129. Nucleotides

Part LIV[1])

Synthesis of Condensed N^1-(2'-Deoxy-β-D-ribofuranosyl)lumazines, New Fluorescent Building Blocks in Oligonucleotide Synthesis

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Dedicated with best personal wishes to Prof. *Dieter Seebach* on the occasion of his 60th birthday

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Various condensed areno[*g*]lumazine derivatives **2**, **3**, and **5**–**7** were synthesized as new fluorescent aglycones for glycosylation reactions with 2-deoxy-3,5-di-*O*-(*p*-toluoyl)-α/β-D-*erythro*-pentofuranosyl chloride (**10**) to form, in a *Hilbert-Johnson-Birkofer* reaction, the corresponding N^1-(2'-deoxyribonucleosides) **15**–**21**. The β-D-anomers **15**, **17**, **19**, and **21** were deblocked to **24**–**27** and, together with N^1-(2'-deoxy-β-D-ribofuranosyl)lumazine (**22**) and its 6,7-diphenyl derivative **23**, dimethoxytritylated in 5'-position to **28**–**33**. These intermediates were then converted into the 3'-(2-cyanoethyl diisopropylphosphoramidites) **34**–**39** which function as monomeric building block in oligonucleotide syntheses as well as into the 3'-(hydrogen succinates) **40**–**45** which can be used for coupling with the solid-support material. A series of lumazine-modified oligonucleotides were synthesized and the influence of the new nucleobases on the stability of duplex formation studied by measuring the T_m values in comparison to model sequences. A substantial increase in the T_m is observed on introduction of areno[*g*]lumazine moieties in the oligonucleotide chain stabilizing obviously the helical structures by improved stacking effects. Stabilization is strongly dependent on the site of the modified nucleobase in the chain.

1. Introduction. – In recent years, the 'antisense' approach [2] as well as DNA-probe technology has stimulated the synthesis of various modified oligonucleotides. Modifications at the base moiety, the sugar part, and the phosphate backbone have been reported. We have focussed our attention on different lumazine N^1-(2'-deoxyribonucleosides) (= 1-(2'-deoxyribofuranosyl)pteridine-2,4(1*H*,3*H*)-diones) which can be regarded as structural analogoues of thymidine. These analogues have been of interest since 1973, when 6,7-dimethyl-, 6,7-diphenyl, and the unsubstituted lumazine (= pteridine-2,4(1*H*,3*H*)-dione) were ribosylated for the first time [3–5]. Considering the well-known propensity for hydroxy- and amino-pteridines to form very strong intermolecular H-bonds, the interaction between a lumazine and a complementary base, *e.g.*, adenine, and the potential stacking effects could probably lead to the formation of relatively stable double strands. The variation of the substituents in the 6,7 position of the molecule allows a broad alteration of physical properties which enable this type of compounds to be a potential indicator for intermolecular interactions, expressed in terms of UV absorp-

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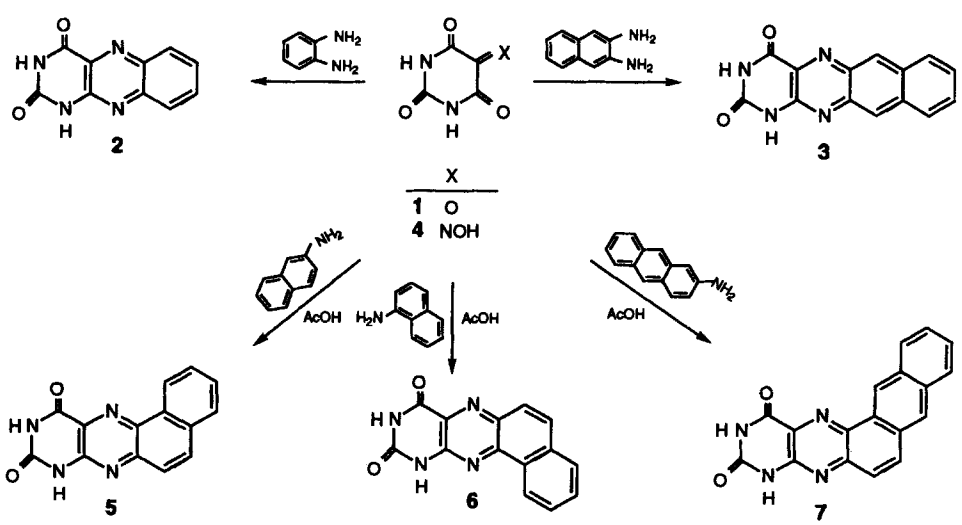
tion and fluorescence. Preliminary investigations to this approach were made by us already since 1979 [6–8] using first a modified phosphotriester method and later phosphoramidite chemistry [9] [10].

In this paper, we wish to report the synthesis of the N^1-[2′-deoxy-5′-*O*-(dimethoxytrityl)-β-D-ribofuranosyl]nucleobase 3′-phosphoramidites starting from the formerly prepared 2′-deoxyribonucleosides derived from the nucleobases lumazine and 6,7-diphenyllumazine [5]. Furthermore, various new types of fluorescent monomeric building blocks were envisaged in the structural analogues derived from alloxazine (benzo[*g*]lumazine), naphtho[1,2-*g*]-, naphtho[2,3-*g*]-, and anthra[1,2-*g*]lumazines by glycosylation and subsequent transformation into the 5′-*O*-(dimethoxytrityl)protected 3′-phosphoramidites by conventional methods.

2. Synthesis. – The areno[*g*]lumazine derivatives **2**, **3**, and **5**–**7** were prepared either according to literature or by slightly modified procedures from alloxan (= pyrimidine-2,4,5,6(1*H*,3*H*)-tetrone; **1**) or from violuric acid (= pyrimidine-2,4,5,6(1*H*,3*H*)-tetrone 5-oxime; **4**) to give the anticipated nucleobases in high yields (*Scheme 1*). Alloxazine (= benzo[*g*]pteridine-2,4(1*H*,3*H*)-dione; **2**) resulted from the condensation of **1** with 1,2-phenylenediamine in acidic medium [11], and in a similar manner, **1** reacted with naphthalene-2,3-diamine in AcOH and in presence of boric acid to naphtho[2,3-*g*]-lumazine (**3**) [12] in 95% yield. The synthesis of naphtho[1,2-*g*]lumazine (**5**) according to the older literature is controversial regarding the structure since the condensations of either **1** and naphthalene-1,2-diamine or uracil-5,6-diamine and 1,2-naphthoquinone [13] [14] led actually to mixtures of the [1,2-*g*] and [2,1-*g*] isomers [15]. The approach of *Timmis* and coworkers [15] to **5** is a regioselective fusion reaction of **2** and naphthalen-2-amine which gave pure **5** in 57% isolated yield. A useful modification thereof was the condensation of **2** with naphthalen-1-amine or anthracen-2-amine in boiling AcOH to give naphtho[2,1-*g*]- (**6**) and anthra[1,2-*g*]lumazine (**7**), respectively.

Scheme 1

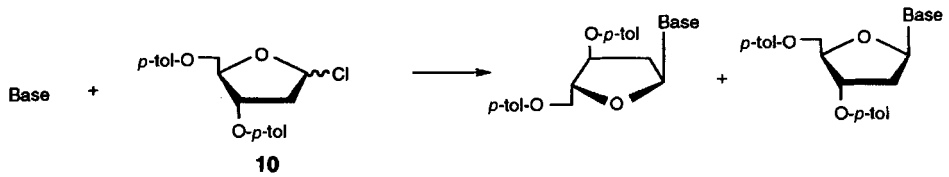


In previous investigations, the chemical synthesis of 1-(2-deoxy-β-D-ribofuranosyl)-lumazine (**22**) and of its 6,7-diphenyl derivative **23** was performed by applying the *Hilbert-Johnson-Birkofer* method in the ribosylation step of lumazine (**8**) and 6,7-diphenyllumazine (**9**) [3–5]. In an analogous manner, the condensed lumazine derivatives **2**, **3**, **5**, and **7** were first silylated by treatment with hexamethyldisilazane (HMDS) and then reacted with 2-deoxy-3,5-di-*O*-(*p*-toluoyl)-α/β-D-*erythro*-pentofuranosyl chloride (**10**) [16] at room temperature under various reaction conditions to improve the α-D/β-D anomeric ratio in preference of the anticipated β-D-form by varying the solvent and adding metal salts as catalysts (*Scheme 2*, *Table 1*). Unfortunately, the successful stereoselective synthesis of 2'-deoxy-β-D-ribonucleosides in the pyrimidine [17] and quinazolinedione [18] series under catalysis with CuI did not influence the α-D/β-D ratio of lumazine glycosylation reactions. Thus, lumazine (**8**) was treated in form of its O^2,O^4-bis(trimethylsilyl) derivative with the halogenose **10** in CH_2Cl_2 for 1 week at room temperature leading to a 1:1 anomeric mixture **11**/**12** in 75% yield (*Table 1*). Addition of CuI or change of the solvent to $CHCl_3$ made the reaction faster, but the formation of the α-D-anomer also increased. The best results regarding the β-D-anomer were achieved in $CHCl_3$ with $ZnCl_2$ as a catalyst yielding a 1:1.6 α-D/β-D ratio after 20 h of treatment at room temperature. Silylated 6,7-diphenyllumazine (**9**) reacted best with **10** in CH_2Cl_2 to give a 1:1.75 α-D/β-D mixture **13**/**14** from which the β-D-anomer **14** could be isolated in pure form in 49% yield. The corresponding ribosylations of alloxazine (**2**) and naphtho[2,3-*g*]lumazine (**3**) were to some extent surprising since a highly regio- and stereospecific reaction to the 2'-deoxy-β-D-ribofuranosides **15** and **17**, respectively, was observed which could be isolated easily by fractional crystallization. Naphtho-[1,2-*g*]- (**5**) and anthra[1,2-*g*]lumazine (**7**) gave under quarternization conditions in $CHCl_3$ and benzene, respectively, experimentally acceptable yields with a preference for the β-D-anomers **19** and **21**. Separation of the two anomers could be achieved either by column chromatography (silica gel) or by fractional crystallization due to the fact that the β-D-forms crystallize in most cases much more easily than the α-D-anomers.

Table 1. *Glycosylations of Lumazine Derivatives*

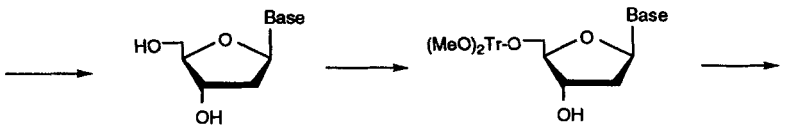
	Solvent/catalyst	Reaction time		α-D/β-D Ratio	Yield [%]	
		h	d		total	β-D
Lumazine (**8**)	CH_2Cl_2		6	1:1	75	29
	CH_2Cl_2/CuI	2		1.6:1	58	
	$CHCl_3$/CuI	15		1.2:1	74	
	$CHCl_3$/$ZnCl_2$	20		1:1.6	55	
6,7-Diphenyllumazine (**9**)	CH_2Cl_2	18		1:1.7	80	49
	CH_2Cl_2/CuI		3	2:1	74	
	toluene		4	1.6:1	73	
Alloxazine (**2**)	$CHCl_3$	18		1:23	93	77
Naphtho[2,3-*g*]lumazine (**3**)	$CHCl_3$	18		1:6	78	58
Naphtho[1,2-*g*]lumazine (**5**)	$CHCl_3$	18		1:3.8	75	47
	CH_2Cl_2/CuI	4		1:1.4	75	
Anthra[1,2-*g*]lumazine (**7**)	$CHCl_3$	3		1:1	93	
	benzene		3	1:2	84	48

Scheme 2

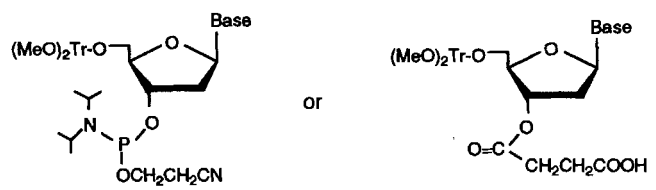


Base	
8	Lumazine
9	6,7-Diphenyllumazine
2	Alloxazine
3	Naphtho[2,3-*g*]lumazine
5	Naphtho[1,2-*g*]lumazine
7	Anthra[1,2-*g*]lumazine

Base		
11	Lumazine	**12**
13	6,7-Diphenyllumazine	**14**
	Alloxazine	**15**
16	Naphtho[2,3-*g*]lumazine	**17**
18	Naphtho[1,2-*g*]lumazine	**19**
20	Anthra[1,2-*g*]lumazine	**21**



Base		
22	Lumazine	**28**
23	6,7-Diphenyllumazine	**29**
24	Alloxazine	**30**
25	Naphtho[2,3-*g*]lumazine	**31**
26	Naphtho[1,2-*g*]lumazine	**32**
27	Anthra[1,2-*g*]lumazine	**33**



Base		
34	Lumazine	**40**
35	6,7-Diphenyllumazine	**41**
36	Alloxazine	**42**
37	Naphtho[2,3-*g*]lumazine	**43**
38	Naphtho[1,2-*g*]lumazine	**44**
39	Anthra[1,2-*g*]lumazine	**45**

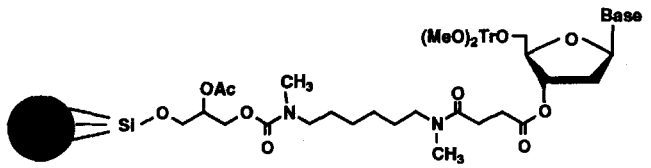
An easy way to assign the anomeric configuration of the (2′-deoxy-D-ribofuranosyl)lumazines consists in the analysis of the chemical-shift differences of the H_α–C(2′) and H_β–C(2′) signals [5]. The ^{1}H-NMR of the α-D-anomers **11**, **13**, **16**, **18**, and **20** are characterized by the appearance of the two H–C(2′) protons close together in the region of 3.1 ppm, whereas, in the β-D-anomers **12**, **14**, **15**, **17**, **19**, and **21**, two separated *m* for H_β–C(2′) and H_α–C(2′) are placed at 3.5 and 2.6 ppm, respectively.

The β-D-anomers were deprotected by treatment with dilute sodium methoxide solution according to *Zemplen et al.* [19] and gave the free β-D-nucleosides **22**–**27** in good yields. Besides their characterizations by UV and ^{1}H-NMR spectra, first informations about their fluorescence properties were derived from the excitation and emission maxima which were measured in $5 \cdot 10^{-1}$M DMF solutions and which were also compared with the corresponding free nucleobases (*Table 2*).

Table 2. *Excitation and Emission Maxima of Areno[g]lumazines and of Their Corresponding 1-(2'-Deoxy-β-D-ribofuranosides) in DMF*

Lumazine	λ_{max} of		1-(2'-Deoxy-β-D-ribofuranoside)	λ_{max} of	
	excitation	emission		excitation	emission
9	360	431	**23**	360	450
2	373	430	**24**	360	455
3	480	570	**25**	480	580
5	400	423	**26**	400	424
7	440	516	**27**	443	464
6	412	509			

Subsequent reactions of **22**–**27** with 4,4'-dimethoxytrityl chloride in dry pyridine at room temperature afforded high yields of the 5'-*O*-(dimethoxytrityl) derivatives **28**–**33** which were used as intermediates for the synthesis of the 3'-phosphoramidites **34**–**39** and the 3'-(hydrogen succinates) **40**–**45**. Phosphitylation was achieved by (2-cyanoethoxy) bis(diisopropylamino)phosphine [20] under 1*H*-tetrazole catalysis in CH_2Cl_2/MeCN mixtures, and functionalization of the 3'-OH group by succinic anhydride worked best in presence of 4-(dimethylamino)pyridine (DMAP). The 3'-(hydrogen succinates) **40**–**45** were then coupled onto the solid-support material LCMAACPG (long-chain(methylamino)alkyl-controlled-pore glass) [21] [22] using as condensing agent *O*-{{[(2-cyanoethoxy)carbonyl]methylidene}amino}-1,1,3,3-tetramethyluronium tetrafluoroborate (TOTU) [23] and *N*-methylmorpholine in MeCN followed by a capping procedure with Ac_2O/DMAP/I_2 in pyridine.



Base	
46	**Lumazine**
47	**6,7-Diphenyllumazine**
48	**Alloxazine**
49	**Naphtho[2,3-*g*]lumazine**
50	**Naphtho[1,2-*g*]lumazine**
51	**Anthra[1,2-*g*]lumazine**

A loading of 25–35 μmol/g was achieved with a 500 Å-CPG material to give the solid supports **46**–**51** for oligonucleotide syntheses.

The oligonucleotide syntheses were performed with an *ABI 380b* DNA synthesizer applying the standard cycle. With the support **46** and **47**, corresponding decamers d(L_{10}) and d[$ph_2^{6,7}L)_{10}$] (dL = 1-(2'-deoxy-β-D-ribofuranosyl)lumazine) were prepared with an optimal coupling yield, and the resulting oligomers were very pure according to the HPLC. The syntheses of mixed oligomers carrying a lumazine moiety (dL or d($ph_2^{6,7}L$) at either the 3'- or 5'-end worked in a similar manner, and the resulting

nonadecamers were then hybridized with a complementary strand showing only a relatively small decrease in the melting temperature in comparison to the unmodified duplex (*Table 3*).

Table 3. *Melting Temperatures of Lumazine-Modified Oligonucleotides* (0.5 *OD*)[a])

Sequence[b])	T_m [°C]	
	Lumazine[c])	6,7-Diphenyllumazine[c])
5′-d(T-T_{16}-T-T)-3′	30.4	
3′-d(A-A_{16}-A-A)-5′		
5′-d(T-T_{16}-T-**Lu**)-3′	28.5	28
3′-d(A-A_{16}-A-**Lu**)-5′		
5′-d(**Lu**-T-T_{16}-T)-3′	27.9	28.6
3′-d(**Lu**-A-A_{16}-A)-3′		
5′-d(T-T_{16}-T-**Lu**)-3′	29	28.7
3′-d(A-A_{16}-A-A)-5′		
5′-d(A-A_{16}-A-**Lu**)-3′	29.7	28.6
3′-d(T-T_{16}-T-T)-5′		

[a]) The T_m were measured at 260 nm in Na_2HPO_4/NaH_2PO_4 buffer pH 7; $[Na^+] = 0.03$M.
[b]) For convenience, d(**Lu**) is used as a general abbreviation for dL (1-(2′-deoxy-β-D-ribofuranosyl)lumazine) and d($ph_2^{6,7}$LK) (1-(2′-deoxy-β-D-ribofuranosyl)-6,7-diphenyllumazine).
[c]) Nucleobase in d(**Lu**).

More extended studies were performed with the self-complementary sequence d(GG-TT-CC-AT-GC-AT-GG-AA-CC) which was modified again with various lumazine nucleobases at the 3′- and 5′-end as well as by substitution of T units in the chain. The syntheses of the mixed oligomers were based on the npe/npeoc strategy [22]

Table 4. *Melting temperatures of Lumazine-Modified Oligonucleotides* (0.5 *OD*)

Sequence[b])	T_m [°C]					
	8[a])	**9**[a])	**2**[a])	**3**[a])	**5**[a])	**7**[a])
5′-d(GG-TT-CC-AT-GC-AT-GG-AA-CC)-3′				60.4		
5′-d(GG-TT-CC-AT-GC-AT-GG-AA-CC-**Lu**)-3′	59	60.2	61.2	62.5	62.3	61.2
5′-d(**Lu**-GG-TT-CC-AT-GC-AT-GG-AA-CC)-3′	59.7	60.3	61.2	62.3	61.9	61.5
5′-d(GG-TT-CC-A**Lu**-GC-AT-GG-AA-CC)-3′	57	59.3	61.5	66.4	66.4	65.5
5′-D(GG-TT-CC-AT-GC-A**Lu**-GG-AA-CC)-3′	57	59.4	61.4	65.5	65.4	66.4
5′-d(GG-TT-CC-A**Lu**-GC-A**Lu**-GG-AA-CC)-3′	55.3	63.2	60.3	> 70	74	> 70
5′-d(GG-**Lu**T-CC-AT-GC-AT-GG-AA-CC)-3′				55.4		
5′-d(GG-T**Lu**-CC-AT-GC-AT-GG-AA-CC)-3′				56.3		
5′-d(GG-**LuLu**-CC-AT-GC-AT-GG-AA-CC)-3′				45.4		
5′-d(GG-T**Lu**-CC-AT-GC-A**Lu**-GG-AA-CC)-3′				61.6		
5′-d(GG-T**Lu**-CC-A**Lu**-GC-AT-GG-AA-CC)-3′				60.7		
5′-d(GG-TT-CC-AT-GC-AT-GG-A**Lu**-CC)-3′				59.1		
5′-d(GG-TT-CC-A**Lu**-GC-At-GG-A**Lu**-CC)-3′					66.8	

[a]) The T_m were measured at 260 nm in Na_2HPO_4/NaH_2PO_4 buffer pH 7; $[Na^+] = 0.03$M.
[b]) For convenience, d(**Lu**) is used as a general abbreviation for all lumazine-derived nucleobases.
[c]) Nucleobase in d(**Lu**).

which guarantees easy isolation, excellent yields, and high purity even of the crude material. The melting temperatures of the various hybrids revealed interesting effects since introduction of the nucleobase lumazine (**8**) showed only small depressions depending on the number of substituents and their site in the chain, whereas 6,7-diphenyllumazine (**9**) did not alter the T_m much but also raised the basic value by 3 degrees when two T substitutions were performed. (*Table 4*).

On the other hand, incorporation of the nucleobases **2**, **3**, **5**, and **7** increased in principle the T_m quite substantially; especially the condensed lumazine systems **3**, **5**, and **7** seem to stabilize the duplexes with an increment of 5°, most likely due to an enforced stacking effect. Two nucleobases in distant positions in the middle of the chain caused so far the highest T_ms of > 70° of this series, whereas adjacent locations and exchange positions towards the 3'- and 5'-ends destabilized the duplex structure. It is also noteworthy that a mismatch by substitution of an A unit by the nucleobase **5** or **7**, respectively, does not affect the stability of the duplexes very much. More studies will be performed in the future to unravel the stabilizing and destabilizing effects of new nucleobases as substitutes of the natural pyrimidine and purine bases.

Experimental Part

General. Products were dried in an oven at 100° or under high vacuum. TLC: Precoated silica gel thin-layer sheets *F1500 LS 254* from *Schleicher & Schuell*. Flash chromatography (FC): silica gel (*Baker*, 30–60 mm); 0.2–0.3 bar. M.p.: *Gallenkamp* or *Büchi* melting point apparatus; no corrections. UV/VIS: *Perkin-Elmer, Lambda 15*; λ_{max} in nm (log ε). Fluorescence spectra: *Aminco SPF 500*. Melting curves: *Perkin-Elmer Lambda 2*; temp. control by *Peltier* element 0.2°/min; programmer *PTP-6*. ^{1}H-NMR: *Bruker AC 250*; in ppm rel. to $SiMe_4$ as internal standard. ^{31}P-NMR: *Joel 400 MHz*; in ppm rel. to H_3PO_4.

1. *Naphthalen-2-amine* [24]. 2-Nitronaphthalene (80% pure; from *Fluka*; 15 g, 87 mmol) was dissolved in EtOH (300 ml) and then reduced with H_2 catalytically over PtO_2 (300 mg) in a shaking apparatus. The mixture was filtered, the filtrate evaporated, and the solid residue crystallized from petroleum ether: 9.8 g (79%). M.p. 109–110° ([24]: 110°). UV (MeOH): 331 (3.34), 288 (sh, 3.68), 279 (3.80), 271 (sh, 3.74), 236 (3.63). ^{1}H-NMR ((D_6)DMSO): 7.49 (*m*, 3 arom. H); 7.48 (*d*, 2 arom. H); 7.21 (*m*, 2 arom. H); 7.06 (*m*, 2 arom. H); 6.95, 6.91 (*dd*, 2 arom. H); 6.81 (*d*, 2 arom. H); 5.35 (*s*, NH_2).

2. *Naphtho[2,3-g]pteridine-2,4(1H,3H)-dione* (**3**) [12]. To a suspension of alloxan tetrahydrate (**1** · $4H_2O$; 3.21 g, 15 mmol) and boric acid (0.186 g, 3 mmol) in AcOH (50 ml) was added naphthalene-2,3-diamine (2.37 g, 15 mmol). The mixture was stirred at r.t. for 3 h. After cooling, the red precipitate was collected, washed with H_2O and EtOH, and dried at 100°: 3.76 g (95%). M.p. > 350° ([12]: 385°). UV (MeOH): 442 (3.24), 389 (4.17), 371 (sh, 3.99), 281 (4.60), 243 (4.60). ^{1}H-NMR ((D_6)DMSO): 11.95 (*s*, NH); 11.76 (*s*, NH); 8.87 (*s*, 1 arom. H); 8.48 (*s*, 1 arom. H); 8.20 (*m*, 2 arom. H); 7.61 (*m*, 2 arom. H).

3. *Naphtho[1,2-g]pteridine-2,4(1H,3H)-dione* (**5**) [15]. In an oil bath naphthalen-2-amine (2.2 g, 15 mmol) was heated to 130°. Then violuric acid monohydrate **4** · H_2O (1.2 g, 7.5 mmol) was added with stirring. The temp. was raised to 155° and kept for 45 min, the melt was allowed to cool and was then extracted with EtOH and hot 2N NaOH. The alkaline soln. was filtered and the filtrate acidified with 2N HCl to pH 2. The precipitated product (1.28 g, 65%) was recrystallized from 80% HCOOH soln. and dried at 100°: 1.2 g (57%). M.p. > 350°. UV (MeOH): 403 (4.13), 386 (4.07), 298 (4.36), 287 (4.30) 280 (4.27), 239 (4.79), 232 (sh, 4.74). ^{1}H-NMR (CF_3COOD): 9.41 (*d*, 1 arom. H); 8.54 (*d*, 1 arom. H); 7.96–8.16 (*m*, 4 arom. H). Anal. calc. for $C_{14}H_8N_4O_2$ (264.24): C 63.64, H 3.05, N 21.21; found: C 63.15, H 3.22, N 20.54.

4. *Naphtho[2,1-g]pteridine-2,4(1H,3H)-dione* (**6**) [14]. Naphthalen-1-amine (0.716 g, 0.5 mmol) and **4** · H_2O (0.876 g, 0.5 mmol) were heated in AcOH under reflux for 24 h. After cooling, the mixture was diluted with H_2O (20 ml), the precipitate, dissolved in hot 1N NaOH, the hot soln. treated with charcoal, filtered, and then, still hot, acidified with 2N HCl to pH 1. The solid was filtered, washed with H_2O and EtOH, and dried at 100°: 0.15 g (11%). M.p. > 350°. UV (MeOH): 412 (3.88), 399 (3.91), 323 (sh, 3.83), 299 (sh, 4.13), 283 (4.44), 275 (4.44), 264 (sh, 4.32), 228 (4.42). ^{1}H-NMR ((D_6)DMSO): 12.12 (*s*, NH); 11.79 (*s*, NH); 8.96 (*d*, 1 arom. H); 8.11 (*m*, 2 arom. H); 7.97 (*d*, 1 arom. H); 7.85 (*m*, 2 arom. H).

5. *Anthra[1,2-g]pteridine-2,4(1H,3H)-dione* (**7**). Anthracen-2-amine (2.13 g, 1.1 mmol) and **4** · H_2O (1.75 mg, 1 mmol) were suspended in AcOH (100 ml) and stirred for 3 h under reflux. After cooling to r.t., the mixture was evaporated, the dark residue dissolved in DMF (300 ml) and treated with charcoal, and then H_2O (175 ml) added to the hot soln. After cooling, the precipitate was filtered, recrystallized from DMF/acetone, and dried at 100°: 2.49 g (70%). M.p. > 350°. UV (MeOH): 443 (4.01), 424 (3.94), 336 (4.28), 323 (sh, 4.19), 275 (4.80), 267 (sh, 4.72), 256 (sh, 4.63), 229 (4.43). Emission spectrum (EtOH): $\lambda_{exc.}$ 440, $\lambda_{em.}$ 543 nm. ^{1}H-NMR ((D$_6$)DMSO): 9.54 (*s*, 1 arom. H); 8.67 (*s*, 1 arom. H); 8.38, 8.34 (2*d*, *2* arom. H); 8.19 (*m*, 1 arom. H); 7.68 (*m*, 3 arom. H). Anal. calc. for $C_{18}H_{10}N_4O_2 \cdot 0.5\ H_2O$ (323.3): C 66.87, H 3.43, N 17.33; found: C 66.65, H 3.55, N 17.18.

6. *1-[2'-Deoxy-3',5'-di-*O*-(p-toluoyl)-β-*D*-ribofuranosyl]benzo[g]pteridine-2,4(1H,3H)-dione* (**15**). To a suspension of alloxazine (**3**; 2.14 g, 10 mmol) [11] in dry CH_2Cl_2 (50 ml), *N,O*-bis(trimethylsilyl)acetamide (10 ml) was added and the mixture stirred for 15 min at reflux temp. The resulting soln. was cooled to r.t. and evaporated, the sirup dissolved in abs. $CHCl_3$ (50 ml) and then 2-deoxy-3,5-di-*O*-(*p*-toluoyl)-α/β-D-*erythro*-pentofuranosyl chloride (**10**; 4.28 g, 11 mmol) [16] added. The soln. was stirred at r.t. overnight. The reaction was quenched with MeOH (10 ml) and the soln. diluted with $CHCl_3$ (100 ml). The org. layer was washed with sat. $NaHCO_3$ soln., the aq. phase extracted with CH_2Cl_2, the combined org. layer dried (Na_2SO_4) and evaporated, and the residue purified by crystallization from toluene: 4.25 g (75%). M.p. 238–239°. UV (MeOH): 370 (3.80), 321 (3.82), 240 (4.79), 213 (sh, 4.57), 203 (4.79). ^{1}H-NMR ($CDCl_3$): 8.74 (*s*, NH); 8.36 (*d*, 1 arom. H); 8.33 (*d*, 1 arom. H); 7.95 (*m*, 3 arom. H); 7.83 (*m*, 3 arom. H); 7.45 (*m*, H–C(1')); 7.26 (*d*, 2 arom. H); 7.10 (*d*, 2 arom. H); 6.19 (*m*, H–C(3')); 4.80, 4.63 (2*m*, H–C(4'), 2 H–C(5')); 3.50 (*m*, 1 H–C(2')); 2.63 (*m*, 1 H–C(2')); 2.44 (*s*, Me); 2.34 (*s*, Me). Anal. calc. for $C_{31}H_{26}N_4O_7$ (566.6): C 65.72, H 4.63, N 9.89; found: C 65.19, H 4.66, N 9.70.

7. *1-[2'-Deoxy-3',5'-di-*O*-(p-toluoyl)-β-*D*-ribofuranosyl]naphtho[2,3-g]pteridine-2,4(1H,3H)-dione* (**17**). As described in *Exper. 6*, with **3** (3.44 g, 13 mmol), *N,O*-bis(trimethylsilyl)acetamide (20 ml), and **10** (5.6 g, 14.3 mmol) [16]. After FC (SiO_2, 2 × 15 cm, toluene/AcOEt 4:1, 2:1, and 1:1), the β-D-isomer **17** crystallized from the product fractions as orange plates: 4.65 g (58%). Evaporation of the mother liquor gave more **17** as a mixture with the α-D-isomer **16** (20%), which could not be separated. M.p. 261° (dec.). UV (MeOH): 404 (3.47), 389 (4.20), 374 (4.04), 242 (4.79), 284 (4.61). ^{1}H-NMR ((D$_6$)DMSO): 12.1 (*s*, NH); 8.94 (*s*, 1 arom. H); 8.68 (*s*, 1 arom. H); 8.29 (*d*, 1 arom. H); 8.17 (*d*, 1 arom. H); 7.92 (*d*, 2 arom. H); 7.78 (*d*, 2 arom. H); 7.67 (*m*, 2 arom. H); 7.35 (*d*, 2 arom. H); 7.30 (*m*, H–C(1')); 7.15 (*d*, 2 arom. H); 6.11 (*m*, H–C(3')); 4.80, 4.60 (2*m*, H–C(4'), 2 H–C(5')); 3.29 (*m*, 1 H–C(2')); 2.58 (*m*, 1 H–C(2')); 2.40 (*s*, Me); 2.28 (*s*, Me). Anal. calc for $C_{35}H_{28}N_4O_7$ (616.6): C 68.17, H 4.58, N 9.09; found: C 68.27, H 4.84, N 9.02.

8. *1-[2'-Deoxy-3',5'-di-*O*-(p-toluoyl)-α-*D*-ribofuranosyl]naphtho[1,2-g]pteridine-2,4(1H,3H)-dione* (**18**) *and 1-[2'-Deoxy-3',5'-di-*O*-(p-toluoyl)-β-*D*-ribofuranosyl]naphtho[1,2-g]pteridine-2,4(1H,3H)-dione* (**19**). As described in *Exper. 6*, with **5** (0.8 g, 3 mmol), *N,O*-bis(trimethylsilyl)acetamide (3 ml), and **10** (1.3 g, 3.33 mmol) [16]. FC (SiO_2, 2 × 15 cm, toluene/AcOEt 6:1, 4:1 and 2:1) gave 1.4 g (75%) of **18**/**19** 1:3.8. The isomers were separated by fractional crystallization from MeOH to give 0.85 g (47%) of β-D-isomer **19**, and after evaporation and recrystallization of the residue from EtOH, 0.178 g (10%) of pure α-D-isomer **18**.

19: M.p. 218–220°. UV (MeOH): 400 (4.18), 389 (sh, 4.11), 298 (4.34), 287 (4.33), 281 (sh, 4.33), 239 (4.94). ^{1}H-NMR ($CDCl_3$): 9.30 (*d*, 1 arom. H); 8.83 (*s*, NH); 8.18 (*d*, 1 arom. H); 7.76–8.0 (*m*, 8 arom. H); 7.48 (*dd*, H–C(1')); 7.27 (*d*, 2 arom. H); 7.03 (*d*, 2 arom. H); 6.22 (*m*, H–C(3')); 4.61–4.86 (*m*, H–C(4'), 2 H–C(5')); 3.55 (*m*, 1 H–C(2')); 2.65 (*m*, 1 H–C(2')); 2.44 (*s*, Me); 2.26 (*s*, Me). Anal. calc. for $C_{35}H_{28}N_4O_7 \cdot H_2O$ (634.7): C 66.24, H 4.76, N 8.83; found: C 66.30, H 4.78, N 8.74.

18: M.p. 191–193°. UV (MeOH): 400 (4.15), 388 (sh, 4.08), 298 (4.30), 287 (sh, 4.31), 280 (4.31), 239 (4.92), 231 (sh, 4.60). ^{1}H-NMR ($CDCl_3$): 9.29 (*d*, 1 arom. H); 8.91 (*s*, NH); 8.16 (*d*, 1 arom. H); 7.77–8.02 (*m*, 8 arom. H); 7.51 (*m*, H–C(1')); 7.26 (*d*, 2 arom. H); 7.18 (*d*, 2 arom. H); 5.66 (*q*, H–C(3')); 5.34 (*m*, H–C(4')); 4.73 (*dd*, 1 H–C(5')); 4.54 (*dd*, 1 H–C(5')); 3.20 (*m*, 2 H–C(2')); 2.43 (*s*, Me); 2.38 (*s*, Me). Anal. calc. for $C_{35}H_{28}N_4O_7$ (616.6): C 68.18, H 4.58, N 9.09; found: C 67.80, H 4.80, N 8.84.

9. *1-[2'-Deoxy-3',5'-di-*O*-(p-toluoyl)-α-*D*-ribofuranosyl]anthra[1,2-g]pteridine-2,4(1H,3H)-dione* (**20**) *and 1-[2'-Deoxy-3',5'-di-*O*-(p-toluoyl)-β-*D*-ribofuranosyl]anthra[1,2-g]pteridine-2,4(1H,3H)-dione* (**21**). To a soln. of **7** (4.71 g, 15 mmol) in abs. dichloroethane (150 ml), *N,O*-bis(trimethylsilyl)acetamide (10 ml) was added and the mixture stirred for 30 min at reflux temp. The resulting soln. was evaporated, the residue dissolved in dry toluene (300 ml), and **10** (6.4 g, 16.5 mmol) [16] added to the soln. After stirring for 3 days at r.t., the reaction was stopped by addition of MeOH (20 ml) and the mixture evaporated. The residue was partitioned between $CHCl_3$ and sat. $NaHCO_3$ soln. and the org. layer washed twice with sat. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated. Purification by FC (SiO_2, 3 × 13 cm, toluene/AcOEt 6:1, 4:1, and 2:1) gave **20**/**21** 1:2 (84%). The isomers were separated by crystallization from toluene yielding first 4.8 g (48%) of β-D-isomer **21**. The mother liquor was

evaporated and the residue crystallized again from toluene to give a mixture **20**/**21** which was not separated. Addition of petroleum ether to the mother liquor gave 1.8 g (18%) of pure α-D-isomer **20** as an amorphous powder.

21: M.p. 167–169°. UV (MeOH): 443 (4.09), 336 (4.31), 324 (sh, 4.19), 276 (4.85), 268 (sh, 7.77), 246 (4.71), 235 (sh, 4.68). ^{1}H-NMR ($CDCl_3$): 9.73 (*s*, 1 arom. H); 8.86 (*s*, NH); 8.36 (*s*, 1 arom. H); 8.25 (*m*, 1 arom. H); 8.17 (*d*, 1 arom. H); 8.06 (*m*, 1 arom. H); 7.99 (*d*, 2 arom. H); 7.84 (*d*, 2 arom. H); 7.75 (*d*, 1 arom. H); 7.66 (*m*, 2 arom. H); 7.46 (*dd*, H–C(1′)); 7.28 (*d*, 2 arom. H); 7.04 (*d*, 2 arom. H); 6.21 (*q*, H–C(3′)); 4.60–4.88 (*m*, H–C(4′), 2 H–C(5′)); 3.55 (*m*, 1 H–C(2′)); 2.64 (*m*, 1 H–C(2′)); 2.44 (*s*, Me); 2.23 (*s*, Me). Anal. calc. for $C_{39}H_{30}N_4O_7$ (666.7): C 68.41, H 4.71, N 8.18; found: C 68.79, H 4.74, N 8.15.

20: UV (MeOH): 443 (4.09), 336 (4.31), 324 (sh, 4.19), 276 (4.85), 267 (sh, 4.77), 246 (4.71), 235 (sh, 4.68). ^{1}H-NMR ((D$_6$)DMSO): 12.1 (*s*, NH); 9.71 (*s*, 1 arom. H); 8.35 (*s*, 1 arom. H); 8.22 (*m*, 1 arom. H); 8.14 (*d*, 1 arom. H); 7.99 (*dd*, 5 arom. H); 7.65 (*m*, 4 arom. H); 7.48 (*m*, H–C(1′)); 7.28 (*d*, 2 arom. H); 7.19 (*d*, 2 arom. H); 5.65 (*q*, H–C(3′)); 5.34 (*m*, H–C(4′)); 4.73 (*dd*, 1 H–C(5′)); 4.56 (*dd*, 1 H–C(5′)); 3.19 (*t*, 2 H–C(2′)); 2.43 (*s*, Me); 2.38 (*s*, Me). Anal. calc. for $C_{39}H_{30}N_4O_7 \cdot H_2O$ (684.7): C 68.41, H 4.71, N 8.18; found: C 68.98, H 4.84, N 7.81.

10. *1-(2′-Deoxy-β-*D*-ribofuranosyl)benzo[*g*]pteridine-2,4(1*H*,3*H*)-dione* (**24**). To a suspension of **15** (3.4 g, 6 mmol) in dry MeOH (50 ml) 2N NaOMe (6.6 ml, 13.2 mmol) was added. The mixture was stirred at r.t. overnight and the reaction stopped by addition of H_2O (80 ml). The soln. was neutralized with 10% AcOH/H_2O and the resulting precipitate filtered and washed with Et_2O. The solid was suspended in MeOH (250 ml), heated a few minutes, filtered after cooling, and dried: 1.55 g (78%). M.p. > 350°. UV (MeOH): 371 (3.82), 322 (3.84), 250 (sh, 4.42), 241 (4.53), 213 (4.51). ^{1}H-NMR ((D$_6$)DMSO): 12.06 (*s*, NH); 8.20 (*d*, 1 arom. H); 8.00 (*m*, 2 arom. H); 7.85 (*m*, 1 arom. H); 7.12 (*m*, H–C(1′)); 5.17 (*d*, OH–C(3′)); 4.59 (*m*, OH–C(5′), 1 H–C(3′)); 3.73 (*m*, H–C(4′), H–C(5′)); 3.57 (*dd*, 1 H–C(5′)); 2.93 (*m*, 1 H–C(2′)); 2.08 (*m*, 1 H–C(2′)). Anal. calc. for $C_{15}H_{14}N_4O_5$ (330.3): C 54.55, H 4.27, N 16.96; found: C 54.38, H 4.33, N 16.87.

11. *1-(2′-Deoxy-β-*D*-ribofuranosyl)naphtho[2,3-*g*]pteridine-2,4(1*H*,3*H*)-dione* (**25**). As described in *Exper. 10*, with **17** (3.8 g, 5 mmol), MeOH (100 ml), 2N NaOMe (6 ml; 18 h at r.t.), and H_2O (17 ml; → clear soln.). The orange precipitate was washed with H_2O, EtOH, and Et_2O, and dried: 1.8 g (95%). M.p. > 360°. UV (MeOH): 442 (3.28), 389 (4.23), 374 (4.05), 382 (sh, 4.68), 244 (4.63), 222 (sh, 4.33). ^{1}H-NMR ((D$_6$)DMSO): 12.03 (*s*, NH); 8.91 (*s*, 1 arom. H); 8.60 (*s*, 1 arom. H); 8.24 (*dd*, 2 arom. H); 8.66 (*m*, 2 arom. H); 7.15 (*dd*, H–C(1′)); 5.21 (*d*, OH–C(3′)); 4.64 (*m*, OH–C(5′), H–C(3′)); 3.80, 3.61 (2*m*, H–C(4′), 2 H–C(5′)); 2.98 (*m*, 1 H–C(2′)); 2.11 (*m*, 1 H–C(2′)). Anal. calc. for $C_{19}H_{16}N_4O_5$ (380.4): C 59.99, H 4.24, N 14.73; found: C 59.47, H 4.35, N 14.56.

12. *1-(2′-Deoxy-β-*D*-ribofuranosyl)naphtho[1,2-*g*]pteridine-2,4(1*H*,3*H*)-dione* (**26**). As described in *Exper. 10*, with **19** (0.616 g, 1 mmol), MeOH (14 ml), 2N NaOMe (1.2 ml, 2.4 mmol; 18 h at r.t.), and H_2O (5 ml). The precipitate was washed with Et_2O and dried: 0.363 g (96%) of yellow crystals. M.p. > 310°. UV (MeOH): 400 (4.17), 388 (4.15), 298 (4.33), 288 (sh, 4.33), 280 (sh, 4.31), 239 (4.75), 232 (sh, 4.63). ^{1}H-NMR ((D$_6$)DMSO): 12.01 (br. *s*, NH); 9.02 (*d*, 1 arom. H); 8.36 (*d*, 1 arom. H); 8.13 (*d*, 1 arom. H); 7.18–7.90 (*m*, 3 arom. H); 7.14 (*m*, H–C(1′)); 5.21 (*s*, OH–C(3′)); 4.59 (*s*, OH–C(5′), H–C(3′)); 3.74–3.81 (*m*, H–C(4′), 1 H–C(5′)); 3.58 (*m*, 1 H–C(5′)); 2.97 (*m*, 1 H–C(2′)); 2.13 (*m*, 1 H–C(2′)). Anal. calc. for $C_{19}H_{16}N_4O_5 \cdot 0.5\,H_2O$ (389.4): C 58.6, H 4.40, N 14.39; found: C 58.38, H 4.32, N 14.38.

13. *1-(2′-Deoxy-β-*D*-ribofuranosyl)anthra[1,2-*g*]pteridine-2,4(1*H*,3*H*)-dione* (**27**). As described in *Exper. 10*, with **21** (2 g, 3 mmol), MeOH (55 ml), 2N NaOMe (3.3 ml, 6.6 mmol; at r.t. overnight), and H_2O (30 ml). The precipitate was heated for a few minutes in MeOH (100 ml), filtered, and dried: 1.15 g (89%) yellow powder. M.p. > 350°. UV (MeOH): 443 (4.11), 426 (sh, 4.05), 361 (sh, 3.75), 336 (4.37), 324 (sh, 4.26), 276 (4.91), 268 (sh, 4.81), 257 (sh, 4.71), 230 (4.48). ^{1}H-NMR ((D$_6$)DMSO): 12.03 (*s*, NH); 9.40 (*s*, arom. H); 8.56 (*s*, arom. H); 8.30 (*d*, 2 arom. H); 8.13 (*m*, 1 arom. H); 7.66 (*dd*, 3 arom. H); 7.12 (*m*, H–C(1′)); 5.22 (*d*, OH–C(3′)); 4.58–4.67 (*m*, H–C(4′), 1 H–C(5′)); 3.58 (*dd*, 1 H–C(5′)); 3.00 (*m*, 1 H–C(2′)); 2.16 (*m*, 1 H–C(2′)). Anal. calc. for $C_{23}H_{13}N_4O_5 \cdot 1/2\,H_2O$ (430.4): C 62.86, H 4.36, N 12.75; found: C 63.11, H 4.45, N 12.80.

14. *1-[2′-Deoxy-5′-*O*-(4,4′-dimethoxytrityl)-β-*D*-ribofuranosyl]pteridine-2,4(1*H*,3*H*)-dione* (**28**). To a soln. of 1-(2′-deoxy-β-D-ribofuranosyl)pteridine-2,4(1*H*,3*H*)-dione (**22**; 0.981 g, 3.5 mmol) [3–5] in dry pyridine (85 ml), 4,4′-dimethoxytrityl chloride (1.5 g, 4.4 mmol) was added and stirred at r.t. for 4 h. The mixture was evaporated and the residue partitioned between CH_2Cl_2 (100 ml) and sat. $NaHCO_3$ soln. (100 ml). The org. layer was washed with sat. $NaHCO_3$ soln. (2 × 50 ml), dried (Na_2SO_4), and evaporated. Purification by FC (SiO_2, 2 × 10 cm, toluene/AcOEt 2:1 , 1:1, 1:2, and 1:4) gave a colourless foam: 1.9 g (92%). UV (MeOH): 317 (3.86), 274 (sh, 3.60), 232 (4.54). ^{1}H-NMR ($CDCl_3$): 9.28 (*s*, NH); 8.56, 8.37 (2*s*, H–C(7), H–C(8)); 7.43 (*m*, 2 arom. H); 7.15–7.39 (*m*, 7 arom. H, H–C(1′)); 6.75–6.84 (*m*, H_o to MeO); 4.78 (*m*, H–C(3′)); 4.01 (*m*, H–C(4′)); 3.75 (*s*,

2 MeO); 3.52 (*dd*, 1 H–C(5')); 3.34 (*dd*, 1 H–C(5')); 2.95 (*m*, 1 H–C(2')); 2.36 (*m*, 1 H–C(2')); 2.29 (*s*, OH–C(3')). Anal. calc. for $C_{32}H_{30}N_4O_7$ (582.6): C 65.97, H 5.19, N 9.62; found: C 65.79, H 5.19, N 9.51.

15. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-D-ribofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione* (**29**). As described in *Exper. 14*, with 1-(2'-deoxy-β-D-ribofuranosyl)-6,7-diphenylpteridine-2,4(1*H*,3*H*)-dione (**23**; 1.87 g, 4.33 mmol) [3–5], 4,4'-dimethoxytrityl chloride (1.84 g, 5.43 mmol) and dry pyridine (10 ml). FC (SiO_2, 3.5 × 10 cm, CH_2Cl_2/MeOH/Et_3N 100:1:1, 98:1:1 and 95:4:1) and evaporation of the main fraction gave a solid foam: 2.9 g (91%). UV (MeOH): 358 (4.10), 273 (4.24), 226 (4.60). ^{1}H-NMR ($CDCl_3$): 7.12–7.45 (*m*, 19 arom. H, H–C(1')); 6.73 (*m*, 4 H_o to MeO); 4.71 (*m*, H–C(3')); 3.94 (*q*, H–C(4')); 3.75 (*s*, 2 MeO); 3.42 (*dd*, 1 H–C(5')); 3.19 (*dd*, 1 H–C(5')); 3.06 (*m*, 1 H–C(2')); 2.39 (*m*, 1 H–C(2')). Anal. calc. for $C_{44}H_{38}N_4O_7$ (734.8): C 71.92, H 5.21, N 7.62; found: C 71.67, H 5.42, N 7.66.

16. *1-[2'-Deoxy'-5-O-(4,4'-dimethoxytrityl)-β-D-ribofuranosyl]benzo[g]pteridine-2,4(1H,3H)-dione* (**30**). To a soln. of **24** (0.826 g, 2.5 mmol) (**24**) in abs. pyridine (20 ml), 4,4'-dimethoxytrityl chloride (0.932 g, 2.75 mmol) was added and the mixture stirred at r.t. for 18 h. MeOH (10 ml) was added, the mixture evaporated, and the resulting residue partitioned between CH_2Cl_2 (60 ml) and sat. $NaHCO_3$ soln. (30 ml). The org. layer was washed with sat. $NaHCO_3$ soln. (30 ml) and H_2O (30 ml), then dried (Na_2SO_4), and evaporated. FC (SiO_2, 1.5 × 20 cm, toluene/AcOEt 4:1, 2:1, and 1:1) gave a pale yellow foam: 1.4 g (89%). UV (MeOH): 372 (3.80), 321 (3.80), 256 (sh, 4.37), 237 (4.67), 212 (sh, 4.67). ^{1}H-NMR ($CDCl_3$): 9.05 (*s*, NH); 8.31 (*m*, 1 arom. H); 7.74–7.86 (*m*, 3 arom. H); 7.15–7.43 (*m*, 9 arom. H, H–C(1')); 6.75 (*m*, 4 H_o to MeO); 4.97 (*m*, H–C(3')); 4.09 (*m*, H–C(4')); 3.74, 3.73 (2*s*, 2 MeO); 3.59 (*dd*, 1 H–C(5')); 3.42 (*dd*, 1 H–C(5')); 3.06 (*m*, 1 H–C(2')); 2.43 (*m*, 1 H–C(2')); 2.17 (*s*, OH–C(3')). Anal. calc. for $C_{36}H_{32}N_4O_7 \cdot H_2O$ (650.7): C 66.45, H 5.23, N 8.61; found: C 66.70, H 5.23, N 8.40.

17. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-D-ribofuranosyl]naphtho[2,3-g]pteridine-2,4(1H,3H)-dione* (**31**). As described in *Exper. 16*, with **25** (1.14 g, 3 mmol), 4,4'-dimethoxytrityl chloride (1.12 g, 3.3 mmol), and dry pyridine (100 ml). Workup with $CHCl_3$ (80 ml), sat. $NaHCO_3$ soln. (2 × 50 ml) and purification by FC (SiO_2, 1.5 × 15 cm), toluene/AcOEt 4:1, 2:1, and 1:1) gave a solid: 1.72 g (84%). M.p. 170–171°. UV (MeOH): 446 (3.23), 390 (4.20), 373 (4.03), 291 (sh, 4.60), 282 (4.64), 239 (4.70), 203 (4.87). ^{1}H-NMR ((D_6)DMSO): 12.05 (*s*, NH); 8.89 (*s*, arom. H); 8.29 (*m*, 1 arom. H); 8.12 (*d*, 1 arom. H); 7.67 (*m*, 1 arom. H); 7.29 (*d*, 1 arom. H); 7.04–7.17 (*m*, 7 arom. H, H–C(1')); 6.64 (*m*, H_o to MeO); 5.23 (*d*, OH–C(3')); 4.65 (*m*, H–C(3')); 4.02 (*m*, H–C(4')); 3.63 (*s*, MeO); 3.57 (*s*, MeO); 3.49 (*m*, 1 H–C(5')); 3.30 (*m*, 1 H–C(5')); 2.92 (*m*, 1 H–C(2')); 2.22 (*m*, 1 H–C(2')). Anal calc. for $C_{40}H_{34}N_4O_7$ (682.7): C 70.37, H 5.02, N 8.21; found: C 70.18, H 5.10, N 7.58.

18. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-D-ribofuranosyl]naphtho[1,2-g]pteridine-2,4(1H,3H)-dione* (**32**). To a soln. of **26** (0.5 g, 1.3 mmol) in dry pyridine (35 ml), 4,4'-dimethoxytrityl chloride (0.542 g, 1.6 mmol) was added and stirred at r.t. for 18 h. The mixture was diluted with MeOH (5 ml) and evaporated. The residue was partitioned between CH_2Cl_2 (120 ml) and sat. $NaHCO_3$ soln. (75 ml). The org. layer was washed with sat. $NaHCO_3$ soln. (75 ml), dried (Na_2SO_4), and evaporated. Purification by FC (SiO_2, 0.5 × 10 cm, toluene/AcOEt 6:1, 2:1, and 1:1) gave an amorphous solid: 0.84 g (94%). UV (MeOH): 400 (4.13), 389 (sh, 4.05), 299 (4.26), 288 (sh, 4.28), 280 (4.30), 238 (4.79), 232 (sh, 4.74). ^{1}H-NMR ((D_6)DMSO): 12.09 (*s*, NH); 9.05 (*d*, 1 arom. H); 8.28 (*d*, 1 arom. H); 8.13 (*d*, 1 arom. H); 7.80–7.91 (*m*, 2 arom. H); 7.53 (*m*, 1 arom. H); 7.31 (*d*, 2 arom. H); 7.02–7.27 (*m*, 7 arom. H, H–C(1')); 6.65 (*m*, H_o to MeO); 5.23 (*d*, OH–C(3')); 4.61 (m, H–C(3')); 4.02 (*m*, H–C(4')); 3.61 (*s*, MeO); 3.51 (*s*, MeO); 3.47 (*m*, 1 H–C(5')); 3.24 (*m*, 1 H–C(5')); 2.94 (*m*, 1 H–C(2')); 2.22 (*m*, 1 H–C(2')). Anal. calc. for $C_{40}H_{34}N_4O_7$ (682.7): C 70.37, H 5.02, N 8.21; found: C 70.72, H 5.26, N 7.60.

19. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-D-ribofuranosyl]anthra[1,2-g]pteridine-2,4(1H,3H)-dione* (**33**). As described in *Exper. 18*, with **27** (0.646 g, 1.5 mmol), dimethoxytrityl chloride (0.56 g, 1.65 mmol), and dry pyridine (15 ml). Purification by FC (SiO_2, 1.5 × 15 cm, toluene/AcOEt 1:4, 2:1, and 1:1) gave an orange solid: 0.960 g (87%). UV (MeOH): 443 (4.09), 336 (4.36), 324 (sh, 4.25), 276 (4.91), 268 (sh, 4.81), 258 (sh, 4.72), 231 (4.72). ^{1}H-NMR ($CDCl_3$): 9.51 (*s*, 1 arom. H); 8.18 (*m*, 2 arom. H); 8.02 (*m*, 1 arom. H); 7.86 (*d*, 1 arom. H); 7.64 (*m*, 2 arom. H); 7.10–7.42 (*m*, 10 arom. H, H–C(1')); 6.76 (*m*, 4 H_o to MeO); 4.98 (*q*, H–C(3')); 4.16 (*q*, H–C(4')); 3.65 (*m*, 2 MeO, 1 H–C(5')); 3.47 (*dd*, 1 H–C(5')); 3.10 (*m*, 1 H–C(2')); 2.48 (*m*, 1 H–C(2')); 2.27 (*s*, OH–C(3')). Anal. calc. for $C_{44}H_{36}N_4O_7 \cdot H_2O$ (750.8): C 70.39, H 5.10, N 7.46; found: C 70.44, H 5.24, N 7.21.

20. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-D-ribofuranosyl]pteridine-2,4(1H,3H)-dione 3'-(2-Cyanoethyl Diisopropylphosphoramidite)* (**34**). To a soln. of **28** (0.437 g, 0.75 mmol) and 1*H*-tetrazole (27 mg, 0.38 mmol) in dry CH_2Cl_2/MeCN 1:1 (10 ml) was added (2-cyanoethoxy)bis(diisopropylamino)phosphine (0.452 g, 1.5 mmol) [20]. The mixture was stirred 4 h at r.t. under N_2 and then diluted with CH_2Cl_2 (10 ml). The org. layer was washed with sat. $NaHCO_3$ soln. (2 × 50 ml), dried (Na_2SO_4), and evaporated. Purification by FC (SiO_2, 2 × 14 cm;

toluene/AcOEt 6:1, 4:1, 1:1, and 1:2) gave an amorphous solid: 0.44 g (76%). UV ($CHCl_3$): 316 (3.79), 274 (sh, 3.57), 233 (4.47). ^{1}H-NMR ($CDCl_3$): 8.56, 8.41 (*2m*, H–C(6), H–C(7)); 7.41 (*q*, 2 arom. H); 7.16–7.33 (*m*, 8 arom. H, H–C(1')); 6.74 (*m*, 4 H_o to MeO); 4.76 (*m*, H–C(3')); 4.21 (*m*, H–C(4')); 3.75 (*s*, 2 MeO); 3.36–3.63 (*m*, CH_2CH$_2$CN, 2 MeC*H*, 2 H–C(5'), 1 H–C(2')); 2.59 (*t*, 1 H, CH$_2$CH_2CN); 2.49 (*m*, 2 H, CH$_2$CH_2CN, 1 H–C(2')); 1.17 (*m*, 8 H, Me); 1.07 (*d*, 4 H, Me). ^{31}P-NMR ($CDCl_3$): 149.08, 149.05. Anal. calc. for $C_{41}H_{47}N_6O_8P$ (782.8): C 62.91, H 6.05, N 10.74; found: C 63.54, N 6.15, H 10.18.

21. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]-6,7-diphenylpteridine-2,4(1*H*,3*H*)-dione 3'-(2-Cyanoethyl Diisopropylphosphoramidite)* (**35**). As described in *Exper. 20*, with **29** (0.515 g, 0.7 mmol), 1*H*-tetrazole (25 mg, 0.35 mmol), (2-cyanoethoxy)bis(diisopropylamino)phosphine (0.422 g, 1.4 mmol) [20], and CH_2Cl_2/MeCN 1:1 (14 ml). FC (SiO_2, 2 × 14 cm, toluene/AcOEt 5:1 and 4:1) gave an amorphous solid: 0.52 g (81%). UV (MeOH): 356 (4.22), 331 (sh, 4.03), 273 (4.41), 224 (4.74). ^{1}H-NMR ($CDCl_3$): 7.11–7.45 (*m*, 19 arom. H, H–C(1')); 6.65 (*m*, 4 H_o to MeO); 4.66 (*m*, H–C(3')); 4.16 (*m*, H–C(4')); 2.98–3.78 (*m*, 2 MeO, 2 MeC*H*, CH_2CH$_2$CN, 2 H–C(5'), 1 H–C(2')); 2.54 (*t*, 1 H, CH$_2$CH_2CN); 2.49 (*m*, 1 H–C(2')); 2.28 (*t*, 1 H, CH$_2$CH_2CN); 1.13 (*m*, 8 H, *Me*$_2$CH); 0.94 (*d*, 4 H, *Me*$_2$CH). ^{31}P-NMR($CDCl_3$): 149.96, 149.56. Anal. calc. for $C_{53}H_{55}N_6O_8P$ (935.0): C 68.08, H 5.93, N 8.99; found: C 68.32, H 5.96, N 8.40.

22. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]benzo[g]pteridine-2,4(1*H*,3*H*)-dione 3'-(2-Cyanoethyl Diisopropylphosphoramidite)* (**36**). As described in *Exper. 20*, with **30** (0.683 g, 1 mmol), 1*H*-tetrazole (35 mg, 0.5 mmol), (2-cyanoethoxy)bis(diisopropylamino)phosphine (0.603 g, 2 mmol) [20], and CH_2Cl_2/MeCN 1:1 (10 ml). FC (SiO_2, 2 × 14 cm, petroleum ether/AcOEt 1:1, 2:1, and 2:3) gave an amorphous solid: 0.77 g (92%). UV ($CHCl_3$): 370 (3.80), 321 (3.79), 256 (sh, 4.39), 237 (4.65). ^{1}H-NMR ($CDCl_3$): 8.32 (*d*, 1 arom. H); 7.39 (*m*, 3 arom. H); 7.40 (*m*, 3 arom. H); 7.23 (*m*, 3 arom. H, H–C(1')); 7.13 (*m*, 3 arom. H); 6.67 (*m*, 4 H_o to MeO); 4.94 (*m*, H–C(3')); 4.32 (*m*, H–C(4')); 3.43–3.89 (*m*, 2 MeO, CH_2CH$_2$CN, 2 MeC*H*, 2 H–C(5')); 3.11 (*m*, 1 H–C(2')); 2.61 (*t*, 1 H, CH$_2$CH_2CN); 2.50 (*m*, 1 H–C(2')); 2.44 (*m*, 1 H, CH$_2$CH_2CN); 1.05–1.29 (*m*, 2 *Me*$_2$CH). ^{31}P-NMR($CDCl_3$): 149.3, 149.5. Anal. calc. for $C_{45}H_{49}N_6O_8P$ (832.9): C 64.89, H 5.93, N 10.09; found: C 64.07, H 6.05, N 9.84.

23. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]naphtho[2,3-g]pteridine-2,4(1*H*,3*H*)-dione 3'-(2-Cyanoethyl Diisopropylphosphoramidite)* (**37**). As described in *Exper. 20*, with **31** (1.03 g, 1.5 mmol), 1*H*-tetrazole (53 mg, 0.75 mmol), (2-cyanoethoxy)bis(diisopropylamino)phosphine (0.904 g, 3 mmol) [20], and CH_2Cl_2/MeCN 1:1 (30 ml). After stirring overnight, the mixture was diluted with CH_2Cl_2 (100 ml), the org. layer washed with sat. $NaHCO_3$ soln. (2 × 50 ml), dried (Na_2SO_4), and evaporated. Purification by FC (SiO_2, 1.5 × 10 cm, petroleum ether/acetone 3:2, 1:1, and 2:3) gave an amorphous solid: 1.20 g (91%). UV ($CHCl_3$): 442 (3.41), 395 (4.27), 375 (4.04), 295 (4.71), 289 (sh, 4.69), 243 (4.66). ^{1}H-NMR ((D$_6$)DMSO): 12.05 (*s*, NH); 8.91 (*s*, 1 arom. H); 8.28 (*d*, 2 arom. H); 8.05 (*t*, 1 arom. H); 7.59–7.78 (*m*, 2 arom. H); 7.05–7.37 (*m*, 9 arom. H, H–C(1')); 6.55–6.76 (*m*, 4 H_o to MeO); 4.93 (*m*, H–C(3')); 4.20 (*m*, H–C(4')); 3.42–3.78 (*m*, 2 MeO, CH_2CH$_2$CN, 2 Me$_2$C*H*, 1 H–C(5')); 3.29 (*m*, with H_2O, 1 H–C(5')); 2.98 (*m*, H–C(2')); 2.65, 2.77 (*2t*, CH$_2$CH_2CN); 2.48 (*m*, with DMSO, 1 H–C(2')); 0.94–1.22 (*m*, 2 *Me*$_2$CH). ^{31}P-NMR ((D$_6$)DMSO): 149.18, 149.36. Anal. calc. for $C_{49}H_{51}N_6O_8P$ (883.0): C 66.66, H 5.82, N 9.52; found: C 66.16, H 6.03, N 9.33.

24. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]naphtho[1,2-g]pteridine-2,4(1*H*,3*H*)-dione 3'-(2-Cyanoethyl Diisopropylphosphoramidite)* (**38**). As described in *Exper. 20*, with **32** (0.1 g, 0.15 mmol), 1*H*-tetrazole (5.6 mg, 0.08 mmol), (2-cyanoethoxy)bis(diisopropylamino)phosphine (0.12 g, 0.39 mmol) [20], and CH_2Cl_2/MeCN 3:1 (4 ml). FC (SiO_2, 1 × 14 cm, petroleum ether/acetone 4:1, 2:1, and 1:1) gave a yellow foam: 0.116 g (87%). UV ($CHCl_3$): 400 (4.16), 386 (4.08), 300 (4.33), 282 (4.38). ^{1}H-NMR ($CDCl_3$): 9.51 (*d*, 1 arom. H); 8.09 (*dd*, 1 arom. H); 7.93 (*dd*, 1 arom. H); 7.81 (*m*, 2 arom. H); 7.58 (*t*, 1 arom. H); 7.41 (*dd*, 3 arom. H); 7.28 (*m*, 2 arom. H); 7.05–7.19 (*m*, 4 arom. H, H–C(1')); 6.65 (*m*, 4 H_o to MeO); 4.97 (*m*, H–C(3')); 4.31 (*m*, H–C(4')); 3.43–3.89 (*m*, 2 MeO, CH_2CH$_2$CN, 2 Me$_2$C*H*, 2 H–C(5')); 3.14 (*m*, 1 H–C(2')); 2.60 (*t*, 1 H, CH$_2$CH_2CN); 2.48 (*m*, 1 H–C(2')); 2.44 (*t*, 1 H, CH$_2$CH_2CN); 1.08–1.25 (*m*, 2 *Me*CH). ^{31}P-NMR ($CDCl_3$): 149.44, 149.22. Anal. calc. for $C_{49}H_{51}N_6O_8P$ (887.0): C 66.36, H 5.79, N 9.48; found: C 66.37, H 5.92, N 9.22.

25. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]anthra[1,2-g]pteridine-2,4(1*H*,3*H*)-dione 3'-(2-Cyanoethyl Diisopropylphosphoramidite)* (**39**). As described in *Exper. 20*, with **33** (0.513 g, 0.7 mmol), 1*H*-tetrazole (25 mg, 0.35 mmol), (2-cyanoethoxy)bis(diisopropylamino)phosphine (0.422 g) [20], and MeCN/CH_2Cl_2 1:1 (4 ml). FC (SiO_2, 1.5 × 14 cm, petroleum ether/AcOEt 1:1 and 2:3) gave an amorphous powder: 0.605 g (93%). UV ($CHCl_3$): 441 (4.10), 424 (sh, 4.04), 336 (4.36), 276 (4.94), 276 (4.94), 268 (sh, 4.82), 258 (sh, 4.70), 232 (4.69). ^{1}H-NMR ($CDCl_3$): 9.77 (*s*, 1 arom. H); 8.39 (*s*, 1 arom. H); 8.27 (*m*, 1 arom. H); 8.11 (*m*, 2 arom. H); 7.67 (*m*, 2 arom. H); 7.43 (*m*, 4 arom. H); 7.30 (*m*, 4 arom. H); 7.12 (*m*, 2 arom. H, H–C(1')); 6.68 (*m*, 4 H_o to MeO); 4.94 (*m*, H–C(3')); 4.34 (*m*, H–C(4')); 3.45–3.88 (*m*, 2 MeO, CH_2CH$_2$CN, 2 Me$_2$C*H*, 2 H–C(5')); 3.15 (*m*, 1 H–C2')); 2.42 (*t*, 1 H, CH$_2$CH_2CN); 2.50 (*m*, 1 H–C(2'); 2.45 (*t*, 1 H, CH$_2$CH_2CN); 1.10–1.23

(*m*, 2 Me_2CH). ^{31}P-NMR ($CDCl_3$): 149.17, 149.48. Anal. calc. for $C_{53}H_{53}N_6O_8P$ (933.0): C 68.23, H 5.73, N 9.00; found: 68.04, H 5.77, N 8.77.

26. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]pteridine-2,4(1*H*,3*H*)-dione 3'-(Hydrogen Butanedioate)* (**40**). After co-evaporation of **28** (0.35 g, 0.6 mmol) with dry pyridine (2 × 10 ml), the residue was dissolved in dry CH_2Cl_2 (10 ml), and then DMAP (8 mg, 0.8 mmol) and succinic anhydride (80 mg, 0.8 mmol) were added. The mixture was stirred for 2 days at r.t. and then diluted with CH_2Cl_2 (10 ml), washed with H_2O (50 ml), 10% citric acid soln. (4 × 10 ml), and again with H_2O (2 × 10 ml). The org. phase was dried (Na_2SO_4) and evaporated to give a colourless foam: 0.384 g (93%). UV (MeOH): 317 (3.76), 233 (4.43). ^{1}H-NMR ($CDCl_3$): 8.62 (*m*, NH), 8.52, 8.22 (2*d*, H–C(6), H–C(7)); 7.17–7.43 (*m*, 8 arom. H); 6.77 (*m*, 4 H_o to MeO); 5.48 (*m*, H–C(3')); 4.32 (*m*, H–C(4')); 3.77 (*s*, 2 MeO); 3.45 (*m*, 1 H–C(5')); 3.35 (*m*, 1 H–C(5')); 3.1 (*m*, 1 H–C(2')); 2.61–2.74 (*m*, CH_2CH_2); 2.37 (*m*, 1 H–C(2')).

27. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]-6,7-diphenylpteridine-2,4(1*H*,3*H*)-dione 3'-(Hydrogen Butanedioate)* (**41**). After co-evaporation of **29** (0.441 g, 0.6 mmol) with dry pyridine (3 × 10 ml), the residue was dissolved in dry pyridine (15 ml) and Et_3N (26 µl, 1.9 mmol), and then DMAP (87 mg, 0.7 mmol) and succinic anhydride (0.188 g, 1.9 mmol) were added and stirred at r.t. for 5 h. After evaporation and coevaporation with toluene (2 × 20 ml), the residue was purified by FC (SiO_2, 1 × 12 cm, CH_2Cl_2/MeOH/Et_3Nt_3). The main fraction was evaporated, the residue dissolved in CH_2Cl_2 (20 ml), and the soln. extracted with 10% citric acid (2 × 20 ml) and H_2O (20 ml), dried (Na_2SO_4), and again evaporated to give a colourless solid: 0.443 g (78%). UV (MeOH): 357 (4.12), 273 (4.29), 224 (4.64). ^{1}H-NMR ($CDCl_3$): 7.40 (*m*, 3 arom. H); 7.16–7.32 (*m*, 3 arom. H); 7.03–7.11 (*m*, 16 arom. H, H–C(1')); 6.63 (*m*, 4 H_o to MeO); 5.34 (*m*, H–C(3')); 4.24 (*m*, H–C(4')); 3.74 (*s*, 2 MeO); 3.33 (*m*, 1 H–C(5')); 3.15 (*m*, 1 H–C(5')); 2.88 (*m*, 1 H–C(2')); 2.57 (*d*, CH_2CH_2); 2.49 (*m*, 1 H–C(2')). Anal. calc. for $C_{48}H_{42}N_4O_{10} \cdot H_2O$ (852.89): C 67.59, H 5.20, N 6.56; found: C 67.87, H 5.17, N 6.52.

28. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]benzo[*g*]pteridine-2,4(1*H*,3*H*)-dione 3'-(Hydrogen Butanedioate)* (**42**). To a soln. of **30** (0.189 g, 0.3 mmol) in dry CH_2Cl_2 (7 ml), DMAP (49 mg, 0.4 mmol) and succinic anhydride (41 mg, 0.4 mmol) were added and stirred for 3 days at r.t. Then the mixture was diluted with CH_2Cl_2 (30 ml), washed with 10% citric acid soln. (3 × 50 ml) and H_2O (3 × 30 ml), dried (Na_2SO_4), and evaporated to give a colourless foam: 0.225 g (99%). UV (MeOH): 371 (3.82), 321 (3.85), 254 (sh, 4.49), 237 (4.69), 213 (4.81). ^{1}H-NMR ($CDCl_3$): 8.27 (*d*, 1 arom. H); 7.78 (*m*, 2 arom. H); 7.62 (*d*, 1 arom. H); 7.37 (*d*, 2 arom. H); 7.08–7.29 (*m*, 7 arom. H, H–C(1')); 6.69 (*m*, 4 H_o to MeO); 5.77 (*m*, H–C(3')); 4.42 (*q*, H–C(4')); 3.73 (*s*, MeO); 3.71 (*s*, MeO); 3.57 (*dd*, 1 H–C(5')); 3.45 (*dd*, 1 H–C(5')); 3.26 (*m*, 1 H–C(2')); 2.55–2.81 (*m*, CH_2CH_2); 2.48 (*m*, 1 H–C(2')). Anal. calc. for $C_{40}H_{38}N_4O_{10} \cdot H_2O$ (752.8): C 63.82, H 5.36, N 7.44; found: C 63.71, H 5.13, N 7.05.

29. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]naphtho[2,3-*g*]pteridine-2,4(1*H*,3*H*)-dione 3'-(Hydrogen Butanedioate)* (**43**). As described in *Exper. 28*, with **31** (0.205 g, 0.3 mmol), DMAP (49 mg, 0.4 mmol), succinic anhydride (41 mg, 0.4 mmol), and CH_2Cl_2 (25 ml). The product (quant.) was further purified by FC (SiO_2, 1.5 × 14 cm, toluene/AcOEt 6:1 to 1:2) to give an amorphous solid: 0.19 g (81%). UV ($CHCl_3$): 446 (3.23), 394 (4.23), 374 (4.04), 295 (4.67), 243 (4.62). ^{1}H-NMR ($CDCl_3$): 8.84 (*s*, 1 arom. H); 8.62 (*d*, 1 arom. H); 8.25 (*s*, 1 arom. H); 8.07 (*d*, 1 arom. H); 7.92 (*d*, 1 arom. H); 7.57 (*m*, 2 arom. H); 7.02–7.34 (*m*, 8 arom. H, H–C(1')); 6.60 (*m*, 4 H_o to MeO); 5.83 (*m*, H–C(3')); 4.38 (*m*, H–C(4')); 3.65 (*m*, 2 MeO, 1 H–C(5')); 3.48 (*m*, 1 H–C(5')); 3.34 (*m*, 1 H–C(2')); 2.62–2.81 (*m*, CH_2CH_2); 2.47 (*m*, 1 H–C(2')). Anal. calc. for $C_{44}H_{38}N_4O_{10} \cdot H_2O$ (800.8): C 65.99, H 5.03, N 6.99; found: C 66.60, H 5.14, N 7.22.

30. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]naphtho[1,2-*g*]pteridine-2,4(1*H*,3*H*)-dione 3'-(Hydrogen Butanedioate)* (**44**). As described in *Exper. 28*, with **32** (68 mg, 0.1 mmol), DMAP (16.4 mg, 0.13 mmol), succinic anhydride (13.4 mg, 0.13 mmol), and CH_2Cl_2 (5 ml): 77 mg (98%) of amorphous solid. UV (MeOH): 400 (4.14), 388 (sh, 4.19), 298 (4.32), 288 (sh, 4.33), 280 (4.34), 238 (4.83). ^{1}H-NMR ($CDCl_3$): 11.21 (br. s, NH); 9.18 (*d*, 1 arom. H); 7.98 (*d*, 1 arom. H); 7.86 (*d*, 1 arom. H); 7.77 (*m*, 2 arom. H); 7.06–7.42 (*m*, 10 arom. H, H–C(1')); 6.66 (*m*, 4 H_o to MeO); 5.79 (*m*, H–C(3')); 4.40 (*q*, H–C(4')); 3.62 (*s*, MeO); 3.66 (*s*, MeO); 3.57 (*m*, 1 H–C(5')); 3.45 (*m*, 1 H–C(5')); 3.45 (*m*, 1 H–C(2')); 2.61–2.85 (*m*, CH_2CH_2); 2.49 (*m*, 1 H–C(2')). Anal. calc. for $C_{44}H_{33}N_4O_{10} \cdot H_2O$ (800.8): C 65.99, H 5.03, N 6.99; found: C 66.05, H 5.18, N 6.86.

31. *1-[2'-Deoxy-5'-O-(4,4'-dimethoxytrityl)-β-*D*-ribofuranosyl]anthra[1,2-*g*]pteridine-2,4(1*H*,3*H*)-dione 3'-(Hydrogen Butanedioate)* (**45**). As described in *Exper. 28*, with **33** (0.205 g, 0.3 mmol), DMAP (49 mg, 0.4 mmol), succinic anhydride (41 mg, 0.4 mmol), and CH_2Cl_2 (7 ml). Workup led to an amorphous solid: 0.248 g (95%). UV (MeOH): 444 (4.08), 336 (4.34), 324 (sh, 4.23), 276 (4.90), 268 (sh, 4.80), 257 (sh, 4.70), 231 (4.69). ^{1}H-NMR ($CDCl_3$): 10.02 (*s*, NH); 9.52 (*s*, 1 arom. H); 8.23 (*s*, 1 arom. H); 8.15 (*m*, 1 arom. H); 7.98 (*m*, 1 arom. H);

7.94 (*d*, 1 arom. H); 7.61 (*m*, 2 arom. H); 7.39 (*d*, 2 arom. H); 7.05–7.28 (*m*, 8 arom. H, H–C(1')); 6.66 (*m*, 4 H_o to MeO); 5.77 (*m*, H–C(3')); 4.39 (*q*, H–C(4')); 3.64 (*s*, MeO); 3.59 (*s*, MeO); 3.55 (*m*, 1 H–C(5')); 3.44 (*m*, 1 H–C(5')); 3.22 (*m*, 1 H–C(2')); 2.68–2.83 (*m*, CH_2CH_2); 2.49 (*m*, 1 H–C(2')). Anal. calc. for $C_{48}H_{40}N_4O_{10} \cdot H_2O$ (851.0): C 67.76, H 4.97, N 6.58; found: C 67.46, H 5.17, N 6.14.

32. *Solid-Support LCMAA-CPG 500-Å Material* **46**–**51**. To a mixture of LCMAA-CPG 500-Å (100 mg) [21] [22] and 16 μmol of **40** (11 mg), **41** (14 mg), **42** (12 mg), **43** (13 mg), **44** (13 mg), or **45** (14 mg), resp., in *N*-methylmorpholine (5 ml) and dry MeCN (3 ml) was added TOTU (6 mg, 18 μmol) [23] with gentle shaking. After reaction for 3 h at r.t., the CPG material was collected and washed with DMF, MeOH, acetone, and Et_2O. Then the nucleoside-functionalized CPG material was capped by gentle shaking with DMAP (25 mg, 0.2 mmol), in dry pyridine (5 ml) and Ac_2O (0.5 ml, 5.3 mmol) at r.t. for 20 min. Thereafter, **46**–**51** were collected and washed with DMF, H_2O, MeOH, acetone, and Et_2O. The loading *L* (in μmol/g support) was determined by UV (498 nm) of the cleaved $(MeO)_2Tr$ group yielding *L* = 28 (**46**), 35 (**47**), 36 (**48**), 18 (**49**), 23 (**50**), and 36 (**51**).

33. *Assembly of Oligonucleotides*. Syntheses were carry out using an *Applied Biosystems 392 DNA/RNA* synthesizer according to the described procedure [25].

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