $[M - 46]^+$), 259 (6), 187 (14), 157 (3).

1,3,4-Tri-O-acetyl-2-deoxy-2-nitro-6-O-pivaloyl-β- and -α-D-psicofuranose (**28** and **29**, resp.). A soln. of 2.63 g (8.25 mmol) of **27** in 75 ml of MeOH was treated with 2.48 g (82.5 mmol) of paraformaldehyde and 1.14 g (8.25 mmol) of K_2CO_3. The mixture was stirred for 15 min at r.t. After usual workup, a soln. of the residue in Ac_2O/pyridine 1:1 (24 ml) was stirred for 30 min at r.t. The mixture was worked up, and a soln. of the residue in 50 ml of aq. 80% AcOH was stirred for 2 h at r.t. The excess of aq. AcOH was evaporated. Residual AcOH and H_2O were removed by co-evaporation with toluene. The soln. of this residue in Ac_2O/pyridine 1:1 (24 ml) was stirred overnight at r.t. Usual workup and CC (AcOEt/hexane 1:3) gave 2.06 g (59%) of **28** and 290 mg (8%) of **29**.

Data of **28**: R_f (AcOEt/hexane 1:1) 0.54. $[\alpha]_D = -26$ ($c = 1.46$). IR: 3040–3020*w* (br.), 2980*w*, 2940*w*, 2915*w*, 2880*w*, 1755*s*, 1590*s*, 1481*w*, 1452*w*, 1370*m*, 1350*w*, 1280*m*, 1240–1200*s*, 1145*s*, 1110*m*, 1090*m*, 1055*s*, 1015*m*, 960*m*, 940*m* (br.), 910*s*, 648*w*. ^{1}H-NMR: 6.03 (*d*, $J = 5.0$, H–C(3)); 5.43 (*t*, $J = 5.0$, H–C(4)); 4.70 (*d*, $J = 12.2$, H–C(1)); 4.62 (*d*, $J = 12.2$, H–C(1)); 4.62–4.59 (*m*, H–C(5)); 4.37 (*dd*, $J = 12.7, 3.0$, H–C(6)); 4.29 (*dd*, $J = 12.7, 3.7$, H–C(6)); 2.18 (*s*, AcO); 2.10 (*s*, AcO); 2.07 (*s*, AcO); 1.20 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 374 (23), 373 (100, $[M - 46]^+$), 331 (5), 271 (7), 253 (15), 229 (5), 213 (4), 212 (9), 211 (71), 171 (4), 169 (19), 157 (15), 153 (9), 109 (6), 101 (4), 85 (5). Anal. calc. for $C_{17}H_{25}NO_{11}$ (419.39): C 48.69, H 6.01, N 3.34; found: C 48.59, H 5.94, N 3.24.

Data of **29**: R_f (AcOEt/hexane 1:3) 0.35. $[\alpha]_D = +57$ ($c = 0.42$). IR: 3040–3020*w*, 2980*m*, 2940*w*, 2910*w*, 2880*w*, 1755*s* (br.), 1567*s*, 1480*w*, 1370*m*, 1275*m*, 1240–1200*s*, 1145*s*, 1092*m*, 1080*m*, 1065*m*, 1050*m*, 1015*m*, 980*w*, 945*w*, 900*w*, 835*w*. ^{1}H-NMR (200 MHz): 5.53 (*d*, $J = 6.4$, H–C(3)); 5.31 (*dd*, $J = 6.4, 3.0$, H–C(4)); 4.96 ('*q*', $J = 3.0$, H–C(5)); 4.79 (*d*, $J = 12.4$, H–C(1)); 4.52 (*d*, $J = 12.4$, H–C(1)); 4.34 (*d*, $J = 3.0$, 2 H–C(6)); 2.13 (*s*, AcO); 2.08 (*s*, AcO); 2.07 (*s*, AcO); 1.25 (*s*, *t*-Bu). ^{13}C-NMR: *Table 5*. MS: 374 (100), 302 (11), 301 (57), 211 (27), 153 (10). Anal. calc. for $C_{17}H_{25}NO_{11}$ (419.39): C 48.69, H 6.01, N 3.34; found: C 48.60, H 5.78, N 3.49.

2. Pyrimidine Nucleosides. – *1-(1-O-Acetyl-3,4-O-isopropylidene-6-O-pivaloyl-β-D-psicofuranosyl)uracil* (**33**). *A*) A soln. of 376 mg (1.0 mmol) of **21** and 307 mg (1.2 mmol) of 2,4-bis(trimethylsilyloxy)pyrimidine [31] (**31**) in 15 ml of MeCN was treated with 487 mg (3.0 mmol) of $FeCl_3$, then heated at 80° for 30 min and cooled to r.t. Usual workup and CC (AcOEt/hexane 1:1) gave **33** (containing 17% of the anomer; 339 mg, 77%). An anal. sample was obtained by crystallization from Et_2O/hexane. R_f (AcOEt/hexane 1:1) 0.20. M.p. 217–218° (dec.). $[\alpha]_D = -42$ ($c = 0.12$). UV: 261 (12320), 209 (33502). CD: 257 (−4.51). IR: 3390*w*, 3110*w*, 3030*w* (sh), 2980*m*, 2935*m*, 2910*w*, 2870*w*, 1750–1700*s*, 1690*s*, 1625*w*, 1615*w*, 1480*m*, 1440*m* (br.), 1378*s*, 1270*s*, 1240–1200*s*, 1145*s*, 1118*s*, 1085*s*, 1048*m*, 1035*m*, 1018*m*, 970*w*, 945*w*, 890*w*, 865*m*, 805*m*, 800–710*m*, 665*w*. ^{1}H-NMR: major anomer: 9.09 (br. *s*, exchangeable with D_2O, NH); 7.64 (*d*, $J = 8.3$, H–C(6)); 5.66 (*d*, $J = 8.3$, H–C(5)); 5.28 (*d*, $J = 6.3$, H–C(3′)); 4.78 (*d*, $J = 12.3$, H–C(1′)); 4.70 (*dd*, $J = 6.3$, 1.7, H–C(4′)); 4.70–4.67 (*m*, H–C(5′)); 4.41 (*d*, $J = 12.3$, H–C(1′)); 4.25 (*dd*, $J = 12.6$, 3.1, H–C(6′)); 416 (*dd*, $J = 12.6$, 4.4, H–C(6′)); 2.00 (*s*, AcO); 1.60 (*s*, Me); 1.36 (*s*, Me); 1.13 (*s*, *t*-Bu); minor anomer: 9.09 (br. *s*, exchangeable with D_2O, NH); 7.66 (*d*, $J = 8.2$, H–C(6)); 5.73 (*d*, $J = 8.2$, H–C(5)); 5.03 (*d*, $J = 5.7$, H–C(3′)); 4.54 (*d*, $J = 11.4$, H–C(1′)); 2.08 (*s*, AcO); 1.38 (*s*, Me); 1.33 (*s*, Me); 1.23 (*s*, *t*-Bu). ^{13}C-NMR: major anomer: 177.67 (*s*), 169.91 (*s*); 163.61 (*s*); 150.11 (*s*); 140.60 (*d*); 114.05 (*s*); 101.00 (*d*); 99.01 (*s*); 86.26 (*d*); 83.40 (*d*); 80.97 (*d*); 63.98 (*t*); 63.73 (*t*); 38.65 (*s*); 26.92 (3*q*); 25.83 (*q*); 24.28 (*q*); 20.56 (*q*); minor anomer: 177.67 (*s*); 169.67 (*s*); 163.85 (*s*); 149.88 (*s*); 139.49 (*d*); 114.10 (*s*); 101.18 (*d*); 97.63 (*s*); 82.92 (*d*); 82.61 (*d*); 81.25 (*d*); 65.13 (*t*); 63.73 (*t*); 38.55 (*s*); 27.08 (3*q*); 25.37 (*q*); 24.28 (*q*); 20.56 (*q*). MS: 441 (24, $[M + 1]^+$), 381 (4), 331 (3), 330 (14), 329 (100), 271 (3), 57 (34), 43 (4). Anal. calc. for $C_{20}H_{28}N_2O_9$ (440.45): C 54.54, H 6.40, N 6.36; found: C 54.61, H 6.49, N 6.39.

B) A soln. of 188 mg (0.5 mmol) of **21** and 154 mg (0.6 mmol) of **31** in 10 ml of MeCN was treated with 391 mg (1.5 mmol) of $SnCl_4$, then heated at 65° for 30 min and cooled to r.t. Usual workup and CC (AcOEt/hexane 1:1) gave **33** (55 mg, 25%) and *1-O-acetyl-2,3-O-isopropylidene-6-O-pivaloyl-α-D-psicofuranose* (**32**; 45 mg, 26%). IR: 3560*w*, 2960*m*, 2935*m*, 2880*w*, 2860*w*, 1745*s*, 1730*s*, 1480*w*, 1455*w* (br.), 1375*m*, 1315*w*, 1275*m*, 1240–1200*s*, 1160*s* (br.), 1145*s*, 1112*s*, 1060*s* (br.), 1033*s*, 1000*m*, 960*m*, 940*m*, 875*m*. ^{1}H-NMR: 4.51 (*d*, $J = 5.0$, H–C(3)); 4.42 (*dd*, $J = 12.5$, 3.0, irrad. at 4.05→*d*, $J = 12.5$, H–C(6)); 4.29 (*d*, $J = 12.0$, H–C(1)); 4.20 (*dd*, $J = 12$, 4.5, irrad. at 4.05→*d*, $J = 12.5$, H–C(6)); 4.15 (*d*, $J = 12.0$, H–C(1)); 4.07–4.03 (*m*, H–C(5)); 3.94–3.88 (*m*, irrad. at 4.05→br. *m*, addn. of D_2O→*dd*, $J = 9.0$, 5.0, irrad. at 4.58→*d*, $J = 9.0$, H–C(4)); 2.41 (*d*, $J = 9.5$, exchangeable with D_2O, OH); 2.18 (*s*, AcO); 1.68 (*s*, Me); 1.43 (*s*, Me); 1.23 (*s*, *t*-Bu). ^{13}C-NMR: 170.07 (2*s*); 113.48 (*s*); 110.68 (*s*); 79.84 (*d*); 79.16 (*d*); 71.99 (*d*); 64.09 (*t*); 62.41 (*t*); 38.88 (*s*); 27.17 (3*q*); 27.08 (*q*); 26.52 (*q*); 20.74 (*q*). MS: 346 (1, M^+), 345 (3), 331 (7, $[M - 15]^+$), 329 (64, $[M - 17]^+$), 289 (100).

1-(1-O-Acetyl-3,4-O-isopropylidene-6-O-trityl-β-D-psicofuranosyl)uracil (**38**) *and 1-O-Acetyl-2,6-anhydro-3,4-O-isopropylidene-β-D-psicofuranose* (**37**). A soln. of 300 mg (0.56 mmol) of **30** [9] and 172 mg (0.67 mmol) of **31** in 10 ml of MeCN was treated with 273 mg (1.68 mmol) of $FeCl_3$ at 80° for 30 min and then cooled to r.t. Usual workup and CC (AcOEt/hexane 1:1) gave **38** (containing *ca.* 10% of diastereoisomer; 230 mg, 68%) and **37** (42 mg, 12%). Compound **38** solidified during drying *in vacuo*.

Data of **38** (from the mixture of diastereoisomers): R_f (AcOEt/hexane 1:1) 0.23. M.p. 102–104°. $[\alpha]_D = -47$ ($c = 0.10$). UV: 260 (8759), 210 (30349). CD: 257 (−3.81). IR: 3390*w*, 3060*w* (sh), 2995*w*, 2960*w*, 2930*w*, 2870*w*, 1750*s*, 1690*s*, 1490*w*, 1450*m*, 1380*m*, 1270*m*, 1255–1200*m*, 1125*m*, 1082*m*, 1050*m*, 1035*m*, 1000*m*, 970*w*, 900*w*, 865*m*, 695*m*, 660*m*, 630*w*. ^{1}H-NMR: 7.94 (*br. s*, NH); 7.63 (*d*, $J = 8.4$, H–C(6)); 7.34–7.28 (*m*, 15 arom. H); 5.47 (*dd*, $J = 8.4$, 2.4, H–C(5)); 5.32 (*d*, $J = 6.2$, H–C(3′)); 4.81 (*d*, $J = 12.1$, H–C(1′)); 4.69–4.61 (*m*, H–C(5′)); 4.55 (*dd*, $J = 6.2$, 1.2, H–C(4′)); 4.34 (*d*, $J = 12.1$, H–C(1′)); 3.34 (*dd*, $J = 10.9$, 3.7, H–C(6′)); 3.26 (*dd*, $J = 10.9$, 4.8, H–C(6′)); 2.00 (*s*, AcO); 1.59 (*s*, Me); 1.34 (*s*, Me). ^{13}C-NMR: major anomer: 169.92 (*s*); 163.30 (*s*); 150.10 (*s*); 143.35 (*s*); 142.89 (*d*); 141.23 (*s*); 139.75 (*s*); 128.81–127.12 (15*d*), 113.46 (*s*); 100.79 (*d*); 99.30 (*s*); 87.74 (*s*); 86.27 (*d*); 85.08 (*d*); 81.71 (*d*); 64.66 (*t*); 63.53 (*t*); 25.84 (*q*); 24.40 (*q*); 20.63 (*q*); minor anomer: 169.62 (*s*); 163.58 (*s*); 149.87 (*s*); 143.35 (*s*); 142.89 (*d*); 141.23 (*s*); 139.75 (*s*); 128.81–127.12 (15*d*); 113.98 (*s*); 101.11 (*d*); 99.30 (*s*); 87.74 (*s*); 84.89 (*d*); 82.74 (*d*); 81.37 (*d*); 65.61 (*t*); 64.08 (*t*); 27.17 (*q*); 25.54 (*q*); 20.53 (*q*). MS: 599 (1, $[M + 1]^+$), 583 (3, $[M - 15]^+$), 539 (11, $[M - 59]^+$), 487 (12, $[M - 111]^+$), 339 (3), 285 (16), 243 (100), 228 (4), 165 (23), 155 (8), 113 (7), 105 (6). Anal. calc. for $C_{34}H_{34}N_2O_8$ (598.66): C 68.22, H 5.72, N 4.68; found: C 68.23, H 5.96, N 4.48.

Data of **37**: R_f (AcOEt/hexane 1:1) 0.50. IR: 3030*m* (sh), 2980*m*, 2940*m*, 2900*m*, 2840*w*, 1750*s*, 1712*m*, 1480*w*, 1455*m*, 1435*m*, 1410*m*, 1385*s*, 1375*s*, 1345*m*, 1310*m*, 1295*m*, 1245–1200*s*, 1160*s*, 1140*m*, 1095*s*, 1055*s* (br.), 1020*s*, 1000*s*, 990*s*, 950*m*, 925*m*, 905*m*, 865*s*, 835*m*, 620*w*. ^{1}H-NMR (200 MHz): 4.71 (*d*, $J = 3.8$, H–C(5)); 4.58 (*d*, $J = 12.2$, H–C(1)); 4.50 (*d*, $J = 12.2$, H–C(1)); 4.44 (*d*, $J = 5.4$, H–C(3)); 4.32 (*d*, $J = 5.4$, H–C(4)); 3.60 (*dd*, $J = 7.2$, 3.8, H–C(6)); 3.44 (*d*, $J = 7.2$, H–C(6)); 2.14 (*s*, AcO); 1.46 (*s*, Me); 1.30 (*s*, Me). ^{13}C-NMR: 170.30 (*s*); 112.63 (*s*); 105.85 (*s*); 81.15 (*d*); 80.13 (*d*); 78.47 (*d*); 64.47 (*t*); 59.49 (*t*); 25.96 (*q*); 25.39 (*q*); 20.69 (*q*). MS: 245 (100, $[M + 1]^+$), 231 (7), 226 (7), 213 (9), 188 (9), 113 (11), 79 (10), 67 (9).

1-(3,4-O-Isopropylidene-6-O-pivaloyl-β-D-psicofuranosyl)uracil (**34**). At r.t., 0.5 ml of 0.1M MeONa in MeOH were added to a soln. of 266 mg (0.59 mmol) of **33** (containing 17% of the anomer) in 10 ml of MeOH. The mixture was stirred for 3 h. Usual workup, CC (AcOEt/hexane 3:1), and crystallization of the residue from AcOEt/hexane gave pure **34** (180 mg, 76%). R_f (AcOEt) 0.45. M.p. 176°. $[\alpha]_D = -24$ ($c = 0.12$). UV: 262 (9140). CD: 252 (+1.19). IR: 3600–3300*w*, 3390*w*, 3200*w* (br.), 3115*w*, 3035*w* (sh), 2980*w*, 2940*w*, 2910*w*, 2875*w*, 1725*s* (sh), 1690*s*, 1625*w*, 1615*w*, 1480*m*, 1450*m* (br.), 1395*w*, 1385*m*, 1375*m*, 1285*m* (sh), 1272*s*, 1240–1195*m*, 1150*s*, 1110*s*, 1085*s*, 1035*m*, 1010*m*, 970*w*, 940*m*, 865*m*, 805*m*, 790–710*m*, 655*w*, 630*w* (br.). ^{1}H-NMR: 9.06 (br. *s*, exchangeable with D_2O, NH); 7.72 (*d*, $J = 8.2$, H–C(6)); 5.63 (*dd*, $J = 8.2$, 1.8, addn. of $D_2O \rightarrow d$, $J = 8.2$, H–C(5)); 5.32 (*d*, $J = 6.1$, H–C(3′)); 4.72–4.68 (*m*, 2 H); 4.28 (*dd*, $J = 12.5$, 6.0, addn. of $D_2O \rightarrow d$, $J = 12.5$, H–C(1′)); 4.24 (*dd*, $J = 12.5$, 3.1, H–C(6′)); 4.16 (*dd*, $J = 12.5$, 4.7, H–C(6′)); 3.84 (*dd*, $J = 12.5$, 6.0, addn. of $D_2O \rightarrow d$, $J = 12.5$, H–C(1′)); 2.80 (*t*, $J = 6.0$, exchangeable with D_2O, OH); 1.58 (*s*, Me); 1.37 (*s*, Me); 1.14 (*s*, *t*-Bu). ^{13}C-NMR: *Table 8*. MS: 399 (68, $[M + 1]^+$), 297 (36), 287 (100), 211 (13), 113 (17). Anal. calc. for $C_{18}H_{26}N_2O_8$ (398.42): C 54.27, H 6.58, N 7.03; found: C 54.14, H 6.71, N 6.98.

1-(6-O-Pivaloyl-β-D-psicofuranosyl)uracil (**35**). A) *From* **33**: A soln. of 133 mg (0.30 mmol) of **33** (containing 17% of the anomer) in 10 ml of MeOH/0.1M H_2SO_4 1:1 was kept at r.t. for 7 d. Usual workup, CC (MeOH/$CHCl_3$ 1:9), and crystallization of the residue from AcOEt/hexane gave pure **35** (71 mg, 66%).

B) *From* **40**: At r.t., 1.5 ml of 0.1M MeONa in MeOH were treated with 49 mg (0.1 mmol) of **40** and stirred for 3 h at r.t. Usual workup and crystallization from MeOH/AcOEt/hexane gave 30 mg (83%) of **35**. R_f (AcOEt/AcOH 19:1) 0.38. M.p. 217–218° (dec.). $[\alpha]_D = -11.9$ ($c = 0.17$). UV: 262 (11344), 209. CD: 260 (+1.51). IR (KBr): 3470*s*, 3450–3430*s*, 3100*m*, 3040–3020*m*, 2980*m*, 2960*m*, 2930*w*, 2905*w*, 2870*w*, 2835–2805*w*, 1720–1710*s*, 1688*s* (sh), 1680*s*, 1480*m*, 1470*m*, 1428*m*, 1395*m*, 1375*w*, 1315*w*, 1282*m*, 1250*w*, 1168*m*, 1125*m*, 1108*m*, 1095*w*, 1064*m*, 1047*m*, 1025*w*, 870*w*, 840*w*, 822*m*, 790*w*, 770–762*w*, 640*w*, 622*w*. ^{1}H-NMR: ((D_6)DMSO): 11.19 (br. *s*, exchangeable with D_2O, NH); 7.71 (*d*, $J = 8.2$, H–C(6)); 5.48 (*d*, $J = 8.2$, H–C(5)); 5.39 (*d*, $J = 4.8$, exchangeable with D_2O, OH–C(3′)); 5.13 (*d*, $J = 6.3$, exchangeable with D_2O, OH–C(4′)); 4.81 (*t*, $J = 6.3$, exchangeable with D_2O, OH–C(1′)); 4.68 (*t*, $J = 4.6$, addn. of $D_2O \rightarrow d$, $J = 4.8$, H–C(3′)); 4.23–4.13 (*m*, 3 H); 4.06 (*dd*, $J = 12.0$, 6.2, addn. of $D_2O \rightarrow d$, $J = 12.0$, H–C(1′)); 3.90–3.87 (*m*, addn. of $D_2O \rightarrow$signal overlapped with DHO, addn. of DCl→*t*, $J = 5.6$, H–C(4′)); 3.63 (*dd*, $J = 12.0$, 6.2, addn. of $D_2O \rightarrow d$, $J = 12.0$, H–C(1′)); 1.11 (*s*, *t*-Bu). ^{13}C-NMR: *Table 8*. MS: 359 (82, $[M + 1]^+$), 331 (7), 289 (11), 247 (100), 229 (17), 113 (76), 57 (89), 43 (24). Anal. calc. for $C_{15}H_{22}N_2O_8$ (358.35): C 50.28, H 6.19, N 7.82; found: C 50.25, H 6.05, N 8.03.

1-(β-D-Psicofuranosyl)uracil (**36**). A) *From* **33**: A soln. of 485 mg (1.10 mmol) of **33** (containing 17% of the anomer) in 10 ml of dioxane/H_2O 1:1 was treated with *ca.* 5 ml of Bu_4NOH (40% in H_2O), stirred for 3 h, treated with an excess of *Dowex 50 W X8* (H^+ form), and filtered. The filtrate was neutralized with *Dowex 1 X 8* (OH^- form), concentrated to remove dioxane, and lyophilized. Crystallization of the residue from MeOH/$CHCl_3$ gave 190 mg (76%) of **36**.

B) *From* **40**: A soln. of 100 mg (0.2 mmol) of **40** in 10 ml of dioxane was treated with 10 ml of H_2O and 3 ml of Bu_4NOH (40% in H_2O). The mixture was stirred for 5 h at r.t. Dioxane was removed by evaporation, the residual soln. was treated with *Dowex 50 W X 8* (6 g, H^+ form), filtered, and lyophilized. Crystallization of the residue (35 mg) from MeOH/AcOEt gave **36** (29 mg, 51%).

Data of **36**: R_f (MeOH/$CHCl_3$ 3:7) 0.31. M.p. 64–65°. $[\alpha]_D = +2.9$ ($c = 0.24$, H_2O). UV (H_2O): 263 (8250). CD (H_2O): 259 (+0.75). IR (KBr): 3400*s* (br.), 1680*s* (br.), 1460*m* (br.), 1410–1400*w*, 1385*w*, 1295*m*, 1260*w* (br.), 1095*m*, 1035*m*, 928*w*, 815*w*, 765*w*. ^{1}H-NMR ((D_6)DMSO): 11.10 (*s*, exchangeable with D_2O, NH); 7.97 (*d*, $J = 8.2$, H–C(6)); 5.43 (*d*, $J = 8.2$, H–C(5)); 5.32 (*d*, $J = 4.8$, exchangeable with D_2O, OH–C(3′)); 4.95–4.90 (*m*, exchangeable with D_2O, OH–C(4′), OH–C(6′)); 4.75 (*t*, $J = 6.2$, exchangeable with D_2O, OH–C(1′)); 4.59 (*t*, $J = 4.8$, addn. of $D_2O \rightarrow d$, $J = 4.8$, H–C(3′)); 4.11 (*dd*, $J = 11.9$, 6.7, addn. of $D_2O \rightarrow d$, $J = 12.1$, H–C(1′)); 3.93–3.90 (*m*, H–C(5′)); 3.85–3.81 (*m*, addn. of $D_2O \rightarrow dd$, $J = 7.5$, 4.8, H–C(4′)); 3.70–3.61 (*m*, 2 H, addn. of $D_2O \rightarrow d$ at 3.64, $J = 12.1$, H–C(1′) and *dd* at 3.65, $J = 12.7$, 2.8, H–C(6′)); 3.48–3.43 (*m*, addn. of $D_2O \rightarrow dd$, $J = 12.7$, 4.7, H–C(6′)). ^{13}C-NMR: *Table 8*. MS: 275 (0,6, $[M + 1]^+$), 187 (10), 163 (17), 145 (16), 113 (100).

1-(1,3,4-Tri-O-acetyl-6-O-pivaloyl-α- and -β-D-psicofuranosyl)uracil (**39** and **40**, resp.). A soln. of 900 mg (2.15 mmol) of **28** and 660 mg (2.58 mmol) of **31** in 5 ml of MeCN was warmed to 60°, treated with 1.22 g (6.45 mmol) of $SnCl_2$ and stirred for 30 min at 60°. Usual workup and CC (AcOEt/hexane 1:1) gave **39**/**40** (6:1; 125 mg, 12%) and **40** (500 mg, 48%). An anal. sample of **40** was obtained after crystallization from Et_2O/hexane.

Data of **39**/**40** (6:1): R_f (AcOEt/hexane 3:1) 0.39. $[\alpha]_D = +6.4$ ($c = 0.16$). UV: 260 (10046), 204 (11275). CD: 254 (−2.38). IR: 3580–3500*w*, 3390*w*, 3180*w* (br.), 3110*w*, 3035–3005*w*, 2980*m*, 2940*w*, 2910*w*, 2870*w*, 1750*s* (br.), 1715*s*, 1692*s*, 1625*w*, 1615*w*, 1480*w*, 1440*m* (br.), 1375*m*, 1278*m*, 1240–1200*s*, 1145*s*, 1120*s*, 1095*s*, 1045*m*, 1015*m* (sh), 965*w*, 950*w*, 935*w* (br.), 900*w*, 808*w*, 800–710*w*, 655*w*, 620*w*. ^{1}H-NMR (only values of **39** listed): 8.55 (*s*, exchangeable with D_2O, NH); 7.68 (*d*, $J = 8.4$, irrad. at 5.77→NOE of 10%, H–C(6)); 5.89 (*d*, $J = 4.8$, irrad. at

5.43→NOE of 10%, irrad. at 4.60→NOE of 10%, H–C(3′)); 5.77 (*d*, *J* = 8.4, irrad. at 7.68→NOE of 20%, H–C(5)); 5.43 (*dd*, *J* = 9.1, 4.8, irrad. at 5.89→NOE of 10%, irrad. at 4.60→NOE of 10%, H–C(4′)); 4.60 (*d*, *J* = 11.5, irrad. at 5.43→NOE of 2%, H–C(1′)); 4.40 (*d*, *J* = 11.5, irrad. at 4.60→NOE of 20%, H–C(1′)); 4.38–4.15 (*m*, 3 H); 2.13 (*s*, AcO); 2.03 (*s*, AcO); 2.01 (*s*, AcO); 1.24 (*s*, *t*-Bu). ^{13}C-NMR: *Table 8*.

Data of **40**: R_f (AcOEt/hexane 3:1) 0.30. M.p. 163–165°. $[\alpha]_D = -9.9$ (*c* = 0.7). UV: 259 (8867). CD: 252 (–1.04). IR: 3580–3460*w*, 3390*w*, 3180*w* (br.), 3110*w*, 3030–3000*w* (sh), 2975*m*, 2940*w* (sh), 2910*w*, 2875*w*, 1755*s* (br.), 1720*s*, 1695*s*, 1625*w*, 1480*m*, 1440*m* (br.), 1370*m*, 1280*m*, 1240–1200*s*, 1150*s*, 1125*s*, 1075*s*, 1050*m*, 1015–1005*m*, 985*m*, 970*m*, 900*w* (br.), 808*w*, 800–705*w*, 655*w*, 620*w*. ^{1}H-NMR: 8.68 (br. *s*, NH); 7.74 (*d*, *J* = 8.4, irrad. at 5.69→NOE of 10%, irrad. at 5.36→NOE of 6%, H–C(6)); 6.05 (*d*, *J* = 5.6, irrad. at 7.74→NOE of 2%, irrad. at 5.36→NOE of 12%, H–C(3′)); 5.69 (*dd*, *J* = 8.4, 2.2, irrad. at 7.74→NOE of 14%, H–C(5)); 5.36 (*dd*, *J* = 5.6, 4.4, irrad. at 6.05→NOE of 14%, H–C(4′)); 4.70 (*d*, *J* = 12.1, H–C(1′)); 4.57 (*d*, *J* = 12.1, H–C(1′)); 4.57–4.53 (*m*, irrad. at 5.36→NOE of 6%, H–C(5′)); 4.26 (*d*, *J* = 3.0, irrad. at 5.36→NOE of 3%, 2 H–C(6′)); 2.16 (*s*, AcO); 2.10 (*s*, AcO); 2.04 (*s*, AcO); 1.18 (*s*, *t*-Bu). ^{13}C-NMR: *Table 8*. MS: 485 (65, $[M + 1]^+$), 441 (0.4), 425 (0.6), 373 (100). Anal. calc. for $C_{21}H_{28}N_2O_{11}$ (484.46): C 52.06, H 5.83, N 5.78; found: C 52.29, H 5.80, N 5.60.

*[1-(2,3-Dideoxy-5,6-*O*-isopropylidene-8-*O*-pivaloyl-β- and -α-*D*-oct-4-ulofuranosyl)uracil]ononitrile* (**41** and **42**, resp.). A soln. of 356 mg (1 mmol) of **23** and 282 mg (1.1 mmol) of **31** in 5 ml of MeCN was treated at –30° with a soln. of 651 mg (2.5 mmol) of $SnCl_4$ in 5 ml of MeCN. The mixture was allowed to warm to 0° within 20 min and treated with 5 ml of sat. aq. $NaHCO_3$ soln. Usual workup and CC (AcOEt/hexane 1:1) yielded 170 mg (40%) of **41**/**42** (3:2 according to ^{1}H-NMR). R_f (AcOEt/hexane 3:1) 0.41. UV: 261 (10580), 207 (9851). IR: 3390*w*, 3115*w*, 3035*w* (sh), 2980*m*, 2940*w*, 2910*w* (sh), 2880*w*, 2255*w*, 1692*s* (br.), 1630*w*, 1620*w*, 1480*m*, 1442*m* (br.), 1388*m*, 1380*m*, 1288–1272*s*, 1255–1200*m*, 1150*s*, 1110*s*, 1085*s*, 1035*m*, 1010*w*, 970*w*, 955*w*, 865*m*, 810*m*, 800–710*m*, 655*w*. ^{1}H-NMR: **41**: 8.45 (br. *s*, exchangeable with D_2O, NH); 7.69 (*d*, *J* = 8.3, H–C(6)); 5.72 (*dd*, *J* = 8.3, 2.0, addn. of D_2O→*d*, *J* = 8.4, H–C(5)); 5.10 (*d*, *J* = 6.2, H–C(5′)); 4.68 (*dd*, *J* = 6.2, 2.2, H–C(6′)); 4.65–4.62 (*m*, H–C(7′)); 4.34–4.18 (2 H–C(8′)); 3.40–2.00 (4*m*, 4 H); 1.61 (*s*, Me); 1.38 (*s*, Me); 1.16 (*s*, *t*-Bu); **42**: 8.39 (br. *s*, exchangeable with D_2O, NH); 7.62 (*d*, *J* = 8.4, H–C(6)); 5.76 (*dd*, *J* = 8.4, 2.2, addn. of D_2O→*d*, *J* = 8.3, H–C(5)); 4.94 (*d*, *J* = 5.8, H–C(5′)); 4.76 (*dd*, *J* = 5.8, 4.4, H–C(6′)); 4.44 (*q*, *J* = 4.1, H–C(7′)); 4.34–4.18 (*m*, 2 H–C(8′)); 3.40–2.00 (4*m*, 4 H); 1.38 (*s*, Me); 1.33 (*s*, Me); 1.26 (*s*, *t*-Bu). ^{13}C-NMR: *Table 8*. MS: 422 (28, $[M + 1]^+$), 311 (18), 310 (100), 188 (5), 155 (8), 153 (5), 113 (10). Anal. calc. for $C_{20}H_{27}N_3O_7$ (421.45): C 57.00, H 6.46, N 9.97; found: C 56.95, H 6.38, N 9.85.

*[1-(2,3-Dideoxy-5,6-*O*-isopropylidene-β- and -α-*D*-oct-4-ulofuranosyl)uracil]ononitril* (**43** and **44**, resp.). A soln. of 211 mg (0.5 mmol) of **41**/**42** (3:2) in 10 ml of MeOH/25% aq. NH_3 1:1 was stirred for 6 d at r.t. The mixture was neutralized with 0.1N H_2SO_4 and extracted with AcOEt (3 × 50 ml). Usual workup and CC (AcOEt/hexane 3:1) gave 96 mg (57%) of **43** and 64 mg (38%) of **44**, which were crystallized from AcOEt/hexane.

Data of **43**: R_f (AcOEt) 0.12. M.p. 92–94°. $[\alpha]_D = -21$ (*c* = 0.5). UV: 261 (8158): CD: 262 (+0.51). IR: 3670*w*, 3535*m*, 3500*m*, 3420*m*, 3200*w* (br.), 3110*w*, 3035*m* (sh), 3000*m*, 2940*w*, 2880*w*, 2820*w*, 2257*w*, 1710–1675*s*, 1600*m*, 1520*m* (br.), 1475*m*, 1425*s*, 1385*s*, 1335*m*, 1270*s*, 1230–1200*s*, 1160*m*, 1110*s*, 1080*s*, 1045–1035*s*, 970*w*, 930*s*, 865*s*, 850*m*, 800–710*s*, 675–665*s*, 625*m*. ^{1}H-NMR ((D_6)DMSO): 11.22 (*d*, *J* = 2.0, NH); 7.79 (*d*, *J* = 8.3, H–C(6)); 5.51 (*dd*, *J* = 8.3, 2.0, irrad. at 7.79→NOE of 13.4%, H–C(5)); 5.06 (*t*, *J* = 4.8, irrad. at 7.79→NOE of 1.4%, irrad. at 4.67→collective NOE of 8.3%, OH); 5.03 (*d*, *J* = 6.1, irrad. at 4.67→collective NOE of 8.3%, irrad. at 1.27→NOE of 1.8%, H–C(5′)); 4.67 (*dd*, *J* = 6.1, 1.4, irrad. at 4.32→*d*, *J* = 6.1, irrad. at 1.27→NOE of 2.6%, H–C(6′)); 4.32 (*m*, irrad. at 4.67→NOE of 3%, irrad. at 1.47→NOE of 0.7%, H–C(7′)); 3.50–3.40 (*m*, irrad. at 4.67→NOE of 4%, 2 H–C(8′)); 2.60–2.46 (*m*, irrad. at 1.47→NOE of 0.2%, 2 H); 2.38–2.33 (*m*, 1 H); 2.02–1.97 (*m*, irrad. at 1.47→NOE of 0.5%, 1 H); 1.47 (*s*, irrad. at 1.27→NOE of 2.6%, Me); 1.27 (*s*, irrad. at 4.67→NOE of 1.7%, irrad. at 1.47→NOE of 1.5%, Me). ^{13}C-NMR: *Table 8*. MS: 338 (51, $[M + 1]^+$), 227 (12), 226 (100), 199 (9), 168 (19), 113 (33). Anal. calc. for $C_{15}H_{19}N_3O_6$ (337.34): C 53.41, H 5.68, N 12.46; found: C 53.28, H 5.85, N 12.26.

Data of **44**: R_f (AcOEt) 0.21. M.p. 78–79°. $[\alpha]_D = -104$ (*c* = 0.42). UV: 262 (8888). CD: 262 (–5.23). IR: 3635*w*, 3540*w* (br.), 3390*m*, 3200*w* (br.), 3115*w*, 3040*w* (sh), 3000*m*, 2940*m*, 2880*w*, 2257*w*, 1715*s*, 1690*s*, 1625*w* (br.), 1520*m* (br.), 1475*m*, 1445*s*, 1425*s*, 1385*m*, 1375*m*, 1335*w*, 1290*s*, 1230–1200*s*, 1160*m*, 1125–1110*s*, 1080*s*, 1045–1030*s*, 970*w*, 930*s*, 875*m*, 850*m*, 800–710*s*, 675–665*s*, 625*m*. ^{1}H-NMR ((D_6)DMSO): 11.13 (br. *s*, NH); 7.71 (*d*, *J* = 8.3, irrad. at 1.23→NOE of 0.3%, H–C(6)); 5.56 (*dd*, *J* = 8.3, 2.2, H–C(5)); 5.12 (*t*, *J* = 5.3, irrad. at 4.80→NOE of 1%, OH); 4.83–4.78 (*m*, irrad. at 1.23→NOE of 1.3%, H–C(5′), H–C(6′)); 4.24 (*m*, irrad. at 4.80→NOE of 0.8%, irrad. at 1.23→NOE of 0.4%, H–C(7′)); 3.60–3.50 (*m*, 2 H–C(8′)); 3.04–2.96 (*m*, irrad. at 4.80→NOE of 1.5%, 1 H); 2.50–2.40 (*m*, irrad. at 4.80→NOE of 1.1%, 2 H); 2.20–2.10 (*m*, irrad. at 4.80→NOE of 3.0%, 1 H); 1.23 (*s*, irrad. at 4.80→NOE of 3.8%, 2 Me). ^{13}C-NMR: *Table 8*. MS: 338 (96, $[M + 1]^+$), 227 (11), 226 (100), 168 (5), 155 (11), 153 (8), 113 (43), 102 (29). Anal. calc. for $C_{15}H_{19}N_3O_6$ (337.43): C 53.41, H 5.68, N 12.46; found: C 53.41, H 5.55, N 12.27.

[1-(2,3-Dideoxy-β-D-oct-4-ulofuranosyl)uracil]ononitrile (**45**). A soln. of 90 mg (0.26 mmol) of **43** in 5 ml of 80% aq. CF_3COOH was stirred for 1 h at r.t. Evaporation, drying of the residue by azeotropic distillation with toluene, and crystallization from MeOH/AcOEt gave 75 mg (94%) of **45**. R_f (MeOH/AcOEt 2:8) 0.51. M.p. 86–88°. $[\alpha]_D = +13$ ($c = 0.15$, DMSO). UV (H_2O): 263 (8472). CD: 265 (+0.27). IR (KBr): 3440*s*, 3410*s*, 3380*s*, 3190*m*, 3150*m*, 3110*m*, 3040*m*, 2960*w*, 2940*w*, 2885*w*, 2830*w*, 2250*m*, 1980*w*, 1710*s*, 1680*s* (br.), 1625*m*, 1557*w*, 1540*w*, 1470*s*, 1443*m*, 1420*s*, 1375*s*, 1362*m*, 1340*m*, 1355*m*, 1290*s*, 1250*m*, 1230*m*, 1220*s*, 1188*w*, 1155*m*, 1125*s*, 1115*s*, 1090*m*, 1070*s*, 1050*s*, 1040*s*, 1005*s*, 988*w*, 950*s*, 910*m*, 860*s*, 815*m*, 785*w*, 770*w*, 760*w*, 740*w*, 712*m*, 675*m* (br.), 645*m*. ^{1}H-NMR ((D$_6$)DMSO): 11.17 (br. *s*, exchangeable with D_2O, NH); 8.05 (*d*, $J = 8.3$, H–C(6)); 5.62 (*d*, $J = 4.8$, exchangeable with D_2O, OH–C(5′)); 5.50 (*d*, $J = 8.3$, H–C(5)); 5.00 (*t*, $J = 5.2$, exchangeable with D_2O, OH–C(8′)); 4.93 (*d*, $J = 6.5$, exchangeable with D_2O, OH–C(6′)); 4.41 (*t*, $J = 4.5$, addn. of $D_2O \rightarrow d$, $J = 4.3$, H–C(5′)); 3.93–3.83 (*m*, addn. of $D_2O \rightarrow$ 3.93–3.86 (*m*, H–C(7′)) and 3.84 (*dd*, $J = 8.4, 4.4$, H–C(6′))); 3.71 (*ddd*, $J = 12.4, 5.5, 2.3$, addn. of $D_2O \rightarrow dd$, $J = 12.4, 2.3$, H–C(8′)); 3.50 (*dt*, $J = 12.4$, **4.4**, addn. of $D_2O \rightarrow$signals overlapped by HDO peak, H–C(8′)); 2.68–2.20 (4*m*, 4 H). ^{13}C-NMR: *Table 8*. MS: 298 (13, $[M + 1]^+$), 226 (9), 225 (8), 212 (3), 204 (3), 187 (16), 186 (99), 185 (9), 169 (8), 168 (65), 159 (46), 153 (10), 141 (68), 126 (12), 114 (13), 113 (100), 79 (11). Anal. calc. for $C_{12}H_{15}N_3O_6$ (297.27): C 48.49, H 5.09, N 14.14; found: C 48.71, H 5.30, N 14.10.

[1-(2,3-Dideoxy-α-D-oct-4-ulofuranosyl)uracil]ononitrile (**46**). Similarly as described for **45**, 84 mg (94%) of **46** were obtained from 101 mg (0.3 mmol) of **44**. R_f (MeOH/AcOEt 3:7) 0.55. M.p. 90°. $[\alpha]_D = -92$ ($c = 0.06$, DMSO). UV (H_2O): 263 (12305), 208 (10175). CD (H_2O): 261 (−2.60). IR (KBr): 3420*s* (br.), 3330*s* (br.), 3150*s*, 3100*s*, 3045*s*, 2970*m*, 2925*m*, 2890*m*, 2820*m*, 2250*w*, 1785*m* (br.), 1708*s*, 1682*s*, 1610*m*, 1560*w*, 1542*w*, 1465*s*, 1442*m*, 1412*s*, 1380*m*, 1360*m*, 1320*m*, 1293*s*, 1265*s*, 1230*m*, 1210*s*, 1175*m*, 1158*m*, 1100*s*, 1090*s*, 1070*m*, 1050*s*, 1028*m*, 995*m*, 965*m*, 948*m*, 895*m*, 880*m*, 822*m*, 780*w*, 770*m*, 735*m*, 700*w* (br.), 660*m*, 630*m*, 618*m*. ^{1}H-NMR ((D$_6$)DMSO): 11.11 (*d*, $J \approx 2.0$, exchangeable with D_2O, NH); 7.63 (*d*, $J = 8.2$, H–C(6)); 5.52 (*dd*, $J = 8.2$, *ca.* 2.0, addn. of $D_2O \rightarrow d$, $J = 8.2$, H–C(5)); 5.39 (br. *s*, exchangeable with D_2O, OH); 4.98 (br. *s*, exchangeable with D_2O, OH); 4.80 (br. *s*, exchangeable with D_2O, OH); 4.13 (br. *d*, $J = 4.1$, irrad. at 4.03→br. *s*, H–C(5′)); 4.05–4.01 (*m*, irrad. at 3.82→br. *s*, H–C(6′)); 3.83–3.80 (*m*, irrad. at 3.44→br. *d*, $J = 9.1$, irrad. at 3.70→*dd*, $J = 8.9$, 3.8, irrad. at 4.03→br. *s*, H–C(7′)); 3.70 (br. *d*, $J \approx 12.3$, addn. of $D_2O \rightarrow$br. *d*, $J \approx 12.3$, irrad. at 3.44→br. *s*, irrad. at 3.82→*d*, $J = 12.3$, H–C(8′)); 3.44 (br. *dd*, $J = 12.3$, 4.1, addn. of $D_2O \rightarrow dd$, $J = 12.3$, 4.1, irrad. at 3.70→br. *d*, $J \approx 3.0$, irrad. at 3.82→*d*, $J = 12.3$, H–C(8′)); 2.88–1.85 (3*m*, 4 H). ^{13}C-NMR: *Table 8*. MS: 298 (23, $[M + 1]^+$), 225 (16), 187 (8), 186 (99), 168 (42), 159 (28), 141 (40), 114 (7), 113 (100). Anal. calc. for $C_{12}H_{15}N_3O_6$ (297.27): C 48.49, H 5.09, N 14.14; found: C 48.31, H 5.26, N 13.89.

Methyl [1-(2,3-Dideoxy-5,6-O-isopropylidene-8-O-pivaloyl-β- and -α-D-oct-2-en-4-ulofuranosyl)uracil]onate (**47** and **48**, resp.). A soln. of 225 mg (0.58 mmol) of **25** and 163 mg (0.64 mmol) of **31** in 10 ml of MeCN was treated dropwise at −30° with a soln. of 0.2 ml (1.74 mmol) of $SnCl_4$ in 2 ml of MeCN. The mixture was allowed to warm to 0° within 1 h and treated with 5 ml of sat. aq. $NaHCO_3$ soln. Usual workup and CC (AcOEt/hexane 1:1) gave 80 mg (30%) of **47**/**48** (1.2:1). R_f (AcOEt/hexane 3:1) 0.52. UV: 262 (9122). IR: 3540*w* (br.), 3390*w*, 3115*w*, 3030*w* (sh), 2980*m*, 2955*m*, 2940*m*, 2910*w*, 2880*w*, 1725*s* (br.), 1695*s*, 1628*w*, 1615*w*, 1537*w*, 1482*m*, 1440*m*, 1400*m*, 1387*m*, 1380*m*, 1315*m*, 1280*s* (br.), 1250–1200*m*, 1175*m* (sh), 1150*s* (br.), 1108*s*, 1090*s*, 1035*m*, 1010*w*, 985*m*, 940*w*, 867*m*, 808*w*, 800–710*w*, 655*w*. ^{1}H-NMR: 9.14, 9.10 (2 br. *s*, exchangeable with D_2O, NH); 7.69, 7.62 (2*d*, $J = 8.2$, H–C(6)); 7.50, 7.29 (2*d*, $J = 15.7$, H–C(3′)); 6.21, 6.19 (2*d*, $J = 15.7$, H–C(2′)); 5.71, 5.67 (2*d*, $J = 8.3$, H–C(5)); 5.34 (*d*, $J = 5.8$), 5.11 (*d*, $J = 5.1$, H–C(5′)); 4.72–4.69 (3 H); 4.48 (*m*, H–C(7′)); 4.29–4.16 (4 H); 3.74, 3.73 (2*s*, MeO); 1.45 (*s*, Me); 1.38 (*s*, Me); 1.34 (*s*, Me); 1.32 (*s*, Me); 1.21 (*s*, *t*-Bu); 1.14 (*s*, *t*-Bu). ^{13}C-NMR: 177.82 (*s*); 177.67 (*s*); 165.90 (*s*); 165.71 (*s*); 163.62 (*s*); 163.18 (*s*); 149.98 (*s*); 149.54 (*s*); 143.67 (*d*); 142.06 (*d*); 138.89 (*d*); 138.76 (*d*); 123.68 (*d*); 121.80 (*d*); 114.29 (2*s*); 102.14 (*d*); 101.00 (*d*); 99.75 (*s*); 96.25 (*s*); 87.39 (*d*); 84.53 (*d*); 83.66 (*d*); 83.01 (*d*); 81.20 (*d*); 80.26 (*d*); 63.91 (*t*); 62.96 (*t*); 51.91 (*q*); 51.86 (*q*); 38.82 (*s*); 38.70 (*s*); 27.08 (3*q*); 26.97 (3*q*); 26.87 (*q*); 25.90 (*q*); 25.20 (*q*); 24.81 (*q*). MS: 453 (80, $[M + 1]^+$), 386 (10), 357 (6), 343 (24), 342 (23), 341 (100), 314 (9), 273 (26), 272 (6), 113 (20). Anal. calc. for $C_{21}H_{28}N_2O_9$ (452.46): C 55.75, H 6.24, N 6.19; found: C 55.73, H 6.35, N 6.39.

Methyl [1-(2,3-Dideoxy-8-O-pivaloyl-β- and -α-D-oct-2-en-4-ulofuranosyl)uracil]onate (**49** and **50**, resp.). A soln. of 200 mg (0.44 mmol) of **47**/**48** (1.2:1) in 5 ml of MeOH was treated with 5 ml of aq. 30% H_2SO_4. The mixture was stirred for 60 min at r.t. Usual workup and CC (AcOEt/hexane 3:1, AcOEt) gave 69 mg (38%) of **49** and 46 mg (25%) of **50**, which were crystallized from AcOEt/hexane.

Data of **49**: R_f (AcOEt) 0.41. M.p. 81–82°. $[\alpha]_D = -87$ ($c = 0.15$). UV: 262 (7360). CD: 256 (−8.69). IR: 3540–3460*w*, 3390*w*, 3200*w* (br.), 3115*w*, 3040*w* (sh), 2980*m*, 2960*m*, 2940*w*, 2915*w*, 2880*w*, 1730–1700*s*, 1690*s*, 1620*w* (sh), 1480*m*, 1440*m*, 1397*m*, 1385*m*, 1340*m* (sh), 1315*m*, 1280*s*, 1245–1200*m*, 1175*m* (sh), 1150*s*, 1090*s*, 1037*m*, 1010*w*, 997*w*, 982*m*, 940*w*, 910–890*w*, 860*w*, 810*w*. ^{1}H-NMR: 8.55 (br. *s*, exchangeable with D_2O, NH); 7.69 (*d*, $J = 8.4$, H–C(6)); 7.16 (*d*, $J = 15.6$, irrad. at 4.87→NOE of 7%, irrad. at 2.94→NOE of 5%, H–C(3′)); 6.14 (*d*,

J = 15.6, H–C(2′)); 5.76 (*d*, J = 8.4, H–C(5)); 4.87 (*d*, J = 2.6, exchangeable with D_2O, irrad. at 4.67→NOE of 1.5%, OH–C(5′)); 4.67 (*dd*, J = 5.1, 2.5, addn. of D_2O→*d*, J = 5.1, irrad. at 4.87→NOE of 10%, irrad. at 4.36→NOE of 4.7%, irrad. at 2.94→NOE of 7.8%, H–C(5′)); 4.66–4.64 (*m*, irrad. at 4.36→NOE of 1.9%, H–C(7′)); 4.36 (br. *d*, J = 5.1, *ca.* 1.1, after addn. of D_2O→*dd*, J = 5.1, < 2.0, irrad. at 4.87→NOE of 6%, irrad. at 4.67→NOE of 6%, irrad. at 2.94→NOE of 6%, H–C(6′)); 4.29 (*dd*, J = 12.5, 3.3, H–C(8′)); 4.15 (*dd*, J = 12.5, 3.8, irrad. at 4.36→NOE of 1.6%, H–C(8′)); 3.76 (*s*, MeO); 2.94 (br. *s*, exchangeable with D_2O, OH–C(6′)); 1.14 (*s*, *t*-Bu). ^{13}C-NMR: *Table 8*. MS: 413 (24, $[M + 1]^+$), 302 (17), 301 (100), 199 (16), 181 (25), 113 (6). Anal. calc. for $C_{18}H_{24}N_2O_9$ (412.40): C 52.42, H 5.86, N 6.79; found: C 52.17, H 5.64, N 6.67.

Data of **50**: R_f (AcOEt/MeOH 9:1) 0.56. M.p. 159–160°. $[\alpha]_D = -12$ (c = 0.11). UV: 264 (10860). CD: 258 (+7.18). IR: 3390*m* (br.), 3220*m* (br.), 3115*w*, 3040*w* (sh), 2980*m*, 2960*m*, 2910*w*, 2880*w*, 1730*s* (br.), 1690*s* (br.), 1480*m*, 1450*m*, 1440*m*, 1400*m*, 1385*m* (sh), 1315*m*, 1280*s* (br.), 1240–1200*m*, 1150*s*, 1095*m*, 1085*m*, 1040*m*, 990*m*, 975*m* (sh), 940*w*, 910*w*, 860*w* (br.), 640*w* (br.). ^{1}H-NMR: 9.84 (br. *s*, exchangeable with D_2O, NH); 7.73 (*d*, J = 8.4, H–C(6)); 7.32 (*d*, J = 15.6, irrad. at 4.76→NOE of 1.3%, H–C(3′)); 6.31 (*d*, J = 15.6, irrad. at 4.76→NOE of 1%, H–C(2′)); 5.76 (*d*, J = 8.4, H–C(5)); 4.88 (br. *s*, exchangeable with D_2O, OH–C(5′)); 4.76 (br. *s*, addn. of D_2O→*d*, J = 4.7, H–C(5′)); 4.52 (*dd*, J = 12.8, 2.1, H–C(8′)); 4.35 (*dd*, J = 12.8, 4.0, H–C(8′)); 4.22 (*ddd*, J = 9.3, 4.0, 2.1, H–C(7′)); 4.17–4.11 (*m*, addn. of D_2O→*dd*, J = 9.2, 4.7, H–C(6′)); 3.75 (*s*, MeO); 3.12 (*d*, J = 9.2, exchangeable with D_2O, OH–C(6′)); 1.25 (*s*, *t*-Bu). ^{13}C-NMR: *Table 8*. MS: 413 (7, $[M + 1]^+$), 385 (35), 301 (17), 285 (6), 283 (5), 199 (24), 183 (7), 145 (5), 113 (100), 103 (16). Anal. calc. for $C_{18}H_{24}N_2O_9$ (412.40): C 52.42, H 5.86, N 6.79; found: C 52.13, H 5.83, N 6.77.

*[1-(2,3-Dideoxy-β-*D*-oct-2-en-4-ulofuranosyl)uracil]onic Acid* (**51**). A soln. of 50 mg (0.12 mmol) of **49** in 2 ml of dioxane/H_2O 1:1 was treated with excess Bu_4NOH (40% in H_2O). After completion of the reaction (*ca.* 30 min), the mixture was treated with *Dowex 50 W X 8* (H^+ form, 3.0 g), filtered, concentrated to remove dioxane, and lyophilized. CC (AcOEt/MeOH/AcOH 8:1.5:0.5) of the residue gave 26.5 mg (70%) of **51**. An anal. sample of **51** was obtained by crystallization from MeOH/AcOEt. R_f (AcOEt/MeOH/H_2O 7:2:1) 0.20. M.p. 172–173° (dec.). $[\alpha]_D = -148$ (c = 0.13, H_2O). UV (H_2O): 264 (8844), CD (H_2O): 259 (–4.64), 219 (–5.49). IR (KBr): 3420*s* (br.), 1710*s*, 1660*m*, 1560*m*, (br.), 1460*w*, 1405*m* (br.), 1385*m*, 1290*m*, 1240–1220*w*, 1105w, 1085*w*, 1050*w*, 990*w*, 940*w* (br.), 760*w*, 645*w* (br.). ^{1}H-NMR (CD_3OD): 8.17 (*d*, J = 8.2, H–C(6)); 7.11 (*d*, J = 15.6, H–C(3′)); 6.09 (*d*, J = 15.6, H–C(2′)); 5.62 (*d*, J = 8.2, H–C(5)); *ca.* 4.82 (*d*, overlapped with DHO signal, addn. of DCl→J = 4.6, H–C(5′)); 4.17–4.13 (*m*, H–C(7′)); 4.10 (*dd*, J = 7.4, 4.6, H–C(6′)); 3.88 (*dd*, J = 12.5, 2.6, H–C(8′)); 3.68 (*dd*, J = 12.5, 4.1, H–C(8′)). ^{13}C-NMR: *Table 8*.

3. Purine Nucleosides. – *9-(1-*O*-Acetyl-3,4-*O*-isopropylidene-6-*O*-pivaloyl-α- and -β-*D*-psicofuranosyl)-N^6-benzoyladenine* (**54** and **53**, resp.). At 80°, 796 mg (4.2 mmol) of $SnCl_2$ were added to a soln. of 500 mg (1.4 mmol) of **21** and 591 mg (1.54 mmol) of **52** [38] in 15 ml of MeCN. The mixture was stirred for 30 min at 80° and cooled to r.t. Usual workup and CC (AcOEt/hexane 1:1) gave 32 mg (4%) of **54** and 320 mg (40%) of **53**. Anal. samples were prepared by recrystallization from AcOEt/hexane.

Data of **54**: R_f (AcOEt/hexane 3:1) 0.31. M.p. 81–83°. $[\alpha]_D = +19$ (c = 0.16). UV: 279 (17954). CD: 274 (+2.77), 228.0 (–0.50). IR: 3410*w*, 3340–3240*w*, 2990*m*, 2940*w*, 2875*w*, 1730*s* (br.), 1708*s*, 1610*s*, 1585*m*, 1480*m*, 1452*s*, 1400*w* (sh), 1385*w*, 1375*w*, 1330*w*, 1275*m*, 1250–1195*s*, 1155*s*, 1130*s*, 1088*s*, 1065*s* (sh), 1035–1018*m*, 990*w*, 965*w* (br.), 945*w*, 900–885*w*, 865*w*, 640*w*. ^{1}H-NMR: 9.10 (*s*, exchangeable with D_2O, NH); 8.82 (*s*, H–C(2)); 8.23 (*s*, H–C(8)); 8.03 (*d*, J = 7.3, 2 arom. H); 7.61 (br. *t*, J = 7.3, 1 arom. H); 7.53 (br. *t*, J = 7.5, 2 arom. H); 5.09 (*d*, J = 5.6, H–C(3′)); 5.04 (*d*, J = 11.7, H–C(1′)); 5.01 (*d*, J = 11.7, H–C(1′)); 4.84–4.79 (*m*, 2 H); 4.35 (*dd*, J = 12.0, 4.7, H–C(6′)); 4.27 (*dd*, J = 12.0, 4.5, H–C(6′)); 2.01 (*s*, AcO); 1.28 (*s*, *t*-Bu); 1.23 (*s*, Me); 0.78 (*s*, Me). ^{13}C-NMR: *Table 10*. MS: 569 (30, $[M + 1]^+$), 568 (100, M^+), 464 (13), 346 (22), 330 (20), 329 (96), 287 (16), 240 (64), 57 (70).

Data of **53**: R_f (AcOEt/hexane 3:1) 0.43. M.p. 88°. $[\alpha]_D = -24$ (c = 0.29). UV: 279 (20728). CD: 283 (–1.37), 245 (+0.38). IR: 3410*m*, 3340–3240*w*, 3140*w*, 3065*w* (sh), 3035*m* (sh), 2990*s*, 2940*m*, 2910*w* (sh), 2875*w*, 1730*s* (br.), 1710*s*, 1610*s*, 1585*s*, 1500*s*, 1480*s*, 1455*s*, 1380*s*, 1365*s*, 1355*s*, 1330*s*, 1280*s*, 1250–1200*s*, 1150*s* (br.), 1125*s*, 1090*s* (br.), 1065*s*, 1050*s*, 1028*s*, 990*m*, 970*m*, 942*m*, 888*m*, 865*s*, 700–660*m*, 640*m*. ^{1}H-NMR: 9.13 (*s*, exchangeable with D_2O, NH); 8.87 (*s*, H–C(2)); 8.23 (*s*, H–C(8)); 8.01 (*d*, J = 7.3, 2 arom. H); 7.60 (br. *t*, J = 7.4, 1 arom. H); 7.51 (br. *t*, J = 7.5, 2 arom. H); 5.90 (*d*, J = 6.1, H–C(3′)); 4.81 (*dd*, J = 6.1, 2.0, H–C(4′)); 4.76–4.73 (*m*, H–C(5′)); 4.68 (*d*, J = 12.3, H–C(1′)); 4.64 (*d*, J = 12.3, H–C(1′)); 4.20 (*dd*, J = 12.4, 4.0, H–C(6′)); 4.15 (*dd*, J = 12.4, 5.5, H–C(6′)); 1.87 (*s*, AcO); 1.66 (*s*, Me); 1.45 (*s*, Me); 1.00 (*s*, *t*-Bu). ^{13}C-NMR: *Table 10*. MS: 569 (21, $[M + 1]^+$), 568 (83, M^+), 330 (7), 329 (43), 240 (40), 57 (100), 43 (18). Anal. calc. for $C_{28}H_{34}N_5O_8$ (568.61): C 59.15, H 6.03, N 12.32; found: C 59.18, H 6.21, N 12.08.

9-(3,4-O-Isopropylidene-6-O-pivaloyl-β-D-psicofuranosyl)adenine (**55**) *and 9-(3,4-O-Isopropylidene-β-D-psicofuranosyl)adenine* (**56**). A soln. of 280 mg (0.49 mmol) of **53** in 10 ml of MeOH/25% aq. NH_3 1:1 was stirred for 7 d at r.t. Usual workup and CC (MeOH/AcOEt 1:19) gave 80 mg of **55** (38%) and 80 mg of **56** (48%) which were recrystallized in AcOEt/hexane.

Data of **55**: R_f (MeOH/AcOEt 1:19) 0.37. M.p. 172–173°. $[\alpha]_D = -66$ ($c = 0.29$). UV: 259 (13805). CD: 256 (−2.28), 230 (0.00), 213 (−4.81). IR: 3530*w*, 3490*w*, 3418*m*, 3340*w* (br.), 3190*w* (br.), 3040*w* (sh), 2990*m*, 2940*m*, 2880*w*, 1732*s*, 1635*s*, 1590*m*, 1575*m*, 1480–1470*m*, 1410*m*, 1388*m*, 1378*m*, 1331*m*, 1280*m*, 1240–1200*m*, 1152*s*, 1120*s*, 1090*s*, 1037*m*, 982*m*, 935*m* (br.), 865*m*, 645*m*. ^{1}H-NMR: 8.29 (*s*, H–C(8)); 8.07 (*s*, H–C(2)); 5.85 (*d*, $J = 6.2$, H–C(3′)); 5.68 (br. *s*, exchangeable with D_2O, NH_2); 4.81 (*dd*, $J = 6.2, 2.2$, irrad. at 4.68→*d*, $J = 6.1$, H–C(4′)); 4.70–4.67 (*m*, H–C(5′)); 4.24 (*d*, $J = 12.5$, H–C(1′)); 4.21 (*dd*, $J = 12.3, 5.6$, irrad. at 4.68→*d*, $J = 12.3$, H–C(6′)); 4.15 (*dd*, $J = 12.3, 5.6$; irrad. at 4.68: *d*, $J = 12.3$, H–C(6′)); 4.07 (*d*, $J = 12.5$, H–C(1′)); 3.48 (br. *s*, exchangeable with D_2O, OH); 1.65 (*s*, Me); 1.43 (*s*, Me); 1.03 (*s*, *t*-Bu). ^{13}C-NMR: *Table 10*. MS: 422 (100, $[M + 1]^+$), 363 (5), 348 (13), 320 (2), 287 (3), 256 (4), 299 (5). Anal. calc. for $C_{19}H_{27}N_5O_6$ (421.45): C 54.15, H 6.46, N 16.62; found: C 54.04, H 6.74, N 16.45.

Data of **56**: R_f (MeOH/AcOEt 3:17) 0.26. M.p. 131–132°. $[\alpha]_D = -83$ ($c = 0.25$, DMSO). UV: 259 (11524). CD: 257 (−0.81). IR (KBr): 3420*s*, 3340*s*, 3150*s*, 2980*m*, 2940*w*, 2900*w*, 1670*s*, 1613*m*, 1567*m*, 1480*m*, 1418*w*, 1385*m*, 1375*m*, 1330*m*, 1318*m*, 1275*m*, 1250*m*, 1235*m*, 1212*m*, 1180*w*, 1160*m*, 1130*m*, 1115*m*, 1080*s*, 1040*m*, 988*w*, 968*w*, 935*m*, 895*w*, 870*m*, 815*w*, 795*m*, 732*w*, 700*m*, 665*m*, 640*m*. ^{1}H-NMR ((D_6)DMSO): 8.12 (*s*); 8.10 (*s*, H–C(2), H–C(8)); 7.15 (*s*, exchangeable withD_2O, NH_2); 5.72 (*d*, $J = 6.1$, H–C(3′)); 5.01 (*t*, $J = 5.1$, exchangeable with D_2O, OH–C(6′)); 4.90 (*dd*, $J = 7.0, 5.3$, exchangeable with D_2O, OH–C(1′)); 4.77 (*dd*, $J = 6.1, 1.5$, H–C(4′)); 4.32–4.29 (*m*, H–C(5′)); 3.91 (*dd*, $J = 12.0, 7.0$, add. of D_2O→*d*, $J = 12.0$, H–C(1′)); 3.75 (*dd*, $J = 12.0, 5.3$, addn. of D_2O→*d*, $J = 12.0$, H–C(1′)); 3.36–3.26 (*m*, addn. of D_2O→*dd*, at 3.34, $J = 11.7, 6.2$, *dd* at 3.28 $J = 11.7, 5.6$, 2 H–C(6′)); 1.48 (*s*, Me); 1.31 (*s*, Me). ^{13}C-NMR: *Table 10*. MS: 338 (100, $[M +]^+$), 203 (7), 193 (6), 179 (8), 176 (6), 137 (6), 136 (64), 135 (5). Anal. calc. for $C_{14}H_{19}N_5O_5$ (337.34): C 49.85, N 5.68, N 20.76; found: C 49.68, H 5.51, N 20.55.

9-(1,3,4-Tri-O-acetyl-6-O-pivaloyl-α- and -β-D-psicofuranosyl)-N^6*-benzoyladenine* (**57** and **58**, resp.). At 80°, 1.54 g (8.1 mmol) of $SnCl_2$ were added to a soln. of 1.14 g (2.70 mmol) of **28** and 1.14 g (2.97 mmol) of **52** in 15 ml of MeCN. The mixture was stirred for 30 min and cooled to r.t. Usual workup and CC (Et_2O) gave 332 mg (20%) of **57** and 500 mg (30%) of **58**. The anal. samples were prepared by crystallization from Et_2O/hexane.

Data of **57**: R_f (AcOEt) 0.65. M.p. 79°. $[\alpha]_D = +42$ ($c = 0.44$). UV: 279 (20451). CD: 275 (+2.24), 223 (−1.68). IR: 3415*w*, 3038*w* (sh), 3005*m*, 2985*m*, 2945*w*, 2915*w*, 2880*w*, 1755*s* (br.), 1615*s*, 1587*m*, 1505*m*, 1482*s*, 1457*s*, 1400*m*, 1375*m*, 1340*m*, 1275*m*, 1240–1200*s*, 1155*m*, 1135*s*, 1068*m*, 1048*m*, 1030*m*, 975*m*, 950*m*, 900*m*, 642*m*. ^{1}H-NMR: 9.10 (*s*, exchangeable with D_2O, NH); 8.73 (*s*, H–C(2)); 8.24 (*s*, H–C(8)); 8.04 (*d*, $J = 7.3$, 2 arom. H); 7.64–7.52 (*m*, 3 arom. H); 6.01 (*d*, $J = 5.2$, H–C(3′)); 5.47 (*dd*, $J = 5.2, 4.1$, irrad. at 4.72→*d*, $J = 5.2$, H–C(4′)); 4.96 (*d*, $J = 11.9$, H–C(1′)); 4.92 (*d*, $J = 11.9$, H–C(1′)); 4.72 (*q*, $J = 4.1$, H–C(5′)); 4.34–4.33 (*m*, irrad. at 4.72→br. *s*, 2 H–C(6′)); 2.03 (*s*, AcO); 1.89 (*s*, AcO); 1.75 (*s*, AcO); 1.29 (*s*, *t*-Bu). ^{13}C-NMR: *Table 10*. MS: 612 (100, $[M + 1]^+$), 611 (8, M^+), 373 (47), 241 (8), 240 (53), 211 (12), 119 (13), 117 (7), 103 (13). Anal. calc. for $C_{29}H_{33}N_5O_{10}$ (611.60): C 56.95, H 5.44, N 11.45; found: C 56.91, H 5.38, N 11.17.

Data of **58**: R_f (AcOEt) 0.67. M.p. 77°. $[\alpha]_D = -56$ ($c = 0.15$). UV: 279 (21436), 231 (13585). CD: 279 (−3.87), 235 (0.38), 222 (−2.96). IR: 3410*w* (br.), 3040*w* (sh), 3005*m*, 2980*m*, 2880*m*, 1755*s* (br.), 1710*m* (sh), 1615*s*, 1585*m*, 1480*m*, 1452*s*, 1370*m*, 1332*m*, 1280*m* (sh), 1240–1200*s*, 1150*m*, 1115*m*, 1095*m*, 1070*m*, 1050*m* (sh), 1030*m*, 945*w* (br.), 890*w* (br.), 640*m*. ^{1}H-NMR: 9.01 (*s*, exchangeable with D_2O, NH); 8.76 (*s*, H–C(2)); 8.29 (*s*, H–C(8)); 8.03 (*d*, $J = 7.1$, 2 arom. H); 7.62–7.51 (*m*, 3 arom. H); 6.45 (*d*, $J = 5.3$, H–C(3′)); 5.41 (*t*, $J = 5.3$, H–C(4′)); 4.83 (*s*, 2 H–C(1′)); 4.65–4.61 (*m*, H–C(5′)); 4.35 (*d*, $J = 3.3$, 2 H–C(6′)); 2.26 (*s*, AcO); 2.12 (*s*, AcO); 1.91 (*s*, AcO); 1.06 (*s*, *t*-Bu). ^{13}C-NMR: *Table 10*. MS: 612 (90, $[M + 1]^+$), 611 (12, M^+), 509 (12), 508 (54), 391 (10), 375 (9), 374 (15), 373 (90), 372 (27), 257 (10), 241 (15), 240 (100), 211 (19), 153 (10). Anal. calc. for $C_{29}H_{33}N_5O_{10}$ (611.60): C 56.95, H 5.44, N 11.45; found: C 57.01, H 5.56, N 11.39.

9-(β-D-Psicofuranosyl)adenine [2] (**1**). A) *From* **56**: A soln. of 10 mg (0.03 mmol) of **56** in 2 ml of H_2O was treated with excess *Dowex 50 W X 8* (H^+ form) for 3 h. Filtration, lyophilization, and crystallisation from MeOH gave 6.5 mg (74%) of **1**.

B) From **58**: A soln. of 30 mg (0.05 mmol) of **58** and 2 ml of aq. 25% NH_3 in 2 ml of MeOH was stirred for 7 d at r.t., and the solvents were evaporated. Crystallization of the residue from MeOH gave 13 mg (89%) of **1**. R_f (MeOH/$CHCl_3$ 3:7) 0.31. M.p. 210–212° ([2]: 212–214°). $[\alpha]_D = -65$ ($c = 1.1$, DMF). UV (H_2O): 260 (14967). CD H_2O): 2.59 (−1.44). IR (KBr): 3420–3200 (br. bands with maxima at 3420*s*, 3340*s*, 3200*s*), 2950–2930*m*, 1968*w*, 1650*s* (br.), 1610*s*, 1570*s*, 1505*m*, 1480*s*, 1450*m*, 1418*s*, 1330*s*, 1280*m*, 1235*m*, 1215*m*, 1175*m*, 1140*s*, 1130*s*, 1110*m*, 1090*s*, 1060*s*, 1035*m*, 985*m*, 940*m* (br.), 915*m*, 892*m*, 832*m*, 808*m*, 798*m*, 740*m*, 725*m*, 690*m*, 670*m*. ^{1}H-NMR

((D$_6$)DMSO): 8.24 (*s*, H–C(8)); 8.09 (*s*, H–C(2)); 7.15 (*s*, exchangeable with D_2O, NH_2); 5.61 (*d*, $J = 4.8$, exchangeable with D_2O, OH–C(3′)); 5.04 (*t*, $J = 5.5$, exchangeable with D_2O, OH–C(6′)); 4.98 (*d*, $J = 6.8$, exchangeable with D_2O, OH–C(4′)); 4.88 (*t*, $J = 4.7$, addn. of $D_2O \rightarrow d$, $J = 4.6$, H–C(3′)); 4.73 (*dd*, $J = 6.8$, 5.3, exchangeable with D_2O, OH–C(1′)); 4.10 (*dd*, $J = 12.1$, 6.8, addn. of $D_2O \rightarrow d$, $J = 12.2$, H–C(1′)); 4.00–3.97 (*m*, H–C(5′)); 3.89 (*dd*, $J = 12.1$, 5.3, addn. of $D_2O \rightarrow d$, $J = 12.2$, H–C(1′)); 3.86–3.83 (*m*, addn. of $D_2O \rightarrow dd$, $J = 7.9$, 4.5, irrad. at 4.88 $\rightarrow d$, $J \approx 8.0$, H–C(4′)); 3.73 (*ddd*, $J = 12.3$, 5.5, 2.5, addn. of $D_2O \rightarrow dd$, $J = 12.5$, 2.4, H–C(6′)); 3.49 (*ddd*, $J = 12.3$, 5.5, 4.2, addn. of $D_2O \rightarrow dd$, $J = 12.5$, 4.1, H–C(6′)). ^{13}C-NMR: *Table 10*. MS: 298 (88, $[M + 1]^+$), 178 (8), 176 (9), 163 (23), 145 (12), 137 (7), 136 (100), 135 (19), 127 (7).

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