Stereocontrolled General Synthesis of Pyrimidine C-Nucleosides Having Branched-chain Sugar Moieties[1)]

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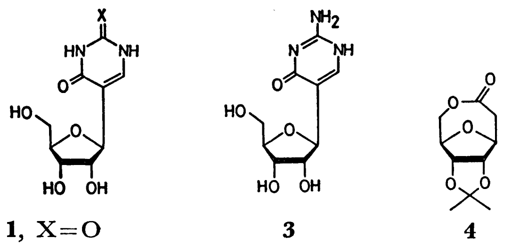
A variety of pyrimidine *C*-nucleosides bearing branched-chain sugars can be synthesized starting from adequately substituted (1*R**,6*S**,7*S**,8*R**)-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-ones. The general procedure consists of condensation with *t*-butoxybis(dimethylamino)methane, giving the corresponding α-dimethylaminomethylene lactones, base-catalyzed heterocycle formation with urea, thiourea, or guanidine, and acid-promoted removal of the isopropylidene protective group. The overall transformation proceeds with retention of the stereochemistry to afford only *C*-β-glycosyl nucleoside structures.

We have recently developed a novel method[2)] for the synthesis of pseudouridine (**1**), a component of tRNA, and its analogues such as 2-thiopseudouridine (**2**) and pseudoisocytidine (**3**)[3)] *via* a common intermediate, (1*R*,6*S*,7*S*,8*R*)-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**4**), which possesses a rigid *C*-β-glycoside structure. Realization of this method relies on the efficiency of the transition metal aided [3+4] annulation using polybromo ketones and furans[4)] and the stereoregulation of the subsequent oxidative transformation. The great flexibility of this new procedure prompted us to prepare a variety of the synthetic analogues. So far interest in the synthesis of *C*-nucleoside analogues has centered around the compounds having an arabionsyl or deoxyribosyl residue.[5)] Being stimulated by the discovery of the antibiotics, angustomycin A and C[6)] and nucleosidin,[7)] which exhibit cytostatic or virostatic activity, we were particularly interested in *C*-nucleosides bearing a branched-chain ribofuranosyl moiety. Although a number of routes to branched-chain sugars have been developed during the past few years,[8)] there were reported no efficient total syntheses which gave directly and stereospecifically such sugar derivatives. The present paper describes a completely stereocontrolled entry to pyrimidine *C*-nucleosides containing branched-chain sugar moieties.



1, X=O **3** **4**
2, X=S

Results and Discussion

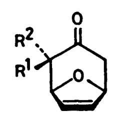
Synthesis of 5′-Modified Pyrimidine C-*Nucleosides.*[9)] The iron carbonyl- or Zn/Ag couple-promoted cyclocoupling of polybromo ketones and furan provides a general way to give the adducts of type **5**.[4)] The bicyclic ketone **5a** thus obtained can be transformed oxidatively to **6a** under perfect stereo- and regiochemical control.[1)] Heating of a mixture of the lactone **6a** and a Bredereck reagent, *t*-$C_4H_9OCH[N(CH_3)_2]_2$[10)] (excess), in DMF at 50 °C afforded the dimethylaminomethylene lactone **7a** (*Z*:*E*=70:30) in a good yield. Condensation of **7a** and urea with ethanolic sodium ethoxide formed the uracil derivative **8a** in 48% yield. The β stereochemistry at the anomeric 1′ position was confirmed by the ^{1}H NMR analysis in pyridine-d_5. The isopropylidene methyl signals appeared at δ 1.41 and 1.67 (Δδ=0.26 ppm), in accord with the Imbach's empirical rule.[11)] The spin-spin coupling constant, $J_{4',5'}$=3.7 Hz, also supported this assignment.[12)] Subsequent treatment of **8a** with 10% HCl in methanol at 25 °C furnished (±)-5′,5′-dimethylpseudouridine (**9a**). No pyranose derivatives were formed by this deprotection procedure.

When **7a** was treated with thiourea in refluxing ethanolic sodium ethoxide, the thiouracil derivative **10a** was obtained. The glycol protective group was then removed by 10% HCl in methanol to give (±)-5′,5′-dimethyl-2-thiopseudouridine (**11a**).

The base-catalyzed condensation of **7a** with guanidine furnished the pseudoisocytidine derivative **12a**, which, by treatment with 10% HCl in methanol, afforded (±)-5′,5′-dimethylpseudoisocytidine (**13a**) in quantitative yield.

In a similar manner, the 5′-monoalkylated or -phenylated pseudouridines **9b—d**, the 5′-monosubstituted 2-thiopseudouridines **11b—d**, and 5′-monosubstituted pseudoisocytidines **13b—d** were prepared from the corresponding ketones **5b—d**. In addition to the complete stereochemical control achieved in this synthesis, the configurational relationship between the carbonyl α position in **5** and the 5′ carbon of the resulting nucleosides, **9**, **11**, and **13**, is noteworthy. Since the chiral center created in the initial reductive [3+4] cyclocoupling of polybromo ketones and furan remains intact during the subsequent transformation, the stereochemistry inherent in **5b**, for example, leads to the 6′-deoxyallofuranosyl structure, **9b**, **11b**, and **13b**. Thus this approach allows a general entry to pyrimidine *C*-nucleosides possessing various carbon substituents at the 5′ position.[13)]

Synthesis of 1′- and 4′-Modified Pyrimidine C-*Nucleosides. A. 4′-Alkylated Pyrimidine* C-*Nucleosides*:[14,15)] The readily available lactone **14a**[1)] was condensed with *t*-$C_4H_9OCH[N(CH_3)_2]_2$ to afford the dimethylaminomethylene derivative **15a** in 70% yield. Conversion of **15a** to a uracil derivative **16a** was accomplished by heating **15a** with urea (10 equiv) in ethanolic sodium ethoxide in a fair yield. The assignment of



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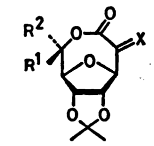
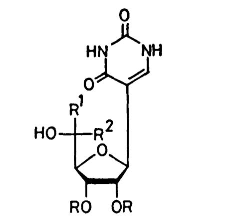
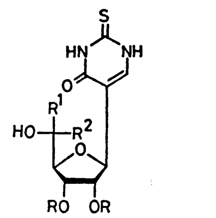
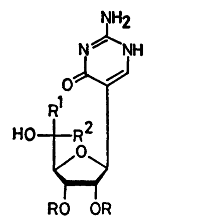


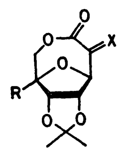
6, X=H_2
7, X=$CHN(CH_3)_2$

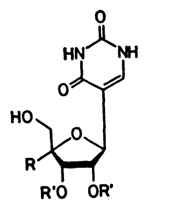


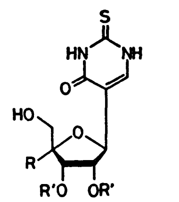


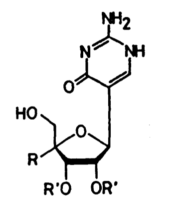


8, R-R=$C(CH_3)_2$ **10**, R-R=$C(CH_3)_2$ **12**, R-R=$C(CH_3)_2$
9, R=H **11**, R=H **13**, R=H (HCl salt)
a, $R^1=R^2=CH_3$ **b**, $R^1=CH_3$; $R^2=H$ **c**, $R^1=(CH_2)_4CH_3$; $R^2=H$
d, $R^1=C_6H_5$; $R^2=H$









14, X=H_2 **16**, R'-R'=$C(CH_3)_2$ **18**, R'-R'=$C(CH_3)_2$ **20**, R'-R'=$C(CH_3)_2$
15, X=$CHN(CH_3)_2$ **17**, R'=H **19**, R'=H **21**, R'=H (HCl salt)
a, R=CH_3 **b**, R=$(CH_2)_4CH_3$ **c**, R=C_6H_5

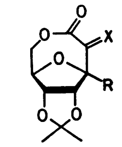
β configuration of the uracil base was made on the basis of the ^{1}H NMR chemical shifts of the isopropylidene methyls (δ 1.40 and 1.66, $\Delta\delta$=0.26 ppm).[11] Exposure of **16a** to 10% HCl in methanol formed (±)-4'-methylpseudouridine (**17a**) in quantitative yield. Preparation of (±)-4'-methyl-2-thiopseudouridine (**19a**) was effected by heating **15a** with thiourea in ethanolic sodium ethoxide, followed by acidic removal of the isopropylidene group. Condensation of **15a** with guanidine followed by removal of the isopropylidene protective group produced (±)-4'-methylpseudoisocytidine (**21a**) in 64% yield.

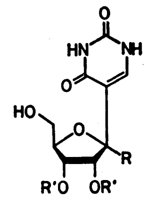
When an alkylated lactone **14b**[1] was used as the starting material, the 4'-pentyl pyrimidine *C*-nucleosides, **17b**, **19b**, and **21b**, were obtained according to similar synthetic procedures.

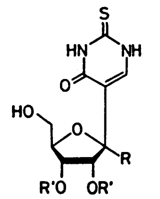
The otherwise unaccessible 4'-arylated pyrimidine *C*-nucleoside analogues, **17c**, **19c**, and **21c**, have been prepared by this completely stereocontrolled recipe starting from the phenylated lactone **14c**, derived from 2-phenylfuran and $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone.[18]

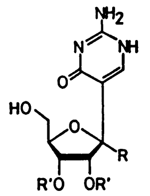
B. 1'-Alkylated Pyrimidine C-*Nucleosides*:[14] When the methylated lactone **22a**[1] was treated with t-$C_4H_9OCH[N(CH_3)_2]_2$ (neat, 90 °C), there was obtained the dimethylaminomethylene lactone **23a**, displaying IR absorptions at 1670 (C=O) and 1590 cm^{-1} (C=C). This was subjected immediately to the condensation with urea in ethanolic sodium ethoxide to afford **24a**. The reaction proceeded only sluggishly and the yield was only 7% based on **22a**. The ^{1}H NMR spectrum of **24a** indicated that the product has β configuation at C-1' position; the singlets due to the isopropylidene methyls occurred at δ 1.39 and 1.65 ($\Delta\delta$=0.26 ppm).[11] Removal of the isopropylidene block with 10% HCl in methanol yielded (±)-1'-methylpseudouridine (**25a**). The lactone **23a** underwent the sodium ethoxide-promoted condensation with thiourea in refluxing ethanol to produce the acetonide **26a**. Subsequent deprotection with 10% HCl in methanol liberated (±)-1'-methyl-2-thiopseudouridine (**27a**). Construction of the heterocyclic nucleus with guanidine gave rise to **28a**, methanolysis of which catalyzed by HCl afforded hydrochloride salt of **29a**. In a like manner, 1'-pentyl pyrimidine *C*-nucleosides, **25b**, **27b**, and **29b**, were obtained by employing the lactone **22b**.[1] Elaboration of heterocycles onto **22** was achieved less effectively because of the severe steric hindrance caused by the C-1' alkyl substitution. Nevertheless, this method realized the first synthesis of 1'-alkylated *C*-nucleosides.[22]

C. 1'- and 4'-Hydroxymethylated Pyrimidine C-*Nucleosides*:[23] Condensation of the lactone **30**[1] with t-$C_4H_9OCH[N(CH_3)_2]_2$ in DMF at 90 °C provided the dimethylaminomethylene compound **31** in 91% yield.

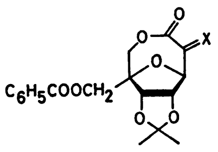


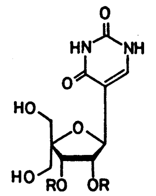


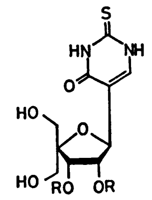




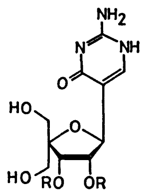
22, X=H_2 **24**, R'-R'=$C(CH_3)_2$ **26**, R'-R'=$C(CH_3)_2$ **28**, R'-R'=$C(CH_3)_2$
23, X=$CHN(CH_3)_2$ **25**, R'=H **27**, R'=H **29**, R'=H (HCl salt)
a, R=CH_3 **b**, R=$(CH_2)_4CH_3$

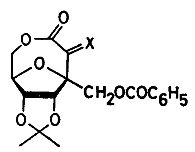


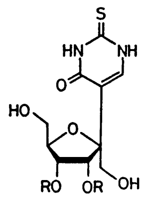




30, X=H_2 **32**, R-R=$C(CH_3)_2$ **34**, R-R=$C(CH_3)_2$
31, X=$CHN(CH_3)_2$ **33**, R=H **35**, R=H







36, R-R=$C(CH_3)_2$ **38**, X=H_2 **40**, R-R=$C(CH_3)_2$
37, R=H (HCl salt) **39**, X=$CHN(CH_3)_2$ **41**, R=H

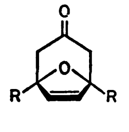
Treatment of **31** with urea in the presence of sodium ethoxide constructed the uracil skeleton and simultaneous removal of the benzoyl moiety gave **32** in a moderate yield. Deprotection of the isopropylidene group by 10% HCl in methanol formed (±)-4'-hydroxymethylpseudouridine (**33**) in 89% yield. Similarly, treatment of **31** with thiourea under the basic conditions, giving **34**, followed by deprotection afforded (±)-4'-hydroxymethyl-2-thiopseudouridine (**35**). The base-catalyzed cyclization of **31** with guanidine, giving **36**, followed by removal of the isopropylidene block furnished (±)-4'-hydroxymethylpseudoisocytidine (**37**) as hydrochloride salt.

In a parallel fashion, the lactone **39**, derived from **38** by the reaction with t-$C_4H_9OCH[N(CH_3)_2]_2$, was convertible to 1'-hydroxymethylated pyrimidine *C*-nucleosides such as (±)-1'-hydroxymethyl-2-thiopseudouridine (**41**). Thus the base-promoted condensation of **39** and thiourea affording the acetonide **40** and subsequent removal of the protective group gave the *C*-nucleoside **41** which consists of psicose and a pyrimidine base.[22)]

D. 1',4'-Dialkylated Pyrimidine C-*Nucleosides*:[24)] Bishydroxylation of **42a**[25)] using hydrogen peroxide (3 equiv) in the presence of a catalytic amount of osmium tetraoxide in a 10:1:1 mixture of acetone, *t*-butyl alcohol, and ether, followed by acetonidation with $CuSO_4$ and *p*-toluenesulfonic acid in acetone gave **43a**. The α stereochemical assignment was made on the basis of the ^{1}H NMR spectrum which exhibited the H_6 and H_7 signal as a singlet at δ 4.30.[26)] Then exposure of **43a** to trifluoroperacetic acid gave the lactone **44a** in 77% yield. Subsequent reaction with neat tris(dimethylamino)methane[27)] at 90 °C afforded the (*Z*)-dimethylaminomethylene lactone **45a** in 38% yield (88% based on consumed **44a**) as a single isomer. Condensation of **45a** with urea with ethanolic sodium ethoxide formed **46a** in 28% yield, which was then treated with 10% methanolic HCl to give (±)-1',4'-dimethylpseudouridine (**47a**). The ^{1}H NMR spectrum giving the isopropylidene methyl signals at δ 1.28 and 1.50 (Δδ=0.22 ppm) confirmed the β heterocycle stereochemistry assigned for **46a**.[11,28)] When thiourea was employed for the analogous cyclization, there was obtained in 60% yield the 2-thiouracil derivative **48a**, leading to **49a** after deprotection. Use of guanidine in place of urea gave rise to **51a** as HCl salt *via* **50a** in 75% yield.

In a usual manner, the 1',4'-dipentyl analogues, **47b**, **49b**, and **51b**, have also been prepared starting with **42b**.

Thus present way appears to provide a facile, general entry to 1',4'-disubstituted pyrimidine *C*-nucleosides which are not available by the conventional approaches



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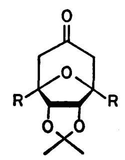

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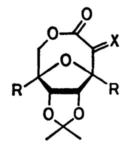
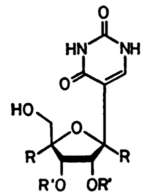
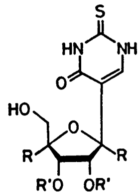


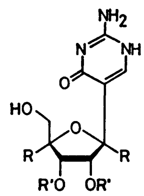
44, $X=H_2$
45, $X=CHN(CH_3)_2$



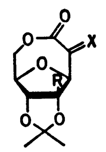
46, R'-$R'=C(CH_3)_2$
47, $R'=H$
a, $R=CH_3$ **b**, $R=(CH_2)_4CH_3$



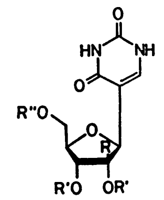
48, R'-$R'=C(CH_3)_2$
49, $R'=H$



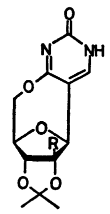
50, R'-$R'=C(CH_3)_2$
51, $R'=H$ (HCl salt)



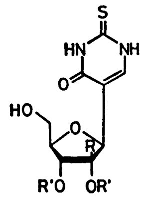
52a, $R=CH_2OTBDMS$; $X=H_2$
52b, $R=CH_3$; $X=H_2$
53a, $R=CH_2OTBDMS$; $X=CHN(CH_3)_2$
53b, $R=CH_3$; $X=CHN(CH_3)_2$



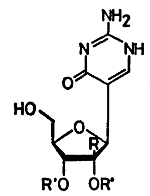
54a, $R=CH_2OTBDMS$; R'-$R'=C(CH_3)_2$; $R''=H$
54b, $R=CH_3$; R'-$R'=C(CH_3)_2$; $R''=H$
55a, $R=CH_2OH$; $R'=R''=H$
55b, $R=CH_3$; $R'=R''=H$
56a, $R=CH_2OTBDMS$; R'-$R'=C(CH_3)_2$; $R''=SO_2CH_3$
56b, $R=CH_3$; R'-$R'=C(CH_3)_2$; $R''=SO_2CH_3$



57a, $R=CH_2OTBDMS$
57b, $R=CH_3$



58a, $R=CH_2OTBDMS$; R'-$R'=C(CH_3)_2$
58b, $R=CH_3$; R'-$R'=C(CH_3)_2$
59a, $R=CH_2OH$; $R'=H$
59b, $R=CH_3$; $R'=H$
$TBDMS=Si(CH_3)_2$-t-C_4H_9



60a, $R=CH_2OTBDMS$; R'-$R'=C(CH_3)_2$
60b, $R=CH_3$; R'-$R'=C(CH_3)_2$
61a, $R=CH_2OH$; $R'=H$ (HCl salt)
61b, $R=CH_3$; $R'=H$ (HCl salt)

reported to date.

Synthesis of 2′-Alkylated Pyrimidine C-*Nucleosides*:[29] Treatment of **52a**[1] with excess t-$C_4H_9OCH[N(CH_3)_2]_2$ at 70 °C afforded the corresponding condensation product **53a** in 52% yield. The base-aided reaction with excess urea led to the uracil derivative **54a** in 20% yield, deprotection of which by methanolic HCl gave (±)-2′-hydroxymethylpseudouridine (**55a**) in 95% yield. The β stereochemistry at the anomeric position was established chemically by converting the acetonide **54a** to the cyclo-*C*-nucleoside **57a**. Thus reaction of **54a** and methanesulfonyl chloride in pyridine and subsequent treatment with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in acetonitrile gave **57a** in *ca.* 60% yield.[30] Formation of the expected product was substantiated by comparison of the UV spectrum in methanol (λ_{max} 295 nm, ε 3720) showing a well-known, characteristic bathochromic shift, with that of the starting open-form **54a** (λ_{max} 266 nm, ε 7150).[21]

When the lactone **53a** was annulated with thiourea, the protected nucleoside **58a** was obtained in high yield. Brief treatment of **58a** with methanolic HCl afforded (±)-2′-hydroxymethyl-2-thiopseudouridine (**59a**). Similarly, treatment of **53a** with guanidine, giving **60a**, and acid-assisted deprotection under the standard conditions led to (±)-2′-hydroxymethylpseudoisocytidine (**61a**) as HCl salt.

In a like fashion, 2′-methylated pyrimidine *C*-nucleosides, **55b**, **59b**, and **61b**, were synthesized by use of **52b**.[1)]

This method allows ready construction of the difficult-to-make hamamelose and 2′-methylribofuranose skeletons and introduction of pyrimidine rings at the 1′-position.[31)]

As has been outlined above, this approach is synthetically very flexible and a variety of *C*-nucleoside analogues can be made by parallel routes. The possibility was examined only with achiral or racemic precursors, but the optical resolution of the intermediates, leading to the "natural" configurations, could be done most conveniently at the stage of the lactones of type **4**.[2)]

Experimental

General. All melting and boiling points are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrometer in $CHCl_3$ solution unless otherwise stated. ^1H NMR spectra were obtained using a Varian NV-21 or HA-100 spectrometer, and ^{13}C NMR spectra were recorded at 20 MHz on a Varian CFT-20 spectrometer or at 25 MHz on a JEOL FX-100 spectrometer. The chemical shifts are recorded in parts per million relative to tetramethylsilane as an internal standard. Singlet, doublet, triplet, and multiplet are abbreviated to s, d, t, and m, respectively. Exact mass spectra were obtained at Central Research Laboratory of Ono Pharmaceutical Co. Elemental analyses were performed at the Research Laboratory of Fujisawa Pharmaceutical Co. and Faculty of Engineering of Nagoya University. Drying of organic extracts was done over anhydrous Na_2SO_4. For concentration of organic solvents, a vacuum (50—100 mmHg)** rotary evaporator was used.

Chromatography. Thin-layer chromatography (TLC) was done using a glass plate coated with 0.25-mm layers of silica gel 60 PF_{254} obtained from E. Merck and for preparative TLC, 20×20-cm glass plates coated with a 1.0-mm layer of silica gel 60 PF_{254} were employed. Analytical plates were visualized by spraying with a solution of 2% $Ce(SO_4)_2$ in 5% H_2SO_4 or 2% *p*-anisaldehyde in 5% ethanolic H_2SO_4 followed by heating on a hot plate. The position of spots are shown by R_f values. For column chromatography, E. Merck Kieselgel 60 (70—230 mesh) was used. For separation of the dimethylaminomethylene lactones, silica gel treated with diluted aqueous ammonia was used.[33)]

Solvents and Materials. DMF, acetonitrile, *t*-C_4H_9OH, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used after distillation from CaH_2. Acetone and CH_2Cl_2 were distilled from P_2O_5. Ethanoı was distilled over magnesium ribbons. THF and ether were distilled from sodium benzophenone ketyl. Preparations of Zn/Ag couple,[34)] Zn/Cu couple,[35)] 2-pentylfuran,[1)] α,α,α′,α′-tetrabromoacetone,[36)] *t*-butoxybis(dimethylamino)methane,[10)] and tris(dimethylamino)methane[27)] were performed according to the known procedures. Other commercially supplied materials and solvents were used as received.

Preparation of Methyl [(2S,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-phenyltetrahydrofuran-2-yl]acetate.* A mixture of **14c** (111 mg, 0.383 mmol),[1)] sodium methoxide (31.0 mg, 0.574 mmol), and CH_3OH (3 ml)*** was stirred at 0 °C for 1 h under argon and to this was added oxalic acid (100 mg). Evaporation followed by extraction with chloroform afforded the title compound (115 mg, 91%) as a white solid. R_f=0.28 (1:1 hexane–ethyl acetate); IR 3580 (OH), 1732 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.04 and 1.28 (s, isopropylidene CH_3), 2.74 (dd, *J*=6.0, 14.5 Hz, $\underline{H}_aH_bCC=O$), 2.96 (dd, *J*=4.8, 14.5 Hz, $H_a\underline{H}_bCC=O$), 3.62 (d, *J*=12.5 Hz, $\underline{H}_aH_bCOH$), 3.77 (s, OCH_3), 3.86 (d, *J*=12.5 Hz, $H_a\underline{H}_bCOH$), 4.40 (m, H_2), 4.56 (t-like, *J*=6.0 Hz, H_3), 5.02 (br, OH), 5.16 (d, *J*=6.0 Hz, H_4), 7.35 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 25.80, 26.70, 37.21, 51.94, 69.33, 79.65, 83.86, 84.06, 90.23, 114.44, 126.50, 127.27, 127.82, 138.12, 171.69. Found: *m/z*, 291.1231. Calcd for $C_{16}H_{19}O_5$: ($M-OCH_3$), 291.1232.

Preparation of 2,5-Dipentylfuran. To a mixture of *n*-C_4H_9Li (1.6 mol dm^{-3} hexane solution, 288 ml, 0.461 mol) and THF (350 ml) was added 2-pentylfuran (60.6 g, 0.439 mol) at −10 °C under argon. After the mixture was stirred at the same temperature for 6 h, pentyl iodide (91.3 g, 0.461 mol) was added. The reaction mixture was stirred at 20 °C for 12 h and then poured into ice-water (200 ml). The organic layer was separated and the aqueous layer was extracted with ether (150 ml×3). The combined organic extracts were dried ($MgSO_4$) and evaporated to leave a yellow oil, which was distilled under reduced pressure to give 2,5-dipentylfuran (68.2 g, 75%, bp 103—108 °C/9 mmHg (lit,[37)] 99—100 °C/5 mmHg)) as a colorless oil. ^1H NMR ($CDCl_3$) δ 0.91 (t, *J*=6.3 Hz), 1.1—1.8 (m), 2.57 (t, *J*=7.0 Hz), 5.84 (s); MS *m/z* 208 (M^+).

*1,5-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**42a**).* To a mixture of Zn/Ag couple (26.0 g, 0.40 g-atom) and 2,5-dimethylfuran (21.3 ml, 0.20 mol) in THF (150 ml) was added a solution of α,α,α′,α′-tetrabromoacetone (224 g, 0.60 mol) in THF (200 ml) over 30 min at −10 °C under argon. The mixture was allowed to warm up to 20 °C and stirred at the same temperature for 12 h. The mixture was evaporated and the residue was dissolved in CH_3OH saturated with NH_4Cl (400 ml). To this was added portionwise Zn/Cu couple (130 g, 2.0 g-atom) over 2 h at 0 °C. The mixture was stirred at 20 °C for an additional 1 h and diluted with water (400 ml) and saturated disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2edta) solution (400 ml). The insoluble material was removed by filtration and the filtrate was extracted with CH_2Cl_2 (300 ml×3). The combined organic layers were dried (Na_2SO_4) and concentrated. Chromatography of the residue on a silica-gel column using a 3:1 hexane–ethyl acetate mixture afforded **42a** (20.0 g, 66%) as a white solid. Mp 64—66 °C (hexane–chloroform); R_f= 0.47 (3:1 hexane–ethyl acetate); IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.50 (s, CH_3), 2.32 (d, *J*=16.1 Hz, H_{2a} and H_{4a}), 2.51 (d, *J*=16.1 Hz, H_{2b} and H_{4b}), 5.97 (s, H_6 and H_7); ^{13}C NMR ($CDCl_3$) δ 23.30, 51.12, 83.83, 136.42, 207.07. Found: C, 71.55, H, 8.06%. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95%.

*1,5-Dipentyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**42b**).* A mixture of Zn/Ag couple (39.0 g, 0.60 g-atom), 2,5-dipentylfuran (62.4 g, 0.30 mol), α,α,α′,α′-tetrabromoacetone (337 g, 0.9 mol), and THF (400 ml) was stirred at 20 °C for 24 h. Reduction of the reaction mixture with Zn/Cu couple (292 g, 4.50 g-atom) in CH_3OH (500 ml) saturated with NH_4Cl

** 1 mmHg≈133.322 Pa.

*** 1 ml=0.001 dm^3.

followed by extractive workup with CH_2Cl_2 gave a brown oil. Chromatography of the residue on a silica-gel column using a 10:1 hexane–ethyl acetate mixture afforded **42b** (32.5 g, 41%) as a colorless oil. R_f=0.35 (10:1 hexane–ethyl acetate); IR (neat) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.5 Hz, CH_3), 1.1—1.9 (m, CH_2), 2.28 (d, J=16.0 Hz, H_{2a} and H_{4a}), 2.48 (d, J=16.0 Hz, H_{2b} and H_{4b}), 5.95 (s, H_6 and H_7); ^{13}C NMR ($CDCl_3$) δ 14.00, 22.59, 23.65, 32.18, 36.65, 50.53, 86.59, 135.42, 207.25. Found: m/z, 264.2092. Calcd for $C_{17}H_{28}O_2$: M, 264.2089. In addition, unreacted 2,5-dipentylfuran (12.9 g) was recovered.

(1S,5R*,6S*,7R*)-1,5-Dimethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (43a).* To a mixture of **42a** (25.0 g, 0.164 mol) and OsO_4 (300 mg, 1.18 mmol) in acetone (200 ml), t-C_4H_9OH (20 ml), and ether (20 ml) was added 30% H_2O_2 (36.2 ml, 0.329 mol). The mixture was stirred at 19 °C for 15 h and to this was added renewedly 30% H_2O_2 (18.1 ml, 0.165 mol). The mixture was stirred for an additional 12 h and cooled to 0 °C. To this was added powder of $Na_2S_2O_3\cdot 5H_2O$ (77 g) and stirring was continued at 20 °C for 3 h. The residue obtained by evaporation was extracted with ethyl acetate (250 ml×3). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was dissolved in acetone (250 ml) and to this was added $CuSO_4$ (30 g) and p-toluenesulfonic acid (250 mg). The resulting mixture was stirred at 20 °C for 12 h. The insoluble material was removed by filtration and the filtrate was concentrated to afford a dark oil, which was chromatographed on a silica-gel column using a 3:1 hexane–ethyl acetate mixture to afford **43a** (22.5 g, 61%). Mp 67—68 °C (hexane–chloroform); R_f=0.32 (3:1 hexane–ethyl acetate); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30 and 1.52 (s, isopropylidene CH_3), 1.41 (s, CH_3), 2.28 (d, J=15.0 Hz, H_{2a} and H_{4a}), 2.50 (d, J=15.0 Hz, H_{2b} and H_{4b}), 4.30 (s, H_6 and H_7); ^{13}C NMR ($CDCl_3$) δ 20.12, 25.00, 26.12, 51.71, 82.59, 85.30, 112.42, 206.90. Found: m/z, 211.0971. Calcd for $C_{11}H_{15}O_4$: (M−CH_3), 221.0970.

(1S,5R*,6S*,7R*)-1,5-Dipentyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (43b).* A mixture of **42b** (11.8 g, 44.7 mmol), acetone (70 ml), t-C_4H_9OH (7 ml), ether (7 ml), OsO_4 (100 mg), and 30% H_2O_2 (14.7 ml, 134 mmol) was stirred at 20 °C for 12 h and to this was added $Na_2S_2O_3\cdot 5H_2O$ (33.5 g) at 0 °C. The resulting mixture was stirred at 20 °C for 3 h. After the usual workup, the residue was dissolved in acetone (150 ml). To this was added $CuSO_4$ (15 g) and p-toluenesulfonic acid (100 mg). After stirring at 20 °C for 24 h, the usual workup and chromatographic isolation (silica gel, 10:1 hexane–ethyl acetate) yielded **43b** (6.50 g, 43%) as a colorless oil. R_f=0.36 (10:1 hexane–ethyl acetate); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.0 Hz, CH_3), 1.28 and 1.50 (s, isopropylidene CH_3), 1.1—1.9 (m, CH_2), 2.30 (d, J=14.5 Hz, H_{2a} and H_{4a}), 2.48 (d, J=14.5 Hz, H_{2b} and H_{4b}), 4.30 (s, H_6 and H_7); ^{13}C NMR ($CDCl_3$) δ 16.64, 25.19, 26.12, 27.78, 28.80, 35.03, 36.43, 52.18, 87.39, 87.59, 114.78, 210.07.

(1R,6S*,7R*,8S*)-1,6-Dimethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (44a).* Trifluoroperacetic acid prepared from trifluoroacetic anhydride (46.5 ml, 0.328 mol) and 90% H_2O_2 (11.8 ml, 0.312 mol) in CH_2Cl_2 (150 ml) was added dropwise to a stirred, ice-cooled mixture of Na_2HPO_4 (140 g, 0.984 mol), Na_2H_2edta (1 g), and **43a** (35.2 g, 0.156 mol) in CH_2Cl_2 (200 ml). The mixture was stirred at 20 °C for 13 h and diluted with CH_2Cl_2 (200 ml). To this was added $Na_2S_2O_3\cdot 5H_2O$ (78 g) at 0 °C and the resulting mixture was stirred at 20 °C for 3 h. The insoluble material was removed by filtration and the filtrate was evaporated. Chromatography of the residue on a silica-gel column using a 3:1 to 2:1 hexane–ethyl acetate mixture afforded **44a** (28.9 g, 77%). Mp 123—124 °C (hexane–chloroform); R_f=0.15 (3:1 hexane–ethyl acetate); IR 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.27 and 1.35 (s, CH_3), 1.35 and 1.51 (s, isopropylidene CH_3), 2.83 (d, J=16.0 Hz, H_{5a}), 3.07 (d, J=16.0 Hz, H_{5b}), 4.11 (d, J=13.5 Hz, H_{2a}), 4.33 (d, J=13.5 Hz, H_{2b}), 4.56 (d, J=6.0 Hz, H_7), 4.88 (d, J=6.0 Hz, H_8); ^{13}C NMR ($CDCl_3$) δ 17.95, 22.16, 24.73, 26.01, 49.44, 75.96, 81.12, 83.63, 85.52, 112.57, 172.09. Found: C, 59.47; H, 7.60%. Calcd for $C_{12}H_{18}O_5$: C, 59.49, H, 7.49%.

(1R,6S*,7R*,8S*)-1,6-Dipentyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (44b).* To a mixture of **43b** (15.5 g, 45.9 mmol), Na_2HPO_4 (64.8 g, 0.456 mol), and CH_2Cl_2 (100 ml) was added trifluoroperacetic acid in CH_2Cl_2 (1.08 mol dm^{-3} solution, 128 ml, 0.138 mol) at 0 °C. After stirring at 20 °C for 12 h, the reaction mixture was worked up to give a white solid, which was purified on a silica-gel column (10:1 hexane–ethyl acetate) to give **44b** (12.2 g, 77%) as a white solid. Mp 60—62 °C (chloroform–hexane); R_f=0.37 (5:1 hexane–ethyl acetate); IR 1736 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.89 (t, J=6.0 Hz, CH_3), 1.31 and 1.49 (s, isopropylidene CH_3), 1.1—1.9 (m, CH_2), 2.28 (d, J=15.5 Hz, H_{5a}), 2.99 (d, J=15.5 Hz, H_{5b}), 4.17 (d, J=13.9 Hz, H_{2a}), 4.32 (d, J=13.9 Hz, H_{2b}), 4.52 (d, J=5.9 Hz, H_7), 4.98 (d, J=5.9 Hz, H_8); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.41, 23.52, 24.57, 25.92, 32.26, 32.86, 35.56, 46.74, 75.06, 83.17, 85.11, 85.30, 112.12, 173.12. Found: C, 67.79; H, 9.76%. Calcd for $C_{20}H_{34}O_5$: C, 67.76; H, 9.67%. In addition, unreacted ketone **43b** (1.90 g) was recovered.

Preparation of the α-Dimethylaminomethylene Lactones. General Procedure: Unless otherwise stated, the dimethylaminomethylenation was performed as follows. A mixture of a lactone, t-butoxybis(dimethylamino)methane or tris(dimethylamino)methane, and DMF (in some reactions, DMF was not used) was magnetically stirred at the stated temperature under argon. After stirring for the stated period, the mixture was concentrated under reduced pressure (0.01 mmHg) at 25—50 °C. Chromatography was done on a silica-gel column using the described solvent system as eluent. Elution course of the column chromatography was monitored by TLC and fractions including the desired product were combined and evaporated. A sample for elemental analysis was obtained by recrystallizations of the chromatographed product.

(1S,6R*7R*,8S*)-2,2-Dimethyl-5-(dimethylaminomethylene)-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (7a).* A mixture of **6a**[1)] (520 mg, 1.75 mmol), DMF (5 ml), and t-butoxybis(dimethylamino)methane (2.5 ml) was heated at 50 °C for 3 h. The reaction mixture was subjected to the usual workup. Pure **7a** (442 mg, 85%) was obtained by silica-gel column chromatography (5:1 to 1:1 hexane–ethyl acetate). Mp 136.5—137.2 °C (ether); R_f=0.35 (ethyl acetate); IR 1670 (C=O), 1590 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.33 and 1.51 (s, isopropylidene CH_3), 1.44 and 1.47 (s, CH_3), 2.93 and 3.14 (s, $N(CH_3)_2$, 3:7 ratio), 6.58 and 7.39 (s, =C$\underline{H}$N$(CH_3)_2$, 3:7 ratio); MS m/z 297 (M^+); UV λ_{max} (CH_3OH) 300 nm (ε 15850). Found: C, 60.24; H, 7.79; N, 4.55%. Calcd for $C_{15}H_{23}O_5N$: C, 60.59; H, 7.80; N, 4.71%.

(1R,2R*,6R*,7R*,8R*)-5-(Dimethylaminomethylene)-7,8-isopropylidenedioxy-2-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (7b).* A mixture of **6b**[1)] (35 mg, 0.15 mmol), t-butoxybis(dimethylamino)methane (0.3 ml), and DMF (1 ml) was stirred at 50 °C for 1 h. After the usual workup, the crude product was purified by preparative TLC (ethyl acetate) to give

7b (20 mg, 47%). Mp 120.1—121.3 °C (ether–hexane); R_f=0.33 (ethyl acetate); IR 1680 (C=O), 1590 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.34 and 1.53 (s, isopropylidene CH_3), 1.38 (d, J=7.3 Hz, CH_3), 2.94 and 3.14 (s, $N(CH_3)_2$, 35:65 ratio), 6.66 and 7.34 (s, =C$\underline{H}$N$(CH_3)_2$, 35:65 ratio); MS m/z 283 (M^+); UV λ_{max} (CH_3OH) 298 nm (ε 16590). Found: C, 59.42; H, 7.64; N, 4.85%. Calcd for $C_{14}H_{21}O_5N$: C, 59.35; H, 7.47; N, 4.94%.

(1R,2R*,6R*,7R*,8R*)-5-(Dimethylaminomethylene)-7,8-isopropylidenedioxy-2-pentyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**7c**).* A mixture of **6c**[1)] (2.37 g, 8.36 mmol), *t*-butoxybis(dimethylamino)methane (12.0 ml), and DMF (15 ml) was stirred at 50 °C for 5 h. After the usual workup, the crude product was chromatographed on silica gel using ethyl acetate as the eluent to give **7c** (2.45 g, 86%). Mp 86.2—87.8 °C (ether–hexane); R_f=0.53 (ethyl acetate); IR 1680 (C=O), 1595 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 0.89 (t-like, J=6.0 Hz, CH_3), 1.32 and 1.50 (s, isopropylidene CH_3), 2.94 and 3.12 (s, $N(CH_3)_2$, 37:63 ratio), 6.65 and 7.32 (s =C$\underline{H}$N$(CH_3)_2$, 37:63 ratio); MS m/z 339 (M^+); UV λ_{max} (CH_3OH) 298 nm (ε 23980). Found: C, 63.62; H, 8.75; N, 4.01%. Calcd for $C_{18}H_{29}O_5N$: C, 63.69; H, 8.61; N, 4.13%.

(1S,2S*,6R*,7R*,8R*)-5-(Dimethylaminomethylene)-7,8-isopropylidenedioxy-2-phenyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**7d**).* A mixture of **6d**[1)] (98 mg, 0.338 mmol), *t*-butoxybis(dimethylamino)methane (0.5 ml), and DMF (2 ml) was stirred at 50 °C for 3.5 h. The usual workup and preparative TLC (2:1 ethyl acetate–hexane) yielded **7d** (74.0 mg, 64%) as a foam. R_f=0.51 (ethyl acetate); IR 1680 (C=O), 1590 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.28 and 1.47 (s, isopropylidene CH_3), 2.94 and 3.15 (s, $N(CH_3)_2$, 38:62 ratio), 6.73 (s, =C$\underline{H}$N$(CH_3)_2$, *E*-isomer); MS m/z 345 (M^+); UV λ_{max} (CH_3OH) 299 nm (ε 13810).

(1R,6R*,7S*,8S*)-5-(Dimethylaminomethylene)-7,8-isopropylidenedioxy-1-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**15a**).* A mixture of **14a**[1)] (952 mg, 4.18 mmol), tris(dimethylamino)methane (4.5 ml), and DMF (1 ml) was stirred at 70 °C for 1 h. To this was renewedly added tris(dimethylamino)methane (1.2 ml). After 2 h, tris(dimethylamino)methane (0.5 ml) was added again and stirring was continued for 3 h. The usual workup and chromatography on silica gel with a 1:1 hexane–ethyl acetate mixture to pure ethyl acetate afforded **15a** (831 mg, 70%). Mp 118—120 °C (ether); R_f=0.37 (ethyl acetate); IR 1680 (C=O), 1590 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.26 and 1.51 (s, isopropylidene CH_3), 1.33 (s, CH_3), 2.94 and 3.11 (s, $N(CH_3)_2$, 33:67 ratio), 6.67 and 7.34 (s, =C$\underline{H}$N$(CH_3)_2$, 33:67 ratio); MS m/z 297 (M^+); UV λ_{max} (CH_3OH) 297 nm (ε 19800). Found: C, 59.18; H, 7.79; N, 4.92%. Calcd for $C_{14}H_{21}O_5N$: C, 59.35; H, 7.47; N, 4.92%.

(1R,6R*,7S*,8S*)-5-(Dimethylaminomethylene)-7,8-isopropylidenedioxy-1-pentyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**15b**).* A mixture of **14b**[1)] (754 mg, 2.23 mmol), tris(dimethylamino)methane (2.6 ml) was stirred at 70 °C for 1 h. The reaction mixture was worked up and purified by silica gel column chromatography (1:1 hexane–ethyl acetate to ethyl acetate) to give **15b** (683 mg, 91%). Mp 117—118 °C (ether); R_f=0.46 (ethyl acetate); IR 1680 (C=O), 1595 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 0.89 (t-like, J=6.0 Hz, CH_3), 1.30 and 1.50 (s, isopropylidene CH_3), 2.94 and 3.13 (s, $N(CH_3)_2$, 31:69 ratio), 6.67 and 7.34 (s, =C$\underline{H}$N$(CH_3)_2$, 31:69 ratio); MS m/z 339 (M^+); UV λ_{max} (CH_3OH) 297 nm (ε 18500). Found: C, 63.38; H, 8.94; N, 4.09%. Calcd for $C_{18}H_{29}O_5N$: C, 63.69; H, 8.61; N, 4.09%.

(1R,6R*,7S*,8S*)-5-(Dimethylaminomethylene)-7,8-isopropylidenedioxy-1-phenyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**15c**).* A mixture of **14c**[1)] (987 mg, 3.40 mmol), tris(dimethylamino)methane (3.5 ml), and DMF (2 ml) was stirred at 70 °C for 1 h. Purification of the reaction mixture by silica-gel column chromatography (1:1 hexane–ethyl acetate to ethyl acetate) gave **15c** (1.08 g, 92%). Mp 233—235 °C (acetone); R_f=0.48 (ethyl acetate); IR 1680 (C=O), 1598 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.30 and 1.33 (s, isopropylidene CH_3), 2.98 and 3.20 (s, $N(CH_3)_2$, 37:63 ratio), 6.80 (s, =C$\underline{H}$N$(CH_3)_2$, *E*-isomer); MS m/z 345 (M^+); UV λ_{max} (CH_3OH) 298 nm (ε 18300). Found: C, 66.21; H, 6.68, N, 4.02%. Calcd for $C_{19}H_{23}O_5N$: C, 66.07; H, 6.71, N, 4.06%.

(1R,6R*,7S*,8S*)-1-Benzoyloxymethyl-5-(dimethylaminomethylene)-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**31**).* A mixture of **30**[1)] (350 mg, 1.00 mmol) and *t*-butoxybis(dimethylamino)methane (1 ml) in DMF (1 ml) was stirred at 90 °C for 30 min. Workup followed by column chromatography (1:1 hexane–ethyl acetate to pure ethyl acetate) afforded **31** (368 mg, 91%) as a white foam. R_f=0.28 (1:2 hexane–ethyl acetate); IR 1725 and 1683 (C=O), 1590 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.31 and 1.50 (s, isopropylidene CH_3), 2.94 and 3.11 (s, $N(CH_3)_2$, 37:63 ratio), 6.70 (s, =C$\underline{H}$N$(CH_3)_2$, *E*-isomer).

(1R,6R*,7R*,8R*)-6-Benzoyloxymethyl-5-(dimethylaminomethylene)-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**39**).* A mixture of **38**[1)] (696 mg, 2.0 mmol), *t*-butoxybis(dimethylamino)methane (2 ml), and DMF (1.5 ml) was stirred at 60 °C for 4 h. Chromatography on a silica-gel column using a 1:1 to 3:1 ethyl acetate–hexane mixture gave **39** (223 mg, 29%, 57% based on consumed starting material) as a white foam. R_f=0.46 (ethyl acetate); IR 1722 and 1690 (C=O), 1600 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.32 and 1.51 (s, isopropylidene CH_3), 2.84 and 3.16 (s, $N(CH_3)_2$, 80:20 ratio), 6.75 (s, =C$\underline{H}$N$(CH_3)_2$, *E*-isomer). In addition, unreacted **38** was recovered (340 mg).

(1R,5Z,6R*,7R*,8S*)-5-(Dimethylaminomethylene)-1,6-dimethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**45a**).* A mixture of **44a** (7.92 g, 32.7 mmol) and tris(dimethylamino)methane (30 ml) was stirred at 90 °C for 8 h. Workup gave a solid, which was purified on a silica-gel column (1:1 hexane–ethyl acetate to pure ethyl acetate) to give **45a** (3.70 g, 38%). Mp 116—118 °C (ether); R_f=0.41 (ethyl acetate); IR 1680 (C=O), 1595 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.25 and 1.47 (s, CH_3), 1.33 and 1.53 (s, isopropylidene CH_3), 2.87 (s, $N(CH_3)_2$), 3.97 (d, J=13.0 Hz, H_{2a}), 4.16 (d, J=13.0 Hz, H_{2b}), 4.59 (d, J=5.9 Hz, H_7), 4.72 (d, J=5.9 Hz, H_8), 6.79 (s, =C$\underline{H}$N$(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 17.48, 20.41, 24.69, 26.04, 44.22, 75.17, 82.15, 84.26, 84.87, 88.33, 100.57, 112.10, 149.13, 170.40. Found: C, 60.25; H, 7.87; N, 4.57%. Calcd for $C_{15}H_{23}O_5N$: C, 60.59; H, 7.80; N, 4.71%. In addition, unreacted **44a** (4.51 g) was recovered.

(1R,5Z,6R*,7R*,8S*)-5-(Dimethylaminomethylene)-1,6-dipentyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**45b**).* A mixture of **44b** (1.76 g, 4.97 mmol) and tris(dimethylamino)methane (5 ml) was stirred at 90 °C for 4 h. The usual workup of the reaction mixture gave an oily product, which was subjected to silica-gel chromatography with a 1:1 hexane–ethyl acetate mixture to pure ethyl acetate to afford **45b** (1.23 g, 61%) as a yellow oil. R_f=0.39 (1:1 hexane–ethyl acetate); IR 1688 (C=O), 1601 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 0.88 (t, J=6.0 Hz, CH_3), 1.33 and 1.51 (s, isopropylidene CH_3), 1.1—1.9 (m, CH_2), 2.84 (s, $N(CH_3)_2$), 3.88 (d, J=13.1 Hz, H_{2a}), 4.15 (d, J=13.1 Hz, H_{2b}), 4.52 (s, H_7 and H_8), 6.39 (s, =C$\underline{H}$N$(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.41, 23.37, 24.87, 26.09, 32.44, 33.00, 35.19, 43.61, 71.50, 83.22, 85.29, 86.45, 88.98, 99.58, 112.03, 146.50, 171.43.

(1R,6S*,7R*,8R*)-5-(Dimethylaminomethylene)-7,8-isopropylidenedioxy-7-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**53b**).* A mixture of **52b**[1)] (1.00 g, 4.41 mmol), *t*-butoxybis(dimethylamino)methane (11 ml), and DMF (1 ml) was stirred at 70 °C for 1 h. Purification of the crude product by silica-gel chromatography (1:1 hexane–ethyl acetate to pure ethyl acetate) afforded **53b** (789 mg, 63%). Mp 137—138 °C (hexane–ethyl acetate); R_f=0.45 (ethyl acetate); IR 1672 (C=O), 1592 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ 3.44 and 3.52 (s, $N(CH_3)_2$, 3:2 ratio), 6.64 and 7.46 (s, =C$\underline{H}$N-$(CH_3)_2$, 3:2 ratio); UV λ_{max} (CH_3OH) 300 nm (ε 16400). Found: C, 59.18; H, 7.41; N, 4.86%. Calcd for $C_{14}H_{21}O_5N$: C, 59.35; H, 7.47; N, 4.94%.

(1R,6S*,7R*,8R*)-7-t-Butyldimethylsiloxymethyl-5-(dimethylaminomethylene)-7,8-isopropylidenedioxy-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**53a**).* A mixture of **52a**[1)] (1.86 g, 5.20 mmol), *t*-butoxybis(dimethylamino)methane (14.7 ml), and DMF (1.2 ml) was stirred at 70 °C for 1 h. Usual workup followed by silica-gel chromatography (2:1 to 1:2 hexane–ethyl acetate) afforded **53a** (1.12 g, 52%). Mp 139—142 °C (hexane–ethyl acetate); R_f=0.37 (1:2 hexane–ethyl acetate); IR 1675 (C=O), 1581 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ 2.95 and 3.14 (s, $N(CH_3)_2$, 1:2 ratio), 6.68 and 7.50 (s, =C$\underline{H}$$N(CH_3)_2$, 1:2 ratio). Found: C, 57.64; H, 8.57; N, 3.21%. Calcd for $C_{20}H_{35}O_6NSi$: C, 58.08; H, 8.53; N, 3.39%.

Reaction of Dimethylaminomethylene Lactones with Urea, Thiourea, and Guanidine. General Procedure: Method A: A mixture of a dimethylaminomethylene lactone, urea, and a C_2H_5ONa in C_2H_5OH solution was heated at reflux under argon until the reaction completed. The mixture was cooled to room temperature and evaporated to dryness. The resulting residue was dissolved in H_2O. After careful neutralization with diluted hydrochloric acid, the aqueous solution was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4. The organic solution was concentrated under reduced pressure (50—90 mmHg), giving a crude material. The residue was subjected to preparative TLC. In TLC separation, silica-gel layer of the product area absorbing the 254-nm light was collected and extracted with a 1:1 chloroform–CH_3OH mixture. A sample for elemental analysis was obtained by repeated preparative TLC or recrystallization of the chromatographed product.

Method B: The reaction was carried out according to Method A. After the reaction was complete, the mixture was cooled to room temperature. The reaction mixture was evaporated and the resulting residue was taken up in water. To this was carefully added diluted hydrochloric acid until the solution was neutralized by monitoring with a pH test paper. The aqueous solution was concentrated and the resulting residue was diluted with ethanol. The insoluble material was removed by the filtration through a short column of Celite 545 and concentrated with a rotary evaporator under reduced pressure (50—90 mmHg) at 25—50 °C. The residue was subjected to preparative TLC and worked up as described above.

The same procedure was applied for the reaction using thiourea and guanidine hydrochloride instead of urea.

With Urea. 5-[(2R,3R*,4S*,5S*)-5-(1-Hydroxy-1-methylethyl)-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**8a**)*: A mixture of **7a** (906 mg, 3.05 mmol), urea (1.90 g, 30.5 mmol), and 2.3 mol dm^{-3} C_2H_5ONa in C_2H_5OH solution (13 ml) was stirred for 5 h. The reaction mixture was subjected to the usual workup according to Method A. Pure **8a** (438 mg, 48%) was obtained by preparative TLC (5:1 chloroform–CH_3OH). Mp 153.1—156.8 °C (CH_3OH); R_f= 0.42 (7:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 1.41 and 1.67 (s, isopropylidene CH_3), 1.48 and 1.53 (s, CH_3), 4.12 (d, J=3.7 Hz, H_5), 5.08 (d, J=3.7 Hz, H_2), 5.30 (m, H_3 and H_4), 7.93 (s, =CH); UV λ_{max} (CH_3OH) 263 nm (ε 3890), λ_{max} (0.1 mol dm^{-3} NaOH) 286 nm (ε 5370). Found: C, 53.96; H, 6.40; N, 9.05%. Calcd for $C_{14}H_{20}O_6N_2$: C, 53.84; H, 6.45; N, 8.97%.

5-[(2R,3R*,4R*,5R*)-5-[(R*)-1-Hydroxyethyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**8b**)*: A mixture of **7b** (975 mg, 3.45 mmol), urea (2.10 g, 34.5 mmol), and 2.30 mol dm^{-3} C_2H_5ONa in C_2H_5OH (15 ml) was stirred for 5 h. After the usual workup according to Method A, the crude product was purified by preparative TLC (5:1 chloroform–CH_3OH) to afford **8b** (464 mg, 47%). Mp 264.5—266 °C (CH_3OH); R_f=0.37 (7:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 1.40 and 1.66 (s, isopropylidene CH_3), 1.43 (d, J=5.2 Hz, CH_3), 4.27 (dd, J=3.0, 3.5 Hz, H_5), 4.30 (m, C$\underline{H}$OH), 4.90 (br, OH), 5.10 (d, J=3.6 Hz, H_2), 5.30 (m, H_3 and H_4), 7.90 (s, =CH); UV λ_{max} (CH_3OH) 262 nm (ε 8310), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 7410). Found: C, 52.10; H, 5.97; N, 9.40%. Calcd for $C_{13}H_{18}O_6N_2$: C, 52.34; H, 6.08; N, 9.39%.

5-[(2R,3R*,4R*,5R*)-5-[(R*)-1-Hydroxyhexyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**8c**)*: A mixture of **7c** (546 mg, 1.61 mmol), urea (981 mg, 16.1 mmol), and 1.6 mol dm^{-3} C_2H_5ONa in C_2H_5OH (10 ml) was stirred for 5 h. The usual workup according to Method A and preparative TLC (5:1 chloroform–CH_3OH) gave **8c** (197 mg, 35%). Mp 209.5—212.0 °C (acetone); R_f=0.44 (7:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 0.83 (t-like, J=6.0 Hz, CH_3), 1.10—1.90 (m, CH_2), 1.42 and 1.67 (s, isopropylidene CH_3), 4.19 (m, C$\underline{H}$OH), 4.37 (t, J=3.0 Hz, H_5), 5.10 (d, J=4.5 Hz, H_2), 5.34 (m, H_3 and H_4), 7.91 (s, =CH); UV λ_{max} (CH_3OH) 263 nm (ε 6760), λ_{max} (0.1 mol dm^{-3} NaOH) 286 nm (ε 7400). Found: C, 57.47; H, 7.35; N, 7.98%. Calcd for $C_{17}H_{26}O_6N_2$: C, 57.61; H, 7.40; N, 7.91%.

5-[(2R,3R*,4R*,5S*)-5-[(S*)-α-Hydroxybenzyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**8d**)*: A mixture of **7d** (205 mg, 0.594 mmol), urea (361 mg, 5.94 mmol), and 2.0 mol dm^{-3} C_2H_5ONa in C_2H_5OH (3 ml) was stirred for 4 h. The reaction mixture was worked up according to Method A and separated by preparative TLC (5:1 ethyl acetate–hexane) to afford **8d** (90 mg, 42%). Mp 250.4—251.5 °C (CH_3OH); R_f=0.48 (7:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 1.27 and 1.55 (s, isopropylidene CH_3), 4.75 (dd, J=2.2, 4.2 Hz, H_5), 5.08 (dd, J=1.9, 4.0 Hz, H_3), 5.40 (m, H_2, H_4, and C$\underline{H}$OH), 7.30—7.80 (m, C_6H_5), 7.88 (s, =CH); UV λ_{max} (CH_3OH) 263 nm (ε 2390), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 7580). Found: C, 60.09; H, 6.02; N, 7.90%. Calcd for $C_{18}H_{20}O_6N_2$: C, 59.99; H, 5.59; N, 7.77%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-methyltetrahydrofuran-2-yl]uracil (**16a**)*: A mixture of **15a** (537 mg, 1.90 mmol), urea (1.14 g, 19.0 mmol), and 1.58 mol dm^{-3} C_2H_5ONa in C_2H_5OH (12 ml) was stirred for 2 h. The reaction mixture was worked up according to Method A and purified by preparative TLC (10:1 chloroform–CH_3OH) to give **16a** (175 mg, 31%). Mp 200—205 °C (CH_3OH); R_f=0.60 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.16 (s, CH_3), 1.24 and 1.51 (s, isopropylidene CH_3), 3.55 (br s, C$\underline{H}_2$OH), 4.48—4.86 (m, H_2, H_3, and H_4), 7.56 (s, =CH), 10.94 (br, NH); (C_5D_5N) δ 1.40 and 1.66 (s, isopropylidene CH_3), 1.50 (s, CH_3), 3.79 (d, J=11.0 Hz, $\underline{H}_aH_b$COH), 3.95 (d, J=11.0 Hz, $H_a\underline{H}_b$COH), 5.07 (d, J=5.5 Hz, H_4), 5.15 (d, J=6.5 Hz, H_2), 5.44 (dd, J=5.5, 6.5 Hz, H_3), 7.92 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 18.18, 25.22, 26.80, 67.19, 79.12, 82.99, 84.28, 85.13, 110.38, 112.70, 140.27, 151.07, 163.61; UV λ_{max} (CH_3OH) 266 nm (ε 7230), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 7510). Found: C, 52.03; H, 6.14; N, 9.22%. Calcd for $C_{13}H_{18}O_6N_2$: C, 52.34; H, 6.08; N, 9.39%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-pentyltetrahydrofuran-2-yl]uracil (**16b**)*: A mixture of **15b** (571 mg, 1.68 mmol), urea (1.01 g, 16.8 mmol), and 1.4 mol dm^{-3} C_2H_5ONa in C_2H_5OH (12 ml) was stirred for 2 h. Workup according to Method A followed by preparative TLC (10:1 chloroform–CH_3OH) gave **16b** (169 mg, 28%). Mp 219—221 °C (CH_3OH); R_f=0.72 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.88 (t, J=5.7 Hz, CH_3), 1.27 and 1.49 (s, isopropylidene CH_3), 1.2—1.9 (m, CH_2), 3.36 (br s, $C\underline{H}_2OH$), 4.55 (d, J=5.0 Hz, H_4), 4.63 (d, J=6.2 Hz, H_2), 4.78 (dd, J=5.0, 6.2 Hz, H_3), 7.55 (s, =CH), 11.03 (br, NH); (C_5D_5N) δ 0.84 (t, J=6.0 Hz, CH_3), 1.1—2.2 (m, CH_2), 1.41 and 1.67 (s, isopropylidene CH_3), 3.86 (d, J=11.3 Hz, $\underline{H}_aH_bCOH$), 4.07 (d, J=11.3 Hz, $H_a\underline{H}_bCOH$), 5.03 (d, J=6.0 Hz, H_4), 5.20 (d, J=6.0 Hz, H_2) 5.51 (t, J=6.0 Hz, H_3), 7.96 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 13.71, 21.92, 22.66, 25.30, 26.95, 31.31, 32.15, 64.77, 79.66, 83.68, 86.74, 90.03, 110.30, 112.41, 140.37, 151.00, 163.52; UV λ_{max} (CH_3OH) 264 nm (ε 7830), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 7930). Found: C, 54.75; H, 7.32; N, 7.45%. Calcd for $C_{17}H_{26}O_6N_2\cdot H_2O$: C, 54.82; H, 7.58; N, 7.52%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-phenyltetrahydrofuran-2-yl]uracil (**16c**)*: A mixture of **15c** (43.2 mg, 0.125 mmol), urea (75 mg, 1.25 mmol), and 0.83 mol dm^{-3} C_2H_5ONa in C_2H_5OH (1.5 ml, 1.25 mmol) was stirred for 2 h. Workup according to Method A gave an oil, which was purified by preparative TLC (5:1 chloroform–CH_3OH) to give **16c** (13.0 mg, 29%). Mp 282—285 °C (CH_3OH); R_f=0.62 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.02 and 1.21 (s, isopropylidene CH_3), 3.50 (m, $C\underline{H}_2OH$), 4.78 (d, J=5.1 Hz, H_2), 4.84 (m, H_3), 5.08 (d, J=5.1 Hz, H_4), 7.32 (m, C_6H_5), 7.77 (s, =CH), 11.20 (br, NH); (C_5D_5N) δ 1.24 and 1.35 (s, isopropylidene CH_3), 4.01 (d, J=6.8 Hz, $\underline{H}_aH_bCOH$), 4.24 (d, J=6.8 Hz, $H_a\underline{H}_bCOH$), 5.20 (m, H_3), 5.62 (m, H_2 and H_4), 7.2—7.8 (m, C_6H_5), 8.13 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 25.59, 26.72, 68.29, 80.40, 83.38, 83.81, 89.50, 109.64, 112.51, 126.43, 127.24, 139.90, 141.34, 151.01, 164.00; UV λ_{max} (CH_3OH) 263 nm (ε 7990), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 7640). Found: C, 59.62; H, 5.50; N, 7.64%. Calcd for $C_{18}H_{20}O_6N_2$: C, 59.99; H, 5.59; N, 7.77%.

5-[(2R,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-2-methyltetrahydrofuran-2-yl]uracil (**24a**)*: A mixture of **22a** (619 mg, 2.72 mmol), and *t*-butoxybis(dimethylamino)methane (2.8 ml) was stirred at 90 °C for 5 h under argon. The resulting solution was evaporated to give (1*R**,6*S**,7*R**,8*R**)-5-(dimethylaminomethylene)-7,8-isopropylidenedioxy-6-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**23a**) as a brown oil, which was used to the next step without purification. A mixture of crude **23a**, urea (2.45 g, 40.9 mmol), and 2 mol dm^{-3} C_2H_5ONa in C_2H_5OH (20 ml) was stirred. After 2 h, the reaction mixture was worked up according to Method A to give a brown solid, which was purified by preparative TLC (10:1 chloroform–CH_3OH) to give **24a** (54.2 mg, 7% based on **22a**) as a yellow foam. R_f=0.42 (5:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 1.39 and 1.65 (s, isopropylidene CH_3), 1.94 (s, CH_3), 4.02 (m, $C\underline{H}_2OH$), 4.56 (m, H_5), 5.00 (dd, J=4.1, 6.2 Hz, H_4), 5.31 (d, J=6.2 Hz, H_3), 8.19 (s, =CH); UV λ_{max} (CH_3OH) 263 nm (ε 8450), λ_{max} (0.1 mol dm^{-3} NaOH) 288 nm (ε 10790). Found: m/z, 298.1156. Calcd for $C_{13}H_{18}O_6N_2$: M, 298.1149.

5-[(2R,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-2-pentyltetrahydrofuran-2-yl]uracil (**24b**)*: A mixture of **23b** prepared from **22b** (963 mg, 3.39 mmol) and *t*-butoxybis(dimethylamino)methane (3.4 ml), urea (2.03 g, 33.9 mmol), and 2.26 mol dm^{-3} C_2H_5ONa in C_2H_5OH (15 ml) was stirred for 2 h. Workup according to Method A and preparative TLC (7:1 chloroform–CH_3OH) afforded **24b** (45.8 mg, 4% based on **22b**) as a yellow foam. R_f=0.43 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.81 (t, J=6.0 Hz, CH_3), 1.0—1.7 (m, CH_2), 1.28 and 1.46 (s, isopropylidene CH_3), 3.44 (m, $C\underline{H}_2OH$), 3.89 (m, H_5), 4.50 (dd, J=4.3, 5.8 Hz, H_4), 4.72 (d, J=5.8 Hz, H_3), 7.44 (s, =CH); UV λ_{max} (CH_3OH) 264 nm (ε 7930), λ_{max} (0.1 mol dm^{-3} NaOH) 289 nm (ε 5670). Found: m/z, 336.1731. Calcd for $C_{17}H_{24}O_5N_2$: (M$-H_2O$), 336.1777.

5-[(2R,3S*,4S*)-5,5-Bis(hydroxymethyl)-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**32**)*: A mixture of **31** (594 mg, 1.47 mmol), urea (442 mg, 7.37 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (7 ml) was stirred for 5 h. After workup according to Method B, the residue was subjected to preparative TLC (5:1 chloroform–CH_3OH) to afford **32** (164 mg, 39%) as a white foam. R_f=0.37 (3:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.23 and 1.46 (s, isopropylidene CH_3), 3.50 (m, $C\underline{H}_2OH$), 4.53—4.86 (m, H_2, H_3, and H_4), 7.51 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 25.11 26.86, 60.39, 63.19, 79.81, 82.87, 84.00, 86.76, 110.19, 112.54, 140.54, 151.05, 163.55; UV λ_{max} (CH_3OH) 263 nm (ε 4910), λ_{max} (0.1 mol dm^{-3} NaOH) 284 nm (ε 4670). Found: m/z, 299.0879. Calcd for $C_{12}H_{15}O_7N_2$: (M$-CH_3$), 299.0880.

5-[(2R,3R*,4S*,5R*)-2,5-Dimethyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**46a**)*: A mixture of **45a** (118 mg, 0.397 mmol), urea (119 mg, 1.99 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (2 ml) was stirred for 24 h. The workup of the reaction product according to Method A gave an oil, which was subjected to preparative TLC (8:1 chloroform–CH_3OH) to afford **46a** (35.1 mg, 28%) as a white foam. Mp 126—134 °C (CH_3OH); R_f=0.51 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.18 and 1.28 (s, CH_3), 1.28 and 1.50 (s, isopropylidene CH_3), 3.19 (m, $C\underline{H}_2OH$), 4.45 (d, J=6.2 Hz, H_3), 4.82 (d, J=6.2 Hz, H_4), 4.95 (br, OH), 7.47 (s, =CH), 10.80 (br, NH); (C_5D_5N) δ 1.42 and 1.70 (s, isopropylidene CH_3), 1.70 and 1.92 (s, CH_3), 3.78 (s, $C\underline{H}_2OH$), 4.85 (d, J=6.2 Hz, H_3), 5.46 (d, J=6.2 Hz, H_4), 8.32 (br s, =CH), 12.45 (br, NH), 13.04 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 19.65, 24.41, 24.94, 25.59, 66.30, 82.95, 83.12, 84.71, 85.18, 111.36, 117.30, 138.01, 151.48, 163.18; UV λ_{max} (CH_3OH) 264 nm (ε 6680), λ_{max} (0.1 mol dm^{-3} NaOH) 217 nm (ε 10070), 287 (7610). Found: C, 53.29; H, 6.61; N, 8.24%. Calcd for $C_{14}H_{20}O_6N_2$: C, 53.84; H, 6.45; N, 8.97%.

5-[(2R,3R*,4S*,5R*)-2,5-Dipentyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**46b**)*: A mixture of **45b** (2.00 g, 4.89 mmol), urea (2.93 g, 48.9 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (49 ml) was stirred for 5 h. The reaction mixture was worked up according to Method A and the crude product was purified by preparative TLC (8:1 chloroform–CH_3OH) to give **46b** (472 mg, 23%) as a white foam. Mp>250 °C (CH_3OH); R_f=0.53 (10:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.84 (m, CH_3), 1.0—1.7 (m, CH_2), 1.26 and 1.46 (s, isopropylidene CH_3), 3.22 (m, $C\underline{H}_2OH$), 4.47 (d, J=6.6 Hz, H_3), 4.63 (br, OH), 4.77 (d, J=6.6 Hz, H_4), 7.37 (s, =CH), 10.82 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 13.66, 21.96, 22.93, 31.73, 32.15, 24.44, 25.35, 63.89, 83.49, 84.90, 86.17, 111.16, 114.96, 138.88, 151.47, 162.89; UV λ_{max} (CH_3OH) 265 nm (ε 5820), λ_{max} (0.1 mol dm^{-3} NaOH) 289 nm (ε 4240). Found: C, 62.02; H, 8.57; N, 6.33%. Calcd for $C_{22}H_{36}O_6N_2$: C, 62.24; H, 8.55; N, 6.60%.

5-[(2S,3R*,4R*,5R*)-3-t-Butyldimethylsiloxymethyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]uracil (**54a**)*: A mixture of **53a** (1.18 g, 2.86 mmol), urea (1.20 g, 8.58 mmol), and 0.41 mol dm^{-3} C_2H_5ONa in C_2H_5OH (21 ml) was stirred for 3 h. Workup according to Method B and preparative TLC (10:1 chloroform–CH_3OH) afforded **54a** (246 mg, 20%). Mp 238—242 °C (CH_3OH–acetone–petroleum ether); R_f=0.27 (10:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.06 (s, t-$C_4H_9(C\underline{H}_3)_2Si$), 0.84 (s, t-$C_4\underline{H}_9(CH_3)_2Si$), 1.33 and 1.51 (s, isopropylidene CH_3), 3.49 (s, CH_2OSi), 3.57 (m, $C\underline{H}_2OH$), 3.96 (m, H_5), 4.52 (d, J=2.8 Hz, H_4), 4.82 (s, H_2), 7.34 (br, =CH), 10.86 (br, NH), 11.02 (br s, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 17.74, 25.49, 26.84, 28.31, 61.01, 61.60, 80.44, 82.73, 83.02, 91.54, 107.86, 113.08, 138.68, 150.78, 162.56; UV λ_{max} (CH_3OH) 266 nm (ε 7150), λ_{max} (0.1 mol dm^{-3} NaOH) 289 nm (ε 6150). Found: C, 53.40; H, 7.54; N, 6.78%. Calcd for $C_{19}H_{32}N_2O_7Si$: C, 53.25; H, 7.53; N, 6.54%.

5-[(2S,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-3-methyltetrahydrofuran-2-yl]uracil (**54b**)*: A mixture of **53b** (730 mg, 2.58 mmol), urea (1.08 g, 18.1 mmol), and 0.9 mol dm^{-3} C_2H_5ONa in C_2H_5OH (20 ml, 18 mmol) was stirred for 3 h. Workup according to Method B followed by preparative TLC (4:1 chloroform–CH_3OH) gave **54b** (245 mg, 32%). Mp 126—128 °C; R_f=0.50 (4:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.12 (s, CH_3), 1.32 and 1.51 (s, isopropylidene CH_3), 3.52 (d-like, J=4.0 Hz, $C\underline{H}_2OH$) 3.92 (m, H_5), 4.30 (d, J=3.0 Hz, H_4), 4.80 (s, H_2), 7.34 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 20.37, 27.16, 28.38, 61.53, 81.39, 82.68, 87.28, 89.36, 109.17, 112.79, 139.33, 151.13, 162.89; UV λ_{max} (CH_3OH) 265 nm (ε 7430), λ_{max} (0.1 mol dm^{-3} NaOH) 289 nm (ε 7750). Found: m/z, 283.0939. Calcd for $C_{12}H_{15}N_2O_6$: (M−CH_3), 283.0930.

With Thiourea. *5-[(2R*,3R*,4S*,5S*)-5-(1-Hydroxy-1-methylethyl)-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil (**10a**)*: A mixture of **7a** (423 mg, 1.42 mmol), thiourea (868 mg, 9.94 mmol), and 1.14 mol dm^{-3} C_2H_5ONa in C_2H_5OH (10 ml) was stirred for 5 h. The reaction mixture was worked up according to Method A. Pure **10a** (332 mg, 71%) was obtained by preparative TLC (5:1 chloroform–CH_3OH). Mp 161.0—162.0 °C (ethyl acetate); ^{1}H NMR (acetone-d_6) δ 1.20 (s, CH_3), 1.32 and 1.51 (s, isopropylidene CH_3), 3.79 (d, J=3.1 Hz, H_5), 4.68 (dd, J=3.3, 4.5 Hz, H_3), 4.80 (d, J=3.3 Hz, H_2), 4.82 (dd, J=3.1, 4.5 Hz, H_4), 7.71 (s, =CH); UV λ_{max} (CH_3OH) 213 nm (ε 11100), 276 (13800), 290 (13000), λ_{max} (0.1 mol dm^{-3} NaOH) 222 nm (ε 14700), 264 (12000), 285 (9490). Found: C, 48.07; H, 6.29; N, 8.00%. Calcd for $C_{14}H_{20}O_5N_2S\cdot1.2H_2O$: C, 48.04; H, 6.45; N, 8.00%.

5-[(2R,3R*,4R*,5R*)-5-[(R*)-1-Hydroxyethyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil (**10b**)*: A mixture of **7b** (305 mg, 1.08 mmol), thiourea (660 mg, 8.64 mmol), and 1.23 mol dm^{-3} C_2H_5ONa in C_2H_5OH (7 ml) was stirred for 5 h. The reaction mixture was subjected to the Method A workup and preparative TLC (7:1 chloroform–CH_3OH) afforded **10b** (277 mg, 82%). Mp 201.2—202.5 °C (ether–CH_3OH); ^{1}H NMR (acetone-d_6) δ 1.19 (d, J=7.0 Hz, CH_3), 1.32 and 1.52 (s, isopropylidene CH_3), 3.87 (m, H_5 and $\underline{H}COH$), 4.66 (d, J=4.2 Hz, H_2), 4.82 (m, H_3 and H_4), 7.66 (s, =CH); UV λ_{max} (CH_3OH) 213 nm (ε 12500), 274 (14400), 286 (13100), λ_{max} (0.1 mol dm^{-3} NaOH) 223 nm (ε 16220), 264 (15140), 284 (11480). Found: C, 49.06; H, 5.85; N, 8.44%. Calcd for $C_{13}H_{18}O_5N_2S$: C, 49.67; H, 5.77; N, 8.91%.

5-[(2R,3R*,4R*,5R*)-5-[(R*)-1-Hydroxyhexyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil (**10c**)*: A mixture of **7c** (491 mg, 1.45 mmol), thiourea (776 mg, 10.2 mmol), and 1.16 mol dm^{-3} C_2H_5ONa in C_2H_5OH (10 ml) was stirred for 5 h. After the Method A workup, the crude product was purified by preparative TLC (7:1 chloroform–CH_3OH) to give **10c** (365 mg, 68%). Mp 203.0—204.5 °C (ether); ^{1}H NMR (acetone-d_6) δ 0.91 (t, J=6.0 Hz, CH_3), 1.10—1.70 (m, CH_2), 1.31 and 1.51 (s, isopropylidene CH_3), 3.76 (m, $\underline{H}COH$), 3.95 (dd, J=3.1, 6.1 Hz, H_5), 4.65 (d, J=4.1 Hz, H_2), 4.86 (m, H_3 and H_4), 7.67 (s, =CH), 11.23 (br, NH); UV λ_{max} (CH_3OH) 214 nm (ε 12880), 276 (15850), 291 (14800), λ_{max} (0.1 mol dm^{-3} NaOH) 222 nm (ε 16990), 264 (13490), 283 (10960). Found: C, 54.56; H, 7.04; N, 7.39; S, 8.68%. Calcd for $C_{17}H_{26}O_5N_2S\cdot0.25H_2O$: C, 54.45; H, 7.12; N, 7.46; S, 8.55%.

5-[(2R,3R*,4R*,5S*)-5-[(S*)-α-Hydroxybenzyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil (**10d**)*: A mixture of **7d** (74 mg, 0.214 mmol), thiourea (115 mg, 1.50 mmol), and 0.85 mol dm^{-3} C_2H_5ONa in C_2H_5OH (2 ml) was stirred. After stirring for 5 h, the workup according to Method A and preparative TLC (5:1 chloroform–CH_3OH) afforded **10d** (59 mg, 73%). Mp 240—241 °C; ^{1}H NMR (C_5D_5N) δ 1.29 and 1.55 (s, isopropylidene CH_3), 4.75 (dd, J=3.9, 5.0 Hz, H_5), 5.17 (d, J=4.0 Hz, H_2), 5.38 (m, H_3, H_4, and $\underline{H}COH$), 7.3—7.9 (m, C_6H_5), 7.94 (s, =CH); UV λ_{max} (CH_3OH) 276 nm (ε 7940), 289 (7240), λ_{max} (0.1 mol dm^{-3} NaOH) 264 nm (ε 10970), 280 (8510). Found: C, 50.29; H, 5.57; N, 6.36%. Calcd for $C_{18}H_{20}O_5N_2S\cdot3H_2O$: C, 50.22; H, 6.09; N, 6.51%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-methyltetrahydrofuran-2-yl]-2-thiouracil (**18a**)*: A mixture of **15a** (284 mg, 1.00 mmol), thiourea (532 mg, 7.0 mmol), and 1.4 mol dm^{-3} C_2H_5ONa in C_2H_5OH (5 ml) was stirred for 2 h. The Method A workup and preparative TLC (5:1 chloroform–CH_3OH) gave **18a** (248 mg, 79%) as a yellow foam. R_f=0.67 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.17 (s, CH_3), 1.28 and 1.50 (s, isopropylidene CH_3), 3.35 (br s, $C\underline{H}_2OH$), 4.54—4.86 (m, H_2, H_3, and H_4), 7.56 (s, =CH); (C_5D_5N) δ 1.40 and 1.65 (s, isopropylidene CH_3), 1.55 (s, CH_3), 3.77 (d, J=11.5 Hz, $\underline{H}_aH_bCOH$), 3.93 (d, J=11.5 Hz, $H_a\underline{H}_bCOH$), 5.09 (d, J=6.0 Hz, H_4), 5.17 (d, J=5.0 Hz, H_2), 5.36 (dd, J=5.0, 6.0 Hz, H_3), 8.05 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 18.20, 25.21, 26.70, 67.06, 78.93, 82.97, 84.56, 85.64, 112.69, 116.16, 139.44, 160.57, 175.38; UV λ_{max} (CH_3OH) 215 nm (ε 9490), 276 (14390), 290 (13190), λ_{max} (0.1 mol dm^{-3} NaOH) 223 nm (ε 9640), 264 (8700), 289 (6740). Found: C, 47.89; H, 5.67; N, 8.40%. Calcd for $C_{13}H_{18}O_5N_2S\cdot0.7H_2O$: C, 47.75; H, 5.98; N, 8.57%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-pentyltetrahydrofuran-2-yl]-2-thiouracil (**18b**)*: A mixture of **15b** (330 mg, 0.973 mmol), thiourea (517 mg, 6.81 mmol), and 0.85 mol dm^{-3} C_2H_5ONa in C_2H_5OH (8 ml) was stirred for 2 h. The reaction mixture was worked up according to Method A. Preparative TLC (10:1 chloroform–CH_3OH) gave **18b** (247 mg, 69%). Mp 181—183 °C (ether); R_f=0.64 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.89 (t, J=5.7 Hz, CH_3), 1.28 and 1.50 (s, isopropylidene CH_3), 1.1—1.7 (m, CH_2), 3.38 (br s, $C\underline{H}_2OH$), 4.56—4.94 (m, H_2, H_3, and H_4), 7.55 (s, =CH), 12.40 (br, NH); (C_5D_5N) δ 0.89 (t, J=6.0 Hz, CH_3), 1.2—2.2 (m, CH_2), 1.45 and 1.70 (s, isopropylidene CH_3), 3.90 (d, J=11.2 Hz, $\underline{H}_aH_bCOH$), 4.06 (d, J=11.2 Hz, $H_a\underline{H}_bCOH$), 5.16 (d, J=6.0 Hz, H_4), 5.18 (d, J=5.0 Hz, H_2), 5.46 (dd, J=5.0, 6.0 Hz, H_3), 8.14 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 13.80, 21.93, 22.78, 25.42, 27.30, 31.67, 32.15, 65.62, 81.68, 82.99, 83.87, 86.52, 111.67, 112.39, 154.54, 156.20, 163.03; UV λ_{max} (CH_3OH) 213 nm (ε 13640), 276 (17330), 290 (sh, 15820), λ_{max} (0.1 mol dm^{-3} NaOH) 220 nm (ε 17230), 264 (13530), 282 (sh, 10910). Found: C, 55.06; H, 7.24; N, 7.56; S, 8.70%. Calcd for $C_{17}H_{26}O_5N_2S$: C, 55.12; H, 7.07; N, 7.56; S, 8.65%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-phenyltetrahydrofuran-2-yl]-2-thiouracil* (**18c**): A mixture of **15c** (36.8 mg, 0.107 mmol), thiourea (57 mg, 0.749 mmol), and 0.38 mol dm^{-3} C_2H_5ONa in C_2H_5OH (2 ml) was stirred for 2 h. The reaction mixture was worked up according to Method A. Preparative TLC (5:1 chloroform–CH_3OH) afforded **18c** (23.5 mg, 58%). Mp 210—213 °C; R_f=0.64 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.01 and 1.21 (s, isopropylidene CH_3), 3.45 (d, J=11.1 Hz, $\underline{H}_aH_bCOH$), 3.72 (d, J=11.1 Hz, $H_a\underline{H}_bCOH$), 4.86 (m, H_2 and H_3), 5.05 (m, H_4), 7.33 (m, C_6H_5), 7.76 (s, =CH); (C_5D_5N) δ 1.20 and 1.34 (s, isopropylidene CH_3), 4.04 (d, J=12.0 Hz, $\underline{H}_aH_bCOH$), 4.25 (d, J=12.0 Hz, $H_a\underline{H}_bCOH$), 5.36 (m, H_3), 5.60 (m, H_2 and H_4), 7.2—7.9 (m, C_6H_5), 8.30 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 25.42, 26.47, 67.94, 80.05, 83.23, 83.92, 89.72, 112.35, 114.97, 126.31, 126.65, 127.09, 139.62, 141.23, 160.83, 175.59; UV λ_{max} (CH_3OH) 275 nm (ε 12780), 291 (sh, 11250), λ_{max} (0.1 mol dm^{-3} NaOH) 264 nm (ε 11530), 281 (sh, 9880). Found: C, 53.98; H, 5.78; N, 6.62; S, 7.70%. Calcd for $C_{18}H_{20}O_5N_2S\cdot1.2H_2O$: C, 54.31; H, 5.67; N, 7.04; S, 8.06%.

5-[(2R,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-2-methyltetrahydrofuran-2-yl]-2-thiouracil* (**26a**): A mixture of **23a** obtained from 1.03 g (4.50 mmol) of **22a** and t-butoxybis(dimethylamino)methane (4.5 ml) as described above and thiourea (2.39 g, 31.5 mmol) in 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (31.5 ml) was stirred for 2 h. Workup according to Method A followed by column chromatography (20:1 to 15:1 chloroform–CH_3OH) afforded **26a** (268 mg, 20% based on **22a**) as a yellow foam. R_f=0.60 (5:1 chloroform–CH_3OH); ^1H NMR (C_5D_5N) δ 1.95 (s, CH_3), 1.42 and 1.66 (s, isopropylidene CH_3), 3.90 (dd, J=5.0, 11.0 Hz, $\underline{H}_aH_bCOH$), 4.07 (dd, J=4.0, 11.0 Hz, $H_a\underline{H}_bCOH$) 4.59 (ddd, J=4.0, 4.0, 5.0 Hz, H_5), 4.99 (dd, J=4.0, 6.0 Hz, H_4), 5.27 (d, J=6.0 Hz, H_3), 8.29 (s, =CH); UV λ_{max} (CH_3OH) 214 nm (ε 9540), 275 (12850), 290 (11920), λ_{max} (0.1 mol dm^{-3} NaOH) 223 nm (ε 11880), 261 (11680), 292 (6800). Found: m/z, 314.0930. Calcd for $C_{13}H_{18}N_2O_5S$: M, 314.0936.

5-[(2R,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-2-pentyltetrahydrofuran-2-yl]-2-thiouracil* (**26b**): A mixture of **23b** obtained from **22b** (577 mg, 2.03 mmol) and t-butoxybis(dimethylamino)methane (3 ml), thiourea (1.08 g, 14.2 mmol), and 2.0 mol dm^{-3} C_2H_5ONa in C_2H_5OH (7 ml) was stirred for 2 h. Workup according to Method A followed by column chromatography (30:1 to 20:1 chloroform–CH_3OH) gave **26b** (88.1 mg, 12% based on **22b**) as a foam. R_f=0.62 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.80 (t, J=6.5 Hz, CH_3), 1.0—1.8 (m, CH_2), 1.25 and 1.45 (s, isopropylidene CH_3), 3.91 (m, H_5), 4.50 (dd, J=4.5, 6.0 Hz, H_4), 4.70 (d, J=6.0 Hz, H_3), 7.40 (s, =CH), $C\underline{H}_2OH$ peaks obscured by H_2O peak; UV λ_{max} (CH_3OH) 214 nm (ε 9430), 276 (13690), 289 (12700), λ_{max} (0.1 mol dm^{-3} NaOH) 232 nm (ε 13400), 261 (16840), 303 (8480). Found: C, 53.19; H, 6.90; N, 7.50%. Calcd for $C_{17}H_{26}O_5N_2S\cdot H_2O$: C, 52.56; H, 7.26; N, 7.21%.

5-[(2R,3S*,4S*)-5,5-Bis(hydroxymethyl)-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil* (**34**). A mixture of **31** (337 mg, 0.84 mmol), thiourea (447 mg, 5.88 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (6 ml) was stirred for 3 h. The Method B workup gave a solid, which was purified by preparative TLC (5:1 chloroform–CH_3OH) to give **34** (160 mg, 63%) as a white foam. R_f=0.39 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.24 and 1.46 (s, isopropylidene CH_3), 3.50 (d-like, J=7.5 Hz, $C\underline{H}_2OH$), 4.67 (m, H_2, H_3, and H_4), 5.5—8.0 (br, HN and OH), 7.56 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 25.11, 26.84, 60.42, 63.07, 79.80, 82.85, 84.25, 87.23, 127.89, 140.77, 160.68; UV λ_{max} (CH_3OH) 276 nm (ε 12770), 297 (11540), λ_{max} (0.1 mol dm^{-3} NaOH) 213 nm (ε 11320), 265 (9060), 292 (7320). Found: m/z, 330.0890. Calcd for $C_{13}H_{18}O_6N_2S$: M, 330.0884.

5-[(2R,3R*,4R*,5R*)-2,5-Bis(hydroxymethyl)-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil* (**40**): A mixture of **39** (220 mg, 0.57 mmol), thiourea (303 mg, 3.99 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (5 ml) was stirred for 3 h. The reaction mixture was worked up according to Method B to give a yellow solid, which was purified by preparative TLC (5:1 chloroform–CH_3OH) to afford **40** (93.0 mg, 51%) as a white foam. R_f=0.50 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.26 and 1.48 (s, isopropylidene CH_3), 3.3—3.8 (br, OH), 3.52 (d-like, J=7.5 Hz, $C\underline{H}_2OH$), 4.56—4.88 (m, H_3, H_4, and H_5), 7.52 (s, =CH); UV λ_{max} (CH_3OH) 214 nm (ε 8780), 276 (11350), 293 (10040), λ_{max} (0.1 mol dm^{-3} NaOH) 223 nm (ε 12910), 264 (8430), 289 (7080). Found: C, 44.63; H, 5.54; N, 8.00%. Calcd for $C_{13}H_{18}O_7N_2S$: C, 45.08; H, 5.24; N, 8.09%.

5-[(2R,3R*,4S*,5R*)-2,5-Dimethyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil* (**48a**): A mixture of **45a** (621 mg, 2.09 mmol), thiourea (1.11 g, 14.6 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (14 ml) was stirred for 5 h. After workup according to Method A, the residue was subjected to preparative TLC (8:1 chloroform–CH_3OH) to give **48a** (426 mg, 61%). Mp 90—95 °C (CH_3OH); R_f=0.67 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.20 and 1.30 (s, CH_3), 1.30 and 1.50 (s, isopropylidene CH_3), 3.22 (m, $C\underline{H}_2OH$), 4.46 (d, J=6.2 Hz, H_3), 4.83 (d, J=6.2 Hz, H_4), 4.96 (t-like, J=4.2 Hz, OH), 7.49 (s, =CH), 12.16 and 12.34 (br, NH); (C_5D_5N) δ 1.42 and 1.70 (s, isopropylidene CH_3), 1.70 and 1.84 (s, CH_3), 3.72 (br s, $C\underline{H}_2OH$), 4.77 (d, J=6.2 Hz, H_3), 5.37 (d, J=6.2 Hz, H_4), 8.41 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 19.47, 24.41, 24.59, 25.59, 66.18, 83.00, 83.12, 84.89, 111.36, 122.89, 137.78, 160.25, 175.13; UV λ_{max} (CH_3OH) 215 nm (ε 12560), 276 (16180), 290 (14820), λ_{max} (0.1 mol dm^{-3} NaOH) 223 nm (ε 14860), 261 (14270), 292 (8650). Found: C, 51.02; H, 6.24; N, 8.67; S, 9.60%. Calcd for $C_{14}H_{20}O_5N_2S$: C, 51.21; H, 6.14; N, 8.53; S, 9.76%.

5-[(2R,3R*,4S*,5R*)-2,5-Dipentyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil* (**48b**): A mixture of **45b** (1.23 g, 2.80 mmol), thiourea (1.49 g, 19.6 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (20 ml) was stirred. After 5 h, the reaction mixture was worked up according to Method A and the crude product was purified by preparative TLC (10:1 chloroform–CH_3OH) to give **48b** (798 mg, 64%). Mp 207—210 °C (CH_3OH); R_f=0.47 (10:1 chloroform–CH_3OH); ^1H NMR (C_5D_5N) δ 0.84 (m, CH_3), 1.1—1.7 (m, CH_2, 14H), 1.44 and 1.74 (s, isopropylidene CH_3), 2.1—2.3 (m, CH_2, 2H), 3.73 (d, J=12.2 Hz, $\underline{H}_aH_bCOH$), 3.94 (d, J=12.2 Hz, $H_a\underline{H}_bCOH$), 4.81

(d, J=6.5 Hz, H_3), 5.37 (d, J=6.5 Hz, H_4), 8.51 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 13.82, 22.06, 23.12, 24.41, 25.35, 31.71, 32.18, 63.59, 83.36, 84.95, 85.71, 86.36, 111.24, 120.77, 138.77, 160.13, 175.18; UV λ_{max} (CH_3OH) 215 nm (ε 12820), 276 (16450), 290 (sh, 15290), λ_{max} (0.1 mol dm^{-3} NaOH) 227 nm (ε 9570), 261 (10640), 305 (6030). Found: C, 59.03; H, 8.06; N, 5.93%. Calcd for $C_{22}H_{36}O_5N_2S\cdot 0.5H_2O$: C, 58.76; H, 8.29; N, 6.23%.

5-[(2S,3R*,4R*,5R*)-3-t-Butyldimethylsiloxymethyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]-2-thiouracil (58a)*: A mixture of **53a** (500 mg, 1.21 mmol), thiourea (645 mg, 8.47 mmol), and 0.94 mol dm^{-3} C_2H_5ONa in C_2H_5OH (9 ml) was stirred for 3 h. The Method B workup gave a crude product which was subjected to preparative TLC (10:1 chloroform–CH_3OH) to afford **58a** (333 mg, 62%). Mp 208—210 °C (acetone–hexane); R_f=0.27 (10:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.06 (s, t-$C_4H_9(C\underline{H}_3)_2Si$), 0.84 (s, t-$C_4\underline{H}_9(CH_3)_2Si$), 1.34 and 1.51 (s, isopropylidene CH_3), 3.30 (br, OH), 3.4—3.7 (m, $C\underline{H}_2OH$ and CH_2OSi), 4.00 (m, H_5), 4.51 (d, J=3.0 Hz, H_4), 4.82 (s, H_2), 7.34 (s, =CH), 12.30 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 17.74, 25.49, 26.90, 28.25, 60.95, 61.65, 80.21, 82.91, 83.14, 91.65, 113.26, 113.61, 138.22, 159.52, 174.61; UV λ_{max} (CH_3OH) 216 nm (ε 9160), 275 (11800), 299 (11200), λ_{max} (0.1 mol dm^{-3} NaOH) 224 nm (ε 9990), 262 (9110), 296 (6780). Found: C, 50.74; H, 7.55; N, 6.53%. Calcd for $C_{19}H_{32}O_6N_2SSi\cdot 0.5H_2O$: C, 50.30; H, 7.33; N, 6.18%.

5-[(2S,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-3-methyltetrahydrofuran-2-yl]-2-thiouracil (58b)*: A mixture of **53b** (200 mg, 0.707 mmol), thiourea (377 mg, 4.95 mmol), and 0.92 mol dm^{-3} C_2H_5ONa in C_2H_5OH (5.4 ml) was stirred for 3 h. The Method B workup and preparative TLC (4:1 chloroform–CH_3OH) afforded **58b** (155 mg, 70%). Mp 142—144 °C (CH_3OH); 'R_f=0.62 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.14 (s, CH_3), 1.32 and 1.50 (s, isopropylidene CH_3), 3.56 (d-like, J=4.0 Hz, $C\underline{H}_2OH$), 3.96 (m, H_5), 4.31 (d, J=2.8 Hz, H_4), 4.80 (s, H_2), 7.38 (s, =CH), ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 20.26, 27.07, 28.32, 61.47, 81.21, 82.91, 87.30, 89.36, 112.84, 114.74, 138.92, 159.82, 175.16; UV λ_{max} (CH_3OH) 215 nm (ε 12600), 275 (15800), 297 (14900), λ_{max} (0.1 mol dm^{-3} NaOH) 221 nm (ε 13700), 262 (12100), 298 (8110). Found: m/z, 314.0949. Calcd for $C_{13}H_{18}O_5N_2S$: M, 314.0936.

With Guanidine Hydrochloride. *5-[(2R*,3R*,4S*,5S*)-5-(1-Hydroxy-1-methylethyl)-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine (12a)*: Guanidine hydrochloride (1.11 g, 11.8 mmol) was dissolved in 1.69 mol dm^{-3} C_2H_5ONa in C_2H_5OH (7 ml). To this was added **7a** (436 mg, 1.47 mmol) and the mixture was stirred for 5 h. The Method A workup followed by trituration of the residue with ether afforded **12a** (334 mg, 73%). Mp 242.0—243.1 °C (CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.10 (s, CH_3), 1.28 and 1.49 (s, isopropylidene CH_3), 3.67 (d, J=3.0 Hz, H_5), 4.51 (m, H_3), 4.68 (m, H_2 and H_4), 6.64 (br, NH_2), 7.66 (s, =CH); UV λ_{max} (CH_3OH) 227 nm (ε 5330), 290 (5370), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 7420), 276 (5940). Found: C, 54.16; H, 6.67; N, 13.30%. Calcd for $C_{14}H_{21}O_5N_3$: C, 54.01; H, 6.80; N, 13.50%.

5-[(2R,3R*,4R*,5R*)-5-[(R*)-1-Hydroxyethyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine (12b)*: A mixture of **7b** (952 mg, 3.36 mmol), guanidine hydrochloride (2.54 g, 26.9 mmol), and 2.69 mol dm^{-3} C_2H_5ONa in C_2H_5OH (10 ml) was stirred for 5 h. The reaction mixture was worked up according to Method A, and the product was subjected to trituration with ethyl acetate to give **12b** (665 mg, 67%). Mp 219.8—220.9 °C (CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.06 (d, J=6.0 Hz, CH_3), 1.27 and 1.48 (s, isopropylidene CH_3), 3.71 (m, H_5 and $C\underline{H}_2OH$), 4.71 (m, H_3), 4.74 (m, H_2 and H_4), 6.66 (br, NH_2), 7.64 (s, =CH); UV λ_{max} (CH_3OH) 226 nm (ε 7240), 290 (7240), λ_{max} (0.1 mol dm^{-3} NaOH) 232 nm (ε 9120), 276 (6920). Found: C, 52.50; H, 6.50; N, 13.97%. Calcd for $C_{13}H_{19}O_5N_3$: C, 52.51; H, 6.44; N, 14.13%.

5-[(2R,3R*,4R*,5R*)-5-[(R*)-1-Hydroxyhexyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine (12c)*: A mixture of **7c** (428 mg, 1.26 mmol), guanidine hydrochloride (951 mg, 10.1 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (10 ml) was stirred for 5 h. Workup according to Method A followed by trituration (ether) of the crude product gave pure **12c** (327 mg, 74%). Mp 212.0—213.9 °C (CH_3OH); ^{1}H NMR (C_5D_5N) δ 0.81 (t, J=6.0 Hz, CH_3), 1.2—1.8 (m, CH_2), 1.40 and 1.68 (s, isopropylidene CH_3), 4.18 (m, $C\underline{H}_2OH$), 4.42 (t-like, J=4.1 Hz, H_5), 5.06 (d, J=4.2 Hz, H_2), 5.38 (m, H_3 and H_4), 8.04 (s, =CH), 8.10 (br, NH_2); UV λ_{max} (CH_3OH) 227 nm (ε 10720), 290 (10720), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 11480), 277 (9330). Found: C, 57.05; H, 7.50; N, 11.91%. Calcd for $C_{17}H_{27}O_5N_3$: C, 57.77; H, 7.70; N, 11.89%.

5-[(2R,3R*,4R*,5S*)-5-[(S*)-α-Hydroxybenzyl]-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine (12d)*: A mixture of **7d** (206 mg, 0.597 mmol), guanidine hydrochloride (394 mg, 4.18 mmol), and 3.2 mol dm^{-3} C_2H_5ONa in C_2H_5OH (1.5 ml) was stirred for 5 h. After workup according to Method A, the crude product was purified by trituration with ether to give **12d** (44 mg, 21%). Mp 273.8—275.0 °C (CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.18 and 1.42 (s, isopropylidene CH_3), 4.10 (dd, J=2.0, 4.0 Hz, H_5), 4.50 (d, J=4.3 Hz, H_2), 4.90 (m, H_3 and H_4) 5.82 (dd, J=2.0, 4.0 Hz, $C\underline{H}OH$), 6.60 (br, NH_2), 7.30 (m, C_6H_5), 7.64 (s, =CH), 11.0 (br, NH); UV λ_{max} (CH_3OH) 227 nm (ε 12310), 290 (13180), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 5490), 277 (4360). Found: C, 59.98; H, 6.05; N, 11.38%. Calcd for $C_{18}H_{21}O_5N_3$: C, 60.16; H, 5.89; N, 11.69%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-methyltetrahydrofuran-2-yl]isocytosine (20a)*: A mixture of **15a** (705 mg, 2.49 mmol), guanidine hydrochloride (1.89 g, 19.9 mmol), and 1.4 mol dm^{-3} C_2H_5ONa in C_2H_5OH (14 ml) was stirred for 2 h. The workup according to Method A and trituration with ethyl acetate gave **20a** (434 mg, 64%). Mp 252—254 °C (CH_3OH); R_f=0.44 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.14 (s, CH_3), 1.27 and 1.50 (s, isopropylidene CH_3), 3.34 (br s, $C\underline{H}_2OH$), 4.53 (d, J=5.2 Hz, H_4), 4.64 (d, J=6.0 Hz, H_2), 4.85 (dd, J=5.2, 6.0 Hz, H_3), 5.08 (br, OH), 6.82 (br, NH_2), 7.64 (s, =CH), 11.14 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 18.14, 25.31, 27.10, 67.70, 80.83, 83.29, 83.50, 84.72, 111.88, 112.56, 154.10, 156.09, 163.00; UV λ_{max} (CH_3OH) 225 nm (ε 13890), 289 (11220), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 10320), 276 (7930). Found: C, 52.60; H, 6.27; N, 13.85%. Calcd for $C_{13}H_{19}O_5N_3$: C, 52.51; H, 6.44; N, 14.13%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-pentyltetrahydrofuran-2-yl]isocytosine (20b)*. A mixture of **15b** (471 mg, 1.39 mmol), guanidine hydrochloride (1.06 g, 11.1 mmol), and 0.93 mol dm^{-3} C_2H_5ONa in C_2H_5OH (12 ml) was stirred for 2 h. The reaction mixture was worked up according to Method A. Trituration with ethyl acetate afforded pure **20b** (356 mg, 73%). Mp 228—230 °C (CH_3OH); R_f=0.51 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.88 (t, J=6.0 Hz, CH_3), 1.28 and 1.51 (s, isopropylidene CH_3), 1.1—1.7 (m, CH_2), 3.39 (br s, $C\underline{H}_2OH$), 4.46 (d, J=6.0 Hz, H_4), 4.68 (d, J=6.0 Hz, H_2), 4.87 (t, J=6.0 Hz, H_3), 5.14 (br, OH), 6.81

(br, NH_2), 7.64 (s, =CH); (C_5D_5N) δ 0.83 (t, J=6.0 Hz, CH_3), 1.2—2.1 (m, CH_2), 1.38 and 1.68 (s, isopropylidene CH_3), 3.85 (d, J=11.5 Hz, $\underline{H}_aH_bCOH$), 4.01 (d, J=11.5 Hz, $H_a\underline{H}_bCOH$), 4.99 (d, J=5.5 Hz, H_4), 5.20 (d, J=5.5 Hz, H_2), 5.59 (t, J=5.5 Hz, H_3), 8.06 (s, =CH), 8.06 (br, NH_2); UV λ_{max} (CH_3OH) 227 nm (ε 9510), 290 (9540), λ_{max} (0.1 mol dm^{-3} NaOH) 216 nm (ε 9210), 233 (9750), 276 (7740). Found: C, 57.98; H, 7.78; N, 11.36%. Calcd for $C_{17}H_{27}O_5N_3$: C, 57.77; H, 7.70; N, 11.89%.

5-[(2R,3S*,4S*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-5-phenyltetrahydrofuran-2-yl]isocytosine* (**20c**): A mixture of **15c** (537 mg, 1.56 mmol), guanidine hydrochloride (1.19 g, 12.5 mmol), and 0.78 mol dm^{-3} C_2H_5ONa in C_2H_5OH (16 ml) was stirred for 2 h. Trituration with ethyl acetate gave **20c** (436 mg, 78%). Mp 270—272 °C (CH_3OH); R_f=0.53 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.14 and 1.24 (s, isopropylidene CH_3), 4.63 (d, J=6.0 Hz, H_4), 5.01 (dd, J=5.8, 6.0 Hz, H_3), 5.13 (d, J=5.8 Hz, H_2), 6.75 (br, NH_2), 7.40 (m, C_6H_5), 7.67 (s, =CH), 11.50 (br, NH), $C\underline{H}_2OH$ peaks obscured by H_2O peaks; ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 25.66, 27.21, 68.71, 82.89, 83.84, 89.40, 111.99, 112.35, 126.22, 126.54, 127.37, 140.02, 154.47, 156.77, 164.22; UV λ_{max} (CH_3OH) 226 nm (ε 12330), 289 (10390), λ_{max} (0.1 mol dm^{-3} NaOH) 211 nm (ε 15210), 234 (11940), 276 (9020). Found: C, 60.00; H, 5.88; N, 11.69%. Calcd for $C_{18}H_{21}O_5N_3$: C, 60.16; H, 5.89; N, 11.69%.

5-[(2R,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-2-methyltetrahydrofuran-2-yl]isocytosine* (**28a**): A mixture of crude **23a** [prepared from **22a** (248 mg, 1.09 mmol) and *t*-butoxybis(dimethylamino)methane (2 ml)], guanidine hydrochloride (1.06 g, 8.72 mmol), and 1.25 mol dm^{-3} C_2H_5ONa in C_2H_5OH (7 ml) was stirred for 2 h. Workup according to Method A followed by preparative TLC (5:1 chloroform–CH_3OH) afforded **28a** (53.4 mg, 17% based on **22a**) as a yellow foam. R_f=0.40 (5:1 chloroform–CH_3OH), ^1H NMR (C_5D_5N) δ 1.36 and 1.62 (s, isopropylidene CH_3), 1.91 (s, CH_3), 4.00 (d, J=5.2 Hz, $C\underline{H}_2OH$), 4.54 (m, H_5), 5.01 (dd, J=4.1, 6.0 Hz, H_4), 5.39 (d, J=6.0 Hz, H_3), 8.04 (br, NH_2), 8.33 (s, =CH); UV λ_{max} (CH_3OH) 224 nm (ε 10400), 290 (8450), λ_{max} (0.1 mol dm^{-3} NaOH) 231 nm (ε 7710), 278 (5950). Found: m/z, 297.1312. Calcd for $C_{13}H_{19}N_3O_5$: M, 297.1325.

5-[(2R,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-2-pentyltetrahydrofuran-2-yl]isocytosine* (**28b**): A mixture of crude **23b** [prepared from **22b** (632 mg, 2.23 mmol) and *t*-butoxybis(dimethylamino)methane (3 ml)], guanidine hydrochloride (1.69 g, 17.8 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (18 ml) was stirred for 2 h. Workup according to Method A and column chromatography (20:1 to 10:1 chloroform–CH_3OH) afforded **28b** (31.6 mg, 4% based on **22b**) as a yellow foam. R_f=0.42 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.77 (t, J=6.0 Hz, CH_3), 1.0—2.0 (m, CH_2), 1.22 and 1.42 (s, isopropylidene CH_3), 3.38 (d, J=2.7 Hz, $C\underline{H}_2OH$), 3.82 (m, H_5), 4.43 (dd, J=2.0, 6.0 Hz, H_4), 4.81 (d, J=6.0 Hz, H_3), 6.78 (br, NH_2), 7.61 (s, =CH); UV λ_{max} (CH_3OH) 225 nm (ε 5770), 292 (3680), λ_{max} (0.1 mol dm^{-3} NaOH) 230 nm (ε 6720), 278 (4770). Found: m/z, 335.1842. Calcd for $C_{17}H_{25}O_4N_3$: ($M-H_2O$), 335.1840.

5-[(2R,3S*,4S*)-5,5-Bis(hydroxymethyl)-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine* (**36**): A mixture of **31** (368 mg, 0.91 mmol), guanidine hydrochloride (608 mg, 6.37 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (7 ml) was stirred for 5 h. Workup according to Method B gave a yellow solid, which was purified by preparative TLC (3:1 chloroform–CH_3OH) to give **36** (128 mg, 45%). Mp 245—247 °C (CH_3OH); R_f=0.39 (3:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.25 and 1.46 (s, isopropylidene CH_3), 3.53 (m, $C\underline{H}_2OH$), 4.0—5.0 (br, OH), 4.47 (d, J=5.5 Hz, H_4), 4.70 (d, J=5.5 Hz, H_2), 4.82 (t, J=5.5 Hz, H_3), 6.85 (br, NH_2), 7.63 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 25.24, 27.16, 60.71, 64.01, 81.74, 83.09, 86.44, 111.44, 112.46, 154.41, 156.45, 163.18, UV λ_{max} (CH_3OH) 227 nm (ε 5960), 290 (5720), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 10250), 277 (7770). Found: C, 49.54; H, 6.10; N, 13.40%. Calcd for $C_{13}H_{19}O_6N_3$: C, 49.83; H, 6.11; N, 13.41%.

5-[(2R,3R*,4S*,5R*)-2,5-Dimethyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine* (**50a**): A mixture of **45a** (1.07 g, 3.60 mmol), guanidine hydrochloride (2.74 g, 28.8 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (30 ml) was stirred for 5 h. Workup according to Method A followed by trituration with ethyl acetate afforded **50a** (878 mg, 77%). Mp 255—257 °C (CH_3OH), R=0.43 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.19 and 1.32 (s, CH_3), 1.32 and 1.49 (s, isopropylidene CH_3), 3.18 (d-like, J=4.8 Hz, $C\underline{H}_2OH$), 4.48 (d, J=6.3 Hz, H_3), 4.91 (d, J=6.3 Hz, H_4), 6.46 (br, NH_2), 7.72 (s, =CH), 10.90 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 19.82, 24.59, 24.94, 25.71, 66.71, 83.24, 83.30, 83.42, 84.59, 111.30, 119.42, 156.01; UV λ_{max} (CH_3OH) 225 nm (ε 9930), 292 (8160), λ_{max} (0.1 mol dm^{-3} NaOH) 231 nm (ε 8750), 278 (6930). Found: C, 52.90; H, 6.75; N, 12.89%. Calcd for $C_{14}H_{21}O_5N_3\cdot0.5H_2O$: C, 52.49; H, 6.92; N, 13.12%.

5-[(2R,3R*,4S*,5R*)-2,5-Dipentyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine* (**50b**): A mixture of **45b** (1.31 g, 3.20 mmol), guanidine hydrochloride (2.43 g, 25.6 mmol), and 1 mol dm^{-3} C_2H_5ONa in C_2H_5OH (25 ml) was stirred. After 5 h, the mixture was worked up according to Method A to give an oil, which was triturated with ethyl acetate to give **50b** (528 mg, 39%). Mp 168—170 °C (CH_3OH); R_f=0.54 (5:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.86 (m, CH_3), 1.0—2.0 (m, CH_2), 1.26 and 1.46 (s, isopropylidene CH_3), 3.34 (m, $C\underline{H}_2OH$), 4.49 (d, J=6.2 Hz, H_3), 4.74 (br, OH) 4.87 (d, J=6.2 Hz, H_4), 6.60 (br, NH_2), 7.62 (s, =CH), 11.10 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 13.80, 22.02, 22.66, 23.13, 24.36, 25.42, 31.76, 32.11, 34.70, 63.58, 83.34, 85.01, 85.66, 85.95, 110.78, 116.83, 155.52; UV λ_{max} (CH_3OH) 225 nm (ε 7530), 292 (5810), λ_{max} (0.1 mol dm^{-3} NaOH) 231 nm (ε 5440), 279 (3980). Found: C, 61.28; H, 8.79; N, 9.39%. Calcd for $C_{22}H_{37}O_5N_3\cdot0.5H_2O$; C, 61.09, H, 8.86; N, 9.71%.

5-[(2S,3R*,4R*,5R*)-3-t-Butyldimethylsiloxymethyl-5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl]isocytosine* (**60a**): A mixture of **53a** (500 mg, 1.21 mmol), guanidine hydrochloride (809 mg, 8.47 mmol), and 0.94 mol dm^{-3} C_2H_5ONa in C_2H_5OH (9 ml) was stirred for 3 h. After the Method B workup, the residue was subjected to preparative TLC (10:1 chloroform–CH_3OH) to give **60a** (339 mg, 67%). Mp 231—233 °C (CH_3OH–acetone–hexane); R_f=0.25 (10:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.06 (s, t-$C_4H_9(C\underline{H}_3)_2Si$), 0.85 (s, t-$C_4\underline{H}_9(CH_3)_2Si$), 1.34 and 1.51 (s, isopropylidene CH_3), 3.4—3.7 (m, $C\underline{H}_2OH$ and CH_2OSi), 3.97 (m, H_5), 4.54 (d, J=3.0 Hz, H_4), 4.89 (s, H_2), 6.67 (br, NH_2), 7.59 (s, =CH), 11.00 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 17.62, 25.37, 26.72, 28.31, 61.42, 81.03, 82.50, 82.73, 91.59, 108.92, 112.79, 128.29, 153.70, 155.18; UV λ_{max} (CH_3OH) 228 nm (ε 9500), 294 (8840), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 5090), 280 (3910). Found: C, 52.15; H, 7.67; N, 9.58%. Calcd for $C_{19}H_{33}O_6N_3Si\cdot0.5H_2O$: C, 52.27; H, 7.85; N, 9.62%.

5-[(2S,3R*,4R*,5R*)-5-Hydroxymethyl-3,4-isopropylidenedioxy-3-methyltetrahydrofuran-2-yl]isocytosine* (**60b**): A mixture of **53b** (200 mg, 0.707 mmol), guanidine hydrochloride (473 mg, 4.95 mmol), and 0.92 mol dm^{-3} C_2H_5ONa in C_2H_5OH (5.4 ml) was stirred for 3 h. The Method B workup of the reaction mixture gave a crude product which was subjected to preparative TLC (4:1 chloroform–CH_3OH) to afford **60b** (132 mg, 63%). Mp 178—180 °C (CH_3OH); R_f=0.45 (5:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.14 (s, CH_3), 1.34 and 1.51 (s, isopropylidene CH_3), 3.56 (d-like, J=5.0 Hz, $C\underline{H}_2OH$), 3.93 (m, H_5), 4.32 (d, J=2.8 Hz, H_4), 4.88 (s, H_2), 6.80 (br, NH_2), 7.58 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 20.55, 27.23, 28.44, 61.72, 82.22, 82.50, 87.37, 89.47, 110.76, 112.62, 152.83, 155.77, 162.22; UV λ_{max} (CH_3OH) 226 nm (ε 6830), 293 (6290), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 11000), 280 (8690). Found: C, 50.11; H, 6.51; N, 13.30%. Calcd for $C_{13}H_{19}O_5N_3 \cdot 0.8H_2O$: C, 50.09; H, 6.66; N, 13.48%.

Deprotection of the 5-(5-Hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl)pyrimidine C-*Nucleosides by Methanolic Hydrogen Chloride. General Procedure*: Unless otherwise stated, removal of the isopropylidene group was performed as follows. A mixture of a 5-(5-hydroxymethyl-3,4-isopropylidenedioxytetrahydrofuran-2-yl)pyrimidine *C*-nucleoside and 10% methanolic hydrogen chloride solution was stirred at the room temperature until the reaction was complete (TLC analysis). The reaction mixture was concentrated under reduced pressure (50—90 mmHg), giving a crude material, which was coevaporated with C_2H_5OH. The resulting solid was triturated with ether or ethyl acetate to give the desired deprotection product. A pure sample was collected by recrystallization.

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-[(R*)-1-hydroxyethyl]tetrahydrofuran-2-yl]uracil ((±)-5′-Methylpseudouridine) (**9b**)*: To a solution of **8b** (51.2 mg, 0.172 mmol) in CH_3OH (2 ml) was added 10% HCl in CH_3OH (2 ml) and the mixture was stirred for 10 min. The above described workup gave **9b** (42.8 mg, 96%). Mp 237.2—239.1 °C (aqueous C_2H_5OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.06 (d, J=6.0 Hz, CH_3), 3.50 (m, H_5 and $C\underline{H}OH$), 4.0 (m, H_3 and H_4), 4.37 (d, J=6.0 Hz, H_2), 7.70 (d, J=6.0 Hz, =CH), 10.87 (d, J=6.0 Hz, NH), 11.08 (s, NH); UV λ_{max} (CH_3OH) 264 nm (ε 5620), λ_{max} (0.1 mol dm^{-3} HCl) 263 nm (ε 8130), λ_{max}(0.1 mol dm^{-3} NaOH) 287 nm (ε 8510). Found: C, 46.67; H, 5.39; N, 10.71%. Calcd for $C_{10}H_{14}O_6N_2$: C, 46.51; H, 5.47; N, 10.85%.

5-[(2R,3R*,4S*,5S*)-3,4-Dihydroxy-5-(1-hydroxy-1-methylethyl)tetrahydrofuran-2-yl]uracil ((±)-5′,5′-Dimethylpseudouridine) (**9a**)*: To a solution of **8a** (218 mg, 0.699 mmol) in CH_3OH (4 ml) was added 10% HCl in CH_3OH (3 ml) and the resulting mixture was stirred for 10 min. Workup in a usual manner left pure **9a** (185 mg, 97%). Mp 221.4—224.8 °C; ^{1}H NMR (C_5D_5N) δ 1.53 and 1.57 (s, CH_3), 4.32 (dd, J=3.0, 5.0 Hz, H_4), 4.34 (d, J=3.0 Hz, H_5), 5.12 (dd, J=5.0, 6.5 Hz, H_3), 5.25 (d, J=6.5 Hz, H_2), 5.75 (br, OH and NH), 8.00 (s, =CH); UV λ_{max} (CH_3OH) 212 nm (ε 7940), 263 (6600), λ_{max} (0.1 mol dm^{-3} HCl) 264 nm (ε 8310), λ_{max} (0.1 mol dm^{-3} NaOH) 218 nm (ε 8310), 287 (10960). Found: C, 48.42; H, 6.02; N, 10.11%. Calcd for $C_{11}H_{16}O_6N_2$: C, 48.52; H, 5.92; N, 10.29%.

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-[(R*)-1-hydroxyhexyl]tetrahydrofuran-2-yl]uracil ((±)-5′-Pentylpseudouridine) (**9c**)*: A mixture of **8c** (134 mg, 0.379 mmol) in CH_3OH (3 ml) and 10% HCl in CH_3OH (3 ml) was stirred for 10 min. The usual workup gave **9c** (71 mg, 60%). Mp 193.3—197.7 °C; ^{1}H NMR (C_5D_5N) δ 0.81 (t, J=6.0 Hz, CH_3), 1.10—1.90 (m, CH_2), 4.24 (m, $C\underline{H}OH$), 4.54 (t, J=2.8 Hz, H_5), 4.94 (dd, J=2.8, 4.3 Hz, H_4), 5.15 (m, H_2 and H_3), 5.50 (br, OH and NH), 7.95 (s, =CH); UV λ_{max} (CH_3OH) 212 nm (ε 8510), 265 (6910), λ_{max} (0.1 mol dm^{-3} HCl) 264 nm (ε 3540), λ_{max} (0.1 mol dm^{-3} NaOH) 217 nm (ε 10960), 286 (7240). Found: C, 53.38; H, 7.21; N, 8.78%. Calcd for $C_{14}H_{22}O_6N_2$: C, 53.49; H, 7.05; N, 8.91%.

5-[(2R,3R*,4R*,5S*)-3,4-Dihydroxy-5-[(S*)-α-hydroxybenzyl]tetrahydrofuran-2-yl]uracil ((±)-5′-Phenylpseudouridine) (**9d**)*: To a solution of **8d** (39.0 mg, 0.108 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1.5 ml). The resulting mixture was stirred for 5 min and worked up to yield **9d** (36.3 mg, 100%) as a wax. ^{1}H NMR (C_5D_5N) δ 4.90 (m, H_5 and $C\underline{H}OH$), 5.24 (m, H_3 and H_4), 5.47 (d, J=4.0 Hz, H_2), 7.20—7.50 (m, C_6H_5), 7.83 (s, =CH); UV λ_{max} (CH_3OH) 265 nm (ε 7410), λ_{max} (0.1 mol dm^{-3} HCl) 264 nm (ε 7250), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 9330). Found: C, 56.31; H, 5.23; N, 8.61%. Calcd for $C_{15}H_{16}O_6N_2$: C, 56.25; H, 5.04; N, 8.75%.

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-methyltetrahydrofuran-2-yl]uracil ((±)-4′-Methylpseudouridine) (**17a**)*: To a solution of **16a** (14.0 mg, 0.0392 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml). After stirring for 15 min, usual workup afforded **17a** (11.6 mg, 100%). Mp 226—228 °C (CH_3OH); R_f=0.37 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 1.69 (s, CH_3), 3.90 (d, J=11.5 Hz, $\underline{H}_aH_bCOH$), 4.08 (d, J=11.5 Hz, $H_a\underline{H}_bCOH$), 4.87 (m, H_4), 5.26 (m, H_2 and H_3), 6.32 (br, OH), 7.98 (s, =CH), 12.50 and 13.20 (br, NH); UV λ_{max} (CH_3OH) 264 nm (ε 7760), λ_{max} (0.1 mol dm^{-3} HCl) 264 nm (ε 7510), λ_{max} (0.1 mol dm^{-3} NaOH) 286 nm (ε 7540). Found: *m/z*, 258.0855. Calcd for $C_{10}H_{14}O_6N_2$: M, 258.0852.

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-pentyltetrahydrofuran-2-yl]uracil ((±)-4′-Pentylpseudouridine) (**17b**)*: To a mixture of **16b** (16.0 mg, 0.0452 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml), and the resulting mixture was stirred for 10 min. Workup afforded **17b** (15.7 mg, 100%). Mp 205—209 °C (CH_3OH); R_f= 0.60 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 0.84 (t, J=6.0 Hz, CH_3), 1.2—2.3 (m, CH_2), 3.98 (d, J= 11.8 Hz, $\underline{H}_aH_bCOH$) 4.14 (d, J=11.8 Hz, $H_a\underline{H}_bCOH$) 4.88 (d, J=4.5 Hz, H_4), 5.14 (d, J=8.0 Hz, H_2), 5.34 (dd, J= 4.5, 8.0 Hz, H_3), 5.91 (br, OH), 7.89 (s, =CH), 12.50 and 13.20 (br, NH); UV λ_{max} (CH_3OH) 264 nm (ε 9530), λ_{max} (0.1 mol dm^{-3} HCl) 264 nm (ε 9210), λ_{max} (0.1 mol dm^{-3} NaOH) 287 nm (ε 8390). Found: C, 50.54; H, 6.68; N, 7.68%. Calcd for $C_{14}H_{22}O_6N_2 \cdot H_2O$: C, 50.59; H, 7.28; N, 8.43%.

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-phenyltetrahydrofuran-2-yl]uracil ((±)-4′-Phenylpseudouridine) (**17c**)*: To a solution of **16c** (34.2 mg, 0.095 mmol) in CH_3OH (2 ml) was added 10% HCl in CH_3OH (2 ml). After stirring for 15 min, the mixture was worked up to give **17c** (32.0 mg, 100%). Mp 245—249 °C (CH_3OH); R_f=0.55 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 4.07 (d, J=11.9 Hz, $\underline{H}_aH_bCOH$), 4.17 (d, J=11.9 Hz, $H_a\underline{H}_bCOH$), 5.28 (d, J=5.2 Hz, H_4), 5.35 (d, J=7.5 Hz, H_2), 5.62 (dd, J=5.2, 7.5 Hz, H_3), 5.92 (br, OH), 7.2—8.0 (m, C_6H_5), 8.08 (s, =CH), 13.30 (br, NH); UV λ_{max} (CH_3OH) 264 nm (ε 5380), λ_{max} (0.1 mol dm^{-3} HCl) 263 nm (ε 8790), λ_{max} (0.1 mol dm^{-3} NaOH) 288 nm (ε 5150).[38)]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-2-methyltetrahydrofuran-2-yl]uracil ((±)-1′-Methylpseudouridine) (**25a**)*: A mixture of a solution of **24a** (16.9 mg, 0.128 mmol) in CH_3OH (1 ml) and 10% HCl in CH_3OH (1 ml) was stirred for 30 min. Usual workup gave **25a** (15.9 mg, 100%) as a pale green foam. R_f=0.40 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 2.16 (s, CH_3), 4.22 (dd, J=3.1, 11.2 Hz, $\underline{H}_aH_bCOH$), 4.38 (dd, J=2.5, 11.2 Hz,

H_aH_bCOH), 4.61 (ddd, J=2.5, 3.1, 7.5 Hz, H_5), 4.84 (dd, J=4.7, 7.5 Hz, H_4), 5.00 (d, J=7.5 Hz, H_3), 6.26 (br, OH), 8.52 (s, =CH), 12.42 and 12.96 (br, NH); UV λ_{max} (CH_3OH) 263 nm, λ_{max} (0.1 mol dm^{-3} HCl) 263 nm, λ_{max} (0.1 mol dm^{-3} NaOH) 265 nm (sh), 289, molar extinction coefficient has not been measured because of the extreme hygroscopicity.[38)]

5-[(2R,3R*,4R*,4R*)-3,4-Dihydroxy-5-hydroxymethyl-2-pentyltetrahydrofuran-2-yl]uracil ((±)-1′-Pentylpseudouridine) (**25b**)*: To a solution of **24b** (30.0 mg, 0.0847 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml). After stirring for 30 min, usual workup and preparative TLC (3:1 chloroform–CH_3OH) afforded **25b** (9.6 mg, 36%) as a yellow foam. R_f=0.44 (3:1 chloroform–CH_3OH); ^1H NMR (C_5D_5N) δ 0.80 (t, J=7.0 Hz, CH_3), 1.1—2.0 (m, CH_2), 2.3—3.1 (m, CH_2, 2H), 4.36 (m, C$\underline{H}_2$OH), 4.58 (m, H_5), 4.84 (m, H_4), 5.00 (m, H_3), 8.62 (s, =CH); UV λ_{max} (CH_3OH) 265 nm (ε 5960), λ_{max} (0.1 mol dm^{-3} HCl) 265 nm (ε 6610), λ_{max} (0.1 mol dm^{-3} NaOH) 266 nm (sh, ε 3260), 289 (4840).[38)]

5-[(2R,3S*,4S*)-3,4-Dihydroxy-5,5-bis(hydroxymethyl)-tetrahydrofuran-2-yl]uracil ((±)-4′-Hydroxymethylpseudouridine) (**33**)*: A mixture of **32** (50 mg, 0.175 mmol) and 10% HCl in CH_3OH (1.5 ml) was stirred for 10 min. Workup afforded **33** (38.3 mg, 89%) as a white powder. Mp 76—79 °C; ^1H NMR (dimethyl-d_6 sulfoxide) δ 3.46 (d-like, J=6.0 Hz, C$\underline{H}_2$OH), 4.33 (m, H_2, H_3, and H_4), 4.0—5.0 (br, OH), 7.43 (d, J=5.8 Hz, =CH), 10.87 (d, J=5.8 Hz, NH), 11.05 (br s, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 61.63, 63.88, 72.40, 74.06, 78.33, 86.47, 110.59, 140.44, 150.91, 163.94; UV λ_{max} (CH_3OH) 264 nm (ε 6580), λ_{max} (0.1 mol dm^{-3} HCl) 264 nm (ε 6090), λ_{max} (0.1 mol dm^{-3} NaOH) 287 nm (ε 6780).[38)]

5-[(2R,3R*,4S*,5R*)-3,4-Dihydroxy-2,5-dimethyl-5-hydroxymethyltetrahydrofuran-2-yl]uracil ((±)-1′,4′-Dimethylpseudouridine) (**47a**)*: To a solution of **46a** (313 mg, 0.911 mmol) in CH_3OH (2 ml)was added 10% HCl in CH_3OH (3 ml). The resulting mixture was stirred for 1 h. Usual workup afforded **47a** (274 mg, 100%). Mp 134—138 °C (CH_3OH); R_f=0.45 (3:1 chloroform–CH_3OH); ^1H NMR (C_5D_5N) δ 1.78 and 2.14 (s, CH_3), 3.96 (s, C$\underline{H}_2$OH), 4.87 (d, J=5.5 Hz, H_3), 5.05 (d, J=5.5 Hz, H_4), 6.24 (br, OH), 8.48 (br s, =CH), 12.50 (br, NH), 13.04 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 19.74, 23.46, 67.24, 72.11, 75.80, 82.23, 84.53, 117.80, 139.04, 151.60, 164.15; UV λ_{max} (CH_3OH) 265 nm (ε 6190), λ_{max} (0.1 mol dm^{-3} NaOH) 287 nm (ε 4760). Found: C, 46.52; H, 5.87; N, 8.98%. Calcd for $C_{11}H_{16}O_6N_2\cdot 0.8H_2O$: C, 46.08; H, 6.19; N, 9.77%.

5-[(2R,3R*,4S*,5R*)-3,4-Dihydroxy-2,5-dipentyl-5-hydroxymethyltetrahydrofuran-2-yl]uracil ((±)-1′,4′-Dipentylpseudouridine) (**47b**)*: To a solution of **46b** (100 mg, 0.236 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (3 ml). After stirring for 1.5 h, the mixture was worked up to give **47b** (82.5 mg, 91%). Mp 232—236 °C (CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.86 (m, CH_3), 1.0—2.1 (m, CH_2), 3.51 (br s, C$\underline{H}_2$OH), 4.03 (m, H_3 and H_4), 4.81 (br, OH), 7.51 (m, =CH), 10.88 (m, NH), 11.00 (br s, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 13.73, 21.98, 22.40, 22.58, 31.62, 31.77, 32.35, 32.77, 63.93, 72.11, 76.65, 83.80, 85.65, 115.67, 138.98, 151.07, 163.94; UV λ_{max} (CH_3OH) 265 nm (ε 7240), λ_{max} (0.1 mol dm^{-3} HCl) 265 nm (ε 2300), λ_{max} (0.1 mol dm^{-3} NaOH) 290 nm (ε 7200).[38)]

5-[(2R,3S*,4R*,5R*)-3,4-Dihydroxy-3,5-bis(hydroxymethyl)-tetrahydrofuran-2-yl]uracil ((±)-2′-Hydroxymethylpseudouridine) (**55a**)*: To a solution of **54a** (94 mg, 0.219 mmol) in CH_3OH (0.1 ml) was added 10% HCl in CH_3OH (0.2 ml). After stirring for 30 min, the mixture was worked up to give **55a** (57 mg, 95%) as a white foam. Mp 125—130 °C; R_f= 0.29 (10:10:1 chloroform–CH_3OH–Water); ^1H NMR (dimethyl-d_6 sulfoxide) δ 3.28 (s, C(OH)C$\underline{H}_2$OH), 3.4—3.9 (m, H_4, H_5, and C$\underline{H}_2$OH), 4.68 (s, H_2), 7.50 (d, J=4.8 Hz, =CH), 12.28 (d, J=4.8 Hz, NH), 12.40 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 60.56, 63.21, 70.58, 79.62, 80.42, 82.06, 110.75, 139.17, 150.96, 164.18; UV λ_{max} (CH_3OH) 267 nm (ε 5710), λ_{max} (0.1 mol dm^{-3} HCl) 266 nm (ε 5140), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 3780).[38)]

5-[(2R,3S*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-3-methyltetrahydrofuran-2-yl]uracil ((±)-2′-Methylpseudouridine) (**55b**)*: To a solution of **54b** (30 mg, 0.101 mmol) in CH_3OH (0.5 ml) was added 10% HCl in CH_3OH (0.5 ml) and the resulting mixture was stirred for 1 h. Workup afforded **54b** (25 mg, 96%). Mp 138—142 °C; R_f=0.40 (2:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.99 (s, CH_3), 3.60 (m, H_4, H_5, and C$\underline{H}_2$OH), 4.00 (br, OH), 4.68 (s, H_2), 7.60 (d, J=5.0 Hz, =CH), 10.78 (d, J=5.0 Hz, NH), 10.99 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 20.95, 60.31, 73.57, 77.99, 81.31, 81.53, 112.13, 138.92, 150.90, 163.68; UV λ_{max} (CH_3OH) 264 nm (ε 6420), λ_{max} (0.1 mol dm^{-3} HCl) 263 nm (ε 8760), λ_{max} (0.1 mol dm^{-3} NaOH) 285 nm (ε 8020).[38)]

5-[(2R,3R*,4S*,5S*)-3,4-Dihydroxy-5-(1-hydroxy-1-methylethyl)tetrahydrofuran-2-yl]-2-thiouracil ((±)-5′,5′-Dimethyl-2-thiopseudouridine) (**11a**)*: A mixture of **10a** (158 mg, 0.549 mmol) and 10% HCl in CH_3OH (5 mol) was stirred for 10 min. Usual workup afforded **11a** (135 mg, 97%) as a white powder. Mp 109—115 °C; ^1H NMR (C_5D_5N) δ 1.58 and 1.60 (s, CH_3), 4.34 (d, J=3.8 Hz, H_5), 4.96 (m, H_3 and H_4), 5.31 (d, J=5.0 Hz, H_2), 5.70 (br, OH and NH), 8.19 (s, =CH); UV λ_{max} (CH_3OH) 214 nm (ε 5780), 276 (6660), 292 (5990), λ_{max} (0.1 mol dm^{-3} HCl) 214 nm (ε 7560), 274 (8810), 289 (8890), λ_{max} (0.1 mol dm^{-3} NaOH) 222 nm (ε 7910), 263 (6670), 284 (5020).[38)]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-[(R*)-1-hydroxyethyl]tetrahydrofuran-2-yl]-2-thiouracil ((±)-5′-Methyl-2-thiopseudouridine) (**11b**)*: To a solution of **10a** (52.1 mg, 0.155 mmol) in CH_3OH (2 ml) was added 10% HCl in CH_3OH (2 ml). The resulting mixture was stirred for 5 min and worked up to give **11b** (48.6 mg, 100%) as a wax. ^1H NMR (C_5D_5N) δ 1.51 (d, J=6.0 Hz, CH_3), 4.67 (m, H_5 and $\underline{H}$COH), 4.96 (m, H_3 and H_4), 5.35 (d, J=5.2 Hz, H_2), 6.0 (br, OH and NH), 8.16 (s, =CH); UV λ_{max} (CH_3OH) 215 nm (ε 6610), 277 (8350), 291 (7590), λ_{max} (0.1 mol dm^{-3} HCl) 213 nm (ε 6080), 280 (4630), 295 (5630), λ_{max} (0.1 mol dm^{-3} NaOH) 221 nm (ε 11400), 264 (10200), 285 (7730).[38)]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-[(R*)-1-hydroxyhexyl]tetrahydrofuran-2-yl]-2-thiouracil ((±)-5′-Pentyl-2-thiopseudouridine (**11c**)*: To a solution of **10c** (62.8 mg, 0.170 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (2 ml). After stirring for 10 min, the mixture was worked up to afford **11c** (32.5 mg, 58%). Mp 164—170 °C; ^1H NMR (C_5D_5N) δ 0.81 (t, J=7.0 Hz, CH_3), 1.1—2.0 (m, CH_2), 4.30 (m, $\underline{H}$COH) 4.57 (t-like, J=3.0 Hz, H_5), 5.00 (m, H_3 and H_4), 5.35 (d, J=5.2 Hz, H_2), 5.4—6.8 (br, OH and NH), 8.14 (s, =CH); UV λ_{max} (CH_3OH) 214 nm (ε 4310), 276 (5160), 291 (4670), λ_{max} (0.1 mol dm^{-3} HCl) 215 nm (ε 7090), 276 (8230), 290 (8230), λ_{max} (0.1 mol dm^{-3} NaOH) 222 nm (ε 5300), 264 (4340), 285 (3420).[38)]

5-[(2R,3R*,4R*,5S*)-3,4-Dihydroxy-5-[(S*)-α-hydroxybenzyl]tetrahydrofuran-2-yl]-2-thiouracil ((±)-5′-Phenyl-2-thiopseudouridine) (**11d**)*: To a suspension of **10d** (26.6 mg, 0.071 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml). The resulting mixture was stirred for 10 min and worked up to give **11d** (24.9 mg, 100%). Mp 126—130 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 3.95 (d-like, *J*=3.1 Hz, H_5), 4.46 (d, *J*=3.0 Hz, H_4), 4.70 (m, H_3), 4.90 (m, H_2), 5.59 (d, *J*=3.0 Hz, H̲COH), 7.2—7.5 (m, C_6H_5), 7.44 (s, =CH); UV λ_{max} (CH_3OH) 212 nm (ε 4380), 277 (3620), 290 (3240), λ_{max} (0.1 mol dm^{-3} HCl) 275 nm (ε 6900), 290 (6440), λ_{max} (0.1 mol dm^{-3} NaOH) 264 nm (ε 6510), 285 (5030).[38]

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-methyltetrahydrofuran-2-yl]-2-thiouracil ((±)-4′-Methyl-2-thiopseudouridine) (**19a**)*: To a solution of **18a** (22.1 mg, 0.0704 mmol) in CH_3OH (1.5 ml) was added 10% HCl in CH_3OH (1.5 ml) and the resulting mixture was stirred for 20 min. Usual workup afforded **19a** (18.4 mg, 95%). Mp 157—162 °C (CH_3OH); R_f=0.55 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 1.69 (s, CH_3), 3.93 (d, *J*=11.5 Hz, $\underline{H}_aH_bCOH$), 4.07 (d, *J*=11.5 Hz, $H_a\underline{H}_bCOH$), 4.88 (d, *J*=5.5 Hz, H_4), 5.10 (t, *J*=5.5 Hz, H_3), 5.35 (d, *J*=5.5 Hz, H_2), 8.16 (s, =CH); UV λ_{max} (CH_3OH) 215 nm (ε 10920), 276 (15550), 291 (14070), λ_{max} (0.1 mol dm^{-3} HCl) 214 nm (ε 13150), 276—290 (flat, 15570), λ_{max} (0.1 mol dm^{-3} NaOH) 223 nm (ε 12640), 264 (11240), 286 (8570). Found: *m/z*, 274.0613. Calcd for $C_{10}H_{14}O_5N_2S$: M, 274.0623.

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-pentyltetrahydrofuran-2-yl]-2-thiouracil ((±)-4′-Pentyl-2-thiopseudouridine) (**19b**).* To a suspension of **18b** (17.7 mg, 0.048 mmol) in CH_3OH (1.5 ml) was added 10% HCl in CH_3OH (1.5 ml). After stirring for 30 min, the mixture was worked up in a usual manner to give **19b** (16.9 mg, 100%). Mp 203—205 °C (CH_3OH); R_f=0.74 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 0.81 (t, *J*=6.0 Hz, CH_3), 1.2—2.0 (m, CH_2), 3.96 (d, *J*=11.8 Hz, $\underline{H}_aH_bCOH$), 4.12 (d, *J*=11.8 Hz, $H_a\underline{H}_bCOH$), 4.87 (br s, H_4), 5.20 (m, H_2 and H_3), 6.0 (br, OH), 8.02 (s, =CH); UV λ_{max} (CH_3OH) 215 nm (ε 13320), 276 (18690), 291 (16950), λ_{max} (0.1 mol dm^{-3} HCl) 214 nm (ε 14310), 275—290 (flat, 16500), λ_{max} (0.1 mol dm^{-3} NaOH) 223 nm (ε 13790), 264 (12100), 286 (9340).[38]

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-phenyltetrahydrofuran-2-yl]-2-thiouracil ((±)-4′-Phenyl-2-thiopseudouridine) (**19c**)*: A mixture of **18c** (106 mg, 0.282 mmol) and 9:1 CF_3COOH–H_2O (4 ml) was stirred for 10 min. Usual workup afforded **19c** (84.1 mg, 89%). Mp 249—250 °C (CH_3OH); R_f=0.70 (3:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 3.34 (m, $C\underline{H}_2OH$), 4.57 (m, H_3), 5.10 (m, H_2 and H_4), 7.30 (m, C_6H_5), 7.66 (d, *J*=5.5 Hz, =CH), 12.43 (d, *J*=5.5 Hz, NH), 12.57 (br s, NH); UV λ_{max} (CH_3OH) 276 nm (ε 16620), 290 (14970), λ_{max} (0.1 mol dm^{-3} HCl) 276 nm (ε 13620), 289 (13790), λ_{max} (0.1 mol dm^{-3} NaOH) 216 nm (ε 19540), 264 (13910), 289 (13790). Found: C, 52.75; H, 4.70; N, 8.12; S, 9.68%. Calcd for $C_{15}H_{16}O_5N_2S$: C, 53.36; H, 4.80; N, 8.33; S, 9.53%.

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-2-methyltetrahydrofuran-2-yl]-2-thiouracil ((±)-1′-Methyl-2-thiopseudouridine) (**27a**)*: To a solution of **26a** (54.7 mg, 0.175 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml). After stirring for 30 min, the mixture was worked up to give **27a** (50.3 mg, 100%) as a yellow foam. R_f=0.60 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 2.16 (s, CH_3), 4.21 (dd, *J*=2.0, 11.9 Hz, $\underline{H}_aH_bCOH$), 4.38 (dd, *J*=3.1, 11.9 Hz, $H_a\underline{H}_bCOH$), 4.60 (ddd, *J*=2.0, 3.1, 6.1 Hz, H_5), 4.82 (dd, *J*=4.6, 6.1 Hz, H_4), 4.96 (d, *J*=6.1 Hz, H_3), 6.0—6.9 (br, OH and NH), 8.71 (s, =CH); UV λ_{max} (CH_3OH) 215 nm (ε 10940), 276 (14430), 290 (13270), λ_{max} (0.1 mol dm^{-3} HCl) 215 nm (ε 11000), 275 (14330), 290 (sh, 13320), λ_{max} (0.1 mol dm^{-3} NaOH) 221 nm (sh, ε 12680), 262 (12310), 295 (sh, 6620).[38]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-2-pentyltetrahydrofuran-2-yl]-2-thiouracil ((±)-1′-Pentyl-2-thiopseudouridine) (**27b**)*: To a solution of **26b** (52.6 mg, 0.142 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml). The mixture was stirred for 30 min and worked up to give **27b** (41.6 mg, 89%) as a yellow foam. R_f=0.72 (3:1 chloroform–CH_3OH); ^{1}H NMR (C_5D_5N) δ 0.76 (t, *J*=7.0 Hz, CH_3), 1.0—1.9 (m, CH_2), 2.2—3.1 (m, CH_2, 2H), 4.27 (dd, *J*=2.2, 11.9 Hz, $\underline{H}_aH_bCOH$), 4.44 (dd, *J*=2.3, 11.9 Hz, $H_a\underline{H}_bCOH$), 4.56 (ddd, *J*=2.2, 2.3, 7.0 Hz, H_5), 4.86 (dd, *J*=5.0, 7.0 Hz, H_4), 4.95 (d, *J*=5.0 Hz, H_3), 6.0—7.2 (br, OH and NH), 8.78 (s, =CH); UV λ_{max} (CH_3OH) 215 nm (ε 10910), 277 (14540), 291 (13190), λ_{max} (0.1 mol dm^{-3} HCl) 213 nm (sh, ε 7280), 273 (8440), 295 (sh, 6160), λ_{max} (0.1 mol dm^{-3} NaOH) 220 nm (sh, ε 9340), 262 (9420), 297 (sh, 4590). Found: *m/z*, 330.1244. Calcd for $C_{14}H_{22}O_5N_2S$: M, 330.1249.

5-[(2R,3S*,4S*)-3,4-Dihydroxy-5,5-bis(hydroxymethyl)tetrahydrofuran-2-yl]-2-thiouracil ((±)-4′-Hydroxymethyl-2-thiopseudouridine) (**35**)*: A mixture of **34** (35.8 mg, 0.119 mmol) and 10% HCl in CH_3OH (1 ml) was stirred for 10 min. Usual workup afforded **35** (32.3 mg, 90%) as a white powder. Mp 84—87 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 3.48 (d-like, *J*=5.9 Hz, $C\underline{H}_2OH$), 4.06 (m, H_3), 4.61 (m, H_2 and H_4), 4.3—5.0 (br, OH), 7.52 (d, *J*=5.9 Hz, =CH), 11.84 (d, *J*=5.9 Hz, NH), 11.98 (br s, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 61.68, 63.94, 72.45, 74.09, 78.41, 86.51, 110.62, 140.43, 150.92, 163.95; UV λ_{max} (CH_3OH) 213 nm (ε 14110), 275 (15840), 296 (sh, 13120), λ_{max} (0.1 mol dm^{-3} HCl) 214 nm (ε 13500), 273 (13500), 292 (sh, 12080), λ_{max} (0.1 mol dm^{-3} NaOH) 265 nm (ε 13620), 285 (12920).[38]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-2,5-bis(hydroxymethyl)-tetrahydrofuran-2-yl]-2-thiouracil ((±)-1′-Hydroxymethyl-2-thiopseudouridine) (**41**)*: To a solution of **40** (50 mg, 0.156 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (0.5 ml). After stirring for 10 min, the mixture was worked up in a usual manner to give **41** (39 mg, 87%) as a white powder. Mp 130—135 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 3.49 (d-like, *J*=6.5 Hz, $C\underline{H}_2OH$), 3.9—4.3 (m, H_3, H_4, H_5, and OH), 7.53 (m, =CH), 12.30 (br, NH), 12.44 (br s, NH); UV λ_{max} (CH_3OH) 213 nm (ε 12360), 275 (12540), 299 (sh, 10300), λ_{max} (0.1 mol dm^{-3} HCl) 213 nm (ε 13820), 274 (13340), 297 (sh, 11200), λ_{max} (0.1 mol dm^{-3} NaOH) 265 nm (ε 12580), 284 (10440).[38]

5-[(2R,3R*,4S*,5R*)-3,4-Dihydroxy-2,5-dimethyl-5-hydroxymethyltetrahydrofuran-2-yl]-2-thiouracil ((±)-1′,4′-Dimethyl-2-thiopseudouridine) (**49a**)*: To a solution of **48a** (229 mg, 0.670 mmol) in CH_3OH (2 ml) was added 10% HCl in CH_3OH (3 ml). The resulting mixture was stirred for 1 h and worked up to afford **49a** (192 mg, 98%). Mp 182—186 °C (CH_3OH); ^{1}H NMR (C_5D_5N) δ 1.75 and 2.13 (s, CH_3), 3.98 (s, $C\underline{H}_2OH$), 4.86 (d, *J*=5.2 Hz, H_3), 4.97 (d, *J*=5.2 Hz, H_4), 6.50 (br, OH), 8.65 (s, =CH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 19.59, 22.88, 66.42, 71.24, 75.06, 81.95, 84.30, 123.01, 138.83, 160.89, 175.01; UV λ_{max} (CH_3OH) 216 nm (ε 13430), 277 (18980), 290 (17230), λ_{max} (0.1 mol dm^{-3} HCl) 216 nm (ε 12870), 277 (16560), 285 (16370), λ_{max} (0.1 mol dm^{-3} NaOH) 222 nm (ε 15860), 262 (14800), 290 (9650). Found: C, 45.76; H, 5.74; N, 9.47; S, 10.86%. Calcd for $C_{11}H_{16}O_5N_2S$: C, 45.83; H, 5.59; N, 9.72, S, 11.12%.

5-[(2R,3R*,4S*,5R*)-3,4-Dihydroxy-2,5-dipentyl-5-hydroxymethyltetrahydrofuran-2-yl]-2-thiouracil ((±)-1′,4′-Dipentyl-2-thiopseudouridine) (**49b**)*: To a solution of **48b** (404 mg, 0.910 mmol) in CH_3OH (3 ml) was added 10% HCl in CH_3OH

(3 ml). The mixture was stirred for 1 h and worked up in a usual manner to afford **49b** (392 mg, 100%). Mp 105—110 °C (CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.84 (m, CH_3), 1.0—2.1 (m, CH_2), 3.34 (m, C$\underline{H}_2$OH), 3.8—5.0 (br, OH), 4.04 (m, H_3 and H_4), 7.57 (m, =CH), 12.26 (m, NH), 12.35 (br s, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 13.73, 21.99, 22.50, 31.71, 32.37, 63.71, 71.89, 76.25, 83.89, 85.78, 121.27, 138.93, 160.73, 174.68; UV λ_{max} (CH_3OH) 215 nm (ε 9330), 277 (13170), 290 (sh, 11690), λ_{max} (0.1 mol dm^{-3} HCl) 217 nm (ε 6280), 275 (9980), 289 (9460), λ_{max} (0.1 mol dm^{-3} NaOH) 225 nm (ε 10110), 262 (10790).[38]

5-[(2S,3R*,4R*,5R*)-3,4-Dihydroxy-3,5-bis(hydroxymethyl)-tetrahydrofuran-2-yl]-2-thiouracil ((±)-2'-Hydroxymethyl-2-thio-pseudouridine) (**59a**)*: To a solution of **58a** (237 mg, 0.534 mmol) in CH_3OH (2.8 ml) was added 10% HCl in CH_3OH (5 ml). After stirring for 30 min, the mixture was worked up as usual to afford **59a** (148 mg, 96%). Mp 140—145 °C; R_f=0.48 (10:10:1 chloroform–CH_3OH–water); ^1H NMR (dimethyl-d_6 sulfoxide) δ 3.27 (s, C(OH)C$\underline{H}_2$OH), 3.4—3.7 (m, H_4 and H_5), 3.64 (d, J=8.0 Hz, $\underline{H}_aH_b$COH), 3.85 (d, J=8.0 Hz, $H_a\underline{H}_b$COH), 4.25 (br, OH), 4.68 (s, H_2), 7.50 (d, J=5.5 Hz, =CH), 12.26 (d, J=5.5 Hz, NH), 12.38 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 60.54, 62.70, 70.17, 79.88, 80.16, 82.05, 116.58, 138.54, 160.90, 174.63; UV λ_{max} (CH_3OH) 215 nm (ε 9080), 277 (11700), λ_{max} (0.1 mol dm^{-3} HCl) 215 nm (ε 9400), 276 (11000), λ_{max} (0.1 mol dm^{-3} NaOH) 220 nm (ε 11700), 264 (9060). Found: C, 37.22; H, 5.06; N, 7.42%. Calcd for $C_{10}H_{14}O_6N_2S\cdot 2.3H_2O$: C, 36.21; H, 5.64; N, 8.45%.

5-[(2S,3R*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-3-methyltetrahydrofuran-2-yl]-2-thiouracil ((±)-2'-Methyl-2-thio-pseudouridine) (**59b**)*: To a solution of **58b** (194 mg, 0.618 mmol) in CH_3OH (3 ml) was added 10% HCl in CH_3OH (5 ml). The mixture was stirred for 30 min and worked up to give **59b** (164 mg, 97%). Mp 132—136 °C (CH_3OH–ether); R_f=0.61 (2:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.98 (s, CH_3), 3.6 (m, H_4, H_5, and C$\underline{H}_2$OH), 4.22 (br, OH), 4.70 (s, H_2), 7.68 (d, J=5.5 Hz, =CH), 12.26 (d, J=5.5 Hz, NH), 12.38 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 20.87, 60.18, 73.46, 78.06, 81.05, 81.59, 117.70, 138.51, 160.53, 174.75; UV λ_{max} (CH_3OH) 215 nm (ε 9470), 276 (11600), λ_{max} (0.1 mol dm^{-3} HCl) 215 nm (ε 10200), 275 (11000), λ_{max} (0.1 mol dm^{-3} NaOH) 220 nm (ε 17300), 263 (14500). Found: C, 40.81; H, 5.19; N, 9.44; S, 10.58%. Calcd for $C_{10}H_{14}O_5N_2S\cdot 1.1H_2O$: C, 40.84; H, 5.55; N, 9.53; S, 10.90%.

5-[(2R,3R*,4S*,5S*)-3,4-Dihydroxy-5-(1-hydroxy-1-methylethyl)tetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-5',5'-Dimethylpseudoisocytidine Hydrochloride) (**13a**)*: To a suspension of **12a** (35.2 mg, 0.113 mmol) in CH_3OH (2 ml) was added 10% HCl in CH_3OH (1 ml). The reaction mixture was stirred for 10 min and worked up in a usual way to afford **13a** (40.1 mg, 100%) as a wax. ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.14 (s, CH_3), 3.52 (d, J=4.1 Hz, H_5), 3.97 (m, H_3 and H_4), 4.49 (d, J=5.0 Hz, H_2), 4.6—6.4 (br, OH), 7.91 (s, =CH), 8.53 (br, NH_2); UV λ_{max} (CH_3OH) 223 nm (ε 10500), 265 (7160), 290 (3910), λ_{max} (0.1 mol dm^{-3} HCl) 221 nm (ε 8950), 262 (6890), λ_{max} (0.1 mol dm^{-3} NaOH 233 nm (ε 8670), 276 (6870).[38]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-[(R*)-1-hydroxyethyl]tetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-5'-Methylpseudoisocytidine Hydrochloride) (**13b**)*: To a suspension of **12b** (57.4 mg, 0.193 mmol) in CH_3OH (2 ml) was added 10% HCl in CH_3OH (2 ml). After stirring for 10 min, the mixture was worked up to afford **13b** (53.1 mg, 94%). Mp 198.0—202.0 °C; ^1H NMR (C_5D_5N) δ 1.58 (d, J=5.8 Hz, CH_3), 4.35 (m, H_5 and $\underline{H}$COH), 4.92 (m, H_4), 5.18 (m, H_2 and H_3), 6.50 (br, OH and NH), 8.12 (s, =CH); UV λ_{max} (CH_3OH) 223 nm (ε 10500), 265 (7160), 290 (3910), λ_{max} (0.1 mol dm^{-3} HCl) 221 nm (ε 8950), 262 (6890), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 8670), 276 (6870).[38]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-[(R*)-1-hydroxyhexyl]tetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-5'-Pentylpseudoisocytidine Hydrochloride (**13c**)*: To a suspension of **12c** (106 mg, 0.30 mmol) in CH_3OH (3 ml) was added 10% HCl in CH_3OH (2 ml) and the resulting mixture was stirred for 15 min. Usual workup afforded **13c** (95.1 mg, 91%). Mp 168.0—172.0 °C (CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.88 (t, J=6.0 Hz, CH_3), 1.1—1.6 (m, CH_2), 3.60 (m, H_5 and $\underline{H}$COH), 4.00 (m, H_3 and H_4), 4.47 (d, J=4.9 Hz, H_2), 7.80 (s, =CH), 8.45 (br, NH_2); UV λ_{max} (CH_3OH) 224 nm (ε 9630), 266 (6220), 290 (4180), λ_{max} (0.1 mol dm^{-3} HCl) 220 nm (ε 11800), 262 (9070), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 7340), 276 (5840). Found: C, 47.83; H, 6.90; N, 12.04%. Calcd for $C_{14}H_{23}O_5N_3Cl$: C, 48.21; H, 6.65; N, 12.05%.

5-[(2R,3R*,4R*,5S*)-3,4-Dihydroxy-5-[(S*)-α-hydroxybenzyl]tetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-5'-Phenylpseudoisocytidine Hydrochloride) (**13d**)*: To a suspension of **12d** (29.3 mg, 0.082 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml). After stirring for 15 min, the mixture was worked up in a usual manner to give **13d** (33.4 mg, 100%) as a wax. ^1H NMR (dimethyl-d_6 sulfoxide) δ 3.98 (m, H_3, H_4, and H_5), 4.4—5.7 (br, OH), 4.48 (d, J=6.0 Hz, H_2), 4.70 (m, $\underline{H}$COH), 7.35 (m, C_6H_5), 7.61 (s, =CH), 8.57 (br, NH_2); UV λ_{max} (CH_3OH) 225 nm (ε 12700), 264 (8240), 290 (3960), λ_{max} (0.1 mol dm^{-3} HCl) 263 (ε 10300), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 13200), 277 (10100).[38]

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-methyltetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-4'-Methylpseudoisocytidine Hydrochloride) (**21a**)*: To a solution of **20a** (14.9 mg, 0.05 mmol) in CH_3OH (3 ml) was added 10% HCl in CH_3OH (2 ml) and the resulting mixture was stirred for 30 min. After usual workup, pure **21a** (17.9 mg, 100%) was obtained. Mp 212—215 °C (CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.10 (s, CH_3), 3.25 (d, J=11.5 Hz, $\underline{H}_aH_b$COH), 3.41 (d, J=11.5 Hz, $H_a\underline{H}_b$COH), 3.93 (d, J=5.8 Hz, H_4), 4.10 (dd, J=5.8, 6.0 Hz, H_3), 4.52 (d, J=6.0 Hz, H_2), 7.80 (s, =CH), 8.38 (br, NH_2); UV λ_{max} (CH_3OH) 223 nm (ε 12360), 263 (8050), 290 (5530), λ_{max} (0.1 mol dm^{-3} HCl) 220 nm (ε 14820), 262 (10940), λ_{max} (0.1 mol dm^{-3} NaOH) 238 nm (ε 11760), 280 (4530). Found: C, 40.45, H, 5.30; N, 14.10%. Calcd for $C_{10}H_{15}O_5N_3Cl$: C, 40.89; H, 5.49; N, 14.31%.

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-pentyltetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-4'-Pentyl pseudoisocytidine Hydrochloride) (**21b**)*: To a solution of **20b** (20.3 mg, 0.0575 mmol) in CH_3OH (2 ml) was added 10% HCl in CH_3OH (2 ml). After stirring for 30 min, the mixture was worked up in a usual manner to give **21b** (12.9 mg, 58%). Mp 188—190 °C CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.92 (t, J=6.0 Hz, CH_3), 1.1—1.7 (m, CH_2), 3.42 (br s, C$\underline{H}_2$OH), 4.01 (d, J=5.0 Hz, H_4), 4.23 (dd, J=5.0, 7.0 Hz, H_3), 4.50 (d, J=7.0 Hz, H_2), 7.80 (s, =CH), 8.38 (br, NH_2); UV λ_{max} (CH_3OH) 225 nm (ε 7520), 266 (4910), 290 (3020), λ_{max} (0.1 mol dm^{-3} HCl) 220 nm (ε 10840), 262 (8200), λ_{max} (0.1 mol dm^{-3} NaOH) 231 nm (ε 12550), 276 (8620). Found: C, 46.64; H, 6.65; N, 11.60%. Calcd for $C_{14}H_{23}O_5N_3Cl\cdot 0.5H_2O$: C, 46.99; H, 6.76; N, 11.74%.

5-[(2R,3S*,4S*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-5-phenyl-*

tetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-4′-Phenylpseudoisocytidine Hydrochloride) (**21c**): To a solution of **20c** (35.7 mg, 0.0994 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml) and the resulting mixture was stirred for 10 min. Usual workup gave **21c** (35.0 mg, 99%). Mp 218—221 °C (CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 3.40 (d, J=11.9 Hz, $\underline{H}_aH_bCOH$), 3.69 (d, J=11.9 Hz, $H_a\underline{H}_bCOH$), 4.35 (m, H_2 and H_3), 4.69 (d, J=6.0 Hz, H_4), 7.30 (m, C_6H_5), 7.98 (s, =CH), 8.48 (br, NH_2); UV λ_{max} (CH_3OH) 217 nm (ε 17630), 262 (9530), λ_{max} (0.1 mol dm^{-3} HCl) 263 nm (ε 7880), λ_{max} (0.1 mol dm^{-3} NaOH) 231 nm (ε 14130), 276 (9740).[38]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-2-methyltetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-1′-Methylpseudoisocytidine Hydrochloride)* (**29a**): To a suspension of **28a** (52.4 mg, 0.178 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml). After stirring for 30 min, the mixture was worked up as usual to afford **29a** (48.4 mg, 93%) as a yellow foam. ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.38 (s, CH_3), 3.5—3.9 (m, H_4, H_5, and $C\underline{H}_2OH$), 4.02 (d, J=3.5 Hz, H_3), 7.90 (s, =CH), 8.48 (br, NH_2); UV λ_{max} (CH_3OH) 222 nm (ε 9490), 262 (6290), 300 (sh, 1030), λ_{max} (0.1 mol dm^{-3} HCl) 221 nm (ε 8680), 262 (6450), λ_{max} (0.1 mol dm^{-3} NaOH) 230 nm (ε 11030), 278 (8250).[38]

5-[(2R,3R*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-2-pentyltetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-1′-Pentylpseudoisocytidine Hydrochloride)* (**29b**): To a solution of **28b** (28.2 mg, 0.0799 mmol) in CH_3OH (1 ml) was added 10% HCl in CH_3OH (1 ml) and the resulting mixture was stirred for 30 min. Usual workup afforded **29b** (25.7 mg, 92%) as a yellow foam. ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.81 (t, J=6.0 Hz, CH_3), 1.0—2.0 (m, CH_2), 3.5—3.9 (m, H_4, H_5, and $C\underline{H}_2OH$), 4.04 (d, J=4.0 Hz, H_3), 7.86 (s, =CH), 8.2—8.8 (br, NH_2); UV λ_{max} (CH_3OH) 210 nm (sh, ε 12180), 225 (7940), 261 (4380), 300 (sh, 1170), λ_{max} (0.1 mol dm^{-3} HCl) 210 nm (ε 12310), 225 (sh, 8660), 262 (4780), λ_{max} (0.1 mol dm^{-3} NaOH) 230 nm (sh, ε 7120), 277 (4780).[38]

5-[(2R,3S*,4S*)-3,4-Dihydroxy-5,5-bis(hydroxymethyl)tetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-4′-Hydroxymethylpseudoisocytidine Hydrochloride)* (**37**): A mixture of **36** (56.0 mg, 0.179 mmol) and 10% HCl in CH_3OH (1.5 ml) was stirred for 15 min. Usual workup gave **37** (50.3 mg, 91%) as a white powder. Mp 177—182 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 3.51 (d-like, J=6.1 Hz, $C\underline{H}_2OH$), 4.08 (m, H_3 and H_4), 4.57 (m, H_2), 5.0—6.4 (br, OH), 7.82 (br s, =CH), 8.50 (br, NH_2); UV λ_{max} (CH_3OH) 224 nm (ε 9250), 263 (7870), λ_{max} (0.1 mol dm^{-3} HCl) 222 nm (ε 9580), 263 (7520), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 10870), 278 (8510).[38]

5-[(2R,3R*,4S*,5R*)-3,4-Dihydroxy-2,5-dimethyl-5-hydroxymethyltetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-1′,4′-Dimethylpseudoisocytidine Hydrochloride)* (**51a**): To a suspension of **50a** (202 mg, 0.641 mmol) in CH_3OH (3 ml) was added 10% HCl in CH_3OH (3 ml). After stirring for 1 h, the mixture was worked up to afford **51a** (193 mg, 97%) as a white powder. Mp 215—220 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.12 and 1.39 (s, CH_3), 3.29 (s, $C\underline{H}_2OH$), 3.90 (d, J=5.7 Hz, H_3), 4.11 (d, J=5.7 Hz, H_4), 7.94 (s, =CH), 8.37 (br, NH_2); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 19.47, 22.77, 66.07, 70.95, 74.83, 81.77, 84.24, 122.18, 137.78, 152.54, 159.42; UV λ_{max} (CH_3OH) 223 nm (ε 18460), 263 (12580), 292 (sh, 3300), λ_{max} (0.1 mol dm^{-3} HCl) 222 nm (ε 9550), 263 (6930), λ_{max} (0.1 mol dm^{-3} NaOH) 231 nm (ε 9080), 278 (6860). Found: C, 41.86; H, 5.72; N, 13.33%. Calcd for $C_{11}H_{18}O_5N_3Cl\cdot0.5H_2O$: C, 41.94, H, 6.01; N, 13.34%.

5-[(2R,3R*,4S*,5R*)-3,4-Dihydroxy-2,5-dipentyl-5-hydroxymethyltetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-1′,4′-Dipentylpseudoisocytidine Hydrochloride)* (**51b**): To a suspension of **50b** (269 mg, 0.63 mmol) in CH_3OH (5 ml) was added 10% HCl in CH_3OH (5 ml) and the resulting mixture was stirred for 1 h. Usual workup afforded **51b** (260 mg, 100%). Mp 245—250 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.87 (m, CH_3), 1.0—2.0 (m, CH_2), 3.19 (d, J=7.1 Hz, $\underline{H}_aH_bCOH$), 3.33 (d, J=7.1 Hz, $H_a\underline{H}_bCOH$), 4.04 (m, H_3 and H_4), 4.0—5.2 (br, OH), 7.82 (s, =CH), 8.30 (br, NH_2); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 14.02, 22.28, 22.59, 32.20, 32.64, 63.95, 72.06, 76.55, 84.14, 86.08, 120.55, 139.68, 153.32, 160.33; UV λ_{max} (CH_3OH) 263 nm (ε 5230), λ_{max} (0.1 mol dm^{-3} HCl) 265 nm (ε 3720), λ_{max} (0.1 mol dm^{-3} NaOH) 230 nm (ε 6780), 278 (3920).[38]

5-[(2S,3R*,4R*,5R*)-3,4-Dihydroxy-3,5-bis(hydroxymethyl)-tetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-2′-Hydroxymethylpseudoisocytidine Hydrochloride)* (**61a**): To a solution of **60a** (200 mg, 0.468 mmol) in CH_3OH (2.3 ml) was added 10% HCl in CH_3OH (5 ml). After stirring for 15 min, the mixture was worked up to afford **61a** (139 mg, 96%). Mp 215—217 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 3.30 (s, $C(OH)C\underline{H}_2OH$), 3.4—3.9 (m, H_4 and H_5), 3.67 (d, J=8.8 Hz, $\underline{H}_aH_bCOH$), 3.92 (d, J=8.8 Hz, $H_a\underline{H}_bCOH$), 4.71 (s, H_2), 7.76 (s, =CH), 8.48 (br, NH_2); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 60.70, 62.50, 70.01, 80.20, 82.00, 116.48, 137.80, 152.49, 159.18; UV λ_{max} (CH_3OH) 224 nm (ε 12500), 265 (7770), λ_{max} (0.1 mol dm^{-3} NaOH) 232 nm (ε 8800), 280 (6420). Found: C, 37.81; H, 5.16; N, 13.08%. Calcd for $C_{10}H_{16}O_6N_3Cl\cdot0.5H_2O$: C, 37.68; H, 5.38; N, 13.19%.

5-[(2S,3R*,4R*,5R*)-3,4-Dihydroxy-5-hydroxymethyl-3-methyltetrahydrofuran-2-yl]isocytosine Hydrochloride ((±)-2′-Methylpseudoisocytidine Hydrochloride)* (**61b**): To a solution of **60b** (263 mg, 0.886 mmol) in CH_3OH (3 ml) was added 10% HCl in CH_3OH (5 ml) and the resulting mixture was stirred for 30 min. Usual workup gave **61b** (253 mg, 97%). Mp 222—225 °C (CH_3OH–ether); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.02 (s, CH_3), 3.62 (m, H_4, H_5, and $C\underline{H}_2OH$), 4.70 (s, H_2), 7.88 (s, =CH), 8.48 (br, NH_2); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 20.84, 60.20, 73.35, 78.28, 80.97, 81.64, 117.18, 138.33, 152.50, 159.53; UV λ_{max} (CH_3OH) 244 nm (ε 10700), 265 (6890), λ_{max} (0.1 mol dm^{-3} HCl) 222 nm (ε 5800), 264 (4250), λ_{max} (0.1 mol dm^{-3} NaOH) 233 nm (ε 9010), 280 (6750). Found: C, 40.46; H, 5.52; N, 14.00; Cl, 12.32%. Calcd for $C_{10}H_{16}O_5N_3Cl$: C, 40.89; H, 5.49; N, 14.31; Cl, 12.07%.

5-[(2S,3R*,4R*,5R*)-3-t-Butyldimethylsiloxymethyl-3,4-isopropylidenedioxy-5-mesyloxymethyltetrahydrofuran-2-yl]uracil* (**56a**): To a solution of **54a** (50 mg, 0.117 mmol) in pyridine (0.8 ml) was added methanesulfonyl chloride (28 µl, 0.351 mmol) at 0 °C under argon, and then this mixture was stirred at the same temperature for 30 min and at 15 °C for 12 h. The reaction mixture was concentrated and the resulting residue was coevaporated with C_2H_5OH (2ml×2). Purification of the residue on preparative TLC (10:1 chloroform–CH_3OH) afforded **56a** (40 mg, 67%). Mp 195—197 °C (acetone–hexane); R_f=0.42 (10:1 chloroform–CH_3OH); ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 0.06 (s, t-C_4H_9-$(C\underline{H}_3)_2Si$), 0.84 (s, t-$C_4\underline{H}_9(CH_3)_2Si$), 1.36 and 1.52 (s, isopropylidene CH_3), 3.28 (s, CH_3SO_2), 3.52 (s, CH_2OSi), 4.2—4.6 (m, H_4, H_5, and CH_2OMs), 4.88 (s, H_2), 7.22 (d, J=5.0 Hz, =CH), 10.92 (d, J=5.0 Hz, NH), 11.12 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 17.74, 25.49, 26.84, 28.31, 61.01, 61.60, 80.44, 82.73, 83.02, 91.54, 107.80, 113.08, 138.68, 150.78, 162.56; UV λ_{max} (CH_3OH) 266 nm (ε 7150), λ_{max} (0.1 mol dm^{-3} NaOH) 289 nm (ε 6150). Found: C, 45.11, H, 6.44, N, 4.91%. Calcd for $C_{20}H_{34}O_9N_2SSi \cdot 1.5H_2O$: C, 45.01, H, 6.98; N, 5.25%.

5-[(2S,3R*,4R*,4R*)-3,4-Isopropylidenedioxy-3-methyl-5-mesyloxymethyltetrahydrofuran-2-yl]uracil* (**56b**): A mixture of **54b** (20 mg, 0.067 mmol), methanesulfonyl chloride (26 μl, 0.335 mmol), and pyridine (0.4 ml) was stirred at room temperature for 14 h and worked up as described above. Subsequent preparative TLC (5:1 chloroform–CH_3OH) afforded **56b** (21 mg, 83%). Mp 199—202 °C; R_f=0.47 (1:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.15 (s, CH_3), 1.34 and 1.50 (s, isopropylidene CH_3), 3.22 (s, CH_3SO_2), 4.1—4.5 (m, H_3, H_4, and CH_2OMs), 4.86 (s, H_2), 7.22 (s, =CH), 11.00 (br, NH); UV λ_{max} (CH_3OH) 261 nm (ε 7000).

2'-t-Butyldimethylsiloxymethyl-2',3'-O-isopropylidene-4,5'-cyclopseudouridine (**57a**): To a solution of **56a** (30 mg, 52.9 μmol) in acetonitrile (1.2 ml) was added DBU (9.8 μl, 65.1 μmol) under argon and the mixture was stirred at 80 °C. After stirring for 2 h, DBU (4.9 μl, 32.6 μmol) was renewedly added. The resulting mixture was stirred for an additional 2 h and evaporated to give a yellow solid, which was purified by preparative TLC (10:1 chloroform–CH_3OH) to afford **57a** (22 mg, 90%). Mp 240—241 °C (acetone–hexane); R_f=0.34 (10:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 0.06 (s, t-$C_4H_9(C\underline{H}_3)_2Si$), 0.80 (s, t-$C_4\underline{H}_9$-$(CH_3)_2Si$), 1.38 and 1.45 (s, isopropylidene CH_3), 3.38 (d, J=11.5 Hz, $C\underline{H}_aH_bOSi$), 3.62 (d, J=11.5 Hz, $CH_a\underline{H}_bOSi$), 3.98 (d, J=13.0 Hz, $\underline{H}_aH_bCO$), 4.32 (br s, H_5), 4.52 (d, J=13.0 Hz, $H_a\underline{H}_bCO$), 4.70 (s, H_2), 4.90 (s, H_4), 7.96 (s, =CH); UV λ_{max} (CH_3OH) 295 nm (ε 3720). Found: C, 50.82; H, 7.77; N, 5.94%. Calcd for $C_{19}H_{30}O_6N_2Si \cdot 2H_2O$: C, 51.10; H, 7.67; N, 6.27%.

2',3'-O-Isopropylidene-2'-methyl-4,5'-cyclopseudouridine (**57b**): A mixture of **54b** (20 mg, 0.053 mmol), DBU (8.8 μl, 0.059 mmol), and acetonitrile (1.1 ml) was stirred at 80 °C for 3 h and the resulting mixture was worked up as described above. Subsequent preparative TLC (5:1 chloroform–CH_3OH) gave **57b** (12 mg, 81%). Mp 225—229 °C(CH_3-OH–acetone–hexane); R_f=0.47 (1:1 chloroform–CH_3OH); ^1H NMR (dimethyl-d_6 sulfoxide) δ 1.10 (s, CH_3), 1.40 and 1.43 (s, isopropylidene CH_3), 3.96 (d, J=6.5 Hz, $\underline{H}_aH_bCO$) 4.2—4.5 (m, H_5 and $H_a\underline{H}_bCO$), 4.62 (s, H_2), 4.78 (s, H_4), 8.02 (br s, =CH); UV λ_{max} (CH_3OH) 293 nm (ε 3080). Found: m/z, 280.1049. Calcd for $C_{13}H_{16}O_5N_2$: M, 280.1059.

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tural change, methyl [(2*S*,3*S*,4*R*,5*R*)-3,4-isopropylidenedioxy-5-hydroxymethyltetrahydrofuran-2-yl]acetate[20] to methyl [(2*S**,3*S**,4*S**,5*R**)-3,4-isopropylidenedioxy-5-hydroxymethyl-5-phenyltetrahydrofuran-2-yl]acetate, compatible with the assigned β stereochemistry at the anomeric carbon.

19) Prepared from pseudouridine according to the reported procedure:[21] ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 1.27 and 1.49 (s, isopropylidene CH_3), 3.53 (m, $\underline{CH_2}OH$), 3.91 (q-like, J=4.0 Hz, H_5), 4.6—5.0 (m, H_2, H_3, and H_4), 7.55 (s, =CH), 10.93 and 11.14 (br, NH); ^{13}C NMR (dimethyl-d_6 sulfoxide) δ 25.45, 27.42, 61.74, 80.30, 81.55, 83.91, 84.83, 110.40, 112.81, 140.03, 151.05, 163.27.

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