186. Reactions of Nucleosides with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). Syntheses of N(3)-Methylene-Bridged Bis-uridines and Secouridine-Dinucleoside Analogs

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(19.IV.93)

Diastereoisomeric secouridine derivatives, appropriately protected and activated, served as starting compounds in the reactions with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in various solvents (CH_2Cl_2, MeCN, or dimethylformamide (DMF)). Reactions with DBU/CH_2Cl_2 gave *N*(3)-methylene-bridged bis-secouridines and bis-uridines (*Scheme 3*), while the reactions with DBU in non-alkylating solvents resulted in formation of secodinucleosides as the result of intermolecular 'dimerizations' (*Scheme 2*).

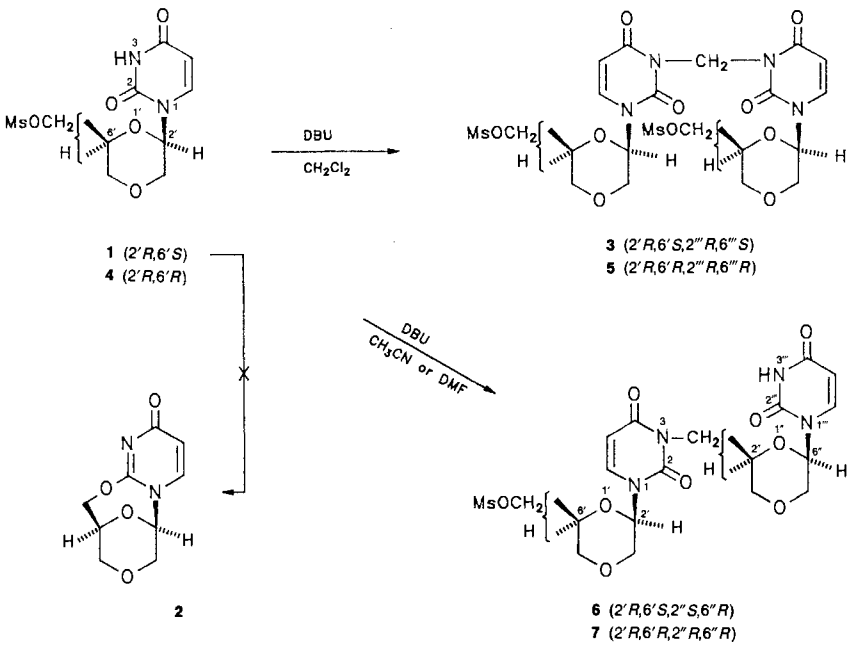
Introduction. – The discovery of acyclovir as an antiviral agent [1] initiated the search for other acyclic nucleosides with potential antiviral activity. Among them are 2′,3′-seconucleosides, the class of compounds that retains the entire C-framework and the chirality at two of four chiral centres of the nucleosidic sugar moiety, but lacking the rigid ring structure. It was rationalized that the flexibility of the acyclic moiety might have prevented their interaction with enzymes to form the corresponding 2′,3′-seconucleotides [2]. However, the free rotation of the acyclic moiety could be restricted by anchoring the chain to the appropriate position of the heterocyclic base giving an anhydro derivative. Aiming to such type of compounds, we planned to prepare 2,3′-anhydro-2′,3′-secouridine and 2,5′-anhydro-2′,3′-secouridine[1]), *i.e.* two diastereoisomeric compounds with a seven-membered dioxazepine ring condensed to uracil. In this respect, we prepared 3′- and 5′-*O*-mesyl derivatives of 2′,3′-secouridines, imagining an intramolecular cyclization through the nucleophilic attack of the pyrimidine C(2)–O^- anion at the C(3′) and C(5′) position, respectively. In the similar intramolecular cyclizations in the uridine series, the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is usually used as a base for proton abstraction from the pyrimidine N(3) [2–4]. We found, however, that instead of the intramolecular cyclizations to dioxazepine structures, intermolecular reactions occurred giving 'dimerization' products or bis-nucleosides with a methylene bridge connecting the N(3) atoms of the two uracil units.

Results and Discussion. – In connection with our work on regioselective transformations of 2′,3′-seconucleosides and their anhydro structures [5] [6], we recently reported on the attempt to perform the intramolecular cyclization of 1-{(2*R*,6*S*)-6-[(mesyloxy)-methyl]-1,4-dioxan-2-yl}uracil[2]) (**1**) into dioxazepine derivative **2** in the presence of DBU

[1]) Nucleoside numbering is used for 2′,3′-secouridines, systematic names are given in the *Exper. Part.*

[2]) Numbering scheme for dioxane derivatives is shown in *Scheme 1.*

Scheme 1



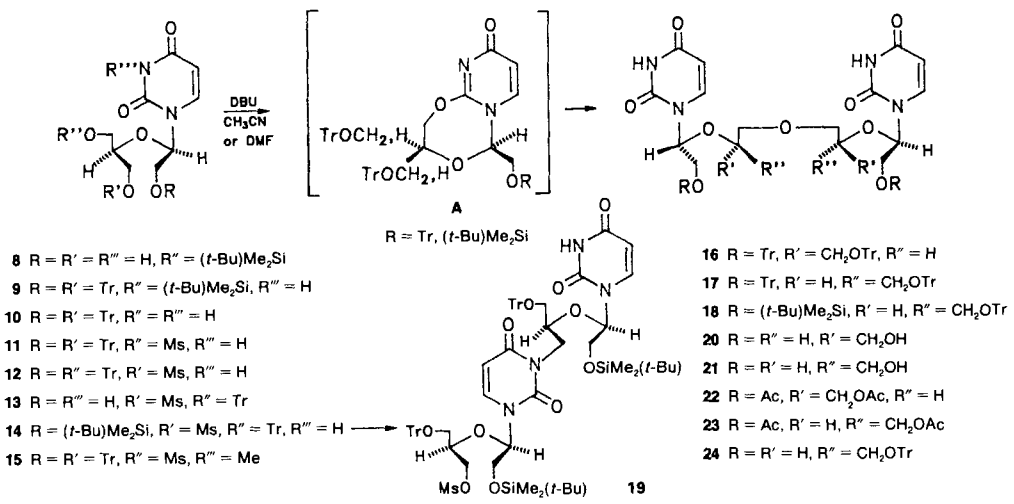
[6] (*Scheme 1*). Instead of the expected cyclized compound **2**, in CH_2Cl_2, the 3,3″-methylenebis{1-{(2*R*,6*S*)-6-[(mesyloxy)methyl]-1,4-dioxan-2-yl}uracil} (**3**) was formed with a methylene bridge connecting the N(3) atoms of two uracil bases. The same type of product, **5**, was obtained on reaction of diastereoisomeric (2*R*,6*R*)-dioxanyl derivative **4** with DBU in CH_2Cl_2. Since it was reported that DBU was efficient in N(3) alkylations of pyrimidine bases with benzyl halides [7], we performed the reactions of **1** and **4** with DBU in non-alkylating solvents such as MeCN or dimethylformamide (DMF) to direct them toward formation of **2**. In both solvents, however, rather complex product mixtures resulted, with 1-{(2*R*,6*S*)-6-[(mesyloxy)methyl]-1,4-dioxan-2-yl}-3-{[(2*S*,6*R*)-6-(uracil-1-yl)-1,4-dioxan-2-yl]methyl}uracil (**6**; 15% yield; *Scheme 1*) and 1-{(2*R*,6*R*)-6-[(mesyloxy)methyl]-1,4-dioxan-2-yl}-3-{[(2*R*,6*R*)-6-(uracil-1-yl)-1,4-dioxan-6-yl]methyl}uracil (**7**; 22%) being the main products. Since both **6** and **7** were formed by intermolecular 'dimerization' of **1** and **4**, respectively, through N(3) alkylation by the (mesyloxy)methyl group, it is obvious that the product mixtures must contain also higher alkylation products.

Apparently, on treatment of **1** and **4** with DBU both in CH_2Cl_2 and in non-alkylating solvents, the intermolecular reactions are more favourable than intramolecular cyclizations to a dioxazepine ring such as in **2**. This may be understood on the basis of the recently reported crystal structure of 1-[(2*R*,6*R*)-6-(hydroxymethyl)-1,4-dioxan-2-yl]-uracil, structurally closely related to **1**, with equatorial positions of both, the pyrimidine base and the 6-(hydroxymethyl) group on the dioxane ring in the chair conformation [8]. Consequently, with **1** in the same conformation, the pyrimidine base and 6-(mesyl-

oxy)methyl group are too far apart for an intramolecular reaction to take place. Inspection of space-filling (*CPK*) molecular models showed that the same holds for diastereoisomeric, *trans*-substituted dioxane **4**.

Since the unfavorable positions of the base and 6-(mesyloxy)methyl group in 1,4-dioxane derivatives **1** and **4** prevented intramolecular cyclizations, we considered the possibility of performing the intramolecular cyclizations on appropriately functionalized, flexible secouridines. Thus, 5′-*O*-[(*tert*-butyl)dimethylsilyl]uridine [9] [10] was oxidized into a dialdehyde and reduced to diol **8** by the usual procedure [11]. Tritylation to **9** (87% yield), desilylation to **10** (83%), and mesylation gave the key intermediate 5′-*O*-mesyl-2′,3′-bis-*O*-(triphenylmethyl)-2′,3′-secouridine (**11**, 87%), being suitably protected and functionalized for the intramolecular cyclization into a dioxazepine ring (*Scheme 2*). The

Scheme 2



diastereoisomeric 3′-*O*-mesyl-2′,5′-bis-*O*-(triphenylmethyl)-2′,3′-secouridine (**12**; 56%) was prepared by tritylation of the known 2′-hydroxy derivative **13** [6]. Alternatively, the silylation of **13** gave 2′,*O*-[(*tert*-butyl)dimethylsilyl] derivative **14** (96%), an intermediate that, having the OH groups protected with different blocking groups offers the possibility for various further functionalizations. Reaction of **11** with diazomethane yielded N(3)-methyl derivative **15**.

It was recently reported that a 1′,2′-secoribosylthymine derivative (tosylated at *O*–C(3′)) underwent intramolecular cyclization into a dioxazepine derivative upon treatment with NaH in DMF or, better, by using DBU in MeCN [12]. Under the latter conditions, **11**, **12**, and **14** gave, as major reaction product, the 'dimeric' 2′,3′-secouridine **16** (68.5%), **17** (50%), and **18** (31%), respectively, consisting of two secouridine moieties connected *via* a 5′-ether linkage (*Scheme 2*). In the case of **14** also product **19**, alkylated at N(3) by the 3′-(mesyloxy)methyl group of **14** was identified. Otherwise some minor products, formed in very low yields, were isolated by prep. TLC. Each of them showed an absorption maximum at *ca.* 260 nm in the UV spectrum, which is characteristic for the

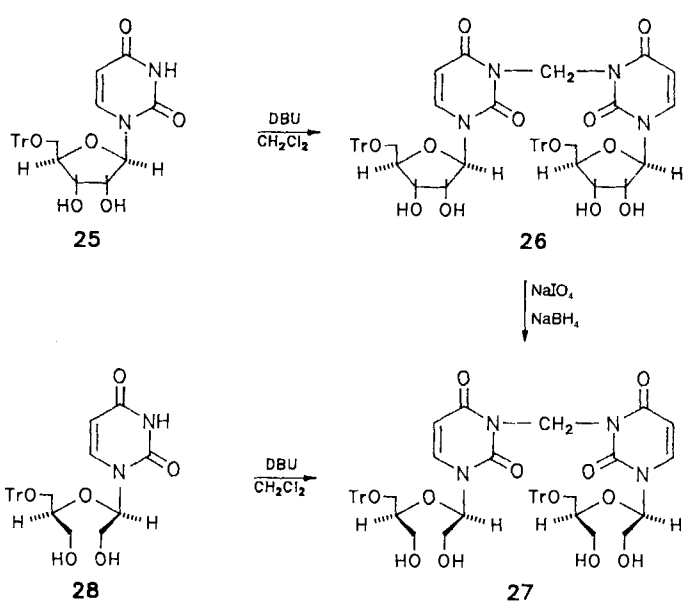
C(2)-carbonyl chromophore of uracil [13]. Thus, we were not able to detect the formation of dioxazepine derivatives in the above reactions. However, dinucleosidic compounds of type **16–18** with two nucleoside units connected directly, apparently have not yet been reported.

The chirality at C(1′) and C(4′) of both secouridine moieties in the 'dimeric' products **16–18** is assumed to be the same as in the starting compounds, as these chiral centres are not involved in the reaction, which occurs at the achiral C(3′) or C(5′).

To elucidate the pathway leading to the 'dimeric' structures **16–18**, we reacted 5′-hydroxy derivative **10** in MeCN with an equimolar amount of **11** and DBU. The 'dimeric' product **16** was isolated in only 24% yield, while the reaction of **11** with DBU gave **16** in 68.5% yield under otherwise identical conditions. Thus, a pathway involving the partial hydrolysis of the 5′-mesyloxy group, formation of the C(5′)–O^- anion, and reaction with unhydrolyzed **11** is possible, but, more probably, in competition with a more favorable route.

The second possible pathway would involve the partial formation of the unstable dioxazepine intermediate **A** (*Scheme 2*) which would open in the presence of a trace of H_2O, generating C(5′)–O^- needed for substitution of the 5′-mesyloxy group. Although we were not able to detect the presence of **A** in the reaction mixture, an indirect proof in favour of its formation emerges from the following experiment. Treatment of N(3)-methyl derivative **15** with DBU in MeCN gave no reaction, only **15** was isolated after 24 h refluxing of the mixture. Apparently, the formation of on anion at N(3) by H-abstraction by DBU and its conversion to the uracil C(2)–O^- anion seems to be of major importance for the formation of **16**. Since the 'dimeric' product **16** contains an ether link between C(5′) and C(5‴), it is reasonable to assume that the C(5′)–O^- anion is formed from

Scheme 3



dioxazepine **A** by its hydrolytic opening. The experiment with **15** also shows that the pathway involving partial hydrolysis of the 5′-mesyloxy group is not probable in the reaction of **11** and DBU: otherwise the N(3)-methylated derivative of **16** should have been formed on reaction of **15** with DBU.

Detritylation of **16** and **17** gave secouridine derivatives **20** and **21**, respectively, as very hygroscopic glassy masses, which were converted into their acetyl derivatives **22** and **23** for analysis. Finally **18** was desilylated to diol **24** which has still two OH groups protected.

Table 1. *^{1}H-NMR Data* ($(CD_3)_2CO$) *of Secouridine Derivatives*[a][b][c][d]). δ in ppm rel. to internal standard Me_4Si, J in Hz.

	H–N(3)[e] (br. *s*)	H–C(6) (*d*)	H–C(1′) (*t*)	H–C(5) (*d*)	H–C(4′) (*m*)	CH_2(3′) (*d*)[f])	CH_2(2′) (*d*)[f])	CH_2(5′) (*d*)[f])
8	10.38	7.57 (J = 7.9)	5.97 (J = 4.1)	5.73 (J = 7.9)		3.74–3.64 (*m*)		
9		7.533 (J = 7.9)	6.58 (J = 6.5)	5.77 (J = 7.9)	4.08–3.92	3.64	3.25 (*m*)	3.73 (J = 5.3)
10		7.53 (J = 8.2)	6.38 (*dd*, J = 4.1, 4.4)	5.61 (J = 7.9)	3.85		3.51–3.00 (*m*)	
11	10.05	7.50 (J = 8.2)	6.33 (J = 5.0)	5.64 (J = 8.2)	4.30–4.12	3.48	3.17 (*m*)	4.30–4.12 (*m*)
12[g])	9.07	7.72 (J = 7.9)	6.04 (J = 5.6)	5.50 (J = 7.9)	3.76–3.66	4.45 (*dd*, J = 3.8, 11.4), 4.28 (*dd*, J = 6.5, 11.4)	3.47 (*dd*, J = 5.0, 10.5), 3.22 (*dd*, J = 5.0, 10.5)	3.21 (J = 5.3)
14[g])	9.14	7.27 (J = 8.2)	5.88 (J = 4.7)	5.58 (J = 8.0)	3.69–3.64	3.85 (*dd*, J = 4.3, 11.2)	4.44 (*dd*, J = 3.0, 11.3)	3.24 (J = 5.5)
15[h])		7.50 (J = 8.2)	6.35 (J = 5.0)	5.71 (J = 8.2)	4.30–4.01 (*m*)		3.55	3.30 (*m*)
16		6.85 (J = 8.2)	6.29 (J = 5.0)	5.46 (J = 7.9)	4.56–4.28		3.69–3.06 (*m*)	
17	10.13	7.45 (J = 8.2)	6.13 (J = 5.9)	5.50 (J = 8.2)	3.96	3.86 (*m*)	3.58	3.20 (*m*)
18		7.69 (J = 7.9)	6.52 (J = 4.7)	5.54 (J = 7.9)		4.26–3.21 (*m*)		
20[i])		7.42 (J = 8.2)	5.90 (J = 5.3)	5.71 (J = 8.2)		3.87–3.30 (*m*)		
21[i])	11.11	7.72 (J = 8.2)	5.92 (J = 5.6)	5.72 (J = 7.9)		3.99–3.34 (*m*)		
22		7.38 (J = 8.2)	6.14 (J = 6.2)	5.66 (J = 7.9)	3.43		4.64–4.09 (*m*)	
23		7.77 (J = 8.2)	6.48 (J = 5.6)	5.85 (J = 8.2)		4.52–3.75 (*m*)		
24[g])		7.44 (J = 7.9)	6.15 (J = 5.0)	5.59 (J = 7.9)		4.15–3.17 (*m*)		
27[j])		7.55 (J = 7.9)	5.96 (J = 5.0)	5.49 (J = 7.9)	3.7	3.68 (J = 5.3)	3.68 (J = 5.3)	3.19 (J = 4.7)

[a]) Ph_3C: 7.75–6.99 (*m*) for **9**–**18**, **24**, and **27**. [b]) $MeSO_2$: 3.27–2.86 (*s*) for **11**–**15**. [c]) MeCO: 2.14–1.89 (*s*) for **22** and **23**. [d]) (*t*-Bu)Me_2Si 0.92–0.83 (*s*) and 0.10–0.02 (*s*) for **8**, **9**, **14**, and **18**. [e]) Disappearing in D_2O. [f]) Unless otherwise stated. [g]) In $CDCl_3$. [h]) Me–N(3): 3.27 (*s*). [i]) In $(CD_3)_2SO$. [j]) N(3)–CH_2–N(3′): 6.06 (*s*).

Table 2. *^{13}C-NMR Data ($(CD_3)_2CO$) of Secouridine Derivatives*[a][b][c][d]). δ in ppm rel. to internal standard Me_4Si.

	C(4) (*s*)	C(2) (*s*)	C(6) (*d*)	C(5) (*d*)	C(1′) (*d*)	C(4′) (*d*)	C(2′) (*t*)	C(3′) (*t*)	C(5′) (*t*)
8[e])	163.82	151.39	140.35	102.26	84.20	81.05	63.16[f])	62.92[f])	61.52
9	163.39	151.99	140.88	102.50	83.31	79.30	64.69	64.69	63.62
10	163.77	152.37	141.31	102.49	83.58	79.85	65.07[f])	64.90[f])	62.81
11	162.87	151.63	140.30	102.37	82.62	75.74	64.05[f])	62.98[f])	69.25
12	162.76	150.62	139.73	102.43	82.39	75.79	63.43[f])	67.55	62.47[f])
14[e])	163.24	150.98	140.32	102.11	83.05	75.66	63.08[f])	67.82	62.36[f])
15[g])	162.36	152.15	138.49	101.52	83.69	76.07	64.11[f])	62.98[f])	69.25
16	161.51	152.03	137.36	103.56	84.54	79.01	65.20	62.42	41.99
17	162.81	151.30	140.18	102.49	82.51	77.27	64.19[f])	43.62	63.27[f])
18	162.02	150.96	139.79	100.57	84.65	77.82	65.69[f])	40.92	64.39[f])
20[h])	161.68	151.40	138.30	102.83	85.95	79.85	62.80	59.89	43.10
21[h])	163.09	151.30	140.92	101.47	83.13	78.56	61.06[f])	41.48	60.72[f])
22	162.02	152.20	137.98	104.46	83.52	78.27	65.41	62.02	41.99
23	161.76	150.82	138.95	100.75	82.01	75.64	63.82	40.13	64.57
24[e])	161.91	152.61	138.27	102.65	84.31	76.69	65.01[f])	41.71	63.60[f])
27[i])	162.42	151.91	140.04	101.96	85.56	80.33	64.80[f])	63.51[f])	62.21

[a]) *Ph_3C* at 144.90–127.20 (*s*, 3*d*) and Ph_3C at 87.70–87.02 (*s*) for **9–18**, **24**, and **27**. [b]) *$MeSO_2$* at 37.32–36.63 (*q*) for **11–15**. [c]) *MeCO* at 170.66–169.23 (*s*) and *MeCO* at 20.71–19.32 (*q*) for **22** and **23**. [d]) *$(Me_3C)Me_2Si$* at 26.03–25.48 (*q*), *$(Me_3C)Me_2Si$* at 18.53–17.90 (*s*), and *$(Me_3C)Me_2Si$* at −5.72 to −5.52 (*q*) for **8**, **9**, **14**, and **18**. [e]) In $CDCl_3$. [f]) Interchangeable. [g]) Me–N(3) at 27.03 (*q*). [h]) In $(CD_3)_2SO$. [i]) N(3)–CH_2–N(3″) at 47.57 (*t*).

The easy preparation of the interesting 3,3″-methylenebis(uracils) **3** and **5** from **1** and **4**, respectively, with DBU in CH_2Cl_2 encouraged us to investigate the synthesis of the hitherto unknown 3,3″-methylene-bridged uridine bis-nucleosides and bis-seconucleosides. Under the same reaction conditions (DBU/CH_2Cl_2), 5′-*O*-trityluridine (**25**) gave 3,3″-methylenebis(uridine) **26** (43% yield and 38% of recovered **25**; *Scheme 3*). The bis-nucleoside **26** was then oxidized by $NaIO_4$ and reduced by $NaBH_4$ to bis-seconucleoside **27** (67%). The latter was also prepared directly from the known 5′-*O*-(triphenylmethyl)-2′,3′-secouridine (**28**) with DBU in CH_2Cl_2, the yield being 18% (58% of recovered **28**). The only hitherto known example of a methylene-bridged pyrimidine bis-nucleoside is that obtained from 5′-*O*-tritylthymidine on reaction with Bu_4NF/CH_2Cl_2 [14].

The 3,2″-bridged compounds **6** and **7** exhibit closely doubled ^1H- and ^{13}C-NMR signals for the two uracil and two 1,4-dioxane moieties, except for a difference of 25 ppm between the signals of O–CH_2–C(6′) and N–CH_2–C(2″). Compounds **16–24** show only one chemical shift for corresponding H- and C-atoms, the two halves of the molecule being identical to each other (*Tables 1* and *2*). The same holds for **26** and **27**, the methylene bridge appearing as *s* at δ (H) *ca.* 6 and δ(C) *ca.* 47 ppm, while all other signals correspond to the parent compounds.

Experimental Part

General. Solvents were dried and redistilled shortly before use. Extracts and filtrates were dried (Na_2SO_4) and evaporated *i.v.* Anal. samples were dried *i.v.* over P_2O_5 for 18 h. FC: silica gel (*Merck 60*, 230–240 mesh ASTM); eluent CH_2Cl_2/MeOH 40:1. Prep. TLC: silica gel activated at 110° for 60 min; eluent CH_2Cl_2/MeOH 9:1 (*A*) or 19:1 (*B*); detection by UV. M.p.: *Kofler* hot-bench apparatus. Optical rotations $[\alpha]_D^{20-25}$: *AA-10* automatic

polarimeter (*Optical Acitvity Ltd.*, England). UV Spectra (λ_{max}(logε) in nm): *Perkin-Elmer* double-beam spectrophotometer, model *124*; in EtOH. IR Spectra (ν in cm^{-1}): *Perkin-Elmer-297* spectrometer; solids in KBr pellets, liquids as thin films. ^{1}H-NMR Spectra (δ in ppm rel. to Me_4Si and J in Hz): *Jeol-FX90Q* spectrometer; at 89.55 MHz. ^{13}C-NMR Spectra ($\delta(CDCl_3) = 77$ with respect to Me_4Si): *Jeol-FX90Q* spectrometer (at 22.5) and *Varian-Gemini-300* instrument; multiplicities from off-resonance decoupled spectra. MS: *Varian-MAT-CH-7* spectrometer; electron energy 70 eV, emission current 100 μA, ion-accelerating voltage 3 kV.

1-{(2R,6S)-6-[(Methylsulfonyloxy)methyl]-1,4-dioxan-2-yl}-3-{[(2S,6R)-6-(1,2,3,4-tetrahydro-2,4-dioxopyrimidin-1-yl)-1,4-dioxan-2-yl]methyl}pyrimidine-2,4(1H,3H)-dione (**6**). To a soln. of **1** [6] (81 mg, 0.26 mmol) in dry DMF (2.6 ml), DBU (0.043 ml, 0.29 mmol) was added and stirred at 75–80° for 8 h. The mixture was evaporated and separated by repeated TLC (*B*): 12.4 mg (15.3%) of **1** and 10 mg (15%) of **6**. R_f 0.7 (*A*). $[\alpha]_D = +73.4$ ($c = 1.28$, Me_2CO). UV: 261 (3.93). IR: 3480*m*, 1720*s*, 1670*s*, 1460*m*, 1390*m*, 1355*m*, 1270*m*, 1240*w*, 1180*m*, 1120*m*, 935*w*, 810*w*. ^{1}H-NMR ($(CD_3)_2CO$): 10.48 (br. *s*, NH); 8.10 (*d*, $J = 8.2$, H–C(6‴)); 8.04 (*d*, $J = 8.2$, H–C(6)); 6.14 (*dd*, $J = 3.2$, 10.0, H–C(6″)); 6.01 (*d*, $J = 8.2$, H–C(5‴)); 5.95 (*dd*, $J = 3.2$, 10.0, H–C(2′)); 5.89 (*d*, $J = 8.2$, H–C(5)); 4.57–3.43 (*m*, 14 H, CH_2(3″), CH_2(5″), H–C(2″), NCH_2–C(2″), CH_2(3′), CH_2(5′), H–C(6′), OCH_2–C(6′)); 3.27 (*s*, Me). ^{13}C-NMR ($(CD_3)_2CO$): 163.29 (*s*, C(4‴)); 162.75 (*s*, C(4)); 151.54 (*s*, C(2‴)); 150.80 (*s*, C(2)); 140.90 (*d*, C(6‴)); 139.55 (*d*, C(6)); 102.72 (*d*, C(5‴)); 102.31 (*d*, C(5)); 80.34 (*d*, C(6″)); 79.65 (*d*, C(2′)); 75.39 (*d*, C(2″)); 74.86 (*d*, C(6′)); 69.14 (*t*, C(3″) or C(5″)); 69.01 (*t*, C(3′) or C(5′)); 68.24 (*t*, C(3″) or C(5″)); 68.06 (*t*, C(3′) or C(5′)); 66.51 (*t*, OCH_2C(6′)); 41.76 (*t*, NCH_2C(2″)); 37.31 (*q*, $MeSO_3$). MS: 517 ($[M + H]^+$), 457, 421, 405 (100), 347, 345, 322, 309, 211, 195, 137. Anal. calc. for $C_{19}H_{24}N_4O_{11}S$ (516.48): C 44.19, H 4.68, N 10.85; found: C 44.36, H 4.79, N 10.68.

1-{(2R,6R)-[(Methylsulfonyloxy)methyl]-1,4-dioxan-2-yl}-3-{[(2R,6R)-6-(1,2,3,4-tetrahydro-2,4-dioxopyrimidin-1-yl)-1,4-dioxan-2-yl]methyl}pyrimidine-2,4(1H,3H)-dione (**7**). To a soln. of **4** [6] (153 mg, 0.50 mmol) in dry MeCN (5 ml), DBU (0.082 ml, 0.55 mmol) was added and stirred at reflux for 7 h. The mixture was evaporated and separated by repeated TLC (*B*): 15 mg of **4** (10%) and 28.6 (22.2%) of oily **7**. R_f 0.7 (*A*). $[\alpha]_D = -42.8$ ($c = 0.57$, Me_2CO). UV: 261 (4.15). IR: 3440*m*, 2930*m*, 1715*s*, 1670*s*, 1630 (sh), 1455*s*, 1400*m*, 1355*s*, 1270*s*, 1240*m*, 1180*s*, 1130*s*, 1075 (sh), 970*m*, 940*m*, 890*w*, 810*m*, 770*m*. ^{1}H-NMR ($(CD_3)_2CO$): 8.08 (*d*, $J = 8.1$, H–C(6‴)); 7.92 (*d*, $J = 8.1$, H–C(6)); 6.01 (*dd*, $J = 3.6$, 5.5, H–C(6″)); 5.95 (*t*, $J = 3.9$, H–C(2′)); 5.71 (*d*, $J = 8.2$, H–C(5‴)); 5.58 (*d*, $J = 8.2$, H–C(5)); 4.47–3.53 (*m*, 14 H, CH_2(3″), CH_2(5″), H–C(2″), NCH_2–C(2″), CH_2(3′), CH_2(5′), H–C(6′), OCH_2–C(6′)); 3.15 (*s*, Me). ^{13}C-NMR ($(CD_3)_2CO$): 163.49 (*s*, C(4‴)); 162.96 (*s*, C(4)); 152.20 (*s*, C(2‴)); 151.13 (*s*, C(2)); 142.48 (*d*, C(6‴)); 141.19 (*d*, C(6)); 102.02 (*d*, C(5‴)); 101.48 (*d*, C(5)); 76.98 (*d*, C(6″)); 76.44 (*d*, C(2′)); 69.76 (*d*, C(2″)); 69.64 (*d*, C(6′)); 69.06 (*t*, C(3″) or C(5″)); 68.63 (*t*, C(3′) or C(5′)); 68.07 (*t*, C(3″) or C(5″)); 67.35 (*t*, C(3′) or C(5′)); 67.01 (*t*, OCH_2C(6′)); 41.38 (*t*, NCH_2C(2″)); 37.46 (*q*, $MeSO_3$). Anal. calc. for $C_{19}H_{24}N_4O_{11}S$ (516.48): C 44.19, H 4.68, N 10.85; found: C 44.36, H 4.79, N 10.68; found: C 44.23, H 4.70, N 10.76.

5′-O-[(tert-Butyl)dimethylsilyl]-2′,3′-secouridine (= *1-{(1R)-1-{(1S)-2-[(tert-Butyl)dimethylsilyloxy]-1-(hydroxymethyl)ethoxy}-2-hydroxyethyl}pyrimidine-2,4(1H,3H)-dione* **8**). To a soln. of *5′-O*-[(*tert*-butyl)-dimethylsilyl]uridine [9] [10] (933 mg, 2.60 mmol) in dioxane/H_2O 5:1 (31 ml), a soln. of $NaIO_4$ (590 mg, 2.76 mmol) in H_2O (5 ml) was added dropwise and stirred at r.t. for 2 h. Dioxane (26 ml) was then added, and after 10 min, $NaIO_3$ was filtered off. To the combined filtrates, $NaBH_4$ (98.5 mg, 2.60 mmol), and after 20 min at r.t., acetone (0.5 ml) were added. The mixture was neutralized with 10% AcOH/H_2O and evaporated to a small volume to be partitioned between CH_2Cl_2 and H_2O. The org. layer was dried and evaporated: 883 mg (94%) of **8**. M.p. 119–122° (Me_2CO/MeOH). $[\alpha]_D = +30.0$ ($c = 1.40$, Me_2CO). UV: 262 (4.32). IR: 3280*s*, 1715*s*, 1630*m*, 1460*s*, 1400*m*, 1360*m*, 1330*m*, 1260*s*, 1120*s*, 1050*s*, 960*m*, 840*s*, 780*m*. Anal. calc. for $C_{15}H_{28}N_2O_6Si$ (360.48): C 49.98, H 7.83, N 7.77; found: C 50.14, H 7.72, N 7.67.

5′-O-[(tert-Butyl)dimethylsilyl]-2′,3′-bis-O-(triphenylmethyl)-2′,3′-secouridine (= *1-{(1R)-1-{(1S)-2-[(tert-Butyl)dimethylsilyloxy]-1-[(triphenylmethoxy)methyl]ethoxy}-2-(triphenylmethoxy)ethyl}pyrimidine-2,4-(1H,3H)-dione*; **9**). To a soln. of **8** (428 mg, 1.19 mmol) in dry pyridine (5 ml), Ph_3CCl (993 mg, 3.56 mmol) was added. The mixture was stirred at 100° for 4 h and evaporated. The residue was mixed with ice/H_2O and extracted with CH_2Cl_2. The org. layer was washed with $NaHCO_3$ soln. and H_2O, dried, and co-evaporated with toluene and Me_2CO and the residue separated by FC (37 × 1.2 cm): 827 mg (86.5%) of **9**. R_f 0.7 (*B*). $[\alpha]_D = +57.7$ ($c = 1.23$, Me_2CO). UV: 261 (3.87). IR: 3060*m*, 2930*s*, 2860*m*, 1700*s*, 1630*m*, 1600*w*, 1495*m*, 1450*s*, 1390*m*, 1270*s*, 1220*m*, 1115*m*, 1100*s*, 1030*m*, 1005*m*, 900*m*, 840*s*, 810*m*, 775*s*, 765*s*, 750*s*, 710*s*. Anal. calc. for $C_{53}H_{56}N_2O_6Si$ (803.30): C 75.31, H 6.68, N 3.32; found: C 75.08, H 6.75, N 3.33.

2′,3′-Bis-O-(triphenylmethyl)-2′,3′-secouridine (= *1-{(1R)-1-{(1R)-2-Hydroxy-1-[(triphenylmethoxy)-methyl]ethoxy}-2-(triphenylmethoxy)ethyl}pyrimidine-2,4(1H,3H)-dione*; **10**). To a soln. of **9** (693 mg, 0.82 mmol) in dry THF (6 ml), 1N Bu_4NF (1.64 ml, 1.64 mmol) was added, and after stirring at r.t. for 22 h, the same quantitity

of 1N Bu_4NF was added once more. The mixture was stirred at r.t. for 24 h, diluted with Et_2O (28 ml), and extracted with 5% $NaHCO_3$ soln. (28 ml) and H_2O (2 × 14 ml). The org. layer was dried and evaporated and the residue separated by FC: 72.5 mg (10.5%) of **9** and 497 mg (82.8%) of **10**. M.p. 110–112° (MeOH). R_f 0.2 (*B*). $[\alpha]_D = +53.9$ ($c = 1.15$, Me_2CO). UV: 261 (4.34). IR: 3440*m*, 1690*s*, 1625*m*, 1490*m*, 1450*s*, 1385*m*, 1270*m*, 1085*m*, 900*m*, 805*m*, 765*m*, 745*m*, 705*s*. Anal. calc. for $C_{47}H_{42}N_2O_5$ (730.86): C 77.24, H 5.79, N 3.83; found: C 77.46, H 5.81, N 3.97.

5'-O-(Methylsulfonyl)-2',3'-bis-O-(triphenylmethyl)-2',3'-secouridine (= *1-{(1R)-1-{(1S)-2-(Methylsulfonyloxy)-1-[(triphenylmethoxy)methyl]ethoxy}-2-(triphenylmethoxy)ethyl}pyrimidine-2,4(1H,3H)-dione*; **11**). To a soln. of **10** (214 mg, 0.29 mmol) in pyridine (1.5 ml) at −20°, MsCl (0.035 ml, 0.47 mmol) was added. The mixture was then kept at +4° for 20 h and evaporated. The residue was mixed with ice/H_2O, and extracted with CH_2Cl_2 (30 ml). The org. layer was washed with aq. $NaHCO_3$ soln. and H_2O, dried, and co-evaporated with toluene and Me_2CO and the residue purified by FC: 205 mg (86.5%) of **11**. M.p. 108–110° (MeOH). R_f 0.6 (*B*). $[\alpha]_D = +43.0$ ($c = 1.07$, Me_2CO). UV: 261 (4.65). IR: 1690*s*, 1630*w*, 1490*m*, 1450*s*, 1360*m*, 1265*m*, 1175*s*, 1080*m*, 1000*m*, 960*m*, 900*w*, 810*w*, 760*m*, 710*s*. Anal. calc. for $C_{48}H_{44}N_2O_8S$ (808.95): C 71.27, H 5.48, N 3.46; found: C 731.35, H 5.51, N 3.37.

3'-O-(Methylsulfonyl)-2',5'-bis-O-(triphenylmethyl)-2',3'-secouridine (= *1-{(1R)-1-{(1R)-2-(Methylsulfonyloxy)-1-[(triphenylmethoxy)methyl]ethoxy}-2-(triphenylmethoxy)ethyl}pyrimidine-2,4(1H,3H)-dione*; **12**). To a soln. of **13** [6] (198 mg, 0.35 mmol) in pyridine (10 ml), TrCl (117 mg, 0.42 mmol) was added. The mixture was stirred at 60° for 18 h and evaporated. The residue was mixed with ice/H_2O and extracted with CH_2Cl_2. The org. layer was washed with aq. $NaHCO_3$ soln. and H_2O, dried, and co-evaporated with toluene and Me_2CO, and the residue separated by FC (37 × 1.2 cm): 64 mg (32.5%) of **13** and 159 mg (56%) of **12**. R_f 0.4 (*B*). $[\alpha]_D = +44.3$ ($c = 1.08$, Me_2CO). UV: 260 (4.04). IR: 1690*s*, 1630*m*, 1490*m*, 1445*s*, 1360*m*, 1260*m*, 1220*m*, 1175*m*, 1030*w*, 960*m*, 900*w*, 810*m*, 760*m*, 745*m*, 705*s*. Anal. calc. for $C_{48}H_{44}N_2O_8S$ (808.95): C 71.27, H 5.48, N 3.46; found: C 71.54, H 5.66, N 3.33.

2'-O-[(tert-Butyl)dimethylsilyl]-3'-O-(methylsulfonyl)-5'-O-(triphenylmethyl)-2',3'-secouridine (= *1-{(1R)-2-([tert-Butyl)dimethylsilyloxy]-1-{(1R)-2-(methylsulfonyloxy)-1-[(triphenylmethoxy)methyl]ethoxy}-ethyl}-ethyl}pyrimidine-2,4(1H,3H)-dione*; **14**). To a soln. of **13** [6] (1.445 g, 2.55 mmol) in CH_2Cl_2 (4.3 ml), 1*H*-imidazole (382 mg, 5.64 mmol) was added. To the mixture cooled to −20°, a soln. of (*t*-Bu)Me_2SiCl (423 mg, 2.81 mmol) in CH_2Cl_2 (1.7 ml) was added dropwise and stirred at 0° for 1 h at r.t. for 24 h. The mixture was partitioned between H_2O (15 ml) and CH_2Cl_2 (3 × 10 ml). The org. layer was dried and evaporated: 1.669 g (96%) of **14**. M.p. 152–154° (MeOH). R_f 0.4 (*B*). $[\alpha]_D = +34.0$ ($c = 1.03$, $CHCl_3$). UV: 261 (3.79). IR: 3060*m*, 2930*m*, 2860*m*, 1700*s*, 1630*m*, 1490*w*, 1450*m*, 1360*s*, 1260*m*, 1180*s*, 1120*s*, 1080*m*, 1000*m*, 960*m*, 840*s*, 775*m*, 745*m*, 710*s*. Anal. calc. for $C_{35}H_{44}N_2O_8SSi$ (680.89): C 61.74, H 6.51, N 4.11; found: C 61.86, H 6.46, N 4.08.

3-Methyl-5'-O-(methylsulfonyl)-2',3'-bis-O-(triphenylmethyl)-2',3'-secouridine (= *3-Methyl-1-{(1R)-1-{(1S)-2-(methylsulfonyloxy)-1-[(triphenylmethoxy)methyl]ethoxy}-2-(triphenylmethoxy)ethyl}pyrimidine-2,4-(1H,3H)-dione*; **15**). To the soln. of diazomethane (3.56 mmol) in Et_2O (15 ml; prepared from Ts-N(NO)Me (1.07 g, 5.0 mmol) and KOH (0.2 g, 3.56 mmol)) [15], the soln. of **11** (153 mmol) in MeOH (2 ml) was added dropwise and allowed to stand at r.t. for 5 h. The mixture was then evaporated and purified by TLC (*B*): 123 mg (79%) of **15**. R_f 0.9 (*B*). $[\alpha]_D = +48.0$ ($c = 0.92$, Me_2CO). UV: 260.4 (3.03). IR: 2910*m*, 1700 (sh), 1660*s*, 1450*m*, 1360*m*, 1290*w*, 1200*w*, 1175*s*, 1070*s*, 995*m*, 960*m*, 805*w*, 760*m*, 700*s*. Anal. calc. for $C_{49}H_{46}N_2O_8S$ (822.98): C 71.51, H 5.63, N 3.40; found: C 71.61, H 5.72, N 3.52.

5',5'''-Dideoxy-5',5'''-oxy-2',2''',3',3'''-tetrakis-O-(triphenylmethyl)bis(2',3'-secouridine) (= *1,1'-{Oxybis-{(R)-1-[(triphenylmethoxy)methyl]ethane-2,1-diyl}bis{oxy{(R)-[(triphenylmethoxy)methyl]methylene}}}bis-[pyrimidine-2,4(1H,3H)-dione]*; **16**). *a*) To a soln. of **11** (240 mg, 0.30 mmol) in MeCN (3 ml), DBU (0.06 ml, 0.39 mmol) was added and stirred at reflux for 24 h. The mixture was evaporated and purified by FC (36 × 1.2 cm): 142 mg (68.5%) of **16**. M.p. 154–156° (Me_2CO/MeOH). R_f 0.7 (*A*). $[\alpha]_D = +100.0$ ($c = 1.32$, Me_2CO). UV: 260 (3.94). IR: 3060*m*, 1715*s*, 1670*s*, 1600*m*, 1490*m*, 1450*s*, 1420*m*, 1395*m*, 1360*m*, 1330*w*, 1270*m*, 1220*m*, 1200*m*, 1150*m*, 1080*s*, 1030*m*, 980*m*, 900*m*, 800*m*, 765*s*, 745*s*, 705*s*. Anal. calc. for $C_{90}H_{82}N_4O_{11}$ (1395.66): C 77.45, H 5.92, N 4.01; found: C 77.40, H 6.05, N 4.17.

b) To a soln. of **11** (115 mg, 0.14 mmol) and **10** (104 mg, 0.14 mmol) in MeCN (3 ml), DBU (0.03 ml, 0.18 mmol) was added and stirred at reflux for 20 h. The mixture was evaporated and separated by FC (36 × 1.2 cm): 39 mg (38%) of **10**, 46 mg (44%) of **11**, and 48 mg (24%) of **16**, identical to the sample described above.

3',3'''-Dideoxy-3',3'''-oxy-2',2''',5',5'''-tetrakis-O-(triphenylmethyl)bis(2',3'-secouridine) (= *1,1'-{Oxybis-{(S)-1-[(triphenylmethoxy)methyl]ethane-2,1-diyl}bis{oxy{(R)-[(triphenylmethoxy)methyl]methylene}}}bis-[pyrimidine-2,4(1H,3H)-dione]*; **17**). To a soln. of **12** (170 mg, 0.210 mmol) in MeCN (2.1 ml), DBU (0.04 ml, 0.27 mmol) was added and stirred at reflux for 24 h. The mixture was evaporated and purified by FC (36 × 1.2 cm):

mg (50%) of **16**. M.p. 94–96° (EtOH). R_f 0.7 (*A*). $[\alpha]_D$ = +48.0 (0.98, Me_2CO). UV: 261 (4.16). IR: 3050*m*, 1690*s*, 1630*m*, 1490*m*, 1450*s*, 1385*m*, 1265*m*, 1220*m*, 1090*m*, 1030*w*, 1000*w*, 900*w*, 805*w*, 760*m*, 740*m*, 705*s*. Anal. calc. for $C_{90}H_{82}N_4O_{11}$ (1395.66): C 77.45, H 5.92, N 4.01; found: C 77.70, H 5.84, N 4.22.

*2',2'''-Bis-*O*-[(*tert*-Butyl)dimethylsilyl]-3',3'''-dideoxy-3',3'''-oxy-5',5'''-tetrakis-*O*-(triphenylmethyl)bis(2',3'-secouridine)* (= *1,1'-{Oxybis{(*S*)-1-[(triphenylmethoxy)methyl]ethane-2,1-diyl}bis{oxy{(*R*)-{[*tert*-butyl)-dimethylsilyloxy]methyl}methylene}}}bis[pyrimidine-2,4(1*H*,3*H*)-dione]*; **18**) *and 2'-*O*-[(*tert*-Butyl)dimethylsilyl]-3'-{2'-*O*-[(*tert*-butyl)dimethylsilyl]-3'-*O*-(methylsulfonyl)-5'-*O*-(triphenylmethyl)-2',3'-secouridin-3-yl}-3'-deoxy-5'-*O*-(triphenylmethyl)-2',3'-secouridine* (= *1-{(1*R*)-2-[(*tert*-Butyl)dimethylsilyloxy]-1-{(1*R*)-2-(methylsulfonyloxy)-1-[(triphenylmethoxy)methyl]ethoxy}ethyl}-3-{(2*R*)-2-{(1*R*)-2-[(*tert*-butyl)dimethylsilyloxy]-1-(1,2,3,4-tetrahydro-2,4-dioxopyrimidin-1-yl)ethoxy}-3-(triphenylmethoxy)propyl}pyrimidine-2,4(1*H,*3*H)-dione*; **19**). To a soln. of **14** (340 mg, 0.50 mmol) in MeCN (5 ml), DBU (0.10 ml, 0.64 mmol) was added under Ar and stirred at reflux for 16 h. The mixture was evaporated and separated by FC (36 × 1.2 cm): 92 mg (31%) of **18**, R_f 0.7 (*B*), 66 mg (21%) of **19**, R_f 0.5 (*B*), and 44 mg (13%) of **14**.

Data of **18**: $[\alpha]_D$ = +28.5 (*c* = 1.84, Me_2CO). UV: 263.2 (4.10). IR: 2920*m*, 2850*m*, 1710*s*, 1660*s*, 1490*w*, 1450*s*, 1390*m*, 1360*m*, 1255*m*, 1200*w*, 1120*s*, 1070*m*, 830*m*, 800*m*, 775*s*, 750*m*, 700*s*. Anal. calc. for $C_{68}H_{82}N_4O_{11}Si$ (1187.59): C 68.77, H 6.96, N 4.72; found: C 69.03, H 6.94, N 4.55.

Data of **19**: $[\alpha]_D$ = +32.4 (*c* = 0.74, MeOH). UV: 263.0 (4.05). IR: 2920*m*, 2850*m*, 1710*s*, 1655*s*, 1490*m*, 1450*s*, 1380*m*, 1360*m*, 1255*m*, 1180*s*, 1120*s*, 1075*m*, 1000*m*, 960*m*, 830*s*, 805*m*, 770*s*, 760*s*, 705*s*. ^{1}H-NMR ($(CD_3)_2CO$): 7.77 (*d*, *J* = 8.2, H–C(6)); 7.72 (*d*, *J* = 8.2, H–C(6″)); 7.68–7.34 (*m*, 30 arom. H); 6.18 (*t*, *J* = 4.8, H–C(1′)); 6.08 (*t*, *J* = 4.8, H–C(1‴)); 5.72 (*d*, *J* = 8.2, H–C(5)); 5.57 (*d*, *J* = 8.2, H–C(5″)); 4.66 (*dd*, *J* = 4.2, 11.1, H–C(4′)); 4.55 (*dd*, *J* = 4.5, 11.1, H–C(4‴)); 4.21–3.89 (*m*, CH_2(2′), CH_2(3′), CH_2(2‴), CH_2(3‴)); 3.41 (*d*, *J* = 4.4, CH_2(5′), CH_2(5‴)); 3.23 (*s*, $MeSO_3$); 1.03 (*s*, *t*-Bu); 0.99 (*s*, *t*-Bu); 0.20 (*s*, Me_2Si); 0.15 (*s*, Me_2). ^{13}C-NMR (CD_3COCD_3): 163.04 (*s*, C(4)); 162.14 (*s*, C(4″)); 151.86 (*s*, C(2)); 150.41 (*s*, C(2″)); 144.14, 143.85 (2*s*, arom. C); 141.25 (*d*, C(6)); 141.08 (*d*, C(6″)); 128.78, 127.94, 127.37, 127.26, 126.92 (5*d*, arom. C); 101.69 (*d*, C(5)); 101.30 (*d*, C(5″)); 87.25 (2*s*, Ph_3C); 84.43 (*d*, C(1′)); 83.07 (*d*, C(1‴)); 76.52 (*d*, C(4′)); 75.96 (*d*, C(4‴)); 68.46 (*t*, C(3‴)); 65.63 (*t*, C(2‴)); 63.64 (*t*, C(2′)); 63.38 (*t*, C(5′)); 63.09 (*t*, C(5‴)); 41.20 (*t*, C(3′)); 36.85 (*q*, $MeSO_3$); 25.56 (*q*, 2 Me_3C); 18.00 (*s*, Me_3C); –5.81 (*q*, 2 Me_2Si). Anal. calc. for $C_{69}H_{84}N_4O_{13}SSi_2$ (1265.68): C 65.48, H 6.69, N 4.43; found: C 65.64, H 6.57, N 4.53.

5',5'''-Dideoxy-5',5'''-oxybis(2',3'-secouridine) (= *1,1'-{Oxybis[(*S*)-1-(hydroxymethyl)ethane-2,1-diyl]bis-{oxy[(*R*)-(hydroxymethyl)methylene]}}bis[pyrimidine-2,4(1*H,*3*H)-dione]*; **20**). A soln. of **16** (48 mg, 0.034 mmol) in 80% AcOH/H_2O (3 ml) was heated at 100° for 10 min. The mixture was evaporated and triturated with Et_2O (3 × 5 ml). The residue was purified by TLC (*A*): 9 mg (55%) of **20**. Very hygroscopic glass. R_f 0.3 (*A*). $[\alpha]_D$ = +77.5 (*c* = 0.51, MeOH). UV: 260.8 (4.67).

To the soln. of **20** (58 mg, 0.122 mmol) in pyridine (1 ml), Ac_2O (0.23 ml, 2.45 mmol) was added and kept at r.t. for 4 days. The mixture was co-evaporated with toluene and EtOH and purified by TLC (*B*, 2 ×): 58 mg (74%) of acetate **22**. M.p. 177–179° (MeOH). R_f 0.5 (*B*). $[\alpha]_D$ = +111.1 (*c* = 0.90, Me_2CO). UV: 257 (4.08). IR: 3450*w*, 3105*w*, 1750*s*, 1718*s*, 1665*s*, 1455*m*, 1370*s*, 1250*s*, 1115*m*, 1080*m*, 1050*m*. Anal. calc. for $C_{26}H_{34}N_4O_{15}$ (642.56): C 48.60, H 5.33, N 8.72; found: C 48.61, H 5.07, N 8.62.

3',3'''-Dideoxy-3',3'''-oxybis(2',3'-secouridine) (= *1,1'-{Oxybis[(*R*)-1-(hydroxymethyl)ethane-2,1-diyl]bis-{oxy[(*R*)-(hydroxymethyl)methylene]}}bis[pyrimidine-2,4(1*H,*3*H)-dione]*; **21**). A soln. of **17** (217 mg, 0.16 mmol) in 80% AcOH/H_2O (10 ml) was heated at 100° for 10 min. The mixture was evaporated and triturated with Et_2O (3 × 10 ml). The residue was purified by TLC (*A*): 55 mg (74.6%) of **21**. Hygroscopic glass. R_f 0.3 (*A*). $[\alpha]_D$ = +52.2 (*c* = 0.90, MeOH). UV: 260.8 (4.65).

The acetate was prepared from **21** (47 mg, 0.10 mmol), pyridine (1 ml), and Ac_2O (0.18 ml, 1.90 mmol) as described above for **22**: 41 mg (67%) of **23**. Colorless foam. R_f 0.5 (*B*). $[\alpha]_D$ = +76.7 (*c* = 0.60, $CHCl_3$). UV: 260 (4.01). IR: 3440*w*, 3105*m*, 1740*s*, 1715*s*, 1660*s*, 1450*s*, 1360*s*, 1230*s*, 1110*s*, 1050*s*. Anal. calc. for $C_{26}H_{34}N_4O_{15}$ (642.56): C 48.60, H 5.33, N 8.72; found: C 48.83, H 5.27, N 8.77.

*3',3'''-Dideoxy-3',3'''-oxy-5',5'''-bis-*O*-(triphenylmethyl)bis(2',3'-secouridine)* (= *1,1'-{Oxybis{(*S*)-1-[(triphenylmethoxy)methyl]ethane-2,1-diyl}bis{oxy[(*R*)-(hydroxymethyl)methylene]}}bis[pyrimidine-2,4(1*H,*3*H)-dione]*; **24**). To a soln. of **18** (44 mg, 0.037 mmol) in dry THF (2 ml), 1N Bu_4NF (0.16 ml, 0.156 mmol) was added. After stirring at r.t. for 22 h, the mixture was diluted with Et_2O (3 ml) and extracted with 5% $NaHCO_3$ soln. (3 ml) and H_2O (2 × 2 ml). The org. layer was dried and evaporated and the residue separated by TLC (*B*): 10 mg (23%) of **18** and 13 mg (37%) of **24**. R_f 0.2 (*B*). $[\alpha]_D$ = +20.7 (*c* = 0.87, Me_2CO). UV: 263.2 (3.62). IR: 3340*m*, 2920*m*, 1700 (sh), 1650*s*, 1450*m*, 1395*m*, 1200*m*, 1065*s*, 970*w*, 805*m*, 755*s*, 700*s*. Anal. calc. for $C_{56}H_{54}N_4O_{11}$ (959.06): C 70.13, H 5.68, N 5.84; found: C 70.25, H 5.85, N 5.98.

3,3''-Methylene-5,5'''-bis-O-(triphenylmethyl)bis(uridine) (**26**). To a soln. of 5'-*O*-(triphenylmethyl)uridine [16] (**25**; 200 mg, 0.41 mmol) in dry CH_2Cl_2/MeCN 4:1 (21 ml), DBU (0.46 ml, 3.06 mmol) was added and heated to reflux for 2 days. The mixture was evaporated and separated by TLC (*B*): 77 mg (38.5%) of **25**, R_f 0.6 (*B*), and 88 mg (43.6%) of **26**, R_f 0.65 (*B*). M.p. 158–160° (Me_2CO). $[\alpha]_D = +1.3$ (*c* = 0.75, Me_2CO). UV: 264 (3.92). IR: 3440*s*, 2915*m*, 1720*s*, 1680*s*, 1495*m*, 1450*s*, 1405*m*, 1345*m*, 1280*m*, 1220*m*, 1105*s*, 1050*s*, 905*w*, 810*w*, 705*m*. ^{1}H-NMR (CD_3COCD_3): 7.85 (*d*, *J* = 8.2, 2 H, H–C(6)); 7.4 (*m*, 2 Ph_3C); 6.02 (*s*, NCH_2N); 5.87 (*d*, *J* = 2.9, 2 H, H–C(1')); 5.31 (*d*, *J* = 8.2, 2 H, H–C(5)); 4.91 (*d*, *J* = 4.7, 2 OH); 4.43–4.09 (*m*, 8 H, H–C(2'), H–C(3'), H–C(4'), OH); 3.47 (*m*, 4 H, CH_2(5')). ^{13}C-NMR ($CDCl_3$): 161.57 (*s*, C(4)); 150.79 (*s*, C(2)); 143.01 (*s*, arom. C); 138.43 (*d*, C(6)); 128.45 (*d*, arom. C); 127.82 (*d*, arom. C); 127.20 (*d*, arom. C); 101.64 (*d*, C(5)); 90.18 (*d*, C(1')); 87.36 (*s*, Ph_3C); 83.24 (*d*, C(4')); 76.19 (*d*, C(2')); 69.47 (*d*, C(3')); 61.21 (*t*, C(5')); 46.39 (*t*, NCH_2N). Anal. calc. for $C_{57}H_{52}N_4O_{12}$ (985.06): C 69.50, H 5.32, N 5.69; found: C 69.66, H 5.32, N 5.49.

3,3''-Methylene-5',5'''-bis-O-(triphenylmethyl)bis(2',3'-secouridine) (= *1,1'-Bis{(1R)-2-hydroxy-1-{(1S)-2-hydroxy-1-[(triphenylmethoxy)methyl]ethoxy}ethyl}-3,3'-methylenebis[pyrimidine-2,4(1H,3H)-dione]*; **27**). *a*) To a soln. of **26** (98.5 mg, 0.10 mmol) in dioxane/H_2O 5:1 (4.2 ml), a soln. of $NaIO_4$ (45.3 mg, 0.21 mmol) in H_2O (0.2 ml) was added and stirred at r.t. for 18 h. A precipitate was filtered off and the filtrate treated with $NaBH_4$ (7.6 mg, 0.20 mmol). After stirring for 20 min, a drop of acetone was added and the mixture neutralized with 10% AcOH/H_2O and evaporated to a small volume to be partitioned between CH_2Cl_2 and H_2O. The org. layer was dried and evaporated and the residue purified by FC: 66 mg (66.7%) of **27**. R_f 0.3 (*B*). $[\alpha]_D = +35.8$ (*c* = 1.48, Me_2CO). UV: 263.3 (4.01). IR: 3430*m*, 2930*m*, 1715*s*, 1680*s*, 1490*w*, 1450*s*, 1345*m*, 1280*m*, 1105*m*, 1065*m*, 900*w*, 760*m*, 745*w*, 710*m*. Anal. calc. for $C_{57}H_{56}N_4O_{12}$ (989.09): C 69.22, H 5.71, N 5.66; found: C 69.08, H 5.98, N 5.52.

b) To a soln. of **28** [6] (100 mg, 0.205 mmol) in CH_2Cl_2 (4 ml), DBU (0.061 ml, 0.41 mmol) was added and heated to reflux for 8 days. The mixture was separated by TLC (*B*, 3 developments): 58 mg (58%) of **28** and 18 mg (18%) of **27**, identical to that described above.

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