

100. Nucleosides

Part L¹⁾

Structure of Lumazine *N*¹-(2'-Deoxy-D-ribonucleosides) (= 1-(2'-Deoxy-D-ribofuranosyl)pteridine-2,4(1*H*,3*H*)-diones): A Revision of the Anomeric Configuration

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The anomeric configuration of the glycosidic bond in lumazine *N*¹-(2'-deoxy-D-ribonucleosides) **1–6** was investigated by NOE difference spectroscopy. The former configurational assignment of the α - and β -D-anomers **1** and **2**, **3** and **4**, and **5** and **6**, respectively, has to be reversed to be in agreement with the physical data. Additional proof is presented by X-ray analysis of **3** and **6**. Chemical interconversions of 1-(2'-deoxy- β -D-ribofuranosyl)-6,7-diphenyllumazine (**6**) into 2,3'-anhydrolumazine 2'-deoxyribonucleosides **16** and **17** are also in agreement with the revised anomeric configuration.

1. Introduction. – Lumazine *N*¹-ribonucleosides and *N*¹-(2'-deoxyribonucleosides) (= 1-(D-ribofuranosyl)- and 1-(2'-deoxy-D-ribofuranosyl)pteridine-2,4(1*H*,3*H*)-diones) can be regarded as structural analogs of uridine and thymidine, respectively, and were therefore, synthesized in our laboratory in 1970 [2], expecting some biological activity. However, so far no antibacterial, antiviral, or antitumor activity was found. The physical properties of these compounds are still of interest due to the fluorescence [3] [4] of the nucleobase.

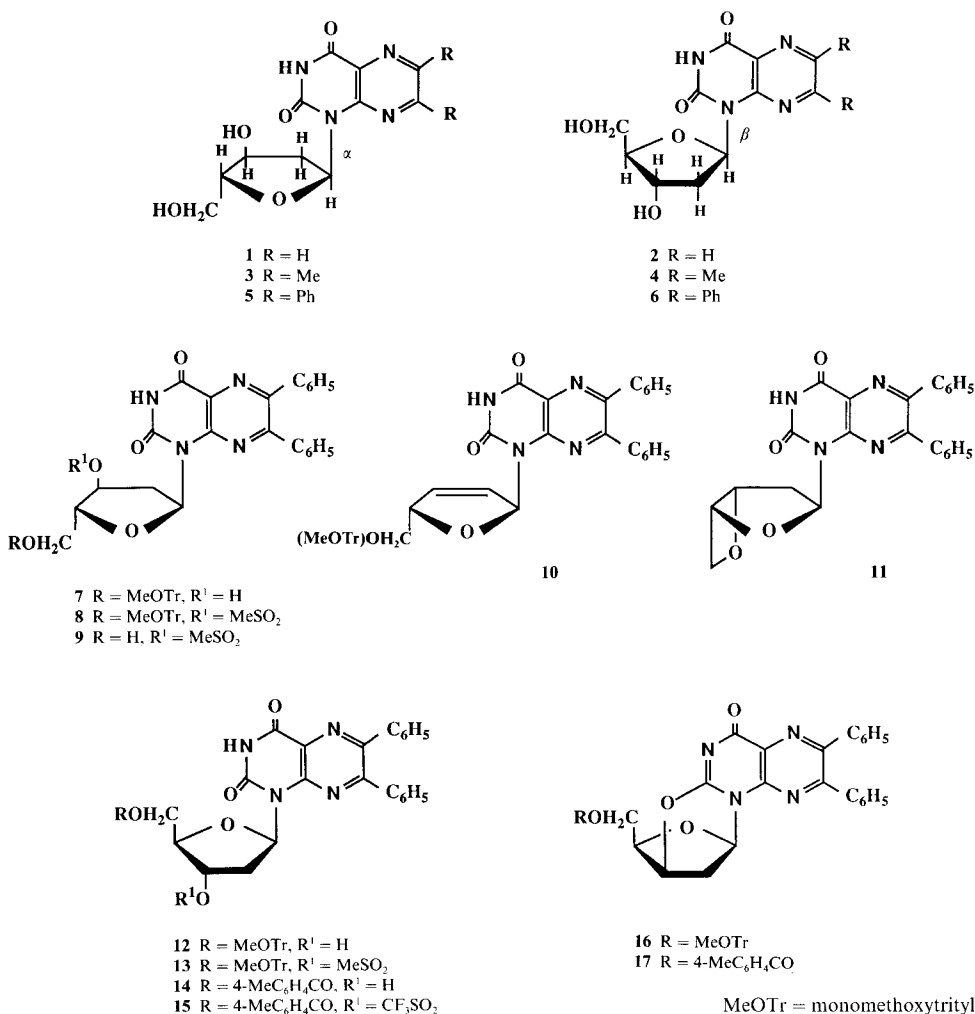
The structural assignment of the *N*-glycosidic bond in the 1-(β -D-ribofuranosyl) lumazines synthesized *via* the *Hilbert-Johnson-Birkofer* procedure [5–7] was based on the *Baker-Tipson* rule [8] (β -D-ribonucleoside formation). Analogous glycosylations in the 2'-deoxyribofuranose series lacking the neighbouring-group-participation effect of the 2'-acyloxy function are less selective and lead usually to α,β -D-anomeric mixtures, which have to be separated by tedious chromatographical techniques.

In an earlier paper [2], the configuration of the glycosidic bond of the 1-(2'-deoxy-D-ribofuranosyl)lumazines was based upon simple chemical-shift data in analogy to the findings in the pyrimidine [9] [10] and purine 2'-deoxy-D-ribofuranoside series [11]. It was stated that the anomeric protons usually appearing as a *quadruplet* (*q*) at lower field is

¹⁾ Part II: [1].

characteristic for the 2'-deoxy- α -D-ribofuranosides, whereas the β -D-anomer shows a *pseudo-triplet* ('t') at higher field. The validity of these assignments has now been questioned by recent studies with the former 1-(2'-deoxy- β -D-ribofuranosyl)-6,7-diphenyllumazine [12], which could not be converted into a 2,3'-anhydronucleoside in the usual manner. Reinvestigation of the configuration of the glycosidic bond became, therefore, necessary by an unambiguous method.

2. Results and Discussion. – The structures in question are the anomeric 1-(2'-deoxy-D-ribofuranosyl)lumazines (**1/2**) and its 6,7-dimethyl and 6,7-diphenyl derivatives **3/4** and **5/6**, respectively. Straightforward results on the assignment of anomeric configurations of nucleosides are available by NOE difference spectroscopy [13] which was now applied to our problem. *Dreiding* models show that in β -D-anomers, H–C(1') and H–C(4') are located in the whole range of N- to S-type conformations [14] in almost the same spacial



proximity on the same side (α) of the sugar moiety. Consequently, H_β -C(2') and H_β -C(3') are positioned on the opposite face. Analogous considerations on 2'-deoxy- α -D-ribonucleosides, bearing H-C(1') and H-C(3') on the β -side of the ribofuranose ring, indicate that the S-type puckered conformation causes a large H-C(1'), H-C(3') distance which is shortened on pseudorotational interconversion towards the N-type conformation.

Saturation of the ^1H -NMR signal ((D_6) DMSO) of the anomeric H-C(1') in the 1-(2'-deoxy- β -D-ribofuranosyl)lumazines **2**, **4**, and **6** causes characteristic NOE's on H-C(4') (1.5–2.7%) and H_α -C(2') (5.5–7.9%), whereas no signal enhancement is observed for H-C(3') and H_β -C(2') (see *Table 1*). The corresponding α -D-anomers **1**, **3**, and **5** exhibit consequently typical NOE's on H-C(3') (1.5–2.8%) and H_β -C(2') (5.5–7.1%) and no signal changes for H-C(4') and H_α -C(2').

Table 1. NOE Data and Chemical Shifts of 2 H-C(2') of 1-(2'-Deoxy- α - and - β -D-ribofuranosyl)lumazines in (D_6) DMSO

	NOE [%] on irradiation of H-C(1')				Chemical shift δ [ppm]		$\Delta\delta$
	H_α -C(2')	H_β -C(2')	H-C(3')	H-C(4')	H_α -C(2')	H_β -C(2')	
1	0	6.7	2.8	0	2.70	2.36	0.34
2	7.9	0	0	2.7	2.03	2.83	0.80
3	0	6.1	2.8	0	2.75	2.35	0.40
4	6.3	0	0	1.5	2.03	2.85	0.82
5	0	5.5	1.5	0	2.83	2.40	0.43
6	5.5	0	0	1.5	2.07	2.95	0.88

A more simple possibility to assign the anomeric configuration in pteridine 2'-deoxy-D-ribonucleosides consists in the analysis of the chemical-shift difference of the H_α -C(2') and H_β -C(2') signals. In the α -D-anomers, these differences are always smaller than in the β -D-anomers [15] (see *Table 1*), which seems to be an indication of a more favoured and more restricted S-type puckered conformation in the β -D-anomer and a more flexibel situation in the α -D-anomer.

The 1-(2'-deoxy- α -D-ribofuranosyl)-6,7-dimethylumazine (**3**) and the 1-(2'-deoxy- β -D-ribofuranosyl)-6,7-diphenylumazine (**6**) could be crystallized and their structures established unambiguously by X-ray analyses (see *Figs. 1* and *2* and *Table 2*).

The data were collected on a Nicolet-R3m four-circle diffractometer fitted with a LT1 cooling apparatus. The structures were determined by direct methods using the SHELXTL PLUS (VAX II) system. The coordinates and geometrical data were deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW, UK.

The correct structural assignments of **5** and **6** enabled us to perform also a series of intramolecular interconversions which could not be achieved before. Thus, α -D-anomer **5** was first converted into 5'-O-monomethoxytrityl derivative **7** [15] and then mesylated ($\rightarrow$ **8**). Treatment of **8** with Et_3N , NaOMe, or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) did not result in any reaction, but *t*-BuOK treatment afforded the elimination product **10**. Acid detritylation of **8** to **9** and subsequent treatment with *t*-BuOK in DMF led to 3',5'-anhydro derivative **11**.

In an analogous series of reactions, β -D-anomer **6** was transformed *via* the 5'-O-monomethoxytrityl derivative **12** [15] into its 5'-O-(monomethoxytrityl)-3'-O-mesyl

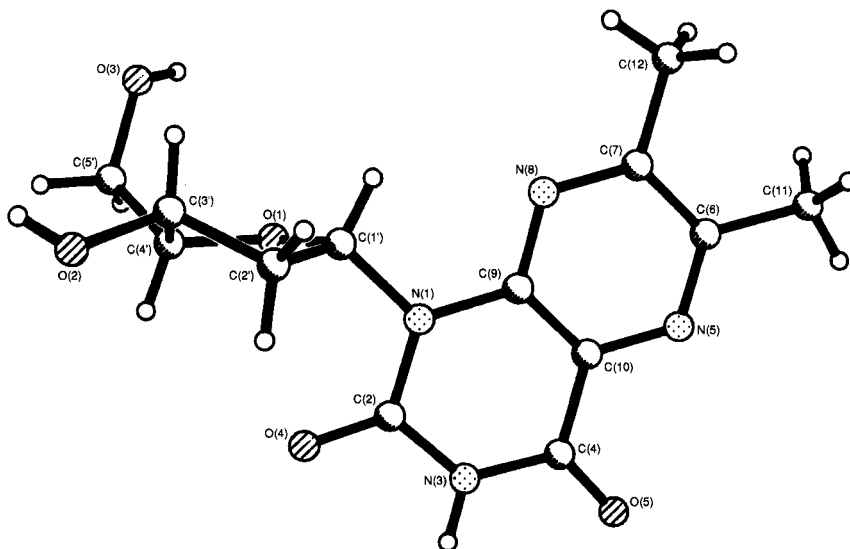


Fig. 1. Crystal structure of 1-(2'-deoxy-α-D-ribofuranosyl)-6,7-dimethylumazine (3). Arbitrary numbering.

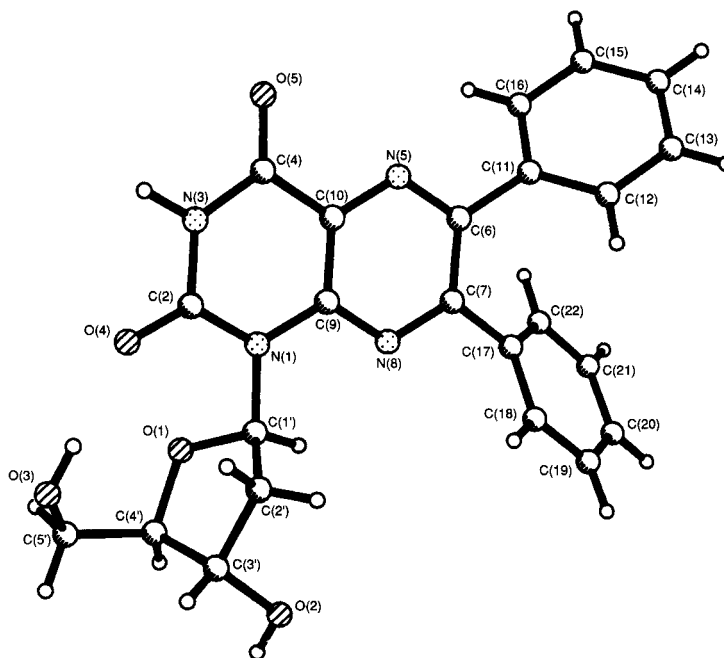


Fig. 2. Crystal structure of 1-(2'-deoxy-β-D-ribofuranosyl)-6,7-diphenyllumazine (6). Arbitrary numbering.

Table 2. *Crystallographic Data of 1-(2'-Deoxy- α -D-ribofuranosyl)-6,7-dimethylumazine (3) and 1-(2'-Deoxy- β -D-ribofuranosyl)-6,7-diphenylumazine (6)*

	3	6
<i>Crystal Data</i>		
Empirical formula	C ₁₃ H ₁₆ N ₄ O ₅	C ₂₃ H ₂₀ N ₄ O ₅
Colour, habit	colourless, prismatic	colourless, prismatic
Crystal size [mm]	0.25 × 0.4 × 0.4	0.25 × 0.25 × 0.4
Crystal system	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit-cell dimensions <i>a</i> [Å]	6.604 (3)	9.523 (5)
<i>b</i> [Å]	10.907 (5)	10.461 (4)
<i>c</i> [Å]	18.975 (8)	21.038 (10)
<i>V</i> [Å ³]	1366.8 (11)	2095.8 (17)
<i>Z</i>	4	4
Molecular weight	308.3	432.4
Density (calc.) [Mg/m ³]	1.498	1.370
Absorption coefficient	0.110 mm ⁻¹	0.092 mm ⁻¹
<i>F</i> (000)	648	904
Radiation MoK _α λ [Å]	0.71073	0.71073
<i>Data Collection</i>		
<i>T</i> [K]	183	183
2 θ range	0.56°	0.56°
Scan type	ω	ω
Scan speed (variable)	0.50–14.65°/min in ω	0.92–14.65°/min in ω
Scan range (ω)	0.76°	1.10°
Standard reflections	2 measured every 120 reflections	2 measured every 120 reflections
Index ranges	0 ≤ <i>h</i> ≤ 8, 0 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 25	–12 ≤ <i>h</i> ≤ 0, 0 ≤ <i>k</i> ≤ 13, –27 ≤ <i>l</i> ≤ 0
Reflections collected	1945	2925
Independent reflections	1921 (<i>R</i> _{int} 0.00%)	2892 (<i>R</i> _{int} 8.24%)
Observed reflections	1839 (<i>F</i> > 5.0 σ (<i>F</i>))	2127 (<i>F</i> > 5.0 σ (<i>F</i>))
Number of parameter	211	297
Final <i>R</i> index (obs. data)	4.06	4.37

derivative **13**. Treatment of **13** with DBU in CHCl₃ under reflux afforded the anticipated 2,3'-anhydro-xylonucleoside **16** in 87% yield. A similar sequence of reactions took place when **6** was first acylated to its 5'-*O*-(4-toluoyl) derivative **14**, which reacted with trifluoromethane sulfonic anhydride in 1,2-dichloroethane/pyridine *via* **15** directly to the 2,3'-anhydro-xylonucleoside **17**.

3. Conclusions. – All structures of the formerly published 1-(2'-deoxy- α - and β -D-ribofuranosyl)lumazines [2] [5] [13] have to be revised from α -D- to β -D-configuration and *vice versa*, according to NOE difference spectroscopic studies, X-ray analyses, and some chemical interconversions.

We would like to thank Mr. P. Iaiza for excellent technical assistance.

Experimental Part

General. TLC: precoated silica-gel thin-layer sheets *F 1550 LS 254* and cellulose thin-layer sheets *F 1440* from Schleicher & Schüll. Prep. TLC: silica gel 60 *PF₂₅₄* (Merck). Prep. column chromatography: silica gel (Merck 60, 0.063–0.2 mesh). M.p.: Büchi apparatus, model Dr. Tottoli; no corrections. UV: *Uvikon 820*, *Kontron*, and *Perkin-Elmer, Lambda 5*; $\lambda_{\max}$ in nm (lg ϵ). $^1\text{H-NMR}$: *Bruker WM 250* and *Bruker AC-250* with *Aspect-3000* computer and array processor; δ in ppm rel. to TMS; for the NOE measurements, the (D_6)DMSO solns. (0.1M) were degassed, and typical spectral conditions were as follows: number of data points 32 K; pre-irradiation delay 1.6 s; relaxation delay 4.5 s; an irradiation time of 1.5 s with an irradiation power of 40–50 dB below 0.2 W yielded a saturation of $\geq 95\%$; evaluation by the NOEDIFF mode of the *Bruker* software package.

1. 1-[2'-Deoxy-3'-O-mesyl-5'-O-(4-monomethoxytrityl)- α -D-ribofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**8**). A soln. of 1.4 g (2 mmol) of 1-[2'-deoxy-5'-O-(4-monomethoxytrityl)- α -D-ribofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**7**) [15] in 15 ml of abs. pyridine was treated with 0.4 ml MeSO_2Cl for 19 h. The mixture was poured on ice, the precipitate collected and then dissolved in CHCl_3 , the soln. washed with H_2O , dried (Na_2SO_4), and evaporated, and the residue crystallized from 20 ml of EtOH: 1.39 g (88%). Colourless crystals. M.p. 168–171°. UV (MeOH): 360 (4.08), 275 (4.18), 228 (sh, 4.53). $^1\text{H-NMR}$ ((D_6) DMSO): 12.07 (s, NH); 7.07 (t, H-C(1')); 6.81–7.52 (m, 24 arom. H); 5.17 (q, H-C(3')); 4.68 (m, H-C(4')); 3.71 (s, MeO); 3.46 (m, $\text{CH}_2(5')$); 3.11 (s, Me); 3.08 (m, H_α -C(2')); 2.83 (m, H_β -C(2')). Anal. calc. for $\text{C}_{44}\text{H}_{38}\text{N}_4\text{O}_8$ (782.8): C 67.51, H 4.89, N 7.16; found: C 67.32, H 4.93, N 7.11.

2. 1-(2'-Deoxy-3'-O-mesyl- α -D-ribofuranosyl)-6,7-diphenylpteridine-2,4(1H,3H)-dione (**9**). To a soln. of 0.2 g of TsOH in 10 ml of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 4:1 were added 0.078 g (0.1 mmol) of **8** and stirred for 2 h. Then H_2O (5 ml) was added, the mixture neutralized by a NaHCO_3 soln. and extracted twice with CH_2Cl_2 , and the org. layer washed with H_2O , dried (Na_2SO_4), and evaporated: 0.042 g (82%). Colourless solid. M.p. 149–150°. UV (MeOH): 360 (4.16), 275 (4.23), 223 (4.47). $^1\text{H-NMR}$ ((D_6) DMSO): 12.07 (s, NH); 7.32–7.52 (m, 10 arom. H); 7.05 (t, H-C(1')); 5.18 (t, H-C(3')); 4.94 (t, OH-C(5')); 4.44 (m, H-C(4')); 3.41–3.61 (m, $\text{CH}_2(5')$); 3.24 (s, MeO); 3.13 (m, H_α -C(2')); 2.84 (m, H_β -C(2')). Anal. calc. for $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_7 \cdot 0.5 \text{H}_2\text{O}$ (519.5): C 55.48, H 4.46, N 10.78; found: C 55.75, H 4.40, N 10.75.

3. 1-[2',3'-Didehydro-2',3'-dideoxy-5'-O-(4-monomethoxytrityl)- α -D-glycero-pentofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**10**). To a soln. of 0.1 g (0.125 mmol) of **8** in 5 ml of abs. DMF, a soln. of 0.2 g of *t*-BuOK in 2 ml of *t*-BuOH was added. The mixture was heated to 90° for 1 h and then evaporated under high vacuum. The residue was chromatographed (silica gel, column 0.7 $\times$ 6 cm, CHCl_3): 0.072 g (82%). Colourless solid. M.p. 125–127°. UV (MeOH): 361 (4.05), 275 (4.13), 226 (4.49). $^1\text{H-NMR}$ ((D_6) DMSO): 12.1 (s, NH); 8.30 (d, H-C(1')); 6.83–7.64 (m, 24 arom. H); 6.40 (d, H-C(3')); 6.06 (d, H-C(2')); 5.12 (m, H-C(4')); 3.71 (s, MeO); 3.05–3.48 (m, $\text{CH}_2(5')$). Anal. calc. for $\text{C}_{43}\text{H}_{34}\text{N}_4\text{O}_5 \cdot 0.5 \text{H}_2\text{O}$ (695.7): C 74.23, H 5.07, N 8.05; found: C 74.03, H 5.35, N 8.13.

4. 1-(3',5'-Anhydro-2'-deoxy- α -D-xylofuranosyl)-6,7-diphenylpteridine-2,4(1H,3H)-dione (**11**). A soln. of 0.52 g (1 mmol) of **9** in 15 ml of abs. DMF was treated with 0.6 g of *t*-BuOK in 2 ml of *t*-BuOH at r.t. for 30 min and then 5 h at 100°. The solvents were evaporated under high vacuum, and the residue was chromatographed (silica gel, column 0.7 $\times$ 20 cm, $\text{CHCl}_3/\text{MeOH}$ 49:1): 0.22 g (56%). Colourless solid. M.p. 193–196°. UV (MeOH): 360 (4.16), 274 (4.24), 223 (sh, 4.46). $^1\text{H-NMR}$ ((D_6) DMSO): 12.0 (s, NH); 7.37–7.52 (m, H-C(1'), 10 arom. H); 5.48 (t, H-C(3')); 5.04 (d, H-C(4')); 4.16–4.62 (m, $\text{CH}_2(5')$); 2.81 (m, H_α -C(2')); 2.56 (m, H_β -C(2')). Anal. calc. for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_4 \cdot 0.5 \text{H}_2\text{O}$ (423.5): C 65.27, H 4.52, N 13.24; found: C 65.04, H 4.38, N 12.95.

5. 1-[2'-Deoxy-3'-O-mesyl-5'-O-(4-monomethoxytrityl)- β -D-ribofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**13**). A soln. of 1.3 g (1.8 mmol) of 1-[2'-deoxy-5'-O-(4-monomethoxytrityl)- β -D-ribofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**12**) [13] in 15 ml of abs. pyridine was treated dropwise with 0.2 ml of MeSO_2Cl . After stirring at r.t. for 2 h, the mixtures was poured on ice, the precipitate filtered off and dissolved in 20 ml of CHCl_3 , and the soln. washed with H_2O , dried (Na_2SO_4), evaporated to a small volume, and then added dropwise into 50 ml of pentane: 1.15 g (82%). Colourless powder. M.p. 138–141°. UV (MeOH): 357 (4.09), 274 (4.14), 225 (sh, 4.50). $^1\text{H-NMR}$ (CDCl_3): 9.58 (s, NH); 6.69–7.47 (m, H-C(1'), 24 arom. H); 5.38 (q, H-C(3')); 4.18 (q, H-C(4')); 3.73 (s, MeO); 3.30 (m, $\text{CH}_2(5')$); 3.13 (m, H_β -C(2')); 2.83 (s, MeSO_2); 2.78 (m, H_α -C(2')). Anal. calc. for $\text{C}_{44}\text{H}_{38}\text{N}_4\text{O}_8\text{S}$ (791.8): C 67.20, H 4.96, N 7.12; found: C 67.51, H 4.89, N 7.16.

6. 1-[2'-Deoxy-5'-O-(4-toluoyl)- β -D-ribofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**14**). A soln. of 0.7 ml (5 mmol) of 4-toluoyl chloride in 10 ml of 1,2-dichloroethane was added at 0° dropwise to 2.15 g (5 mmol) of 1-(2'-deoxy- β -D-ribofuranosyl)-6,7-diphenylpteridine-2,4(1H,3H)-dione (**6**) [2] [5] in 40 ml of abs. pyridine and stirred for 1 h. The mixture was poured on ice and extracted by CHCl_3 , the soln. washed with NaHCO_3 soln., dried

(Na₂SO₄), and evaporated, and the residue purified by column chromatography (3 × 10 cm, silica gel, toluene/AcOEt 1:2): 2.14 g (77%). Colourless solid. M.p. 159–161°. UV (MeOH): 359 (4.09), 274 (4.11), 230 (4.43). ¹H-NMR ((D₆)DMSO): 12.04 (s, NH); 7.26–7.84 (m, 14 arom. H); 7.17 (dd, H–C(1′)); 5.39 (d, OH–C(3′)); 4.01–4.60 (m, H–C(3′), H–C(4′), CH₂(5′)); 2.95 (m, H_β–C(2′)); 2.37 (s, Me); 2.25 (m, H_α–C(2′)). Anal. calc. for C₃₁H₂₆N₄O₆·0.5 H₂O (559.6): C 66.54, H 4.86, N 10.02; found: C 66.82, H 4.82, N 10.33.

7. 2,3′-Anhydro-1-[2′-deoxy-5′-O-(4-monomethoxytrityl)-β-D-xylofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**16**). A soln. of 0.95 g (1.2 mmol) of **13** in 30 ml of abs. CHCl₃ was treated with 0.5 ml of DBU and then refluxed for 4 h. The mixture was washed twice with H₂O, dried (Na₂SO₄), and evaporated: 0.72 g (87%). Chromatographically pure colourless solid. M.p. 154–156°. UV (MeOH): 360 (4.14), 271 (4.14), 228 (4.52). ¹H-NMR ((D₆)DMSO): 6.71–7.55 (m, H–C(1′), 24 arom. H); 5.56 (s, H–C(3′)); 4.57 (m, H–C(4′)); 3.66 (s, MeO); 3.19 (m, CH₂(5′)); 2.75 (m, H_β–C(2′)); 2.54 (m, H_α–C(2′)). Anal. calc. for C₄₃H₃₅N₄O₅·0.5 H₂O (695.7): C 74.23, H 5.07, N 8.05; found: C 74.22, H 5.45, N 8.00.

8. 2,3′-Anhydro-1-[2′-deoxy-5′-O-(4-toluoyl)-β-D-xylofuranosyl]-6,7-diphenylpteridine-2,4(1H,3H)-dione (**17**). To a mixture of 0.28 g (0.5 mmol) of **14** in 10 ml of 1,2-dichloroethane and 1 ml of abs. pyridine was added dropwise a soln. of 0.09 ml (0.5 mmol) of trifluoromethanesulfonic anhydride in 10 ml of 1,2-dichloroethane. After stirring for 10 min, H₂O was added, the org. layer dried (Na₂SO₄) and evaporated, and the residue crystallized from 3 ml of EtOH: 0.23 g (86%). Colourless crystals. M.p. 173–177°. UV (MeOH): 359 (4.09), 269 (4.09), 230 (4.45). ¹H-NMR ((D₆)DMSO): 7.19–7.84 (m, 14 arom. H); 7.11 (d, H–C(1′)); 5.63 (s, H–C(3′)); 4.70 (m, CH₂(5′)); 4.43 (m, H–C(4′)); 2.76 (m, CH₂(2′)); 2.29 (s, Me). Anal. calc. for C₃₁H₂₄N₄O₅ (534.4): C 68.75, H 4.84, N 10.34; found: C 68.75, H 4.73, N 10.46.

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