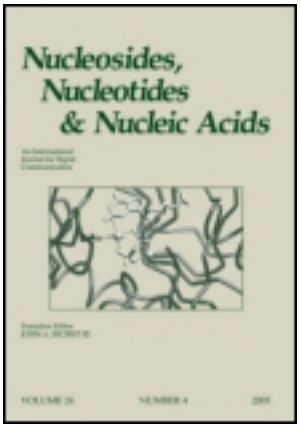

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Nucleosides Part LXVI I[ ]: Synthesis of 4-Amino-7(8H)Pteridinone-N_8-Nucleosides—Structural Analogs of Adenosine

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NUCLEOSIDES PART LXVI I[1]: SYNTHESIS OF 4-AMINO-7(8H)PTERIDINONE-N_8-NUCLEOSIDES—STRUCTURAL ANALOGS OF ADENOSINE

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□ *Various 4-amino-7(8H)pteridones (**6**, **12**, **14**, **15**, **20**, **22**) have been glycosylated with 1-chloro-2′-deoxy-D-ribofuranose derivatives (**25**, **26**) applying the new DBU-salt method to form the N_8-2′-deoxy-D-ribofuranosides (**27–36**) which can be regarded as 2′-deoxyadenosine analogs. Analogously reacted the 2-N,N-dimethyl-amino-methyleneimino-7(8H)pteridones (**43–48**) to give preferentially the corresponding N_8-β-D-anomers (**49–55**). Ribosylation with 1-bromo-2,3,5-tri-O-benzoyl-a-D-ribofuranose (**56**) proceeded as well with **6**, **12**, **15**, **45**, and **46** to yield to N_8-β-D-ribofuranosides **57–61**. Sugar deprotection led to the free N_8-2′-deoxy-β-D-ribofuranosides **37–42** and N_8-β-D-ribofurano-sides **62–65**, respectively. Glycosylations via the silyl-method under Vorbrüggen conditions led with **6**, **12** and **15** to the same results, however, 4-amino-6-phenyl-7(8H)pteridone (**14**) reacted differently forming the N_1-β-D-ribofuranosides (**71**, **79**) and the N_1-2′-deoxy-α-and β-D-ribofuranosides **73**, **74**, **77**, **78**. The assignments of the structures have been achieved by ^{1}H-NMR- and UV-spectra. **C,H,N**-elemental analyses account for the composition.*

Keywords DBU-salt glycosylations; 4-amino-7(8)pteridones; N_1- and N_8-pteridine-nucleosides; silyl glycosylations; UV-spectra; pK_a-determinations

INTRODUCTION

Our interests in the syntheses of pteridine-N(1)- and N(8)-nucleosides[2–24] are based on the structural similarities to the naturally occurring pyrimidine - and purine-nucleosides, respectively. Furthermore, most pteridine derivatives are inherently fluorescent and therefore pteridine-based fluorophores can be applied as new types of building blocks in oligonucleotides synthesis to substitute linker-attached fluorescent probes.[25–27]

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On the occassion of the 70th birthday of Morris J. Robins and in admiration of his important contributions to purine and nucleosides chemistry.

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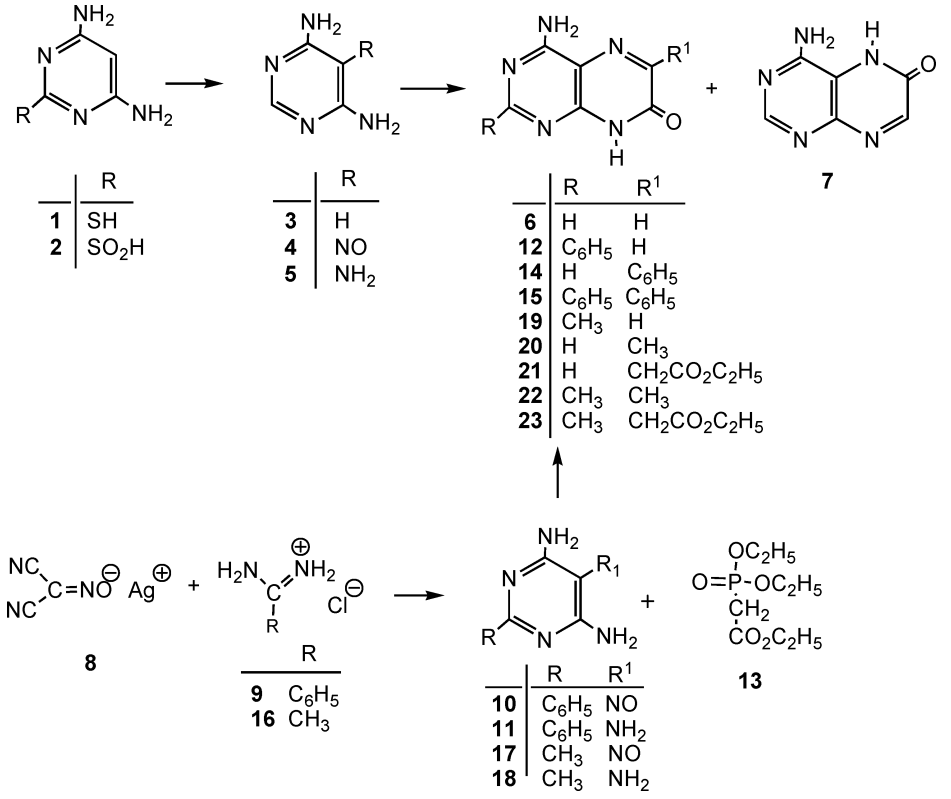
In continuation of our investigations of structural analogs of adenosine and 2′-deoxyadenosine, we concentrated again on glycosylation reactions of 4-amino-7(8H)-pteridone (**6**) and its 2- (**12**) and 6-phenyl-(**14**) as well as 2,6-diphenyl derivatives (**15**).[15] Since the Hilbert-Johnson-Birkofer procedure[28] works well in the ribose series, the synthesis of the corresponding 2′-deoxyribofuranosides leads always to α/ß-anomeric mixture which have to be seperated by tedious chromatographic techniques. Based on the phase-transfer glycosylation procedure introduced by F. Seela et al.[29,30] and the sodium salt approach practised by R.K. Robins et al.[31] we found some improvement in the pteridine series by applying the DBU-salts in acetonitrile yielding with 1-chloro-2-deoxy-3,5-di-O-toluoyl-a-D-ribofuranose in a highly stereospecific manner the blocked 2′-deoxy-ß-D-ribofuranosides via an S_N2-mechanism.

SYNTHESIS

First we improved the syntheses of the starting pteridine derivatives. 4-Amino-7(8H)-pteridone (**6**) was obtained from 4,6-diamino-2(1**H**)pyrimidinethione (**1**) by H_2O_2 oxidation to the corresponding 2-sulfinic acid (**2**), followed by hydrolysis with conc. HCl to give 4,6-diaminopyrimidine (**3**) in almost quantitative yield. The subsequent nitrosation works only well in 2 N HCl yielding 4,6-diamino-5-nitrosopyrimidine (**4**) in 82% yield. Catalytic reduction of **4** with Raney-Nickel gave 4,5,6-triaminopyrimidine (**5**), which was treated with ethyl glyoxylate-hemiethylacetal and cyclized in MeOH with sodium methoxide to give 69% of 4-amino-7(8H)pteridone (**6**) and the isomeric 4-amino-6(5H)-pteridone (**7**) in 18% yield, as a side-product. The attempts to synthesize 4,6-diamino-2-phenylpyrimidine from benzamidine and malononitrile or by the approach of Howard et al.[32] with malonodiamidine and ethyl benzoate worked only in very low yields. The interesting variant of E. C. Taylor et al.[33] starting from the silver salt of isonitrosomalonodintrile (**8**) and benzamidine hydrochloride (**9**) worked in α-picoline almost quantitatively to give 4,6-diamino-5-nitroso-2-phenylpyrimidine (**10**). Reduction to 4,5,6-triamino-2-phenylpyrimidine (**11**) and subsequent condensation with ethyl glyoxylate-hemiethylacetal afforded 4-amino-2-phenyl-7(8H)-pteridone (**12**) in 60% yield. An even simpler and improved approach was found in the Wittig-Horner-reaction[34] between **10** and ethyl 2-(diethoxyphosphoryl)acetate (**13**) yielding compound **12** in 87%. 4-Amino-6-phenyl-7(8H)pteridone (**14**) resulted from a Timmis reaction between 4,6-diamino-5-nitrosopyrimidine (**4**) and ethyl phenyl-acetate in EtOH/C_2H_5ONa in 62% yield. Similarly **10** reacted with ethyl phenylacetate to yield 85% of 4-amino-2,6-diphenyl-7(8H)pteridone (**15**). Besides the phenyl-substituted 4-amino-7(8)pteridones (**12, 14, 15**), we were also interested in the corresponding

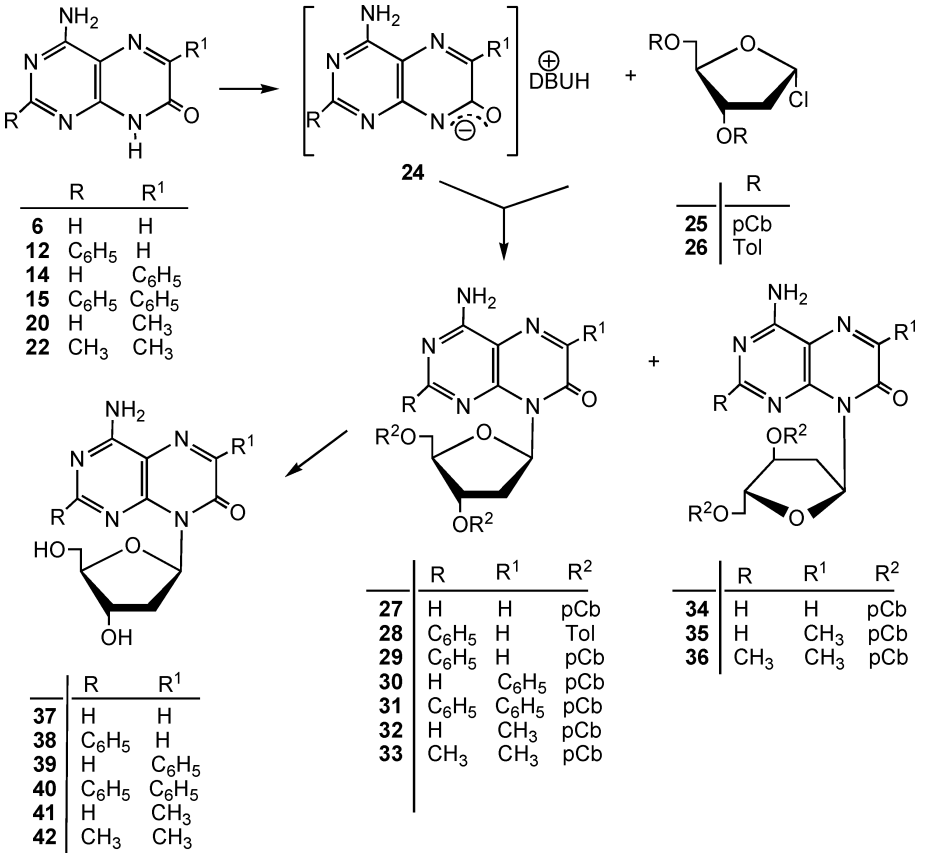


SCHEME 1

methyl derivatives **19**, **20**, and **22**. 4,6-Diamino-2-methyl-5-nitrosopyrimidine (**17**)[33] resulted from the condensation between **8** and **16** and was then reduced catalytically to 4,5,6-triamino-2-methylpyrimidine (**18**). Its reaction with ethyl glyoxylate-hemiethylacetal yielded 37% of 4-amino-2-methyl-7(8H)pteridone (**19**). In contrast to earlier results,[35] 4,5,6-triaminopyrimidine (**5**) reacted with ethyl pyruvate in AcOH regioselectively, to give 4-amino-6-methyl-7(8H)pteridone (**20**) in 44% yield. The same compound resulted also from the condensation of **5** with sodium ethyl oxalylacetate to give, first 4-amino-6-ethoxycarbonylmethyl-7(8H)pteridone (**21**) which further gives under acid hydrolysis ester cleavage and decarboxylation to afford **20**. 4-Amino-2,6-dimethyl-7(8H)pteridone (**22**) was obtained in an analogous manner via both routes in good yields (Scheme 1).

For the glycosylation reactions of the 4-amino-7-(8H)pteridones **6**, **12**, **14**, **15**, **19**, and **20**, we developed a simplified new procedure on the basis of Seela's[29,30] and Robins'[31] ideas by treatment of the DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) salts (**24**) with the haloribose **25** and **26**, respectively, in acetonitrile.

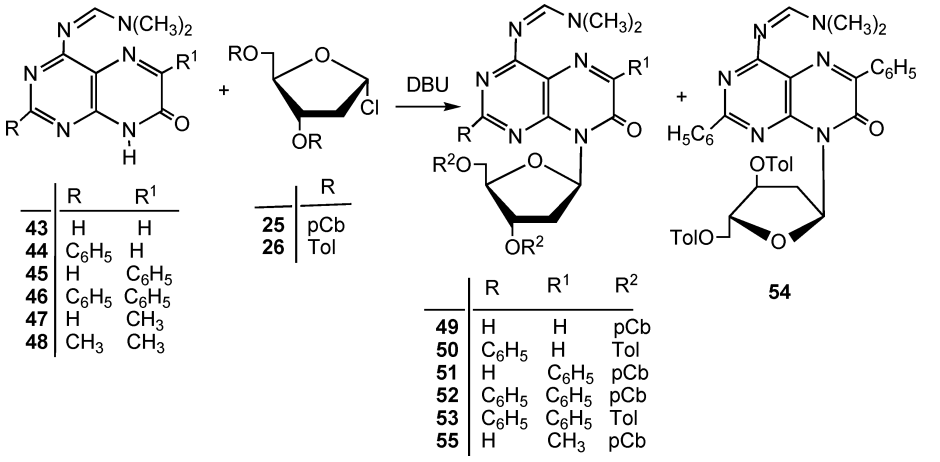
A suspension of the starting material in acetonitrile was treated with one equivalent of DBU and followed by the addition of 1-chloro-3,5-di-



SCHEME 2

O-(4-chlorobenzoyl)-2-deoxy-α-D-*erythro*-pentofuranose (**25**)[36] leading at room temperature in a highly regioselective manner to the corresponding N_8-2′-deoxy-ß-D-ribofuranosides **27**, **29–33**, which were isolated either by crystallization from $CHCl_3$/MeOH or by chromatographic technique in 34–54% yield. The anomeric α-D-ribosides have been detected chromatographically as minor components and have been isolated in pure form only in a few cases (**34–36**). During these reactions it was also noticed that, minor amounts of the starting material did not react due to their low solubility. Glycosylation of **12** with **26** in DMF and DMF/CH_3CN, respectively, proceeded in clear solutions but the yields, even after applying different bases, such as NaH, K_2CO_3 or KOH led to no improvement. But with DBU, the 4-amino-2-phenyl-8-(3,5-di-O-toluoyl-2deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (**28**) resulted in 49% isolated yield (Scheme 2).

A general improvement in the glycosylation reactions was expected from improved solubilities of the starting pteridine derivatives in organic solvents.



	R	R1
43	H	H
44	C_6H_5	H
45	H	C_6H_5
46	C_6H_5	C_6H_5
47	H	CH_3
48	CH_3	CH_3

	R
25	pCb
26	Tol

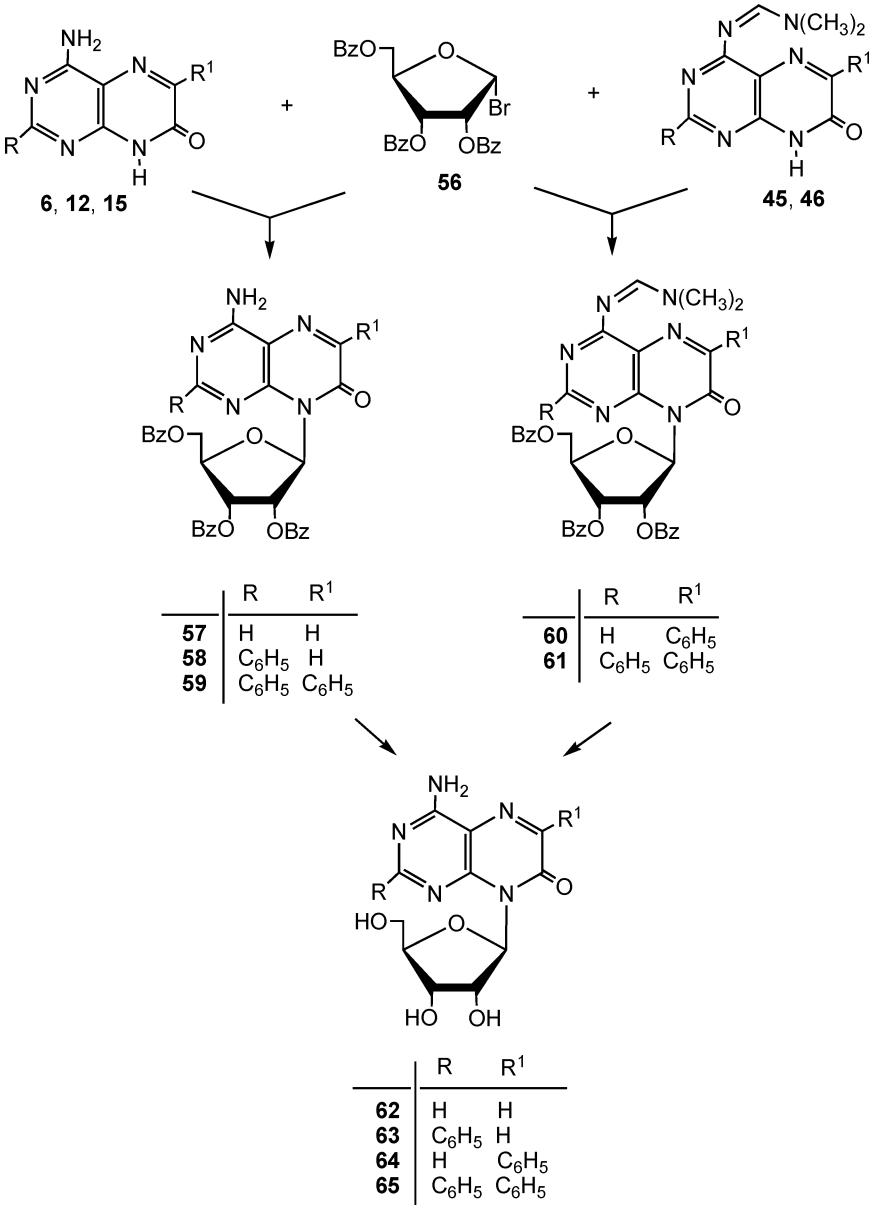
	R	R1	R2
49	H	H	pCb
50	C_6H_5	H	Tol
51	H	C_6H_5	pCb
52	C_6H_5	C_6H_5	pCb
53	C_6H_5	C_6H_5	Tol
55	H	CH_3	pCb

SCHEME 3

Conversion of the 4-amino group into the 4-dimethylaminomethyleneimino function by treatment of **6**, **12**, **14**, **15**, **20**, and **22** with N,N-dimethylformamide dimethylacetal was performed to give **43–48** in yields of 84–91% (Scheme 3). Small amounts of side-products especially on prolonged reaction times were chromatographically detected and identified as the N_8-methyl derivatives.

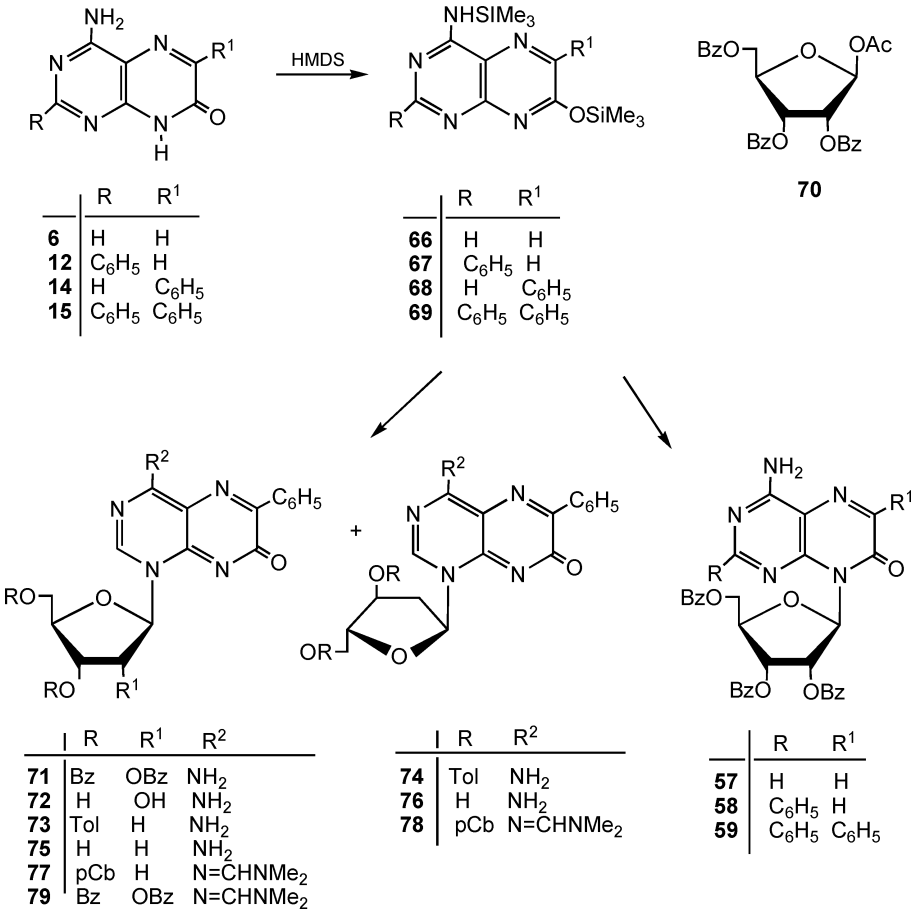
The glycosylations of the DBU-salts of **43–47** worked well and gave very good yields, especially, with **45** to **51** in 60%, with **46** to **52** in 86%, and **53** in 71% yield. The deprotection of the sugar moieties to the free pteridine-N-8-2′-deoxy-ß-D-*erythro*-pentofuranosides **37–42** worked very well in high yields by the Zemplen method[37] in MeOH under CH_3ONa-catalysis. The N,N-dimethylaminomethylene function was rather stable under these conditions but could be cleaved with K_2CO_3 in MeOH (Scheme 2).

The new synthetic method has been found to be applicable equally well for the preparation of the pteridine-N-8-ß-D-ribonucleosides **57–61**, whereas the nucleophilic displacement at the anomeric center of 2,3,5-tri-O-benzoyl-1-bromo-α-D-*erythro*-pentofuranose (**56**)[38] by the attack of the deprotonated aglycons in form of their DBU salts, is controlled by the intermediary formed acyloxonium cation, leading to the formation of a ß-glycosidic linkage (Scheme 4). In the ribo-series, the direct glycosylation by the DBU-salt method is only superior to the formerly reported[15] classical Vorbrüggensilyl approach[39] if the pteridines are amino group protected. Deprotection by the Zemplen method[37] led again in high yields to the corresponding 4-amino-8-ß-D-*erythro*-pentofuranosyl-7(8H)pteridones **62–65** (Scheme 4). During these investigations we also noticed that, the earlier reported 4-amino-6-phenyl-8-ß-D-*erythro*-pentofuranosyl-7(8H)pteridine[15] and its α- and ß-D-2′-deoxyribosides,[40] which were obtained under Hilbert-Johnson-Birkofer conditions,[41] are not in agreement with the physical data of the N-8-ribosides synthesized by the DBU-salt method.



SCHEME 4

We repeated some of the earlier experiments by the silyl method and converted 4-amino-7(8)pteridone (**6**), and its 2-phenyl-(**12**), 6-phenyl-(**14**) and 2,6-diphenyl derivatives (**15**) by treatment with hexamethyl-disilazane (HMDS) into the corresponding 4-trimethyl-silylamino-7-trimethylsilyloxypteridines **66–69**. Reaction of **66, 67** and **69** with 1-O-acetyl-2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranose (**70**)[41] and BF_3-etherate



SCHEME 5

as catalyst in CH_2Cl_2, proceeded in the expected manner under N-8 substitution to **57–59**, which were identical with the products obtained by the DBU-salt method. Unexpectedly, 6-phenyl-4-trimethylsilylamino-7-trimethylsilyloxypteridine (**69**) led to a new type of reaction product to which the revised structure of 4-amino-6-phenyl-1-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (**71**) was assigned by spectroscopic means. Similarly, we reacted **69** with **26** in acetonitrile under catalysis of trimethylsilyl trifluoromethane-sulfonate to give the anomeric mixture of **73** + **74**, which was separated into the pure components. After silylation of 4-N,N-dimethylaminomethyleneimino-6-phenyl-7(8)pteridone (**45**) reaction with **25** in acetonitrile in the presence of $SnCl_4$ proceeded, again under N-1 substitution, to give the α,ß-anomeric mixture **77** + **78**. Compound **71** reacted with dimethylformamide dimethylacetal to give 4-N,N-dimethylaminomethyleneimino-6-phenyl-1-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (**79**) in high yield (Scheme 5).

STRUCTURES

The structural determinations of the various reaction products have been achieved by UV- and ^{1}H-NMR-data. Glycosylations at the 4-amino group could be excluded since the prepared pteridine-nucleosides showed a normal NH_2-signal in the ^{1}H-NMR spectrum integrating for 2 protons. Furthermore, the deprotected nucleosides showed no acidic pK_a-value indicating that substitution most likely occured at the 7,8-lactam function. 7-O-glycosylation could be omitted by the fact that the products revealed no base lability during the deprotection step. The site of glycosylation at N-8 was derived from a comparison of the UV-spectra with the starting nucleobases (Table 1).

The close structural analogies can best be seen from the comparisons of the cations and neutral forms of the nucleobases and their corresponding free nucleosides as, for example, **6**, **37**, **63**, and **12**, **38**, **64**, and **14**, **39**, **65**, and **15**, **40**, **66**. The same similarities are observed in the 4-N,N-dimethylaminomethyleneimino series **43**, **49**, and **44**, **50**, and **45**, **51** and **46**, **52**, **53**, **62**. From the comparisons of the UV-spectra of the N-1 with the N-8-pteridine-nucleosides it is noticed that the longer vinylogous amide resonance between N-1 and the 7-carbonyl group is reflected in a bathochromic shift of the long wavelength absorption band. The structural differences between the N-1-(**77**) and N-8-nucleosides (**51**) are nicely demonstrated by the shape of the UV-spectra (Figure 1).

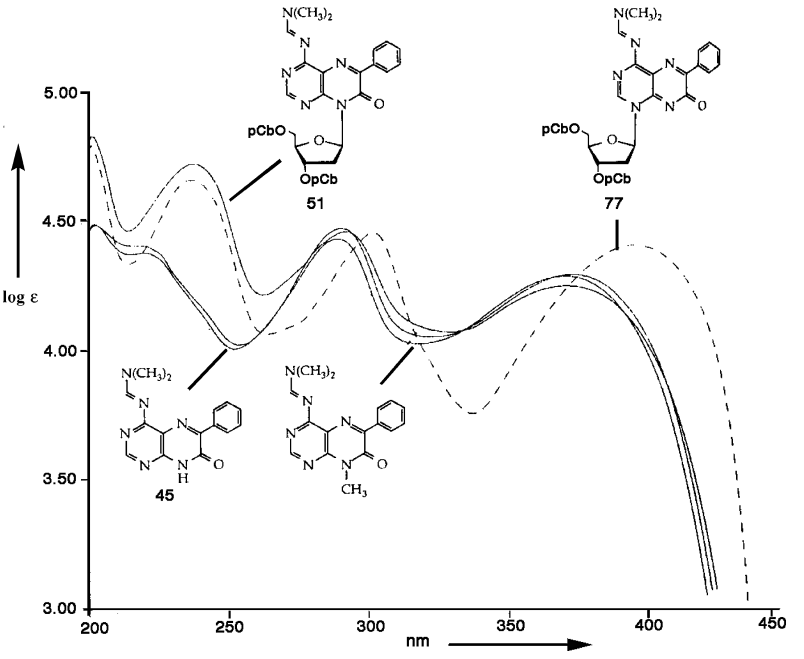


FIGURE 1 UV-spectra of 4-dimethylaminomethyleneimino-6-phenyl-7(8H)pteridone (**45**), its 8-methyl-, N-1-(**77**) and N-8–2′-deoxyribonucleoside (**51**) in MeOH.

TABLE 1 UV-data of 4-amino-7(8H)pteridones and their nucleosides

Compound	pK_a in H_2O	UV-Absorption in λ_{max}						log ε				pH	Form
6	2,27		[245]		290	320		[3.94]		4.07	3.96	0.0	+
	7.52	218	249		[295]	333	4.32	4.00		[3.71]	3.95	5.0	o
			235		[320]	330		4.37		[3.96]	3.98	10.0	−
37	2.36				290	317				4.04	3.94	0.0	+
			250			336		4.07			3.96	5.0	o
			253			331		4.10			3.91	MeOH	o
62	1.74	223	248	283	293	322	4.26	4.00	3.89	3.95	3.81	0.0	+
		218	249		[295]	333	4.38	4.00		[3.70]	3.92	7.0	o
		218	253			337	4.53	4.05			3.86	MeOH	o
27			240			331		4.68			3.93	MeOH	o
34			241			331		4.72			3.96	MeOH	o
57		222	[259]	[273]		343	4.81	[4.15]	[3.84]		3.92	MeOH	o
12	1.97	234	[256]		304	339	4.37	[4.24]		4.15	4.20	0.0	+
	7.45	222	264			348	4.45	4.28			4.20	7.0	o
			243		341	[354]		4.59		4.19	[4.08]	10.0	−
38	2.15	235	[258]		305	341	4.33	[4.21]		4.06	4.14	0.0	+
		222	266		[316]	353	4.39	4.21		[3.89]	4.12	5.0	o
		220	266		[328]	354	4.45	4.26		[3.96]	4.12	MeOH	o
63	1.73	239	[260]		306	346	4.36	[4.26]		4.06	4.17	0.0	+
		221	267		[315]	354	4.43	4.25		[3.91]	4.14	5.0	o
		221	267		[323]	355	4.43	4.30		[3.99]	4.18	MeOH	o
28		[229]	240	[267]	[320]	354	[4.62]	4.64	[4.28]	[3.93]	4.10	MeOH	o
29		229	239	[266]	[323]	355	4.61	4.61	[4.27]	[3.92]	4.10	MeOH	o
58		226		268	[320]	357	4.79		4.30	[3.94]	4.14	MeOH	o
14	2.27	222	[240]		300	354	4.46	[4.19]		4.04	4.23	0.0	+
	7.69	219	[247]	260		358	4.39	[4.06]	4.14		4.22	7.0	o
		233		260		352	4.47		4.24		4.20	10.0	−
39	2.41	222	[241]		301	353	4.39	[4.16]		3.99	4.17	0.0	+
		218	[249]	261		360	4.36	[4.09]	4.14		4.14	7.0	o
		220	[246]	264		366	4.38	[4.12]	4.17		4.16	10.0	−
64		220	[246]	265		369	4.42	[4.13]	4.19		4.19	MeOH	o
30		238		[268		366	4.53		[4.01]		4.20	MeOH	o
15	1.91	229		[250]	[320]	372	4.38		[4.29]	[4.06]	4.40	−0.5	+
	7.99	222		272		378	4.37		4.28		4.37	7.0	o
			250			367		4.59			4.28	11.0	−
40	2.70	232	[242]		[316]	373	4.42	[4.32]		[3.97]	4.37	0.0	+
		222		266		377	4.35		4.26		4.38	7.0	o
		222		270		383	4.50		4.31		4.37	11.0	−
65	1.84	233		[263]	[317]	375	4.28		[4.08]	[3.98]	4.40	0.0	+
		[220]		271		379	[4.35]		4.29		4.36	7.0	o
		[220]		272		385	[4.50]		4.30		4.36	MeOH	o
31		232		[270]		388	4.69		[4.33]		4.37	MeOH	o
59		226		270		387	4.79		4.37		4.39	MeOH	o
19	2.80	220		291	315	[341]	4.31		4.03	3.97	[3.72]	0.0	+
	8.32		250	[290]	334	[345]		4.11	[3.67]	4.03	[3.94]	5.0	o
		235			330	[343]	4.38			4.04	[3.93]	13.0	−
20	2.88	220		291	320	[336]	4.32		4.11	3.98	[3.79]	0.0	+
	8.39	218	243	[291]	326	[343]	4.37	4.07	[3.82]	4.02	[3.89]	5.0	o
		231			326	[338]	4.41			4.08	[3.96]	13.0	−
41			248	[292]	329			4.09	[3.71]	3.93		MeOH	o

TABLE 1 UV-data of 4-amino-7(8H)pteridones and their nucleosides (*Continued*)

Compound	pK_a in H_2O	UV-Absorption in λ_{max}						log ε				pH	Form
32			241		333			4.66		3.96		MeOH	o
35			240		329			4.68		3.94		MeOH	o
22	2.96	220		293	[320]		4.35		4.14	[3.85]		0.0	+
	8.59		245	[291]	331			4.08	[3.77]	4.03		5.0	o
		232	[250]		327		4.41	[4.22]		4.12		13.0	−
42			250	[298]	333			4.08	[3.74]	3.95		MeOH	o
33			241		333			4.66		3.96		MeOH	o
43	2.16	220		290	315		4.37		4.08	3.99		0.0	+
	5.23	217	248		332		4.43	4.07		4.01		4.0	o
		219		281		346	4.24		4.14		4.18	8.0	−
49			241	282	333			4.65	4.03	4.15		MeOH	o
44	1.96	233		270	337	[344]	4.44		4.46	4.33	[4.17]	0.0	+
	5.48	220		263		349	4.43		4.39		4.27	4.0	o
		222		299		355	4.45		4.49		4.28	8.0	−
50			235	301		355		4.68	4.50		4.26	MeOH	o
45	2.22	221		267		345	4.36		4.21		4.25	0.0	+
	5.31	220		258		360	4.35		4.26		4.24	4.0	o
		222		289		371	4.31		4.40		4.25	8.0	−
		222		290		372	4.33		4.44		4.27	MeOH	o
51			238	293		374		4.70	4.50		4.24	MeOH	o
60			228	293		378		4.74	4.47		4.21	MeOH	o
46	1.91	231		272		363	4.43		4.40		4.44	0.0	+
	5.42	233		269		377	4.40		4.46		4.40	4.0	o
		225		302		377	4.47		4.59		4.42	8.0	−
		225		302		383	4.49		4.57		4.41	MeOH	o
52			237	305		388		4.72	4.62		4.38	MeOH	o
53			235	305		386		4.69	4.57		4.33	MeOH	o
54			237	303		379		4.74	4.62		4.37	MeOH	o
61			227	306		390		4.75	4.53		4.31	MeOH	o
47	2.80	220		260	307		4.17		4.19	4.20		0.0	+
	5.82	230	255	[281]	314	[329]	4.03	4.07	[3.93]	4.09	[3.98]	4.0	o
		217		278		342	4.19		4.22		4.28	8.0	−
55		238		281	[325]	336	4.64		4.30	[4.23]	4.24	MeOH	o
48	2.94	220	256		309		4.15	4.19		4.19		0.0	+
	5.90	225	251	[283]	317	[331]	4.03	4.07	[3.93]	4.09	[3.98]	4.0	o
		222		279		344	4.19		4.19		4.29	8.0	−
71		229		263		370	4.83		4.51		4.29	MeOH	o
72	1.56	219		257		354	4.34		4.28		4.22	0.0	+
		229		263		362	4.93		4.37		4.25	7.0	o
		230		265		367	4.40		4.42		4.28	MeOH	o
73		233		[260]		367	4.68		[4.43]		4.20	MeOH	o
74		233		[260]		366	4.71		[4.38]		4.23	MeOH	o
75	2.40	221			300	352	4.40			4.00	4.25	0.0	+
		229		262		361	4.43		4.37		4.25	7.0	o
		230		264		365	4.44		4.39		4.26	MeOH	o
76		231		264		366	4.46		4.39		4.26	MeOH	o
77		238			302	397	4.74		4.50		4.44	MeOH	o
78		237			302	393	4.72		4.47		4.42	MeOH	o
79		228			303	400	4.80		4.53		4.46	MeOH	o

The ^{1}H-NMR-spectra (exper. part) are also in full agreement with the proposed structures of the newly synthesized pteridine-nucleosides. The assignments of the site of glycosylation was derived first from comparisons of the signals of **39** and **75** as well as **64** and **72** indicating that, in the N-1 nucleosides the H-C(2) is shifted to lower field compared to H-C(2) in the N-8-analogs and the H-C(1′) shifted in the opposite direction to higher field in the N-1-compared to the N-8 nucleosides. These shifts are influenced by the sugar moiety in the first and by the 7-carbonyl function in the second case. A confirmation of this assignment was also drawn from the ROESY-spectra which showed no correlation peaks between H-C(2) and the sugar protons in the N-8 nucleosides whereas the cross couplings were detected in the N-1-nucleosides. These relations furthermore proved the ß-configuration of the glycosidic linkage. The ß-configuration in the 2′-deoxynucleosides (**27–33**, **37–42**, **49–55**, **73** and **79**) is based on the $\Delta\delta$ shift difference[43] of the $H_ß$-C(2′) and H_α-C(2′) in D_6-DMSO in the order of 0.63–1.01 ppm whereas the a-anomers (**34–36**, **54**, **74**, **76**, and **78**) show in general no splitting of the signals.

EXPERIMENTAL

Melting points were taken on a Büchi Melting Point B-545 apparatus and are uncorrected. Products were dried under high vacuum. TLC: precoated silica gel thin-layer sheets 60 F 254 from Merck (Darmstadt, Germany) and cellulose sheets F 1440 LS 254 from Schleicher & Schuell. Column chromatography (CC): silica gel 60 from Merck and flash chromatography (FC): silica gel (30–60 μm) from Baker. UV/VIS: Perkin-Elmer Lambda 5; λ_{max} in nm (log ε). ^{1}H-NMR: Bruker AC 250 and Bruker DRX 600; δ in ppm rel. to $SiMe_4$ or $CDCl_3$ (DMSO-d_6) as internal standard. The pK_a-values were determined by the spectrophotometric method.[42] Elemental analyses were performed by the analytical lab of the Department of Chemistry, Konstanz University.

4,6-Diaminopyrimidine-2-sulfinic acid (2)[44]

A solution of 4,6-diamino-2(1H)pyrimidinethione (**1**)[45] (50 g, 0.35 mol) in 2N NaOH (220 ml) was cooled by ice and then within 45 minutes H_2O_2 (3%; 750 ml) was added dropwise with stirring. It was stirred at room temperature for 30 minutes and thern acidified by glacial acetic acid. The resulting precipitate was collected, washed with H_2O and EtOH and dried at 60° to give 58.3 g (96%) of colorless crystals of m.p. 167–170°C (decomp.). UV (MeOH): 263 (3.89). Anal. For $C_4H_6N_4O_2S$ (174.2) Calcd: C 27.58, H 3.47, N 32.17. Found: C 27.19, H 3.34, N 31.88.

4,6-Diaminopyrimidine Hydrochloride (3)[44]

Under vigorous stirring, compound **2** (40 g, 0.23 mol) was added in small portions into conc. HCl (120 ml). After 30 minutes the precipitate was collected, washed with acetone, and ether, and dried at 60° to give 32.4 g (96%) of a colorless solid of compound **3** of m.p. 200–202°C. UV (MeOH): 263 (3.62). Anal. For $C_4H_6N_4 \times HCl$ (146.6) Calcd: C 32.78, H 4.13, N 38.22. Found: C 32.66, H 3.95, N 37.78.

4,6-Diamino-5-nitrosopyrimidine (4)[44]

A solution of **3** (8.0 g, 55 mmol) in 2 N HCl (250 ml) was cooled in ice and then $NaNO_2$ (4.2 g, 62 mmol) in H_2O (15 ml) was added dropwise. Stirring was continued for 30 minutes at 0–5° and then 2 hours at room temperature. The violet solution was neutralized with $NaHCO_3$, the resulting precipitate collected, suspended in H_2O and heated to 80°C, filtered, washed with MeOH and dried to give 6.3 g (82%) of blue crystals of **4** of m.p. >350°C. UV (MeOH): 224 (4.07), 346 (4.02), 643 (1.80). ^{1}H-NMR (DMSO-d_6): 10.05 (s, 1H, NH_2); 9.12 (s, 1H, NH_2); 8.44 (s, 1H, NH_2); 8.05 (s, 1H, NH_2); 7.92 (s, H-C(2)). Anal. For $C_4H_5N_5O$ (139.1) Calcd: C 34.53, H 3.62, N 50.34. Found: C 34.35, H 3.66, N 49.99.

4,5,6-Triaminopyrimidine (5)[46]

A solution of **4** (7.8 g, 56 mmol) in MeOH (200 ml) and 1 N NaOH (10 ml), was reduced with H_2 and Raney-nickel (1.2 g) in a shaking apparatus. After uptake of the theoretical amount of H_2 in 2 days, the catalyst was filtered off, the filtrate evaporated, and the residue was recrystallyzed from H_2O (100 nl) and charcoal. On cooling, 6.78 g (97%) of colorless crystals of **5** of m.p. 257°C were obtained. UV (MeOH): 277 (3.94), 281 (4.00). ^{1}H-NMR (DMSO-d_6): 7.45 (s, H-C(2)); 5.57 (bs, 4H, 2 NH_2); 3.75 (bs, H_2N-C(5)). Anal. For $C_4H_7N_5$ (125.1) Calcd: C 38.39, H 5.64, N 55.96. Found: C 38.31, H 5.59, N 55.87.

4-Amino-7(8H)pteridone (6)[13]

To a solution of Na (10 g) in abs. MeOH (500 ml) 4,5,6-triaminopyrimidine (12.5 g, 0.1 mol) was added and followed by ethyl glyoxylate-ethyl-hemiacetal (30 ml). After stirring the soln for 18 hours at room temperature, the solution was evaporated to half of the volume, then H_2O (500 ml) was added and acidified by AcOH to pH 5. The precipitate was collected and recrystallized from DMF/H_2O to give 11.29 g (69%) of a colorless crystal powder of **6** of m.p. >350°C. ^{1}H-NMR (DMSO-d_6): 12.65 (s, H-N(8)); 8.15 (s, H-C(2)); 7.90 (s, H-C(6)); 7.65 (bs, NH_2). Anal. For

$C_6H_5N_5O$ (163.1) Calcd: C 44.17, H 3.09, N 42.93. Found: C 43.85, H 3.15, N 42.92.

Evaporation of the filtrate and recrystallization of the residue gave 2.94 g (18%) of 4-amino-6(5H)-pteridone (**7**). pK_a: 3.39. UV (pH 0): 225 (4.52), 280 (4.31), [345 (3.20)], [360 (3.08)]. (pH 12): 255 (4.25), [277 (3.89)], 367 (3.86), [384 (3.76)].

Silver Salt of Isonitrosomalononitrile (8)

A solution of malononitrile (20 g, 0.3 mol) in AcOH (60 ml) + H_2O (60 ml) was cooled in ice and then $NaNO_2$ (23 g, 0.33 mol) in H_2O (100 ml) was dropwise added under stirring. The solution was kept at room temperature in the dark overnight and then a solution of $AgNO_3$ (46 g, 0.3 mol) in H_2O (100 ml) was added. The precipitate was collected,washed with H_2O, MeOH, and ether, and dried in high vacuum at 60°C to give 57.6 g (95%) of a yellow solid of **8** of m.p. >350°C. UV (MeOH): 291 (4.07), 407 (1.90). Anal. For C_3AgN_3O (201.9) Calcd: C 17.85, N 20.81. Found: C 17.45, N 20.66.

Benzamidine Salt of Isonitrosomalononitrile[33]

To a soln of benzamidine hydrochloride (**9**) (50.7 g, 0.32 mol) in MeOH (320 ml) **8** was added in small portions (72.0 g, 0.36 mol) under stirring at room temperature. After 1 hour the AgCl was filtered off, the filtrate evaporated to dryness, and the residue was recrystallized from EtOAc (500 ml) to give 50.2 g (87%) of yellowish crystals of m.p. 146°C. UV (MeOH): 228 (4.14), 290 (4.09). Anal. For $C_{10}H_9N_5O$ (215.2) Calcd: C 55.81, H 4.21, N 32.54. Found: C 56.01, H 4.19, N 32.36.

4,6-Diamino-5-nitroso-2-phenylpyrimidine (10)[33]

A solution of the benzamidine salt of isonitrosomalononitrile (66.5 g, 0.31 mol) in 2-methylpyridine (330 ml) was heated in an oilbath to 160°C for 3 hours. After cooling to room temperature H_2O (330 ml) was added to separate a green precipitate which was washed with H_2O and MeOH and dried in vacuum at 80°C to give 63.4 g (95%) of **10** of m.p. 235–237°C. UV (MeOH): 290 (4.13), 353 (4.30), 623 (1.74). ^{1}H-NMR (DMSO-d_6): 10.18 (s, 1H, NH_2); 9.12 (s, 1H, NH_2); 8.49 (s, 1H, NH_2); 8.37 (m, 2H, arom. H); 8.10 (s, 1H, NH_2); 7.49 (m, 3H, arom. H). Anal. For $C_{10}H_9N_5O$ (215.2) Calcd: C 55.81, H 4.21, N 32.54. Found: C 55.66, H 4.24, N 32.29.

4,5,6-Triamino-2-phenylpyrimidine (11)[33]

A suspension of **10** (14.0 g, 65 mmol) in MeOH (200 ml) was reduced under H_2 atmosphere in presence of Pd/C (150 mg, 5%) in a shaking apparatus. The reaction solution was heated, the catalyst filtered off, and the filtrate evaporated to dryness. The residue was recrystallized from H_2O (350 ml) with charcoal to give 10.2 g (78%) of brownish needles of **11** of m.p. 186–188°C. UV (MeOH): 223 (4.50), 290 (4.08). ^{1}H-NMR (DMSO-d_6): 8.14 (m, 2H, arom. H); 7.32 (m, 3H, arom. H); 5.67 (bs, 4H, 2 NH_2); 3.96 (bs, 2H, H_2N-C(5)). Anal. For $C_{10}H_{11}N_5$ (201.2) Calcd: C 59.69, H 5.51, N 34.80. Found: C 59.49, H 5.61, N 34.90.

4-Amino-2-phenyl-7(8H)pteridone (12)[13]

a) To a solution of Na (2.5 g) in absolute MeOH (200 ml) 4,5,6-triamino-2-phenylpyrimidine (**11**) (5 g, 25 mmol) was added and followed by ethyl glyoxylate-ethylhemiacetal (15 ml). After stirring for 24 hours at room temperature was evaporated to half of the volume, then H_2O (300 ml) and charcoal were added. The reaction mixture was heated, filtered hot, and acidified by AcOH to pH 5. After cooling the precipitate was collected and dried at 60°C to give 3.59 g (60%) of a yellowish crystal powder of **12** of m.p. 330–332°C.

b) To a suspension of NaH (0.3 g, 12.5 mmol) in THF (100 ml) ethyl 2-(diethoxyphosphoryl)acetate (**13**) (2.5 ml, 12.5 mmol), dissolved in THF (10 ml), was added dropwise under stirring. After 30 minutes, **10** (2.15 g, 10 mmol) was added and stirring continued for 1 hour. The resulting precipitate was collected and recrystallized from DMF to give 2.1 g (87%) yellowish powder of **12** of m.p. 331–332°C. ^{1}H-NMR (DMSO-d_6): 12.70 (s, H-N(8)); 7.66 (m, 2H, arom. H); 7.21 (s, H-C(6)); 6.98 (bs, NH_2); 6.87 (m, 3H, arom. H). Anal. For $C_{12}H_9N_5O$ (239.2) Calcd: C 60.25, H 3.79, N 29.27. Found: C 60.11, H 3.88, N 28.95.

4-Amino-6-phenyl-7(8H)pteridone (14)[13]

A mixture of **4** (8.0 g, 58 mmol) and ethyl phenylacetate (11.1 ml, 70 mmol), in a solution of Na (3.0 g, 130 mmol) in absolute EtOH (250 ml), was heated under reflux for 3 h. The precipitate was collected after cooling. then dissolved in hot H_2O (300 ml), and acidified with 2 N HCl to pH 3. The precipitate was collected after cooling and recrystallized from DMF to give 8.6 g (62%) of a yellowish powder of **14** of m.p. >350°C. ^{1}H-NMR (DMSO-d_6): 12.82 (s, H-N(8)); 8.47 (m, 2H, arom. H); 8.18 (s, H-C(2)); 7.77 (bs, NH_2); 7.46 (m, 3H, arom. H). Anal. For $C_{12}H_9N_5O$ (239.2) Calcd: C 60.25, H 3.79, N 29.27. Found: C 59.91, H 3.86, N 28.87.

4-Amino-2,6-diphenyl-7(8H)pteridone (15)[13]

a) A mixture of **10** (2.15 g, 10 mmol) and ethyl phenylacetate (1.91 ml, 12 mmol) in a solution of Na (0.28 g, 12 mmol) in absolute EtOH (100 ml), was heated under reflux for 3 hours. The yellow precipitate was collected after cooling. suspended in H_2O (100 ml) and acidified by AcOH to pH 5. The solid was collected, dried at 100°C to give 2.68 g (85%) of a chromatographically pure yellow powder of **15** of m.p. >350°C.

b) A mixture of **11** (2.0 g, 10 mmol) and ethyl phenylglyoxylate (2.0 ml 12 mmol) was heated in EtOH (50 ml) for 2 hours under reflux. After cooling the precipitate was collected and recrystallized from DMF/H_2O 2:1 to give 2.81 g (89%) of a yellow crystal powder of **15** of m.p. >350°C. ^{1}H-NMR (DMSO-d_6): 12.80 (s, H-N(8)); 8.54 (m, 2H, arom. H); 8.36 (m, 2H, arom. H); 7.73 (bs, NH_2); 7.48 (m, 6H, arom. H). Anal. For $C_{18}H_{13}N_5O$ (315.3) Calcd: C 68.56, H 4.16, N 22.21. Found: C 68.23, H 4.21, N 21.97.

Acetamidine Salt of Isonitrosomalononitrile[33]

To a solution of acetamidine hydrochloride (**16**) (15.0 g, 0.157 mol) in MeOH (150 ml), was added in small portions **8** (35.0 g, 0.173 mol) under stirring at room temperature. After 1 hour, the AgCl was filtered off, the filtrate was evaporated to dryness, and the residue was recrystallized from EtOAc (1.3 l) to give 20.8 g (87%) of yellowish crystals of m.p. 138–140°C. UV (MeOH): 290 (4.07). Anal. For $C_5H_7N_5O$ (153.1) Calcd: C 39.22, H 4.61, N 45.73. Found: C 39.39, H 4.61, N 45.77.

4,6-Diamino-5-nitroso-2-methylpyrimidine (17)[33]

A solution of the acetamidine salt of isonitrosomalononitrile (14.43 g, 94 mmol) in 5-ethyl-2-methylpyridine (72 ml) was heated in an oilbath to 180°C for 20 minute. After cooling to room temperature, EtOH (100 ml) was added and the green precipitate was collected, washed with EtOH and ether, and dried in vacuum at 80°C to give 13.62 g (95%) of a green crystal powder of **17** of m.p. 306°C (decomp.). UV (MeOH): [225 (4.17)], 343 (4.10), 622 (1.74). ^{1}H-NMR (DMSO-d_6): 10.02 (s, 1H, NH_2); 8.94 (s, 1H, NH_2); 8.33 (s, 1H, NH_2); 7.94 (s, 1H, NH_2); 2.19 (s, H_3C-C(2)). Anal. For $C_5H_7N_5O$ (153.1) Calcd: C 39.22, H 4.61, N 45.73. Found: C 39.61, H 4.56, N 45.56.

4,5,6-Triamino-2-methylpyrimidine (18)

A suspension of **17** (12.0 g, 13.1 mmol) in MeOH (250 ml) was reduced under H_2 atmosphere in presence of Pd/C (1.0 g, 10%) in a shaking apparatus for 6 hours. The mixture was heated, charcoal was added, the

hot solution was filtered and the filtrate was evaporated to dryness. The residue was dissolved in hot MeOH (60 ml), toluene (150 ml) was added and the solution was then stored in the icebox over night. The precipitate was collected and gave after drying 9.25 g (85%) of a brownish solid of **18** of m.p. 240–242°C. The substance can be sublimed at 190°C/0.001 bar to give a colorless solid. UV (MeOH): 279 (3.91). ^{1}H-NMR (DMSO-d_6): 5.54 (bs, 4H, 2 NH_2); 3.54 (bs, 2H, H_2NC(5)); 2.06 (s, H_3C-C(2)). Anal. For $C_5H_9N_5$ (139.2) Calcd: C 43.15, H 6,52, N 50.33. Found: C 43.33, H 6.54, N 50.71.

4-Amino-2-methyl-7(8H)pteridone (19)

To a solution of Na (1.0 g, 43 mmol) in abs. MeOH (50 ml), 4,5,6-triamino-2-methylpyrimidine (**18**) (2.5 g, 18 mol) was added and followed by ethyl glyoxylate-ethylhemiacetal (5.33 g, 136 mmol). After stirring for 12 hours at room temperature, H_2O (150 ml) was added, heated with charcoal, filtered, and acidified by AcOH to pH 5. After cooling, the precipitate was collected, recrystallized from DMF (350 ml) + H_2O (250 ml) and dried at 60°C to give 1.13 g (37%) of a colorless crystal powder of **19** of m.p. >300°C (decomp.). ^{1}H-NMR (DMSO-d_6): 12.58 (s, H-N(8)); 7.85 (s, H-C(6)); 7.60 (bs, NH_2); 2.32 (s, H_3C-C(2)). Anal. For $C_7H_7N_5O$ (177.2) Calcd: C 47.46, H 3.98, N 39.53. Found: C 47.25, H 4.17, N 39.76.

4-Amino-6-methyl-7(8H)pteridone (20)

a) To a solution of 5 (2.0 g, 16 mmol) in AcOH (20 ml) was added ethyl pyruvate (2.2 ml, 19 mmol) and then heated under reflux for 2 hours. After cooling the precipitate was collected, recrystallized from DMF/H_2O (1:1, 350 ml) and dried at 60°C to give 1.25 g (44%) of a colorless solid of **20** of m.p. >360°C (decomp.).

b) A solution of **21** (2.2 g, 8.8 mmol) in 1 N HCl (70 ml) was heated in an oilbath to 120°C for 1.5 hours. Charcoal was added, filtered hot, and the filtrate buffered by $NaHCO_3$ to pH 5. The precipitate was collected and recrystallized from DMF/H_2O (1:1, 250 ml) to give 1.0 g (64%) of a colorless solid of **20** of m.p. >360°C (decomp.). ^{1}H-NMR (DMSO-d_6): 12.56 (s, H-N(8)); 8.12 (s, H-C(2)); 7.85 (s, H-C(6)); 7.45 (bs, 1H, NH_2); 7.35 (bs, 1H, NH_2); 2.34 (s, H_3C-C(6)). Anal. For $C_7H_7N_5O$ (177.2) Calcd: C 47.46, H 3.98, N 39.53. Found: C 47.10, H 4.17, N 39.29.

4-Amino-6-ethoxycarbonylmethyl-7(8H)pteridone (21)

A solution of **5** (1.46 g, 12 mmol) in AcOH (20 ml) was treated with sodium diethyl oxalylacetate (3.0 g, 14 mmol) in an oilbath at 100°C for 1 hour. The suspension was treated with H_2O (40 ml) and after cooling the precipitate collected and recrystallized from AcOH (20 ml) with charcoal to

give 1.94 g (65%) of a colorless solid of **21** of m.p. >230°C (decomp.). ^{1}H-NMR (DMSO-d_6): 12.78 (s, H-N(8)); 8.17 (s, H-C(2)); 7.71 (bs, 1H, NH_2); 7.50 (bs, 1H, NH_2); 3.74 (s, 2H, CH_2CO); 3.10 (q, 2H, OCH_2CH_3); 1,16 (t, 3H, CH_3CH_2). Anal. For $C_{10}H_{11}N_5O_3$ (249.2) Calcd: C 48.19, H 4.45, N 28.10. Found: C 48.14, H 4.47, N 27.73.

4-Amino-2,6-dimethyl-7(8H)pteridone (22)

a) To a solution of **18** (0.5 g, 3.6 mmol) in AcOH (10 ml) was added ethyl pyruvate (1.0 ml, 9 mmol) and then heated under reflux for 1 hour. After cooling the precipitate was collected, recrystallized from DMF/H_2O (1:1, 90 ml) with charcoal and dried at 60°C to give 0.372 g (54%) of a colorless solid of **22** of m.p. >300°C (decomp.).

b) A solution of **23** (1.31 g, 5 mmol) in 1 N HCl (50 ml) was heated in an oilbath to 120°C for 1.5 hours. Charcoal was added, filtered hot, and the filtrate was buffered by $NaHCO_3$ to pH 5. The precipitate was collected and recrystallized from DMF/H_2O (1:1, 160 ml) to give 0.64 g (65%) of a colorless solid of **22** of m.p. >360°C (decomp.). ^{1}H-NMR (DMSO-d_6): 12.43 (s, H-N(8)); 7.42 (bs, 1H, NH_2); 7.32 (bs, 1H, NH_2); 2.34 (s, 6H, H_3C-C(6), H_3C-C(2)). Anal. For $C_8H_9N_5O$ (191.2) Calcd: C 50.26, H 4.74, N 36.63. Found: C 50.15, H 4.82, N 36.35.

4-Amino-6-ethoxycarbonylmethyl-2-methyl-7(8H)pteridone (23)

A solution of **18** (3.0 g, 22 mmol) in AcOH (20 ml) was treated with sodium diethyl oxalylacetate (5.09 g, 22 mmol) in an oilbath at 100°C for 2 hours. The suspension was diluted with H_2O (40 ml), heated with charcoal, and filtered hot. After cooling the precipitate was collected, dried to give 3.72 g (64%) of a colorless solid of **23** of m.p. >230°C (decomp.). ^{1}H-NMR (DMSO-d_6): 12.66 (s, H-N(8)); 7.65 (bs, 1H, NH_2); 7.35 (bs, 1H, NH_2); 3.71 (s, 2H, CH_2CO); 3.10 (q, 2H, OCH_2CH_3); 2.33 (s, H_3C-C(2)); 1,16 (t, 3H, CH_3CH_2). Anal. For $C_{11}H_{13}N_5O_3$ (263.3) Calcd: C 50.19, H 4.98, N 26.60. Found: C 49.97, H 5.00, N 26.90.

4-Amino-8-(3,5-di-O-4-chlorobenzoyl-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (27) and α-Anomer 34

A suspension of 6 (1.63 g, 10 mmol) in dry CH_3CN (100 ml) was treated at room temperature with DBU (1.49 ml, 10 mmol) for 30 minutes. Then 3,5-di-O-4-chlorobenzoyl-2-deoxy-ß-D-*erythro*-pentofuranosyl chloride (**25**) (4.73 g, 11 mmol) was added and stirring continued for 2.5 hours. The mixture was evaporated to dryness, the residue díssolved in CH_2Cl_2 (100 ml), and then extracted twice with H_2O (40 ml) and saturated NaCl

solution (40 ml). The organic layer was separated, dried over Na_2SO_4, evaporated, the residue dissolved in little toluene, and put onto a silica-gel column (20 × 5 cm). Chromatography with toluene/EtOAc (2:1, 1.5 l) gave a main fraction of 2.28 g (41%) of the a/ß-mixture (1:5).

Fractional crystallization from $CHCl_3$ (25 ml) and MeOH (15 ml) gave as a first fraction 1.89 g (34%) of **27** as colorless crystals of m.p. 210–211°C. From the filtrate were obtained 0.28 g (5%) of **34** as colorless crystals of m.p. 178–180°C.

27: ^{1}H-NMR (DMSO-d_6): 8.26 (s, H-C(2)); 8.00 (s, H-C(6)); 7.78–7.98 (m, 6H, NH_2, 4 arom. H); 7,53 (d, 2H, arom. H); 7.45 (d, 2H, arom. H); 7.27 (m, H-C(1′)); 5.87 (m, H-C(3′)); 4.68 (m, H-C(4′)); 4.48 (m, 2 H-C(5′)); 3.21 (m, H$_ß$-C(2′)); 2.55 (m, H$_\alpha$-C(2′)). Anal. For $C_{25}H_{19}Cl_2N_5O_6$ (556.4) Calcd: C 53.97, H 3.44, N 12.59. Found: C 53.66, H 3.53, N 12.31.

34: ^{1}H-NMR (DMSO-d_6): 7.95 (m, 5H, H-C(6), 4 arom. H); 7.83 (bs, NH_2); 7.59 (d, 2H, arom. H); 7.53 (d, 2H, arom. H); 7.27 (m, H-C(1′)); 5.69 (m, H-C(3′)); 5.06 (m, H-C(4′)); 4.52 (m, 2 H-C(5′)); 2.92 (m, H$_ß$-C(2′), H$_\alpha$-C(2′)). Anal. For $C_{25}H_{19}Cl_2N_5O_6$ (556.4) Calcd: C 53.97, H 3.44, N 12.59. Found: C 53.87, H 3.53, N 12.54.

4-Amino-2-phenyl-8-(3,5-di-O-toluoyl-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (28)

a) A suspension of **12** (4.5 g, 19 mmol) in dry CH_3CN (250 ml) was treated with DBU (2.8 ml, 19 mmol) at room temperature for 30 minutes, then **26** (8.04 g, 2.1 mmol) was added and stirring was continued for 2 hours. The dark reaction solution was evaporated in vacuum, the residue dissolved in CH_2Cl_2 (150 ml), extracted twice with H_2O (60 ml) and then the organic layer dried over Na_2SO_4. After evaporation the residue was dissolved in little toluene, put on a silica-gel column (15 × 5 cm) and eluted by toluene/EtOAc (9:1, 1.2 l). The main fraction was collected, evaporated and the residue recrystallized from $CHCl_3$/MeOH to give 5.5 g (49%) of a colorless solid of **28** of m.p. 196–198°C.

b) A suspension of **12** (0.12 g, 0.5 mmol) in dry DMF (10 ml) and 1,2-dimethoxyethane 80.1 ml) was treated with KOH (56 mg, 1 mmol) to achieve solution. Little KOH was filtered of and to the filtrate, **26** (0.233 g, 0.6 mmol) was added. After stirring at room temperature for 2 hours, the soln was evaporated, the residue dissolved in CH_2Cl_2 (5 ml) and the solution put onto a preparative silica-gel plate (40 × 20 ml) for chromatography with toluene/EtOAc (7:3). The main band (R_f 0.50) was cut out, eluted with $CHCl_3$(MeOH (2:1, 20 ml) to give after drying in vacuum 0.165 g (52%) of a colorless solid of **28** of m.p. 196–198°C. ^{1}H-NMR (DMSO-d_6): 8.40 (m, 2H, arom. H); 7.99 (s, H-C(6)); 7.85 (m, 6H, NH_2, 4 arom. H); 7.68 (m, H-C(1′)); 7.49 (m, 3H, arom H); 7.34 (d, 2 arom. H); 7,21 (d, 2 arom. H); 5.89 (m, H-C(3′)); 4.49–4.66 (m, H-C(4′), H-C(5′)); 3.21 (m, H$_ß$-C(2′));

2.39 (m, H_α-C(2′)); 2.31 (s, 2 CH_3). Anal. For $C_{33}H_{29}N_5O_6$ (591.6) Calcd: C 67.00, H 4.94, N 11.84. Found: C 67.09, H 4.95, N 11.90.

4-Amino-2-phenyl-8-(3,5-di-O-(4-chlorobenzoyl)-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (29)

Analogous to the preceding procedure a) with **12** (4.5 g, 19 mmol) and **25** (8.2 g, 19 mmol) to give 6.0 g (50%) of colorless crystals of **29** of m.p. >120°C (slow decomp.). ^{1}H-NMR (DMSO-d_6): 8.38 (m, 3H, 2 arom. H, H-C(6)); 7.89 (dd, H-C(1′)); 7.85 (2d, 6H, NH_2, 4 arom. H); 7.61 (m, 2 arom. H); 7.53 (m, 5H, arom H); 5.90 (m, H-C(3′)); 4.54–4.65 (m, H-C(4′), H-C(5′)); 3.21 (m, $H_ß$-C(2′)); 2.40 (s, CH_3); 2.33 (s, CH_3); 2.20 (m, H_α-C(2′)). Anal. For $C_{31}H_{23}N_5O_6$ (632.5) Calcd: C 58.87, H 3.67, N 11.07. Found: C 58.79, H 3.65, N 11.00.

4-Amino-6-phenyl-8-(3,5-di-O-(4-chlorobenzoyl)-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (30)

A suspension of **14** (0.5 g, 2.1 mmol) in dry CH_3CN (15 ml) was treated with DBU (313 μl, 2.1 mmol) at room temperature for 30 minutes, then **25** (1.1 g, 2.5 mmol) was added and stirring was continued for 1 hour. The solution was evaporated in vacuum, the residue dissolved in CH_2Cl_2 (50 ml), extracted twice with H_2O (20 ml), and then the organic phase was dried over Na_2SO_4. After evaporation the residue was dissolved in little toluene, put on a silica-gel column (8 × 2.5 cm), and eluted by toluene/EtOAc (3:1, 250 ml). The main fraction was collected and evaporated to give 0.6 g (45%) of a yellowish amorphous solid of **30**. ^{1}H-NMR (DMSO-d_6): 8.34 (m, 2 arom. H); 8.29 (s, H-C(6)); 7.93 (m, 6H, NH_2, 4 arom. H); 7.42–7.63 (m, 8H, NH_2, H-C(1′), 6 arom. H); 5.98 (m, H-C(3′)); 4.72 (m, H-C(4′)); 4.56 (m, 2 H-C(5′)); 3.25 (m, $H_ß$-C(2′)); 2.59 (m, H_α-C(2′)). Anal. For $C_{31}H_{23}N_5O_6$ (632.5) Calcd: C 58.87, H 3.67, N 11.07. Found: C 58.56, H 3.80, N 11.13.

4-Amino-2,6-diphenyl-8-(3,5-di-O-(4-chlorobenzoyl)-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (31)

A suspension of **15** (0.5 g, 1.6 mmol) in dry CH_3CN (25 ml) was treated with DBU (240 μl, 2.1 mmol) at room temperature for 30 minutes, then **25** (0.82 g, 1.9 mmol) added and stirring was continued for 30 minutes. The resulting precipitate was collected and recrystallized from $CHCl_3$/MeOH (2:1, 45 ml) to give 0.61 g (54%) of yellow crystals of **31** of m.p. 224–226°C. ^{1}H-NMR (DMSO-d_6): 8.41 (m, 4 arom. H); 7.93 (2d, 6H, NH_2, 4 arom. H); 7.75 (m, H-C(1′)); 7.62 (m, 2 arom. H); 7.50 (m, 4 arom. H); 6.04 (m, H-C(3′)); 4.75 (m, H-C(4′)); 4.61 (m, 2 H-C(5′)); 3.31 (m, $H_ß$-C(2′)); 2.69 (m,

H_α-C(2′)). ^{1}H-NMR ($CDCl_3$): 8.41 (m, 2 arom. H); 8.18 (m, 2 arom. H); 7.97 (2d, 4H, pClbz); 7.81 (m, H-C(1′)); 7.47 (m, 8H, arom. H); 7.23 (d,2H, pClbz); 6.12 (m, 3H, NH_2, H-C(3′)); 4.83 (m, H-C(4′)); 4.73 (m, 1H, H-C(5′)); 4.57 (m, 1H, H-C(5′)); 3.45 (m, $H_ß$-C(2′)); 2.62 (m, H_α-C(2′)). Anal. For $C_{37}H_{27}Cl_2N_5O_6$ (708.6) Calcd: C 62.72, H 3.84, N 9.88. Found: C 62.62, H 3.88, N 9.81.

4-Amino-6-methyl-8-(3,5-di-O-(4-chlorobenzoyl)-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (32) and α-Anomer 35

A suspension of **20** (1.54 g, 9 mmol) in dry CH_3CN (100 ml) was treated with DBU (1.34 ml, 9 mmol) at room temperature for 30 minutes, then **25** (4.46 g, 10.8 mmol) was added and stirring continued for 2 hours. It was evaporated, the residue dissolved in CH_2Cl_2 (60 ml), extracted twice with saturated NaCl solution (30 ml) and after separation, the organic layer was dried over Na_2SO_4. After another evaporation the crude product was dissolved in toluene (10 ml) and put onto a silica-gel column (11 × 5 cm) for chromatography with toluene/EtOAc (2:1, 600 ml) followed by (1:1, 400 ml). The product fractions were evaporated and the residue crystallized from $CHCl_3$/MeOH to give 0.85 g (17%) of **32**, 0.34 g (7%) of **35** and 1.71 g (33%) of the anomeric mixture 1:1.

32: Colorless crystals of m.p. 187–189°C. ^{1}H-NMR (DMSO-d_6): 8.22 (s, H-C(2)); 7.93 (2d, 4 arom. H); 7.79 (bs, NH_2); 7.59 (d, 2 arom. H); 7.51 (d, 2 arom. H); 7.34 (m, H-C(1′)); 5.94 (m, H-C(3′)); 4.69 (m, H-C(4′)); 4.53 (m, 2 H-C(5′)); 3.18 (m, $H_ß$-C(2′)); 2.55 (m, H_α-C(2′)); 2.38 (s, H_3C-C(6)). Anal. For $C_{26}H_{21}Cl_2N_5O_6$ (570.4) Calcd: C 54.75, H 3.71, N 12.28. Found: C 54.52, H 3.80, N 12.28.

35: Colorless crystals of m.p. 135–136°C. ^{1}H-NMR (DMSO-d_6): 8.23 (s, H-C(2)); 7.95 (2d, 4 arom. H); 7.70 (bs, NH_2); 7.59 (d, 2 arom. H); 7.52 (d, 2 arom. H); 7.29 (m, H-C(1′)); 5.64 (m, H-C(3′)); 5.08 (m, H-C(4′)); 4.52 (m, 2 H-C(5′)); 2.92 (m, 2H, $H_ß$-C(2′), H_α-C(2′)); 2.39 (s, H_3C-C(6)). Anal. For $C_{26}H_{21}Cl_2N_5O_6 \times 0.5\ H_2O$ (579.4) Calcd: C 53.90, H 3.83, N 12.09. Found: C 54.15, H 3.85, N 12.06.

4-Amino-2,6-dimethyl-8-(3,5-di-O-(4-chlorobenzoyl)-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (33)

A suspension of **22** (0.79 g, 4.1 mmol) in dry CH_3CN (30 ml) was treated with DBU (615 μl, 4.1 mmol) at room temperature for 15 minutes, then **25** (2.1 g, 5 mmol) added, and stirring was continued for 2 hours. The precipitate was collected and recrystallized from $CHCl_3$/MeOH (1:2, 45 ml) to give 0.96 g (40%) of colorless crystals of **33** of m.p. 218–220°C (decomp.). The filtrate yielded 0.39 g (16%) of the anomeric mixture **33**/**36** (2:1).

^{1}H-NMR (DMSO-d_6): 7.96 (d, 2 arom. H); 7.89 (d, 2 arom. H); 7.50 (d, 2 arom. H); 7.42 (bs, NH_2); 7.30 (m, H-C(1′)); 6.00 (m, H-C(3′)); 4.69 (m, H-C(4′)); 4.53 (m, 2 HC(5′)); 3.17 (m, $H_ß$-C(2′)); 2.57 (m, $H_α$-C(2′)); 2.40 (s, H_3C-C(6)); 2.36 (s, H_3C-C(2)). Anal. For $C_{27}H_{23}Cl_2N_5O_6$ (584.4) Calcd: C 55.49, H 3.97, N 11.98. Found:C 55.57, H 4.09, N 11.53.

4-Amino-8-(2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (37)

$NaOCH_3$ (0.22 g, 4 mmol) was dissolved in dry MeOH (80 ml) and then **27** (2.24 g, 4 mmol) was added and the mixture stirred for 2 days at room temperature. The suspension was neutralized by AcOH and the precipitate was collected. Drying in vacuum at 80°C yielded 0.96 g (86%) of a colorless powder of **37** of m.p. >180°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.24 (s, H-C(2)); 7.95 (s, H-C(6)); 7.83 (bs, NH_2); 7.12 (m, H-C(1′)); 5.20 (d, HO-C(3′)); 4.71 (d, HO-C(5′)); 4.43 (m, H-C(3′)); 3.76 (m, H-C(4′)); 3.65 (m, 1 H-C(5′)); 3.54 (m, 1 H-C(5′)); 2.89 (m, $H_ß$-C(2′)); 2.02 (m, $H_α$-C(2′)). Anal. For $C_{11}H_{13}Cl_2N_5O_4$ (279.3) Calcd: C 47.31, H 4.69, N 25.08. Found: C 47.31, H 4.72, N 25.05.

4-Amino-8-(2-deoxy-ß-D-*erythro*-pentofuranosyl)-2-phenyl-7(8H)pteridone (38)

Either **28** (0.592 g, 1 mmol) or **29** (0.632 g, 1 mmol) was stirred in dry MeOH (20 ml) in presence of $NaOCH_3$ (54 mg, 1 mmol) for 2 days at room temperature. The suspension was neutralized by AcOH, the precipitate was collected and dried in vacuum at 80°C to give 0.306 g (86%) of a colorless powder of **38** of m.p. >260°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.35 (m, 2 arom. H); 7.93 (s, H-C(6)); 7.78 + 7.87 (2 bs, NH_2); 7.52 (m, 3 arom. H); 7.44 (dd, H-C(1′)); 5.21 (d, HO-C(3′)); 4.62 (d, HO-C(5′)); 4.46 (m, H-C(3′)); 3.81 (m, H-C(4′)); 3.67 (m, 1 H-C(5′)); 3.52 (m, 1 H-C(5′)); 2.94 (m, $H_ß$-C(2′)); 2.11 (m, $H_α$-C(2′)). Anal. For $C_{17}H_{17}N_5O_4 \times H_2O$ (364.4) Calcd: C 56.04, H 4.98, N 19.22. Found: C 55.82, H 4.88, N 18.80.

4-Amino-8-(2-deoxy-ß-D-*erythro*-pentofuranosyl)-6-phenyl-7(8H)pteridone (39)

A suspension of 4-N,N-dimethylaminomethyleneimino-6-phenyl-8-[(3,5-di-O-(4-chlorobenzoyl)-2-deoxy-ß-D-*erythro*-pentofuranosyl]-7(8H) pteridone (**51**) (0.65 g, 1 mmol) in MeOH was treated with K_2CO_3 (70 mg, 0.5 mmol) and conc. NH_3 (0.7 ml) under stirring for 2 days at room temperature. It was evaporated to half of the volumn, then neutralized by AcOH, and the precipiate was collected. Recrystallization from MeOH gave 0.3.16 g (89%) of yellow crystals of **39** of m.p. >165°C (decomp.).

^{1}H-NMR (DMSO-d_6): 8.32 (m, 2 arom. H); 8.20 (s, H-C(2)); 7.81 + 7.88 (2 bs, NH_2); 7.47 (m, 3 arom. H); 7.22 (dd, H-C(1′)); 5.17 (d, HO-C(3′)); 4.71 (d, HO-C(5′)); 4.48 (m, H-C(3′)); 3.79 (m, H-C(4′)); 3.69 (m, 1 H-C(5′)); 3.55 (m, 1 H-C(5′)); 2.95 (m, $H_ß$-C(2′)); 2.06 (m, $H_α$-C(2′)). Anal. For $C_{17}H_{17}N_5O_4$ (355.4) Calcd: C 57.46, H 4.82, N 19.71. Found: C 57.30, H 4.91, N 19.48.

4-Amino-8-(2-deoxy-ß-D-*erythro*-pentofuranosyl)-2,6-diphenyl-7(8H)pteridone (40)

To a solution of $NaOCH_3$ (19 mg, 0.35 mmol) in dry MeOH (15 ml) was added **31** (0.25 g, 0.35 mmol) and the mixture was stirred for 12 hours. It was neutralized by AcOH, the precipitate was collected, and dried in vacuum at 80°C to give 0.145 g (96%) of a yellow powder of **40** of m.p. >220°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.39 (m, 4 arom. H); 7.90 (bs, NH_2); 7.50 (m, 7H, H-C(1′), 6 arom. H); 5.24 (d, HO-C(3′)); 4.65 (d, HO-C(5′)); 4.51 (m, H-C(3′)); 3.82 (m, H-C(4′)); 3.65 (m, 1 H-C(5′)); 3.56 (m, 1 H-C(5′)); 2.98 (m, $H_ß$-C(2′)); 2.17 (m, $H_α$-C(2′)). Anal. For $C_{23}H_{21}N_5O_4$ (431.5) Calcd: C 64.03, H 4.91, N 16.23. Found: C 63.91, H 5.05, N 15.90.

4-Amino-8-(2-deoxy-ß-D-*erythro*-pentofuranosyl)-6-methyl-7(8H)pteridone (41)

a) To a solution of sodium (20 mg, 0.88 mmol) in dry MeOH (20 ml) was added **32** (0.5 g, 0.88 mmol) and the mixture was stirred for 12 hours. It was neutralized by AcOH, concentrated to 10 ml, and the precipitate was collected and dried in vacuum at 80°C to give 0.16 g (62%) of a colorless powder of **41** of m.p. >190°C (decomp.).

b) A suspension of 4-N,N-dimethylaminomethyleneimino-6-methyl-8-[(3,5-di-O-(4-chlorobenzoyl)-2-deoxy-ß-D-*erythro*-pentofuranosyl]-7(8H) pteridone (**55**) (2.0 g, 3.2 mmol) in MeOH was treated with K_2CO_3 (0.44 g, 3.2 mmol) and conc. NH_3 (5 ml) under stirring for 2 days at room temperature. It was evaporated to half of the volumn, then neutralized by AcOH and the precipiate was collected and dried in vacuum at 80°C to give 0.76 g (81%) of colorless crystals of **41** of m.p. >190°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.20 (s, H-C(2));); 7.52+7.70 (2 bs, NH_2); 7.15 (dd, H-C(1′)); 5.17 (d, HO-C(3′)); 4.72 (d, HO-C(5′)); 4.44 (m, H-C(3′)); 3.67 (m, H-C(4′)); 3.60 (m, 1 H-C(5′)); 3.54 (m, 1 H-C(5′)); 2.88 (m, $H_ß$-C(2′)); 2.36 (s, H_3C-C(6)); 2.01 (m, $H_α$-C(2′)). Anal. For $C_{12}H_{15}N_5O_4$ (293.3) Calcd: C 49.13, H 5.16, N 23.88. Found: C 49.13, H 5.03, N 23.73.

4-Amino-8-(2-deoxy-ß-D-*erythro*-pentofuranosyl)-2,6-dimethyl-7(8H)pteridone (42)

a) To a solution of sodium (30 mg, 1.33 mmol) in dry MeOH (20 ml) was added **33** (0.78 g, 1.33 mmol) and the mixture was stirred for 12 hours. It was neutralized by AcOH, concentrated to 10 ml, the precipitate was collected, washed with MeOH, and dried in vacuum at 80°C to give 0.38 g (93%) of a colorless solid of **42** of m.p. >180°C (decomp.). ^{1}H-NMR (DMSO-d_6):); 7.38 + 7.57 (2 bs, NH_2); 7.14 (dd, H-C(1′)); 5.16 (d, HO-C(3′)); 4.66 (d, HO-C(5′)); 4.45 (m, H-C(3′)); 3.74 (m, H-C(4′)); 3.65 (m, 1 H-C(5′)); 3.53 (m, 1 H-C(5′)); 2.88 (m, $H_ß$-C(2′)); 2.37 (s, H_3C-C(6)); 2.34 (s, H_3C-C(2)); 1.99 (m, H_α-C(2′)). Anal. For $C_{13}H_{17}N_5O_4$ (307.3) Calcd: C 50.81, H 5.58, N 22.79. Found: C 50.34, H 5.80, N 23.08.

4-N,N-Dimethylaminomethyleneimino-7(8H)pteridone (43)

A suspension of 4-amino-7(8H)-pteridone (**6**) (1.63 g, 10 mmol) in dry DMF (20 ml) was treated with N,N-dimethylformamide-diethylacetal (2.6 ml, 15 mmol) at 60°C in an oilbath for 5 hours. After cooling, the precipitate was collected, washed with EtOH and dried in vacuum at 80°C. The reaction filtrate was evaporated in vacuum to dryness and the residue was recrystallized from EtOH to give a total of 1.99 g (91%) of a colorless solid of **43** of m.p. 289–291°C. ^{1}H-NMR (DMSOd_6): 12.78 (s, H-N(8)); 8.76 (s, N=CH-N); 8.42 (s, H-C(2)); 8.04 (s, H-C(6)); 3.20 (s, 3H, NCH_3Me); 3.12 (s. 3H, NCH_3Me). Anal. For $C_9H_{10}N_6O$ (218.2) Calcd: C 49.54, H 5.62, N 38.51. Found: C 49.52, H 4.68, N 38.77.

4-N,N-Dimethylaminomethyleneimino-2-phenyl-7(8H)pteridone (44)

Analogous to the preceding procedure with **12** (2.39 g, 10 mmol) to give 2.47 g (84%) of a colorless solid of **44** of m.p. 257–260°C. Recrystallization from isopropanol gave colorless crystals. ^{1}H-NMR (DMSO-d_6): 12.74 (s, H-N(8)); 8.94 (s, N=CH-N); 8.44 (m, 2 arom. H); 8.02 (s, H-C(6)); 7.51 (m, 3 arom. H); 3.33 (s, 3H, NCH_3Me); 3.26, s. 3H, NCH_3Me). Anal. For $C_{15}H_{14}N_6O$ (294.3) Calcd: C 61.21, H 4.79, N 28.55. Found: C 61.12, H 4.86, N 28.77.

4-N,N-Dimethylaminomethyleneimino-6-phenyl-7(8H)pteridone (45)

Analogous to the preceding procedure with **14** (2.39 g, 10 mmol) to give 2.59 g (88%) of a colorless solid of **45** of m.p. 257–260°C. Recrystallization from EtOH gave colorless crystals. ^{1}H-NMR (DMSOd_6): 12.89 (s, H-N(8)); 8.43 (s, N=CH-N); 8.38 (s, H-C(2)); 8.26 (m, 2 arom. H); 7.48 (m, 3 arom.

H); 3.22 (s, 3H, NCH_3Me); 3.17 (s. 3H, NCH_3Me). Anal. For $C_{15}H_{14}N_6O$ (294.3) Calcd: C 61.21, H 4.79, N 28.55. Found: C 60.88, H 5.00, N 28.15.

4-N,N-Dimethylaminomethyleneimino-2,6-diphenyl-7(8H)pteridone (46)

Analogous to the preceding procedure with **15** (3.15 g, 10 mmol) to give 3.14 g (85%) of a colorless solid of **46** of m.p. 269–270°C. Recrystallization from isopropanol gave colorless crystals. ^{1}H-NMR (DMSO-d_6): 12.89 (s, H-N(8)); 8.93 (s, N=CH-N); 8.42 (m, 2 arom. H); 8.31 (m, 2 arom. H); 7.50 (m, 6 arom. H); 3.28 (s, 3H, NCH_3Me); 3.21 (s. 3H, NCH_3Me). Anal. For $C_{21}H_{18}N_6O$ (370.4) Calcd: C 68.10, H 4.90, N 22.69. Found: C 67.86, H 4.98, N 22.86.

4-N,N-Dimethylaminomethyleneimino-6-methyl-7(8H)pteridone (47)

A suspension of **19** (1.0 g, 5.6 mmol) in dry DMF (15 ml) was treated with N,N-dimethylformamide-diethylacetal (1.45 ml, 8.4 mmol) at 60°C in an oilbath for 1.5 hours. After cooling, the precipitate was collected, washed with EtOH and dried in vacuum at 80°C. The reaction filtrate was evaporated in vacuum to dryness, the residue was treated with ether and dried to give a total of 1.13 g (87%) of a colorless solid of **47** of m.p. >220°C (decomp.). ^{1}H-NMR (DMSO-d_6): 12.82 (s, H-N(8)); 8.70 (s, N=CH-N); 8.38 (s, H-C(2)); 3.20 (s, 3H, NCH_3Me); 3.13 (s. 3H, NCH_3Me); 2.38 (s, H_3C-C(6)). Anal. For $C_{10}H_{12}N_6O \times 0.5\ H_2O$ (236.7) Calcd: C 50.73, H 5.32, N 35.50. Found: C 50.56, H 5.39, N 35.09.

4-N,N-Dimethylaminomethyleneimino-2,6-dimethyl-7(8H)pteridone (48)

A suspension of **22** (2.24 g, 11.7 mmol) in dry DMF (20 ml) was treated with N,N-dimethylformamidediethylacetal (3.0 ml, 17.5 mmol) at room temperature for 3 hours. The precipitate was collected, washed with EtOH and dried in vacuum at 80°C. The reaction filtrate was evaporated in vacuum to dryness, the residue was treated with EtOH and ether and dried to give a total of 2.59 g (90%) of a colorless solid of **48** of m.p. 220°C (decomp.). ^{1}H-NMR (DMSO-d_6): 12.49 (s, H-N(8)); 8.61 (s, N=CH-N); 3.18 (s, 3H, NCH_3Me); 3.11 (s. 3H, NCH_3Me); 2.42 (s, $H_3CC(6)$); 2.33 (s, H_3C-C(2)). Anal. For $C_{11}H_{14}N_6O$ (246.3) Calcd: C 53.65, H 5.73, N 34.13. Found: C 53.81, H 5.79, N 34.19.

4-N,N-Dimethylaminomethyleneimino-8-(3,5-di-O-4-chlorobenzoyl- 2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (49)

A suspension of 4-N,N-dimethylaminomethyleneimino-7(8H)pteridone (**43**) (2.18 g, 10 mmol) in dry CH_3CN (150 ml) was treated with DBU (1.49 ml, 10 mmol) and stirred at room temperature for 30 minutes. After addition of **25** (4.73 g, 11 mmol) the mixture was stirred for another 2.5 hours, filtered, and the filtrate evaporated to dryness. The residue was dissolved in CH_2Cl_2 (100 ml), extracted twice with H_2O (40 ml), the organic layer was separated, dried over Na_2SO_4, evaporated, and the residue put onto a silica-gel column (20 × 5 cm) for chromatography with n-hexane/acetone (1:1, 1.5 l). The first fraction (R_f 0.71) consisted of **27** (0.78 g, 14%) and the second fraction (R_f 0.45) gave after evaporation 1.28 g (21%) of **49** of m.p. 152–155°C. ^{1}H-NMR (DMSO-d_6): 8.73 (s, N=CHN); 8.51 (s, H-C(2)); 8.17 (s, H-C(6)); 7.45 (m, 4 arom. H); 7.29–7.48 (2 d, 5H, HC(1′), 4 arom. H); 5.99 (m, H-C(3′)); 4.77 (m, H-C(4′)); 4.68 (m, H-C(5′)); 5.52 (m, H-C(5′)); 3.42 (m, $H_ß$-C(2′)); 3.28 (s, N-CH_3); 3.22 (s, N-CH_3); 2.50 (m, H_α-C(2′)). Anal. For $C_{28}H_{24}Cl_2N_6O_6$ (611.4) Calcd: C 55.00, H 3.96, N 13.75. Found: C 54.86, H 3.92, N 13.92.

4-N,N-Dimethylaminomethyleneimino-2-phenyl-8-(3,5-di-O-toluoyl -2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (50)

A suspension of **44** (1.0 g, 3.4 mmol) in dry CH_3CN (60 ml) was treated with DBU (506 μl, 3.4 mmol) and stirred at room temperature for 20 minutes. After addition of **26** (1.45 g, 3.7 mmol) the mixture was stirred for another 1.5 hours, filtered, and the filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (100 ml), shaken twice with H_2O (40 ml), the organic layer was separated, dried over Na_2SO_4, evaporated, and the residue put onto a silica-gel column (15 × 3 cm) for chromatography with CH_2Cl_2/acetone (9:1, 750 ml). The first fraction consisted of **28** (0.663 g, 33%) and the second fraction (R_f 0.31) gave after evaporation 0.835 g (38%) of **50**. Recrystallization from $CHCl_3$/MeOH gave 0.374 g (17%) of yellowish crystals of of **50** of m.p. 171–173°C. ^{1}HNMR (DMSO-d_6): 8.91 (s, N=CHN); 8.45 (m, 2 arom. H); 8.14 (s, H-C(6)); 7.93 (m, 4 arom. H); 7.80 (m, H-C(1′)); 7.46 (m, 3 arom. H); 7.23 (m, 2 arom. H); 7.12 (m, 2 arom. H); 5.99 (m, H-C(3′)); 4.60–4.76 (m, 3H, H-C(4′), H-C(5′)); 3.44 (m, $H_ß$-C(2′)); 3.31 (s, N-CH_3); 3.26 (s, N-CH_3); 2.33 (m, H_α-C(2′)). Anal. For $C_{36}H_{34}N_6O_6$ (646.7) Calcd: C 66.86, H 5.30, N 13.00. Found: C 66.71, H 5.28, N 12.90.

4-N,N-Dimethylaminomethyleneimino-6-phenyl-8-(3,5-di-O-4-chlorobenzoyl-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (51)

A suspension of **45** (2.94 g, 10 mmol) in dry CH_3CN (60 ml) was treated with DBU (1.49 ml, 10 mmol) and stirred at room temperature for 20 minutes to give a clear solution. After addition of 25 (4.72 g, 11 mmol) the reaction mixture was stirred for another 1 hour and the resulting precipitate was collected, washed with ether, and dried in vacuum at 40°C to give 4.13 g (60%) of a yellow powder of **51** of m.p. 225–227°C. ^{1}H-NMR (DMSO-d_6): 8.74 (s, N=CHN); 8.54 (s, H-C(2)); 8.27 (m, 2 arom. H); 7.98 (m, 4 arom. H); 7.61 (m, H-C(1′)); 7.44 (m, 3 arom. H); 7.26 (d, 2 arom. H); 7.12 (m, 2 arom. H); 6.12 (m, H-C(3′)); 4.82 (m, H-C(4′)); 4.75 (m, H-C(5′)); 4.53 (m, H-C(5′)); 3.46 (m, $H_ß$-C(2′)); 3.31 (s, N-CH_3); 3.22 (s, N-CH_3); 2.55 (m, H_α-C(2′)). Anal. For $C_{34}H_{28}Cl_2N_6O_6$ (687.5) Calcd: C 59.40, H 4.10, N 12.22. Found: C 59.35, H 4.14, N 11.97.

4-N,N-Dimethylaminomethyleneimino-2,6-diphenyl-8-(3,5-di-O-4-chlorobenzoyl-2deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (52)

A suspension of **46** (3.7 g, 10 mmol) in dry CH_3CN (80 ml) was treated with DBU (1.49 ml, 10 mmol) and stirred at room temperature for 20 minutes to give a clear solution. After addition of **25** (4.72 g, 11 mmol) the reaction mixture was stirred for another 1 hour, the resulting precipitate was collected and recrystallized from $CHCl_3$/MeOH and dried in vacuum at 40°C to give 4.2 g (55%) of a yellow powder of **52** of m.p. 225–227°C. ^{1}H-NMR (DMSO-d_6): 8.90 (s, N=CHN); 8.48 (m, 2 arom. H); 8.29 (m, 2 arom. H); 7.96 (m, 5H, H-C(1′), 4 arom. H); 7.45 (m, 8 arom. H); 7.23 (d, 2 arom. H); 6.15 (m, H-C(3′)); 4.58–4.81 (m, H-C(4′), 2 H-C(5′)); 3.45 (m, $H_ß$-C(2′)); 3.32 (s, N-CH_3); 3.25 (s, N-CH_3); 2.58 (m, H_α-C(2′)). Anal. For $C_{40}H_{32}Cl_2N_6O_6$ (763.6) Calcd: C 62.91, H 4.22, N 11.01. Found: C 62.92, H 4.29, N 10.69.

4-N,N-Dimethylaminomethyleneimino-2,6-diphenyl-8-(3,5-di-O-toluoyl-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (53)

A suspension of **46** (3.7 g, 10 mmol) in dry CH_3CN (80 ml) was treated with DBU (1.49 ml, 10 mmol) and stirred at room temperature for 20 minutes to give a clear solution. After addition of **26** (4.28 g, 11 mmol) the reaction mixture was stirred for another 1 hour, the resulting precipitate was collected and recrystallized from $CHCl_3$/MeOH and dried in vacuum at 40°C to give 5.17 g (71%) of a yellow powder of **53** of m.p. 218–220°C.

From the filtrate an α/ß-anomeric mixture (**53**/**54**) 1.52 g (21%) could be isolate but all attempts to get pure **54** failed. ^{1}H-NMR (DMSO-d_6): 8.89 (s, N=CHN); 8.48 (m, 2 arom. H); 8.33 (m, 2 arom. H); 7.93 (m, H-C(1′)); 7.45 (m, 6 arom. H); 7.23 (d, 2 arom. H); 7.08 (d, 2 arom. H); 6.11 (m, H-C(3′)); 4.60–4.85 (m, H-C(4′), 2 H-C(5′)); 3.46 (m, H$_ß$C(2′)); 3.32 (s, N-CH_3); 3.25 (s, N-CH_3); 2.60 (m, H$_\alpha$-C(2′)); 2.41 (s, H_3C-C); 2.32 (s, H_3CC). Anal. For $C_{42}H_{38}N_6O_6$ (722.8) Calcd: C 69.79, H 5.30, N 11.63. Found: C 69.51, H 5.30, N 11.42.

4-N,N-Dimethylaminomethyleneimino-6-methyl-8-(3,5-di-O-4-chlorobenzoyl-2-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (55)

A suspension of **47** (2.16 g, 9.3 mmol) in dry CH_3CN (40 ml) was treated with DBU (1.39 ml, 9.3 mmol) and stirred at room temperature for 20 minutes. After addition of **25** (4.8 g, 11.1 mmol) the reaction mixture was stirred for another 1 hour, the precipitate was filtered off and recrystallized from $CHCl_3$/MeOH (1:1, 30 ml) to give 2.2 g (38%) and from the filtrate 0.44 g (7%) of colorless crystals of **55** of m.p. 171–174°C. ^{1}H-NMR ($CDCl_3$): 8.75 (s, N=CHN); 8.52 (s, H-C(2)); 7.99 (2 d, 4 arom. H); 7.52 (dd, H-C(1′)); 7.43 (d, 2 arom. H); 7.34 (d, 2 arom. H); 6.08 (m, H-C(3′)); 4.68 (m, 1 H-C(5′)); 4.58 (m, H-C(4′)); 3.42 (m, H$_ß$-C(2′)); 3.31 (s, N-CH_3); 3.23 (s, N-CH_3); 2.58 (s, H_3C-C(6)); 2.53 (m, H$_\alpha$-C(2′)). Anal. For $C_{36}H_{34}N_6O_6$ (646.7) Calcd: C 66.86, H 5.30, N 13.00. Found: C 66.71, H 5.28, N 12.90.

4-Amino-8-(2,3,5-tri-O-benzoyl-ß-D-erythro-pentofuranosyl)-7(8H)pteridone (57)

a) A suspension of compound **6** (1.0 g, 6.1 mmol) in dry CH3CN (100 ml) and dry DMF (50 ml) was treated with DBU (0.9 ml, 6.1 mmol) and stirred at room temperature for 15 minutes. After addition of 2,3,5-tri-O-benzoyl-1-bromo-α-D-*erythro*-pentofuranose (**56**) (3.86 g, 7.4 mmol), the reaction mixture was stirred for another 2.5 hours, then evaporated to dryness, the residue was dissolved in CH_2Cl_2 (50 ml), and extracted twice with saturated NaCl solution (30 ml). The organic phase was separated, dried over Na_2SO_4, evaporated again, and the residue dissolved in little toluene and put onto to a silica-gel column (10 × 5 cm) for chromatography with toluene/EtOAc(1:1, 500 ml) and followed by toluene/EtOAc (2:1, 500 ml). The main fraction was collected, evaporated and the solid recrystallized from isopropanol to give 0.8 g (22%) of a colorless powder of **57** of m.p. >105°C (decomp.).

b) A mixture of compound **6** (1.64 g, 10 mmol) and a few crystals of $(NH_4)_2SO_4$ in HMDS (30 ml) was heated under reflux for 2 hours. The excess of HMDS was evaporated in vacuum and the resulting oily mixture

(**66**) dissolved in dry $CHCl_3$ (50 ml). After addition of **70** (5.05 g, 10 mmol) followed by BF_3-etherate (10 ml, 80 mmol), the reaction mixture was stirred at room temperature for 12 hours. The soln was poured into H_2O (100 ml), neutralized with $NaHCO_3$, the organic phase was separated and dried over Na_2SO_4. It was again evaporated, the residue dissoloved in little toluene and put onto a silica-gel column (12 × 5 cm) for chromatography with toluene/EtOAc (3:1, 1.8 l). The product fraction eluted late, was evaporated to give 4.2 g (69%) of a colorless foam of **57** of m.p. >105°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.26 (s,HC(2)); 8.10 (s, H-C(6)); 7.92 (m, 6H, NH_2, 4 arom. H); 7.81 (d, 2 arom. H); 7.61 (m, 3 arom. H); 7.39 (m, 6 arom. H); 7.12 (bs, H-C(1′)); 6.31 (m, 2H, H-C(2′), H-C(3′)); 4.75 (m, 1 HC(5′), H-C(4′)); 4.58 (m, 1 H-C(5′)). Anal. For $C_{32}H_{25}N_5O_8$ (607.6) Calcd: C 63.26, H 4.14, N 11.53. Found: C 63.18, H 4.19, N 11.39.

4-Amino-2-phenyl-8-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (58)

a) A suspension of **12** (1.0 g, 4.24 mmol) in dry CH_3CN (80 ml) was treated with DBU (0.62 ml, 6.1 mmol) and stirred at room temperature for 30 minutes. After addition of 2,3,5-tri-Obenzoyl-1-bromo-α-D-*erythro*-pentofuranose (**56**) (3.62 g, 5.0 mmol), the reaction mixture was stirred for another 2 hours, then evaporated to dryness, the residue was dissolved in CH_2Cl_2 (50 ml) and extracted twice with saturated NaCl solution (30 ml). The organic phase was separated, dried over Na_2SO_4, evaporated again, the residue dissolved in toluene (15 ml) and put onto to a silica-gel column (7 × 5 cm) for chromatography with toluene/EtOAc(3:1, 600 ml). The main fraction was collected, evaporated and the solid recrystallized from MeOH (200 ml) to give 0.97 g (34%) of a colorless solid of **58** of m.p. 157–158°C.

b) A mixture of **12** (2.37 g, 9.9 mmol) and a few crystals of $(NH_4)_2SO_4$ was heated in hexamethyldisilazane (HMDS) (50 ml) under reflux and exclusion of moisture for 5 hours. The HMDS was removed in vacuum and the residue of **67** dissolved in dry CH_2Cl_2 (60 ml). Then compound **70** (5.0 g, 9.9 mmol) was added, followed by BF_3-etherate (8.9 ml, 70 mmol) and the mixture stirred for 3 hours at room temperature. The solution was poured into H_2O (120 ml), neutralized with $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was separated, dried over Na_2SO_4, filtered, evaporated again, the residue dissolved in toluene (30 ml), and put onto a silica-gel column (15 × 5 cm) for chromatography with toluene/EtOAc (3:1, 1000 ml). The main fraction was collected, evaporated, the residue dissolved in CH_2Cl_2 (10 ml), and this solution was added dropwise under stirring into MeOH (150 ml). Cooling over night in the icebox (−20°C) yielded 3.48 g (51%) of **58** and from the filtrate another 0.3 g (5%) of a colorless solid of **58** of m.p. 156–158°C. ^{1}H-NMR (DMSO-d_6): 8.32 (m, 2 arom. H); 8.08 (s, H-C(6)); 7.91 (m, 8H, NH2, 6 arom. H); 7.63 (m, 3 arom. H); 7.47 (m,

H-C(1′), 9 arom. H); 6.27 (m, 2H, H-C(2′), H-C(3′)); 4.84 (m, H-C(4′)); 4.72 (m, 1 H-C(5′)); 4.58 (m, 1 H-C(5′)). Anal. For $C_{38}H_{29}N_5O_8$ (683.7) Calcd: C 66.76, H 4.28, N 10.24. Found: C 67.04, H 4.33, N 10.32.

4-Amino-2,6-diphenyl-8-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)7(8H)pteridone (59)

a) A suspension of **15** (1.0 g, 3.17 mmol) in dry CH_3CN (50 ml) was treated with DBU (0.47 ml, 3.17 mmol) and stirred at room temperature for 30 minutes. After addition of 2,3,5-tri-O-benzoyl-1-bromo-α-D-*erythro*-pentofuranose (**56**) (1.87 g, 3.49 mmol), the reaction mixture was stirred for another 1 hour, the yellow precipitate was collected, heated with $CHCl_3$/MeOH (1:1, 100 ml) and the insoluble educt filtered off. On cooling, yellow needles precipitated to give 0.795 g (33%) of **59** of m.p. 241–243°C.

b) A mixture of **15** (2.1 g, 6.7 mmol) and a few crystals of $(NH_4)_2SO_4$ was heated in hexamethyldisilazane (HMDS) (80 ml) under reflux and exclusion of moisture for 24 hours. The HMDS was removed in vacuum and the residue of **69** was dissolved in dry CH_2Cl_2 (100 ml). Then compound **70** (3.8 g, 7.5 mmol) was added, followed by BF_3-etherate (20 ml, 160 mmol) and the mixture stirred for 24 hours at room temperature. The soln was evaporated to half of its volume, the precipitate was collected, the filtrate was diluted with n-hexane (50 ml), and the second crop again collected. The solids were combined and heated in $CHCl_3$/MeOH (1:1, 200 ml), the insoluble educt filtered off. Cooling over night in the icebox yielded 1.6 g (31%) of yellow needles of **59** of m.p. 240–243°C. ^{1}H-NMR (DMSO-d_6): 8.43 (m, 2 arom. H); 8.35 (m, 2 arom. H); 8.08 (s, H-C(6)); 7.97 (m, 6H, NH_2, 4 arom. H); 7.86 (d, 2 arom. H); 7.63 (m, 4 arom. H); 7.47 (m, H-C(1′), 11 arom. H); 6.43 (m, 2H, H-C(2′), H-C(3′)); 4.84 (m, H-C(4′)); 4.78 (m, 1 H-C(5′)); 4.60 (m, 1 H-C(5′)). Anal. For $C_{44}H_{33}N_5O_8$ (759.8) Calcd: C 69.55, H 4.38, N 9.22. Found: C 69.62, H 4.49, N 9.22.

4-N,N-Dimethylaminomethyleneimino-6-phenyl-8-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (60)

A suspension of **45** (2.0 g, 6.8 mmol) in dry CH_3CN (100 ml) was treated with DBU (1.0 ml, 6.8 mmol) and stirred at room temperature for 15 minutes to give a clear solution. After addition of **56** (3.93 g, 7.5 mmol), the reaction mixture was stirred for another 2 hours and then evaporated, The residue was dissolved in CH_2Cl_2 ((50 ml), shaken twice with saturated NaCl solution (30 ml), the organic phase was separated, dried over Na_2SO_4 and again evaporated. The residue was dissolved in toluene (20 ml) and put onto a silica-gel column (14 × 6 cm) for chromatography with toluene/EtOAc (1:1, 800 ml) and followed by toluene/EtOAc (2:1, 1000 ml) eluting the product fraction. Evaporation and drying in high vacuum gave 2.6 g (52%)

of a yellowish powder of **60** of m.p. 100–110°C. ^{1}H-NMR (DMSO-d_6): 8.83 (s, N=CHN); 8.53 (s, H-C(2)); 8.20 (m, 2 arom. H); 7.95 (m, 4 arom. H); 7.80 (d, 2 arom. H); 7.41–7.65 (m, H-C(1′), 12 arom. H); 6.44 (m, H-C(2′)); 6.36 (m, H-C(3′)); 4.79 (m, H-C(4′)); 4.74 (m, H-C(5′)); 4.57 (m, H-C(5′)); 3.24 (s, N-CH_3); 3.19 (s, N-CH_3). Anal. For $C_{41}H_{34}N_6O_8$ (738.8) Calcd: C 66.66, H 4.64, N 11.38. Found: C 66.57, H 4.74, N 11.39.

4-N,N-Dimethylaminomethyleneimino-6-phenyl-8-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (61)

A suspension of **46** (1.0 g, 2.7 mmol) in dry CH_3CN (50 ml) was treated with DBU (0.4 ml, 2.7 mmol) and stirred at room temperature for 15 minutes to give a clear solution. After addition of **56** (1.59 g, 2.97 mmol), the reaction mixture was stirred for another 1 hour, then evaporated, and the precipitate was collected and washed with MeOH and ether. Recrystallization from $CHCl_3$ (20 ml) and MeOH (25 ml) gave after drying 1.5 g (68%) of a yellow crystals of **61** of m.p. 249–251°C. ^{1}H-NMR (DMSO-d_6): 8.83 (s, N=CHN); 8.32 (m, 4 arom. H); 7.99 (m, 4 arom. H); 7.88 (d, 2 arom. H); 7.63 (m, H-C(1′)); 7.35 (m, 15 arom. H); 6.43 (m, H-C(2′), H-C(3′)); 4.82 (m, H-C(4′), 1 H-C(5′)); 4.66 (m, 1 HC(5′)); 3.29 (s, N-CH_3); 3.21 (s, N-CH_3). Anal. For $C_{47}H_{38}N_6O_8$ (814.9) Calcd: C 69.28, H 4.70, N 10.31. Found: C 69.76, H 4.75, N 10.28.

4-Amino-8-ß-D-*erythro*-pentofuranosyl-7(8H)pteridone (62)

To a solution of CH_3ONa (0.177 g, 3.3 mmol) in absolute MeOH (100 ml), **57** (2.90 g, 3.3 mmol) was added and stirred for 24 hours. The resulting suspension was neutralized with AcOH, the precipitate was collected and dried at 40°C to give 0.92 g (94%) of a colorless powder of **62** of m.p. >199°C (decomp.). ^{1}HNMR (DMSO-d_6): 8.26 (s, H-C(2)); 7.99 (s, H-C(6)); 7.84 + 7.88 (2 bs, NH_2); 6.67 (d, H-C1′)); 5.14 (d, HO-C(2′)); 4.99 (d, HO-C(3′)); 4.70 (m, 2H, HO-C(5′), H-C(2′)); 4.26 (m, HC(3′)); 3.88 (m, H-C(4′)); 3.65 (m, 1 H-C(5′)); 3.47 (m, 1 H-C(5′)). Anal. For $C_{11}H_{13}N_5O_5$ (295.3) Calcd: C 44.75, H 4.44, N 23.72. Found: C 44.68, H 4.48, N 23.59.

4-Amino-2-phenyl-8-ß-D-*erythro*-pentofuranosyl-7(8H)pteridone (63)

To a solution of Na (67 mg, 2.9 mmol) in absolute MeOH (100 ml), **57** (2.0 g, 2.9 mmol) was added and stirred for 12 hours. The resulting suspension was neutralized with AcOH, evaporated to half of the volume and then the precipitate was collected and dried at 80°C in vacuum to give 1.0 g (93%) of a colorless powder of **63** of m.p. 214°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.33 (m, 2 arom. H); 7.97 (s, H-C(6)); 7.85 + 7.91

(2 bs, NH_2); 7.54 (m, 3 arom. H); 6.69 (d, H-C-1′)); 5.20 (d, HO-C(2′)); 5.06 (d, HO-C(3′)); 4.68 (m, 2H, HO-C(5′), H-C(2′)); 4.27 (m, H-C(3′)); 3.82 (m, H-C(4′)); 3.66 (m, 1 H-C(5′)); 3.49 (m, 1 H-C(5′)). Anal. For $C_{17}H_{17}N_5O_5$ (371.4) Calcd: C 54.98, H 4.61, N 18.86. Found: C 55.11, H 4.69, N 18.77.

4-Amino-6-phenyl-8-ß-D-*erythro*-pentofuranosyl-7(8H)pteridone (64)

A suspension of **60** (0.74 g, 1 mmol) and K_2CO_3 (70 mg) in MeOH (20 ml) was treated with conc. NH_3 (0.7 ml, 25%) and stirred for 2 days. It was neutralized with AcOH, evaporated to half of the volume and then the precipitate was collected and dried at 60°C in vacuum to give 0.32 g (86%) of a yellow powder of **64** of m.p. >205°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.32 (m, 2 arom. H); 8.27 (s, H-C(2)); 7.87 + 7.89 (2 bs, NH2); 7.45 (m, 3 arom. H); 6.77 (d, H-C-1′)); 5.12 (d, HO-C(2′)); 4.98 (d, HO-C(3′)); 4.71 (m, 2H, HO-C(5′), H-C(2′)); 4.33 (m, H-C(3′)); 3.81 (m, H-C(4′)); 3.68 (m, 1 H-C(5′)); 3.51 (m, 1 H-C(5′)). Anal. For $C_{17}H_{17}N_5O_5$ (371.4) Calcd: C 54.98, H 4.61, N 18.86. Found: C 54.60, H 4.70, N 18.67.

4-Amino-2,6-diphenyl-8-ß-D-*erythro*-pentofuranosyl-7(8H)pteridone (65)

To a solution of Na (50 mg, 2.17 mmol) in absolute MeOH (100 ml), **59** (1.12 g, 1.47 mmol) was added and the reaction mixture stirred at room temperature for 24 hours. It was neutralized with AcOH, evaporated to half of the volume, and then the precipitate was collected. Recrystallization from DMF/H_2O and drying at 60°C in vacuum gave 0.59 g (88%) of a yellow powder of **65** of m.p. >265°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.37 (m, 4 arom. H); 7.93 + 7.97 (2 bs, NH_2); 7.51 (m, 6 arom. H); 7.03 (d, H-C-1′)); 5.20 (d, HO-C(2′)); 5.03 (d, HO-C(3′)); 4.76 (m, H-C(2′)); 4.67 (dd, HO-C(5′)); 4.36 (m, H-C(3′)); 3.84 (m, H-C(4′)); 3.71 (m, 1 H-C(5′)); 3.51 (m, 1 H-C(5′)). Anal. For $C_{23}H_{21}N_5O_5 \times 0.5\ H_2O$ (456.5) Calcd: C 60.52, H 4.86, N 15.34. Found: C 60.86, H 4.81, N 15.31.

4-Amino-6-phenyl-1-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (71)

A mixture of **14** (3.6 g, 15 mmol) and a few crystals of $(NH_4)_2SO_4$ was heated in hexamethyl-disilazane (HMDS) (50 ml) under reflux and exclusion of moisture for 12 hours. The HMDS was removed in vacuum and the residue of **68** was dissolved in dry CH_2Cl_2 (50 ml). Then compound **70** (7.7 g, 15.2 mmol) was added, followed by BF_3-etherate (13.5 ml, 107 mmol) and the mixture stirred for 24 hours at room temperature. The reaction soln was diluted with CH_2Cl_2 (100 ml), poured into ice-H_2O (200 ml) and

neutralized with $NaHCO_3$. The organic phase was separated, dried over Na_2SO_4, filtered, and evaporated again. The residue was dissolved in toluene (30 ml) and put onto a silica-gel column (15 × 5 cm) for chromatography with toluene/EtOAc (1:1, 1800 ml). The main fraction which eluted late, was collected, evaporated, and the residue was recrystallzed from MeOH (150 ml) to give 2.4 g (23%) of a yellowish solid of **71** of m.p. >157°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.76 + 8.94 (2 s, NH_2); 8.75 (s, H-C(2)); 8.55 (m, 2 arom. H); 7.84 (m, 6 arom. H); 7.64 (m, 3 arom. H); 7.43 (m, 9 arom. H); 6.69 (d, H-C(1′)); 6.30 (m, H-C(2′)); 6.22 (m, H-C(3′)); 4.86 (m, HC(4′)); 4.79 (m, 2 H-C(5′)). Anal. For $C_{38}H_{29}N_5O_8$ (683.7) Calcd: C 66.76, H 4.28, N 10.24. Found: C 66.73, H 4.29, N 10.33.

4-Amino-6-phenyl-1-(ß-D-erythro-pentofuranosyl)-7(8H)pteridone (72)

To a soln of Na (35 mg, 1.5 mmol) in dry MeOH (30 ml), 71 (1.02 g, 1.5 mmol) was added and the reaction mixture stirred at room temperature for 12 hours. It was neutralized by AcOH and the solution cooled in the icebox to −20°C over night. The resulting precipitate was collected and dried in vacuum at 80°C to give 0.36 g (65%) and from the filtrate 0.125 g (22%) of yellowish crystals of **72** of m.p. >225°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.94 (s, H-C(2));); 8.58 + 8.70 (2 bs, NH_2); 8.53 (m, 2 arom. H); 7.41 (m, 3 arom. H); 6.36 (d, H-C(1′)); 5.62 (m, HO-C(2′)); 5.30 (dd, HO-C(5′)); 5.13 (d, HO-C(3′)); 4,25 (m, H-C(2′)); 4.14 (m, H-C(3′)); 3.97 (m, H-C(4′)); 3.79 (m, 1 H-C(5′)); 3.64 (m, 1 H-C(5′)). Anal. For $C_{17}H_{17}N_5O_5$ (371.4) Calcd: C 54.98, H 4.61, N 18.86. Found: C 54.91, H 4.77, N 18.74.

4-Amino-6-phenyl-1-(3,5-di-O-toluoyl-2′-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (73) and the a-anomer (74)

A mixture of **14** (2.39 g, 10 mmol) and a few crystals of $(NH_4)_2SO_4$ was heated in hexamethyldisilazane (HMDS) (60 ml) under reflux and exclusion of moisture for 6 hours. The HMDS was removed in vacuum and the residue of **68** was dissolved in dry CH_3CN (150 ml). Then **26** (4.28 g, 11 mmol) was added, followed by trimethylsilyl trifluoromethanesulfonate (2.26 ml, 11 mmol) and was stirred at room temperature, for 3 hours. The reaction solution was slowly added to saturated $NaHCO_3$ solution (200 ml) and then extracted twice with EtOAc (2 × 80 ml). The organic phase was washed with saturated NaCl solution (80 ml), dried over Na_2SO_4, and evaporated. The residue was dissolved in little CH_2Cl_2, insoluble educt filtered off, and the filtrate put onto a silica-gel column (30 × 5 cm) for chromatography with CH_2Cl_2/acetone (5:1).The ß-anomer (**73**) ($R_f = 0.40$) was eluted first followed by the α-anomer (**74**) ($R_f = 0.30$). The fractions were evaporated and dried in high vacuum to give 3.08 g (52%) of **73** as a

yellowish powder of m.p. 138–140°C and 2.37 g (40%) of **74** as a yellowish solid of m.p. >130°C (decomp.).

73: ^{1}H-NMR (DMSO-d_6): 8.63 + 8.77 (2 s, NH_2); 8.66 (s, H-C(2)); 8.53 (m, 2 arom. H); 7.95 (m, 2H, arom. H); 7.84 (m, 2 arom. H); 7.40 (m, 5 arom. H); 7.29 (d, 2 arom. H); 6.73 (m, H-C(1′)); 5.69 (m, H-C(3′)); 4.71 (m, H-C(4′), 2 H-C(5′)); 2.83 (m, $H_ß$-C(2′), $H_α$-C(2′)); 2.41 (s, CH_3); 2.36 (s, CH_3). Anal. For $C_{33}H_{29}N_5O_6 \times 0.5\ H_2O$ (600.4) Calcd: C 65.99, H 5.03, N 11.66. Found: C 65.50, H 5.02, N 11.92.

74: ^{1}H-NMR (DMSO-d_6): 8.74 (s, H-C(2));); 8.73 (bs,1H of NH_2); 8.54 (bs, 1H of NH_2): 8.51 (m, 2 arom. H); 7.96 (m, 2H, arom. H); 7.65 (m, 2 arom. H); 7.40 (m, 5 arom. H); 7.26 (d, 2 arom. H); 6.70 (d, H-C(1′)); 5.61 (m, H-C(3′)); 5.34 (m, H-C(4′)); 4.54 (m, 2 H-C(5′)); 3.06 (m, $H_α$-C(2′)); 2.69 (d, $H_ß$-C(2′)); 2.41 (s, CH_3); 2.36 (s, CH_3). Anal. For $C_{33}H_{29}N_5O_6 \times 0.5\ H_2O$ (600.4) Calcd: C 65.99, H 5.03, N 11.66. Found: C 66.21, H 5.27, N 11.61.

4-Amino-6-phenyl-1-(2′-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (75)

To a soln of Na (10 mg, 0.04 mmol) in dry MeOH (20 ml), **73** (0.591 g, 1.0 mmol) was added and the reaction mixture was stirred at room temperature for 2 hours. It was neutralized by AcOH and the soln was evaporated to dryness. The residue was recrystallized from little H_2O, the crystals collected and dried in high vacuum to give 0.32 g (90%) of yellowish crystals of **75** of m.p. >200°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.85 (s, H-C(2));); 8.53 + 8.67 (2 bs, NH_2); 8.51 (m, 2 arom. H); 7.40 (m, 3 arom. H); 6.63 (d, H-C(1′)); 5.36 (m, HO-C(3′)); 5.20 (dd, HOC(5′)); 4.31 (m, H-C(3′)); 3.95 (m, H-C(4′)); 3.67 (m, 2 H-C(5′)); 2.44 (m, $H_ß$-C(2′)); 2.44 (m, $H_α$-C(2′)). Anal. For $C_{17}H_{17}N_5O_4 \times 0.5\ H_2O$ (371.4) Calcd: C 56.04, H 4.98, N 19.22. Found: C 56.32, H 4.83, N 19.01.

4-Amino-6-phenyl-1-(2′-deoxy-α-D-*erythro*-pentofuranosyl)-7(8H)pteridone (76)

Analogous to the preceding procedure with **74** (0.591 g, 1 mmol) to give 0.338 g (95%) of a yellowish solid of **76** of m.p. >230°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.56 (s, H-C(2)); 8.52 + 8.62 (2 bs, NH_2); 8.50 (m, 2 arom. H); 7.41 (m, 3 arom. H); 6.63 (d, H-C(1′)); 5.24 (m, HO-C(3′)); 4.96 (dd, HO-C(5′)); 4.45 (m, H-C(4′)); 4.31 (m, H-C(3′)); 3.46 (m, 2 H-C(5′)); 2.68 (m, $H_ß$-C(2′)); 2.18 (m, $H_α$-C(2′)). Anal. For $C_{17}H_{17}N_5O_4 \times 0.5\ H_2O$ (371.4) Calcd: C 56.04, H 4.98, N 19.22. Found: C 56.48, H 4.88, N 19.26.

4-N,N-Dimethylaminomethyleneimino-6-phenyl-1-(3,5-di-O-4-chlorobenzoyl-2′-deoxy-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (77) and the α-anomer (78)

A mixture of compound **45** (1.0 g, 3.4 mmol) and a few crystals of $(NH_4)_2SO_4$ was heated in hexamethyldisilazane (HMDS) (50 ml) under reflux and exclusion of moisture for 3 hours. The HMDS was removed under vacuum and the residue was dissolved in dry CH_3CN (150 ml). Then **25** (2.19 g, 5,1 mmol) and $SnCl_4$ (6 ml, 5.1 mmol) were added and stirred at room temperature for 3 hours. The reaction soln was slowly added to a saturated $NaHCO_3$ solution (150 ml) and then extracted twice with EtOAc (2 × 80 ml). The organic phase was washed with saturated NaCl solution (80 ml), dried over Na_2SO_4, and evaporated. The residue was dissolved in little CH_2Cl_2, and put onto a silica-gel column (30 × 5 cm) for chromatography with CH_2Cl_2/acetone (7:1, 500 ml) and followed by CH_2Cl_2/acetone (6:1, 2 l). The ß-anomer (**77**) ($R_f = 0.36$) was eluted first followed by the α-anomer (**78**) ($R_f = 0.32$). The fractions were evaporated and dried in high vacuum to give 1.22 g (50%) of **77** as a yellowish powder of m.p. 210–212°C and 0.79 g (31%) of **78** as a yellowish solid of m.p. 205–207°C.

77: ^{1}H-NMR (CDCl3): 8.72 (s, N=CHN); 8.48 (s, H-C(2)); 8.34 (m, 2 arom. H); 7.95 (m, 2H, arom. H); 7.85 (m, 2 arom. H); 7.36 (m, 7 arom. H); 6.95 (dd, H-C(1′)); 5.57 (m, H-C(3′)); 4.70 (m, H-C(4′), 2 H-C(5′)); 3.39 (m, H$_ß$-C(2′)); 3.32 (s, N-CH_3); 3.24 (s, N-CH_3); 2.39 (m, H$_\alpha$-C(2′)). Anal. For $C_{34}H_{28}Cl_2N_6O_6$ (687.5) Calcd: C 59.40, H 4.10, N 12.22. Found: C 59.66, H 4.12, N 11.94.

78: ^{1}H-NMR ($CDCl_3$): 8.79 (s, N=CHN); 8.46 (s, H-C(2)); 8.38 (m, 2 arom. H); 8.02 (d, 2H, arom. H); 7.63 (d, 2 arom. H); 7.45 (d, 2 arom. H); 7.39 (m, 3 arom. H); 7.31 (d, 2 arom. H); 6.97 (d, H-C(1′)); 5.65 (m, H-C(3′)); 5.03 (m, H-C(4′)); 4.62 (m, 2 H-C(5′)); 3.40 (s, N-CH_3); 3.31 (s, N-CH_3); 3.14 (m, H$_\alpha$-C(2′)); 2.88 (m, H$_ß$-C(2′)). Anal. For $C_{34}H_{28}Cl_2N_6O_6$ (687.5) Calcd: C 59.40, H 4.10, N 12.22. Found: C 58.96, H 4.09, N 12.11.

4-N,N-Dimethylaminomethyleneimino-6-phenyl-1-(2,3,5-tri-O-benzoyl-ß-D-*erythro*-pentofuranosyl)-7(8H)pteridone (79)

A soln of compound **71** (0.15 g, 0.22 mmol) in dry DMF (5 ml) was treated with dimethylformamide diethylacetal (0.15 ml, 0.88 mmol) at room temperature for 3 hours. It was evaporated in vacuum and the residue was recrystallized from $CHCl_3$ (10 ml) and isopropanol (80 ml) to give 0.155 g (94%) of a yellow solid of **79** of m.p. 214–219°C (decomp.). ^{1}H-NMR (DMSO-d_6): 8.84 (s, N=CHN); 8.83 (s, H-C(2)); 8.34 (m, 2 arom. H); 7.93 (d, 6H, arom. H); 7.65 (d, 3 arom. H); 7.35 (m, 9 arom. H); 6.73 (d, H-C(1′)); 6.34 (m, H-C(2′)); 6.26 (m, H-C(3′)); 4.87 (m, H-C(4′)); 4.83 (m,

2 H-C(5′)); 3.33 (s, N-CH_3); 3.26 (s, N-CH_3). Anal. For $C_{41}H_{34}N_6O_8 \times 0.5$ H_2O (747.8) Calcd: C 65.86, H 4.72, N 10.24. Found: C 65.92, H 4.73, N 10.23.

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