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Transformations of Thiopyrimidine and Thiopurine Nucleosides Following Oxidation with Dimethyldioxirane.

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Abstract: A general and convenient method for the synthesis of several pyrimidine and purine nucleosides by selective oxidation of thionucleosides with dimethyldioxirane is reported. Thioketo moieties in the C-4 position of the pyrimidine ring, and in the C-6, and C-8 positions of the purine ring are the domain of oxidative nucleophilic substitution. Thioketo moieties in the C-2 position of both purine and pyrimidine rings are the domain of desulfurization or formation of disulfides.

In the chemistry of nucleosides general methods for the synthesis of biologically important derivatives starting from thiopyrimidine and thiopurine nucleosides have been developed.[1] Moreover, chemical transformations of thiopyrimidine and thiopurine nucleosides have been proposed as key reactions in a number of biochemical processes including metabolic pathways[2] and structural modifications of transfer-ribonucleic acids (t-RNAs).[3] Among the various synthetic methods reported,[4] only the direct nucleophilic substitution of the mercapto moiety with alcohols or amines in a sealed tube at high temperature[5] has became a standard procedure.[6] In the presence of C-5 substituents on the thiopyrimidine ring, or in the presence of heavily hindered amines,[7] the conversion shows varying degrees of success as well as limitations due to side reactions.[4b]

In the course of our studies on the chemistry of nucleic acid components[8] we have employed the oxidation of 2-thiouracils,[9] pyrimidine-2-thione,[10] 4-thiopyrimidine, and 6-thiopurine nucleosides,[11] with ozone for site-specific introduction of alkoxyl or alkylamino groups at C-2 uracil and pyrimidine or C-6 purine residues, respectively. The method is quite general and affords cytosine and adenosine nucleosides routinely in acceptable yields, even if, the ozonolysis of the C-5,6 uracil double bond to give 5-substituted hydantoin derivatives becames an undesirable side reaction in the presence of C-5 electron-releasing substituents.[11,12,13] Recently, we have also shown that dimethyldioxirane (indicated only as DMDO in the continuation of the paper), a powerful and selective oxidant wich performs under strictly neutral conditions,[14] reacts under mild reaction conditions with the C-5,6 double bond of pyrimidine nucleosides[15,16] and with the *C,N*-7,8 double bond of caffeine and purine nucleosides[17] to give C-5,6 pyrimidine epoxidation or C-8 purine hydroxylation. Preliminary studies on the oxidation of 4-thiopyrimidine and 6-thiopurine nucleosides[18,19] with DMDO have

shown that, unlike the ozone reactivity, the oxidation of the thioketo moiety is faster than the other possible reactions. Cytosine and adenosine nucleosides are also obtained in good yields in the presence of electron-releasing C-5 substituents and for prolonged reaction times.

Table1: Reaction of 2',3',5'-tri-O-acetyl-4-thio uridine **1** with dimethyldioxirane and deacetylation of compounds **3a-f**.[a]

Entry	Product(s)	R1	R2	Yield (%)
1[b]	2a	H	Ac	95
2[c]	2b (2a)	Me	Ac	70 (22)
3[c]	2c (2a)	Et	Ac	65 (18)
4[c]	2d (2a)	n-Pr	Ac	70 (15)
5[c]	2e (2a)	n-Bu	Ac	75 (20)
6[d]	3a	H	Ac	73
7[d]	3b	Me	Ac	64
8[d]	3c	Et	Ac	75
9[d]	3d	n-Pr	Ac	55
10[d]	3e	n-Bu	Ac	58
11[d]	3f	p-Tolyl	Ac	69
12[e]	4a	H	H	93
13[e]	4b	Me	H	90
14[e]	4c	Et	H	82
15[e]	4d	n-Pr	H	87
16[e]	4e	n-Bu	H	72
17[e]	4f	p-Tolyl	H	88

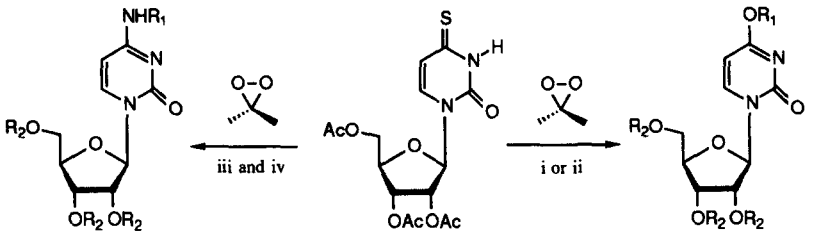
[a]All oxidations were performed with a freshly prepared solution of DMDO (0.07 M,acetone solution). [b] DMDO (1.2 equiv./mol.), CH_2Cl_2, 25 °C. [c] DMDO (1.2 equiv./mol.) dried before use over $MgSO_4$, dry CH_2Cl_2-alcohol (1:1 v/v), 25 °C. [d] DMDO (1.2 equiv./mol.), amine, CH_2Cl_2, 25 °C. [e] Ammonia (2N solution in MeOH, 15 equiv./mol.), 25 °C.

This report describes extensively these results and provides a selective, convenient, and general method, comparable with the triazolo procedure,[20] for the synthesis of biologically important cytosine and adenosine nucleosides. Studies on the chemoselectivity of the oxidation depending on the position of the thioketo moiety on the heterocyclic ring are also reported.

Treatment of 2',3',5'-tri-*O*-acetyl-4-thiouridine **1**[5] with a freshly prepared solution of DMDO (0.07 M;[21] 1.2 equiv./mol.) in CH_2Cl_2 at 25°C gave 2',3',5'-tri-*O*-acetyluridine **2a** in good yields (Scheme 1, Table 1, Entry 1). The same reaction performed in the presence of alcohols (methanol, ethanol, n-propanol and n-butanol) as nucleophiles (CH_2Cl_2/alcohol =1:1 v/v) afforded **2a** as the main product and traces of 2',3',5'-tri-*O*-acetyl-4-alkoxyuridines **2b-e** as by-products. In the formation of compound **2a** the moisture present in the distilled dioxirane-acetone solution is an essential ingredient; in fact, the yield of **2a** decreased when the dioxirane was dried before use over $MgSO_4$.[22] Under these experimental conditions, using dry CH_2Cl_2 and

dried alcohols, the 4-alkoxyuridine derivatives **2b-e** became the main products, and they were obtained in acceptable yields (Scheme 1, Table 1, Entries 2-5).

Scheme 1



3a-f, 4a-f **1** **2a-e**

a: R_1=H; b: R_1=Me; c: R_1=Et; d: R_1=n-Pr; e: R_1=n-Bu; f: R_1=p-Tolyl

3a-f R_2=Ac. **4a-f** R_2=H.

i: DMDO (0.07 M, acetone solution), CH_2Cl_2, 25°C. ii: DMDO (0.07 M, acetone solution), dry CH_2Cl_2/alcohol (1:1 v/v), 25°C. iii: DMDO (0.07 M, acetone solution), amine (stoichiometric amount), CH_2Cl_2, 25°C. iv: Ammonia (2N solution in MeOH; 15 equiv./mol.), 25°C.

Table 2. Reaction of 2',3',5'-tri-O-benzoyl-2-thiouridine **5** and 2',3',5'-tri-*O*-benzoyl-2,4-di-thiouridine **8** with dimethyldioxirane.[a]

Entry	Substrate	Product(s)	Yield(%)
1[b]	5	6	43
		7	20
2[c]	5	6	37
		7	26
3[d]	5	6	24
		7	15
4[b]	8	6	38
		7	22
		5	8

[a]All oxidations were performed with a freshly prepared solution of DMDO (0.07 M acetone solution). [b] DMDO (1.2 equiv./mol.), CH_2Cl_2, 25 °C. [c] DMDO (1.2 equiv./mol.) dried before use over $MgSO_4$, dry CH_2Cl_2-alcohol (1:1 v/v), 25 °C. [d] DMDO (1.2 equiv./mol.), amine, CH_2Cl_2, 25 °C.

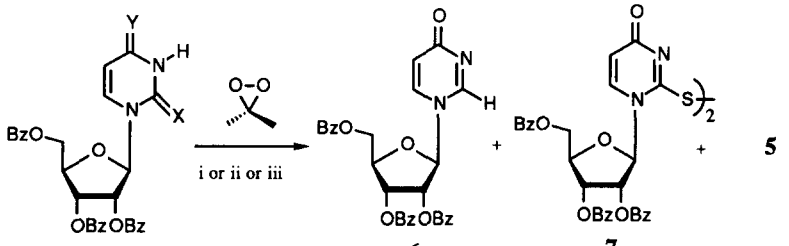
Cytidine derivatives **3a-f** were selectively obtained when compound **1** was allowed to react with DMDO in CH_2Cl_2 at 25°C in the presence of a stoichiometric amount of ammonia, aliphatic amines (methylamine, ethylamine, n-propylamine and n-butylamine) or aromatic amine (p-toluidine) [Scheme 1, Table 1, Entries 6-11]. Deprotection of compounds **3a-f** with an excess of ammonia in methanol afforded cytidine **4a** and N-4-

substituted cytidine derivatives **4b-f** in good yields (Scheme 1, Table 1, Entries 12-17). Moreover, cytidine **4a**, *N*-4-ethylcytidine **4c**, and *N*-4 n-propylcytidine **4d** were also obtained when performing the oxidation in the presence of a large excess of amine for prolonged reaction times.

Having established the protocol for introducing alcohols and amines at the C-4 position of the 4-thiouridine **1**, it was now necessary to examine the chemoselectivity of the oxidation depending on the position of the thioketo moiety on the pyrimidine ring. With this purpose, we started to study the oxidation of 2-thiouridine and 2,4-dithiouridine derivatives with dioxirane.

The reaction of 2',3',5'-tri-*O*-benzoyl-2-thiouridine **5**, prepared from 1-*O*-acetyl-2',3',5'-tri-O-benzoyl-β-D-ribofuranose and 2-thiouracil (not shown) as described by Vorbruggen,[23] with DMDO (1.5 equiv./mol.) in CH_2Cl_2 at 25°C gave 2',3',5'-tri-*O*-benzoyl-4(1H)pyrimidinone nucleoside **6** and the disulfide **7** as the only recovered products (Scheme 2, Table 2, Entry 1).

Scheme 2



5, **8** **6** **7**

5 X= S, Y= O
8 X=Y= S

i: DMDO (1.5 equ iv./mol.), CH_2Cl_2, 25°C. ii: DMDO (1.5 equiv./mol.) dried before use over $MgSO_4$, dry CH_2Cl_2-methanol (1:1 v/v), 25°C. iii: DMDO (1.5 equiv./mol.), ammonia (2N solution in MeOH; 1.2 equiv./mol.), 25°C

Unexpectedly, compounds **6** and **7** were also obtained performing the oxidation in the presence of oxygen or nitrogen nucleophiles (Scheme 2, Table 2, Entries 2 and 3), while products of C-2 nucleophilic substitution were not detected in the reaction mixture. In a similar way, the reaction of 2', 3', 5'-tri-*O*-benzoyl-2,4-dithiouridine **8** [23] with DMDO in CH_2Cl_2 at 25°C gave compounds **6** and **7** as main products, together with a small amount of **5** (Scheme 2, Table 2, Entry 4).

It has long been recognised[24] that the sulphur atom in 2-thiouridine derivatives is much less reactive toward the electrophiles than that present in 4-thiouridine compounds. DMDO is an electrophilic oxidant [25] and the reactivity of the pyrimidine ring may be affected by the position of the thioketo moiety .[26] The initial product in the oxidation of the thioketo moiety is a sulphine[27] that exists in tautomeric equilibrium with the corresponding sulfenic acid.[28] This sulfenic acid, whose stability strictly depends on steric, electronic, intermolecular and intramolecular hydrogen-bonding effects,[29] may be in turn oxidized to give a sulfinic[30] or a sulfonic acid,[31] or it may react with another molecule of thioketo derivative to give a disulfide.[32] The absence of the disulfide in the oxidation of 2',3',5'-tri-*O*-acetyl-4-thiouridine **1** suggests that the transformation of the

sulfenic acid '*transient species*' is the main reaction, and the sulfinic or sulfonic acid intermediates thus formed (but not isolated in our case), may be reactive toward nucleophiles to give products of nucleophilic substitution.[4a,33]

Table 3: Reaction of 3',5'-di-*O*-acetyl-2'-deoxy-4-thiouridine **9**, 3',5'-di-*O*-acetyl-4-thiouridine **10**, and 2',3',5'-tri-*O*-acetyl-β-D-arabinosyl-4-thiouridine **11** with dimethyldioxirane and deacetylation of products **12a-d**, **13a-d** and **14a-e**.[a]

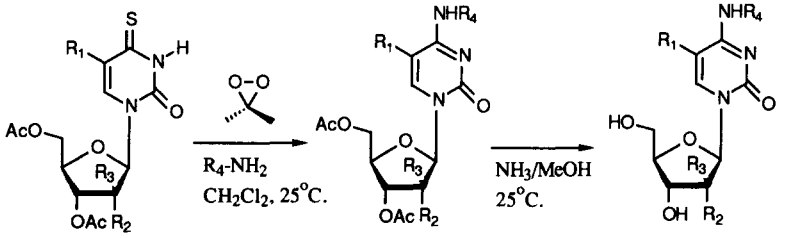
Entry	Substrate	Product	R1	R2	R3	R4	Yield (%)
1	9	12a	H	H	H	H	81
2	9	12b	H	H	H	Me	58
3	9	12c	H	H	H	Et	78
4	9	12d	H	H	H	p-Tolyl	79
5	10	13a	Me	H	H	H	77
6	10	13b	Me	H	H	Me	73
7	10	13c	Me	H	H	Et	61
8	10	13d	Me	H	H	p-Tolyl	68
9	11	14a	H	H	OAc	H	90
10	11	14b	H	H	OAc	Me	72
11	11	14c	H	H	OAc	Et	72
12	11	14d	H	H	OAc	p-Tolyl	76
13	11	14e	H	H	OAc	o-diMe-Ph	81
14	12a	15a	H	H	H	H	93
15	12b	15b	H	H	H	Me	58
16	12c	15c	H	H	H	Et	63
17	12d	15d	H	H	H	p-Tolyl	64
18	13a	16a	Me	H	H	H	85
19	13b	16b	Me	H	H	Me	60
20	13c	16c	Me	H	H	Et	56
21	13d	16d	Me	H	H	p-Tolyl	74
22	14a	17a	H	H	OH	H	88
23	14b	17b	H	H	OH	Me	79
24	14c	17c	H	H	OH	Et	92
25	14d	17d	H	H	OH	p-Tolyl	73
26	14e	17e	H	H	OH	o-diMe-Ph	78

[a]All oxidations were performed with a freshly prepared solution of dimethyldioxirane (0.07 M acetone solution) in the presence of stoichiometric amount of amines. Deacetylations were performed using an excess of ammonia in methanol (2N solution).

On the other hand, the presence of the disulfide **7** in the oxidation of **5** probably reflects a lower reactivity of the C-2 sulfenic acid intermediate toward a further oxidation, because of the enhanched stability of the intermolecular hydrogen-bonding and/or the steric-electronic effects exerted on dioxirane by the neighboring sugar moiety.[34] Moreover, this steric hindrance is probably one of the factors responsible for the loss of the whole C-2 sulfur containing group to yield appreciable amounts of **6**. The latter hypothesis is supported by our data on the oxidation of 2-thiouracils with DMDO.[10] In this case, appreciable amounts of products of nucleophilic substitution were obtained, showing that the sugar moiety exerts an important role in the pattern of the oxidation. Noteworthy, the chemoselectivity observed in the oxidation of 2',3',5'-tri-*O*-benzoyl-2,4-dithiouridine **8** confirms the oxidation pattern independently shown by the C-2 and C-4 thiouridine isomers. The selective nucleophilic substitution is the only operative reaction for the C-4 position, while the formation of the disulfide and the elimination of the whole sulphur containing group are operative reactions for the C-2 position.

The versatility of the C-4 nucleophilic substitution in the oxidation of 4-thiopyrimidine nucleosides is further illustrated by the synthesis of several biologically interesting cytidine nucleosides. 3',5'-Di-*O*-acetyl-2'-deoxy-4-thio uridine **9**, 3',5'-di-*O*-acetyl-4-thiothymidine **10**[2] and 2',3',5'-tri-*O*-acetyl-β-D-arabinofuranosyl-4-thiouridine **11**, react with DMDO in CH_2Cl_2 at 25°C in the presence of a stoichiometric amount of aliphatic and aromatic amines to give the corresponding 3',5'-di-*O*-acetyl-2'-deoxycytidine derivatives **12a-d**, 3', 5'-tri-*O*-acetyl-2'-deoxy-5-methylcytidine derivatives **13a-d**, and 2',3',5'-tri-*O*-acetyl-arabinofuranosylcytidine derivatives **14a-d** in good yields (Scheme 3, Table 3, Entries 1-4, 5-8 and 9-12).

Scheme 3



9, 10, 11 **12a-d, 13a-d, 14a-e** **15a-d, 16a-d, 17a-e**

a: R_4= H. b: R_4= Me. c: R_4= Et. d: R_4= p-Tolyl. e: R_4= 2,6-dimethylphenyl

9, 12a-d, 15a-d: R_1= R_2= R_3= H
10, 13a-d, 16a-d: R_1= CH_3, R_2= R_3= H
11, 14a-e : R_1= R_2= H, R_3= OAc
17a-e: R_1= R_2= H, R_3= OH

Moreover, in the oxidation of **11** a very heavily hindered aromatic amine, 2,6-dimethylaniline, was also used as nucleophile to give the cytidine derivative **14e** in good yield (Scheme 3, Table 3, Entry 13). This data shows that the steric hindrance of the nucleophile does not affect the reaction pathway. Deprotection of the acetylated cytidines with an excess of ammonia in methanol afforded 2'-deoxycytidines **15a-d**, 2'-deoxy-5-methylcytidines **16a-d**, and arabinofuranosylcytidines **17a-e** in satisfactory yields (Scheme 3, Table 3, Entries 14-17, 18-21 and 22-26).

Attention was next turned to the use of 6-thiopurine nucleosides, 6-thio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)purine **18** and 6-thio-2-acetamido-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)purine **19**; 2,6-dithiopurine nucleosides, 2,6-dithio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)xantosine **20** and 8-thiopurine nucleosides, N(4)-acetyl-8-thio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)adenosine **21** as starting materials for the synthesis of adenosine derivatives.

Table 4: Reactions of 6-thio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)purine **18**, 6-thio-2-acetamido-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)purine **19**, and 2,6-dithio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)xantosine **20** with DMDO and deacetylations of products **22a-b** and **23a-d**.

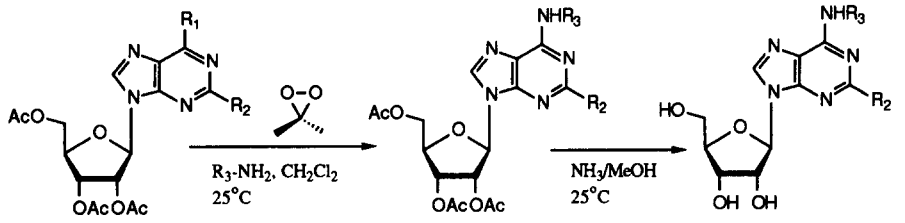
Entry	Substrate	Product	R2	R3	Yield (%)
1	18	22a	H	H	75
2	18	22b	H	Me	55
3	19	23a	NHAc	H	65
4	19	23b	NHAc	Me	63
5	19	23c	NHAc	Et	67
6	19	23d	NHAc	p-Tolyl	69
7	20	22a	H	H	53
8	20	22b	H	Me	46
9	22a	24a	H	H	83
10	22b	24b	H	Me	87
11	23a	25a	NH_2	H	81
12	23b	25b	NH_2	Me	83
13	23c	25c	NH_2	Et	78
14	23d	25d	NH_2	p-Tolyl	61

[a]All oxidations were performed with a freshly prepared solution of DMDO (0.07 M solution) in the presence of amines in CH_2Cl_2 at 25 °C. Deacetylations were performed using an excess of ammonia in methanol (2N solution).

The reaction of compounds **18** and **19** with DMDO in CH_2Cl_2 at 25°C in the presence of stoichiometric amount of amines (ammonia, methylammine, ethylammine, and p-toluidine) gave the acetylated adenosine derivatives **22a-b** and **23a-d** in variable yields (Scheme 4, Table 4, Entries 1-2 and 3-6, respectively). Deprotection of compounds **22a-b**, and **23a-d** afforded adenosine **24a**, 2-amino adenosine (^{NH2}A) **25a** and their N-6-alkyl and N-6-aryl substituted derivatives **24b** and **25b-d** in good yields (Scheme 4, Table 4, Entries 9-10 and 11-14, respectively). Furthermore, treatment of 2,6-dithio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)xantosine **20** with DMDO in the presence of stoichiometric amount of ammonia and methylamine

yielded 2',3',5'-tri-*O*-acetyl adenosine **22a** and N(6)-methyl-2',3',5'-tri-O-acetyl adenosine **22b** in good yields (Scheme 4, Table 4, Entries 7-8).

Scheme 4



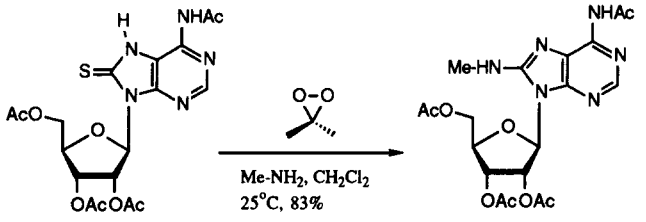
18, 19, 20 **22a-b, 23a-d** **24a-b, 25a-d**

a: R_3=H. b: R_3=Me. c: R_3=Et. d: R_3=p-Tolyl.

18 R_1= SH, R_2= H. **19** R_1= SH, R_2= NHAc. **20** R_1= R_2= SH. **22, 24** R_2= H. **23** R_2= NHAc. **25** R_2= NH_2.

Compounds **22a-b** were easily deprotected to give adenosine **24a** and N(6)-methyl-adenosine **24b** (Table 4, Entries 9-10). Finally, the reaction of N(6)-acetyl-8-thio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)adenosine **21** with DMDO in CH_2Cl_2 at 25°C in the presence of stoichiometric amount of methylamine gave selectively N(6)-acetyl-8-methylamino-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)adenosine **26** in 83% yield (Scheme 5).

Scheme 5



21 **26**

According to the results discussed above, the reaction of thiopurine nucleosides with DMDO furnishes a general, selective, and convenient method for the oxidative nucleophilic functionalization of the purine ring.

In summary, as shown in Fig.1, thioketo moieties present in the C-4 position of the pyrimidine ring, and in the C-6, and C-8 positions of the purine ring, are the domain of nucleophilic substitution. Thioketo moieties present in the C-2 position of both pyrimidine and purine rings are the domain of desulfurization or formation of

disulfide. The great flexibility of the functionalization of thiopurine and thiopyrimidine nucleosides by dioxirane and the possibility to select appropriate conditions (position of the thioketo moiety on the heterocyclic ring) in order to control the regioselectivity of the transformations, makes this procedure useful for the synthesis of new biologically important nucleoside derivatives.

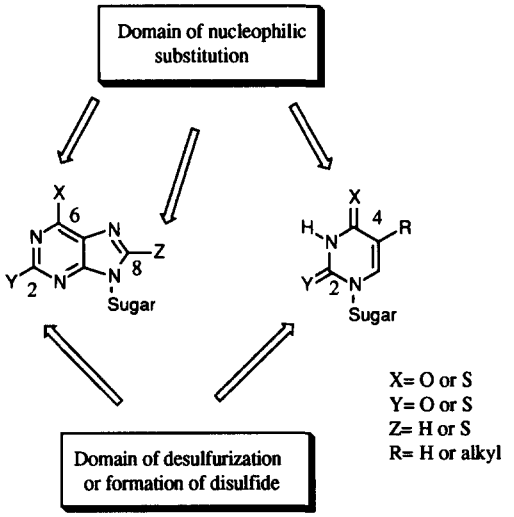


Figure1: General pattern of the oxidation of thiopurine and thiopyrimidine nucleosides with DMDO. Thioketo moieties in the C-2 position of the uracil ring or in the C-6 and C-8 positions of the purine ring are the domain of nucleophilic substitution. Thioketo moities in the C-2 position of both uracil and purine ring are the domain of desulfurization or formation of disulfide.

Experimental

NMR spectra were recorded on a Bruker (200 MHz) spectrometer and are reported in δ values. Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer using NaCl plates. Microanalyses were performed by C. Erba 1106 analyzer. Mass spectra were recorded on a VG 70/250S spectrometer with an electron beam of 70 eV. Melting points were obtained on a Reichert Kofler apparatus and are uncorrected. All solvents were ACS reagent grade and were redistilled and dried according to standard procedures. Chromatographic purifications were performed on columns packed with Merck silica gel 60, 230-400 mesh for flash technique. Thin-layer chromatography was carried out using Merck platten Kieselgel 60 F254.

Starting Compounds

Commercially available 2-acetamido-6-thio-9-(2',3',5',-tri-*O*-acetyl-β-D-ribosyl)purine **10** (Aldrich, Co.) was used without further purification. 2',3',5'-tri-*O*-acetyl-4-thiouridine **1**, 3',5'-di-*O*-acetyl-2'-deoxy-4-thio uridine **9**, 3',5'-di-*O*-acetyl-4-thio thymidine **10**, 2',3',5'-tri-*O*-acetyl-β-D-arabinofuranosyl-4-thio uridine **11**, and

2,6-dithio-9-(2', 3', 5'-tri-*O*-acetyl-β-D-ribosyl)xantosine **20** were synthesized starting from the corresponding pyrimidine and purine nucleosides according to the procedure reported by Fox.[5] 6-Thio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)purine **18** was synthesized according to the procedure reported by Lewis.[35] 2',3',5'-Tri-*O*-benzoyl-2-thiouridine **5**, and 2',3',5'-tri-*O*-benzoyl-2,4-dithiouridine **8** were synthesized sarting from commercially available 2-thio uracil, 2,4-dithio uracil and 1-*O*-acetyl- 2',3',5'-tri-*O*-benzoyl-β-D-ribofuranose (Aldrich, Co.) according to the procedure reported by Vorbruggen.[23] N(6)-Acetyl-8-thio-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)adenosine **21** was prepared starting from N(6)-acetyl-2',3',5'-tri-*O*-acetyl-β-D-ribosyl)adenosine according to the procedure described by Robins.[36]

Oxidation of thiopyrimidine and thiopurine nucleosides **1**, **5**, **8**, **9**, **10**, **11**, **18**, **20** and **21**. General procedure- Dimethyldioxirane solution was prepared using the procedure reported by Adam[21] and the dioxirane content (Ca. 0.07M, acetone solution) was assayed with methyl-phenyl-sulfide yielding the corresponding sulfoxide; the latter being determined by ^{1}H-NMR. The reactions were carried out by adding freslhly prepared solution of the dioxirane to solutions of the required substrate (1 mmol) in the appropriate solvent (CH_2Cl_2 or dry CH_2Cl_2-alcohol 1:1 v/v) in the presence of the nucleophile (dry alcohol or amine) at 25°, until the substrate disappeared (TLC solvent CH_2Cl_2/CH_3OH = 9.0/1.0). The reaction mixture was evaporated and the residue was purified by flash-chromatography using a gradient CH_2Cl_2/CH_3OH as eluent.

2',3',5'-Tri-*O*-acetyl-uridine **2a**- (510 mg, 69%), m. p. 127-129 °C [lit.[37], 128-129 °C]. I.R. ($CHCl_3$) νmax: 3385 (NH), 1750 (C=O), 1680 (C=O) and 1636 cm^{-1} (C=C). δ_H [$CDCl_3$, 200 MHz] 2.10 (9H, s, CH_3), 4.35 (3H, m, H-4', 5', 5"), 5.30 (2H, m, H-2', 3'), 5.75 (1H, d, J 5.0 Hz, H-5), 6.05 (1H, m, H-1'), 7.35 (1H, d, J 5.0 Hz, H-6); m/z 370 (M^+, 12%).

4-*O*-Methyl-1-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)uracil **2b**- (269 mg, 70%), oil. I.R. ($CHCl_3$) νmax: 1760 (C=O), 1680 (C=0), and 1630 cm^{-1} (C=C). δ_H [$CDCl_3$, 200 MHz] 2.09 (9H, s, CH_3), 3.93 (3H, s, CH_3), 4.34 (3H, m, H-4', 5', 5"), 5.31 (2H, m, H-2', 3'), 5.90 (1H, d, J 7.5 Hz, H-5), 6.14 (1H, d, J 4.2 Hz, H-1'), 7.64 (1H, d, J 7.5 Hz, H-6); m/z 384 (M^+, 12%). Anal. Calcd. for $C_{16}H_{20}N_2O_9$: C, 50%; H, 5.24%; N, 7.29%. Found. C, 50.18%, H, 7.32%; N, 7.18%.

4-*O*-Ethyl-1-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)uracil **2c**- (258 mg, 65%), oil. I.R. ($CHCl_3$) ν_{max}: 1760 (C=O), 1680 (C=O), and 1630 cm^{-1} (C=C). δ_H [$CDCl_3$, 200 MHz] 1.32 (3H, m, CH_3), 2.09 (9H, s, CH_3), 4.37 (5H, m, CH_2, H-4', 5', 5"), 5.32 (2H, m, H-2', 3'), 5.90 (1H, d, J 7.2 Hz, H-5), 6.18 (1H, d, J 3.2 Hz, H-1'), 7.65 (1H, d, J 7.2 Hz, H-6) ; m/z 398 (M^+, 18%). Anal. Calcd. for $C_{17}H_{22}N_2O_9$: C, 51.25%; H, 5.57%; N, 7.03%. Found. C, 51.16%, H, 5.52%; N, 7.12%.

4-*O*-n-Propyl-1-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)uracil **2d**- (288 mg, 70%), oil. I.R. ($CHCl_3$) ν_{max}: 1760 (C=O), 1680 (C=O), and 1630 cm^{-1} (C=C). δ_H [$CDCl_3$, 200 MHz] 0.96 (3H, m, CH_3), 1.72 (2H, m, CH_2), 2.07 (3H, s, CH_3), 2.13 (6H, s, CH_3), 4.34 (5H, m, CH_2, H-4', 5', 5"), 5.33 (2H, m, H-2', 3'), 5.92 (1H, d, J 6.3 Hz, H-5), 6.13 (1H, d, J 4.3 Hz, H-1'), 7.63 (1H, d, J 6.3 Hz, H-6) ; m/z 412 (M^+, 11%). Anal. Calcd. for $C_{18}H_{24}N_2O_9$: C, 52.42%; H, 5.86%; N, 6.79%. Found. C, 52.45%, H, 5.87%; N, 6.83%.

4-*O*-n-Butyl-1-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)uracil **2e**- (319 mg, 75%), oil. I.R. ($CHCl_3$) ν_{max}: 1760 (C=O), 1680 (C=O), and 1630 cm^{-1} (C=C). δ_H [$CDCl_3$, 200 MHz] 0.97 (3H, m, CH_3), 1.30-1.70 (4H, m, CH_2), 2.10 (9H, s, CH_3), 4.39 (5H, m, CH_2, H-4', 5', 5''), 5.32 (2H, m, H-2', 3'), 5.91 (1H, d, J 7.7 Hz, H-5), 6.17 (1H, d, J 3.2 Hz, H-1'), 7.65 (1H, d, J 7.7 Hz, H-6) ; m/z 426 (M^+, 8%). Anal. Calcd. for $C_{19}H_{26}N_2O_9$: C, 53.52%; H, 6.14%; N, 6.57%. Found. C, 53.61%, H, 6.10%; N, 6.65%.

2',3',5'-Tri-*O*-acetyl-cytidine **3a**- (269 mg, 73%), m.p. 165-167 °C (from CH_3OH); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1650 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 2.05 (6H, s, CH_3), 2.07 (3H, s, CH_3), 4.27 (3H, m, H-4', 5', 5''), 5.39 (2H, m, H-2', 3'), 5.84 (1H, d, J 3.7 Hz, H-1'), 5.93 (1H, d, J 7.6 Hz, H-5), 7.35 (1H, d, J 7.6 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 20.26 (CH_3), 2048 (CH_3), 20.53 (CH_3), 62.97 (CH_2), 69.95 (CH), 73.40 (CH), 79.10 (CH), 89.97 (CH), 96.12 (CH), 141.15 (CH), 155.88 (C), 166.39 (C), 169.80 (C), 169.92 (C), 170.64 (C); m/z 369 (M^+, 27%).

2',3',5'-Tri-*O*-acetyl-N^4-methyl-cytidine **3b**- (245 mg, 64%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 2.13 (6H, s, CH_3), 2.15 (3H, s, CH_3), 2.64 (3H, s, NCH_3), 4.36 (3H, m, H-4', 5', 5''), 5.34 (2H, m, H-2', 3'), 5.80 (1H, d, J 8.10 Hz, H-5), 6.04 (1H, d, J 2.4 Hz, H-1'), 7.40 (1H, d, J 8.10 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 20.05 (CH_3), 20.08 (CH_3), 20.12 (CH_3), 26.0 (NCH_3), 62.87 (CH_2), 69.80 (CH), 73.7 (CH), 79.90 (CH), 88.80 (CH), 99.90 (CH), 141.60 (CH), 155.88 (C), 169.70 (C), 169.80 (C), 169.92 (C), 170.10 (C); m/z 383 (M^+, 21%). Anal. Calcd. for $C_{16}H_{21}N_3O_8$: C, 50.13%; H, 5.52%; N, 10.96%. Found. C, 50.19%, H, 5.50%; N, 10.98%.

2',3',5'-Tri-*O*-acetyl-N^4-ethyl-cytidine **3c**- (297 mg, 75%), oil; I.R. ($CHCl_3$) ν_{max} 3390 (NH), 1740 (C=O) and 1640 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 1.23 (3H, m, CH_3), 2.08 (6H, s, CH_3), 2.12 (3H, s, CH_3), 3.45 (2H, m, NCH_2), 4.30 (3H, m, H-4', 5', 5''), 5.29 (2H, m, H-2', 3'), 5.65 (1H, d, J 8.85 Hz, H-5), 6.10 (1H, d, J 2.7 Hz, H-1'), 7.31 (1H, d, J 8.85 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 20.78 (CH_3), 26.79 (CH_3), 29.27 (CH_3), 29.71 (CH_3), 63.09 (CH_2), 63.91 (CH_2), 71.95 (CH), 73.79 (CH), 77.46 (CH), 90.68 (CH), 113.60 (CH), 128.85 (CH), 130.90 (C), 133.56 (C), 167.70 (C), 170.13 (C), 189.59 (C); m/z 397 (M^+, 11%). Anal. Calcd. for $C_{17}H_{23}N_3O_8$: C, 51.38%; H, 5.83%; N, 10.57%. Found. C, 51.40%, H, 5.84%; N, 10.53%.

2',3',5'-Tri-*O*-acetyl-N^4-n-propyl-cytidine **3d**- (226 mg, 55%), oil; I.R. ($CHCl_3$) ν_{max} 3390 (NH), 1740 (C=O) and 1640 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 0.88 (3H, m, CH_3), 1.56 (2H, m, CH_2), 2.02 (6H, s, CH_3), 2.09 (3H, s, CH_3), 3.38 (2H, m, NCH_2), 4.28 (3H, m, H-4', 5', 5''), 5.28 (2H, m, H-2', 3'), 5.70 (1H, d, J 7.70 Hz, H-5), 6.13 (1H, d, J 4.4 Hz, H-1'), 7.29 (1H, d, J 7.70 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 11.09 (CH_3), 20.27 (CH_3), 20.53 (CH_3), 22.14 (CH_2), 42.47 (CH_2), 63.23 (CH_2), 70.17 (CH), 73.18 (CH), 79.28 (CH), 88.0 (CH), 96.37 (CH), 138.95 (CH), 156.14 (C), 163.84 (C), 169.87 (C), 170.46 (C); m/z 411 (M^+, 32%). Anal. Calcd. for $C_{18}H_{25}N_3O_8$: C, 52.55%; H, 6.12%; N, 10.21%. Found. C, 52.30%, H, 6.14%; N, 10.24%.

2',3',5'-Tri-*O*-acetyl-N^4-n-butyl-cytidine **3e**- (246 mg, 58%), oil; I.R. ($CHCl_3$) ν_{max} 3390 (NH), 1740 (C=O) and 1640 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 0.86 (3H, m, CH_3), 1.29 (2H, m, CH_2), 1.51 (2H, m,

CH_2), 2.05 (6H, s, CH_3), 2.09 (3H, s, CH_3), 3.30 (2H, m, NCH_2), 4.29 (3H, m, H-4', 5', 5"), 5.29 (2H, m, H-2', 3'), 5.63 (1H, d, J 7.58 Hz, H-5), 6.13 (1H, d, J 3.5 Hz, H-1'), 7.32 (1H, d, J 7.58 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 13.50 (CH_3), 20.29 (CH_3), 20.48 (CH_3), 20.54 (CH_3), 31.01 (CH_2), 40.59 (CH_2), 63.22 (CH_2), 70.0 (CH), 73.34 (CH), 79.31 (CH), 88.15 (CH), 96.19 (CH), 113.46 (CH), 156.09 (C), 163.76 (C), 169.90 (C), 170.49 (C), 190.01 (C); m/z 425 (M^+, 32%). Anal. Calcd. for $C_{19}H_{27}N_3O_8$: C, 53.64%; H, 6.40%; N, 9.88%. Found. C, 53.62%, H, 6.37%; N, 9.90%.

2',3',5'-Tri-*O*-acetyl-N^4-p-tolyl-cytidine **3f**- (317 mg, 69%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1640 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 2.04 (3H, s, CH_3), 2.06 (6H, s, CH_3), 2.29 (3H, s, CH_3), 4.30 (3H, m, H-4', 5', 5"), 5.32 (2H, m, H-2', 3'), 5.95 (1H, d, J 5.38 Hz, H-5), 6.15 (1H, d, J 4.48 Hz, H-1'), 7.12 (4H, m, Ph-H), 7.45 (1H, d, J 5.38 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 20.25 (CH_3), 20.30 (CH_3), 20. (CH_3), 20.53 (CH_3), 29.42 (CH_3), 63.10 (CH_2), 70.11 (CH), 73.36 (CH), 79.47 (CH), 88.26 (CH), 91.25 (CH), 121.0 (CH), 124.39 (CH), 129.92 (CH), 130.86 (C), 169.85 (C), 170.46 (C), 230 (C); m/z 459 (M^+, 32%). Anal. Calcd. for $C_{22}H_{25}N_3O_8$: C, 57.51%; H, 5.48%; N, 9.15%. Found. C, 57.53%, H, 5.51%; N, 9.19%.

2',3',5'-Tri-*O*-benzoyl-β-D-ribosyl-4(1H)pyrimidinone **6**- (232 mg, 43%). I.R. ($CHCl_3$) νmax: 1750 (C=O), and 1636 cm^{-1} (C=C). δ_H [$CDCl_3/CD_3OD$, 200 MHz] 4.80 (3H, m, H-4', 5', 5"), 5.63 (1H, m, H-3'), 5.81 (2H, m, H-5, 2'), 6.15 (1H, d, J 4.26 Hz, H-1'), 7.20-7.50 (10H, m, H-6, and Ph-H), 7.94 (6H, m, Ph-H), 8.40 (1H, s, H-2); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 63.22 (CH_2), 70.78 (CH), 74.29 (CH), 81.25 (CH), 92.41 (CH), 113.26 (CH), 127.89 (C), 128.40 (C), 128.72 (CH), 128.96 (CH) 129.62 (CH), 129.91 (CH), 129.89 (CH), 133.92 (CH), 134.09 (CH), 134.24 (CH), 150.10 (CH), 165.23 (C), 165.38 (C), 166.13 (C), 170.15(C). m/z 540 (M^+, 37%). Anal. Calcd. for $C_{30}H_{24}N_2O_8$: C, 66.66 %; H, 4.47%; N, 5.18 %. Found. C, 66.64 %, H, 4.50 %; N, 4.87 %.

Bis-2-thio-2',3',5'-tri-*O*-benzoyl-β-D-ribosyl-4(1H)pyrimidinone **7**- (297 mg, 26%). I.R. ($CHCl_3$) νmax: 1750 (C=O), and 1636 cm^{-1} (C=C). δ_H [$CDCl_3/CD_3OD$, 200 MHz] 4.75 (6H, m, H-4', 5', 5"), 5.50 (2H, d, J 9.5 Hz, H-5), 5.70 (4H, m, H-2', 3'), 6.15 (2H, d, J 5.0 Hz, H-1'), 7.20-7.50 (20H, m, H-6, and Ph-H), 8.0 (12H, m, Ph-H); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 62.56 (CH_2), 69.76 (CH), 73.47 (CH), 80.32 (CH), 89.38 (CH), 107.49 (CH), 127.82 (C), 128.23 (C), 128.60 (CH), 128.67 (CH), 128.81 (CH), 129.55 (CH), 129.78 (CH), 129.89 (CH), 133.89 (CH), 134.03 (CH), 134.30 (CH), 137.10 (C), 155.23 (C), 165.47 (C), 165.89 (C), 166.26(C). m/z 1143 (MH^+, 15%). Anal. Calcd. for $C_{60}H_{46}N_4O_{16}S_2$: C, 63.04%; H, 4.06%; N, 4.90%. Found. C, 63.10%, H, 4.08%; N, 4.93%.

2'-Deoxy-3',5'-di-*O*-acetyl-N^4-methylcytidine **12b**- (188 mg, 58%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 2.05 (6H, s, CH_3), 2.95 (2H, m, CH_2), 4.25 (3H, m, H-4', 5', 5"), 5.10 (1H, m, H-3'), 5.70 (1H, d, J 10.8 Hz, H-5), 6.25 (1H, m, H-1'), 7.40 (1H, d, J 10.8 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 20.53 (CH_3), 27.66 (CH_2), 38.17 (CH_3), 63.80 (CH_2), 74.29 (CH), 82.01 (CH), 86.13 (CH), 95.78 (CH), 138.10 (CH), 140.90 (C), 156.32 (C), 164.47 (C), 170.65(C); m/z 325 (M^+, 34%). Anal. Calcd. for $C_{14}H_{19}N_3O_6$: C, 51.69%; H, 5.89%; N, 12.91%. Found. C, 51.71%, H, 5.86 %; N, 13.0%.

2'-Deoxy-3',5'-di-*O*-acetyl-N^4-ethyl-cytidine **12c**- (264 mg, 78%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1730 (C=O) and 1640 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 1.19 (3H, m, CH_3), 2.05 (6H, m, CH_3), 2.60 (2H, m, CH_2), 3.49 (2H, m, CH_2), 4.25 (3H, m, H-4', 5', 5''), 5.18 (1H, m, H-3'), 5.60 (1H, d, J 9.0 Hz, H-5), 6.28 (1H, m, H-1'), 7.40 (1H, d, J 9.0 Hz, H-6); m/z 339 (M^+, 17%). Anal. Calcd. for $C_{15}H_{21}N_3O_6$: C, 53.09%; H, 6.24%; N, 12.38%. Found. C, 52.11%; H, 6.30%; N, 12.36%.

2'-Deoxy-3',5'-di-*O*-acetyl-N^4-p-tolyl-cytidine **12d**- (317 mg, 79%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1730 (C=O) and 1640 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 2.02 (3H, s, CH_3), 2.05 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.70 (2H, m, CH_2), 4.26 (3H, m, H-4', 5', 5''), 5.15 (1H, m, H-3'), 5.83 (1H, d, J 9.3 Hz, H-5), 6.250 (1H, q, Ja= 10 Hz, Jb= 9.5 Hz, H-1'), 7.15 (4H, m, Ph-H), 7.53 (1H, d, J 9.3 Hz, H-6); m/z 401 (M^+, 13%). Anal. Calcd. for $C_{20}H_{23}N_3O_6$: C, 59.84%; H, 5.78%; N, 10.47%. Found. C, 59.88%; H, 5.81%; N, 10.50%.

5-Methyl-2'-deoxy-3',5'-di-*O*-acetyl-cytidine **13a**- (250 mg, 77%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3/CD_3OD$, 200 MHz] 1.90 (3H, s, CH_3), 2.06 (6H, s, CH_3), 2.50 (2H, m, CH_2), 4.23 (3H, m, H-4', 5', 5''), 5.18 (1H, m, H-3'), 6.25 (1H, m, H-1'), 7.31 (1H, s, H-6); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 12.58 (CH_3), 20.19 (CH_2), 37.82 (CH_2), 63.58 (CH_2), 74.04 (CH), 81.93 (CH), 85.82 (CH), 102.73 (CH), 137.21 (C), 156.26 (C), 165.56 (C), 170.77 (C), 170.86(C); m/z 325 (M^+, 7%). Anal. Calcd. for $C_{14}H_{19}N_3O_6$: C, 51.69%; H, 5.89%; N, 12.92%. Found. C, 51.73%, H, 6.01%; N, 12.94%.

5-Methyl-2'-deoxy-3',5'-di-*O*-acetyl-N^4-methyl-cytidine **13b**- (247 mg, 73%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3/CD_3OD$, 200 MHz] 1.85 (3H, s, CH_3), 2.03 (6H, s, CH_3), 2.53 (2H, m, CH_2), 2.95 (3H, s, CH_3), 4.20 (3H, m, H-4', 5', 5''), 5.12 (1H, m, H-3'), 6.28 (1H, m, H-1'), 7.20 (1H, s, H-6); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 12.99 (CH_3), 20.59 (CH_3), 28.10 (CH_2), 38.07 (CH_3), 63.86 (CH_2), 74.32 (CH), 81.93 (CH), 85.80 (CH), 102.60 (CH), 135.72 (C), 156.35 (C), 163.94 (C), 170.56 (C), 170.73 (C); m/z 339 (M^+, 23%). Anal. Calcd. for $C_{15}H_{21}N_3O_6$: C, 53.09%; H, 6.23%; N, 12.38%. Found. C, 54.0%, H, 6.24%; N, 12.41%.

5-Methyl-2'-deoxy-3',5'-di-*O*-acetyl-N^4-ethyl-cytidine **13c**- (215 mg, 71%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3/CD_3OD$, 200 MHz] 1.13 (3H, m, CH_3), 2.02 (3H, s, CH_3), 2.10 (6H, s, CH_3), 2.50 (2H, m, CH_2), 3.50 (2H, m, CH_2), 4.20 (3H, m, H-4', 5', 5''), 5.10 (1H, m, H-3'), 6.15 (1H, m, H-1'), 7.18 (1H, s, H-6); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 12.48 (CH_3), 20.47 (CH_3), 35.65 (CH_2), 37.88 (CH_2), 61.97 (CH_2), 63.73 (CH), 70.28 (CH), 81.82 (CH), 102.58 (CH), 137.96 (C), 156.52 (C), 163.21 (C), 170.69 (C), 170.84 (C); m/z 353 (M^+, 41%). Anal. Calcd. for $C_{16}H_{23}N_3O_6$: C, 54.38%; H, 6.56%; N, 11.89%. Found. C, 54.41%, H, 6.51%; N, 11.91%.

5-Methyl-2'-deoxy-3',5'-di-*O*-acetyl-N^4-p-tolyl-cytidine **13d**- (282 mg, 68%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3/CD_3OD$, 200 MHz] 2.0 (3H, s, CH_3), 2.05 (6H, s, CH_3), 2.25 (3H, s, CH_3), 2.50 (2H, m, CH_2), 4.25 (3H, m, H-4', 5', 5''), 5.15 (1H, m, H-3'), 6.30 (1H, m, H-1'), 7.10-7.50 (6H, m, Ph-H and H-6); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 13.40 (CH_3), 20.57 (CH_3),

20.68 (CH_3), 38.26 (CH_2), 63.85 (CH_2), 74.31 (CH), 82.20 (CH), 86.24 (CH), 102.64 (CH), 122.20 (CH), 129.49 (CH), 134.46 (C), 135.30 (C), 137.12 (C), 156.45 (C), 161.67 (C), 170.55 (C), 170.72 (C); m/z 415 (M^+, 11%). Anal. Calcd. for $C_{21}H_{25}N_3O_6$: C, 60.71%; H, 6.07%; N, 10.11%. Found. C, 60.73%, H, 6.09 %; N, 10.09%.

2',3',5'-Tri-*O*-acetyl-arabinofuranosyl-cytidine **14a**- (332 mg, 90%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 1.90 (3H, s, CH_3), 2.06 (6H, s, CH_3), 4.30 (3H, m, H-4', 5', 5''), 5.05 (1H, m, H-2'), 5.49 (1H, m, H-3'), 5.85 (1H, d, J 9.2 Hz, H-5), 6.25 (1H, d, J 4.5 Hz, H-1'), 7.50 (1H, d, J 7.6 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 20.32 (CH_3), 20.52 (CH_3), 62.91 (CH_2), 74.30 (CH_2), 80.35 (CH), 85.46 (CH), 94.69 (CH), 141.47 (CH), 155.63 (C), 166.29 (C), 168.73 (C), 169.96 (C), 170.84 (C); m/z 369 (M^+, 15%). Anal. Calcd. for $C_{15}H_{19}N_3O_8$: C, 48.78%; H, 5.19%; N, 11.38%. Found. C, 48.76%, H, 5.16%; N, 11.43%.

2',3',5'-Tri-*O*-acetyl-arabinofuranosyl-N^4-methyl-cytidine **14b**- (276 mg, 72%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 1.90 (3H, s, CH_3), 2.06 (6H, s, CH_3), 2.90 (3H, s, CH_3), 4.10-4.40 (3H, m, H-4', 5', 5''), 5.0 (1H, m, H-2'), 5.41 (1H, m, H-3'), 5.80 (1H, d, J 9.0 Hz, H-5), 6.28 (1H, d, J 4.5 Hz, H-1'), 7.35 (1H, d, J 9.0 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 20.20 (CH_3), 20.38 (CH_3), 20.44 (CH_3), 27.43 (CH_3), 62.82 (CH_2), 74.23 (CH_2), 80.18 (CH), 85.09 (CH), 95.12 (CH), 139.54 (CH), 155.99 (C), 164.38 (C), 168.54 (C), 169.88 (C), 170.78 (C); m/z 383 (M^+, 22%). Anal. Calcd. for $C_{16}H_{21}N_3O_8$: C, 50.13%; H, 5.52%; N, 10.96%. Found. C, 50.16%, H, 5.48%; N, 10.99%.

2',3',5'-Tri-*O*-acetyl-arabinofuranosyl-N^4-ethyl-cytidine **14c**- (286 mg, 72%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 1.15 (3H, m, CH_3), 1.90 (3H, s, CH_3), 2.06 (6H, s, CH_3), 3.40 (2H, m, CH_2), 4.10-4.40 (3H, m, H-4', 5', 5''), 4.90 (1H, m, H-2'), 5.35 (1H, m, H-3'), 5.80 (1H, d, J 9.2 Hz, H-5), 6.35 (1H, d, J 4.0 Hz, H-1'), 7.40 (1H, d, J 9.2 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 14.15 (CH_3), 20.27 (CH_3), 20.49 (CH_3), 35.54 (CH_3), 62.88 (CH_2), 74.29 (CH_2), 80.36 (CH), 85.16 (CH), 94.81 (CH), 1140.11 (CH), 155.88 (C), 163.71 (C), 168.46 (C), 169.86 (C), 170.77 (C); m/z 397 (M^+, 8%). Anal. Calcd. for $C_{17}H_{23}N_3O_8$: C, 51.38%; H, 5.83%; N, 10.57%. Found. C, 51.41%, H, 5.86%; N, 10.59%.

2',3',5'-Tri-*O*-acetyl-arabinofuranosyl-N^4-p-tolyl-cytidine **14d**- (349 mg, 76%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 1.90 (3H, s, CH_3), 2.06 (6H, s, CH_3), 2.25 (3H, s, CH_3), 4.10-4.40 (3H, m, H-4', 5', 5''), 4.98 (1H, m, H-2'), 5.35 (1H, m, H-3'), 5.90 (1H, d, J 9.3 Hz, H-5), 6.25 (1H, d, J 4.3 Hz, H-1'), 7.20 (4H, m, Ph-H), 7.50 (1H, d, J 9.0 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 18.75 (CH_3), 20.18 (CH_3), 20.44 (CH_3), 20.50 (CH_3), 62.80 (CH_2), 74.21 (CH), 76.46 (CH), 80.51 (CH), 85.33 (CH), 129.92 (CH), 130.0 (CH), 130.23 (CH), 131.10 (C), 140.54 (C), 168.63 (C), 170.05 (C), 170.99 (C); m/z 459 (M^+, 13%). Anal. Calcd. for $C_{22}H_{25}N_3O_8$: C, 57.51%; H, 5.48%; N, 9.15%. Found. C, 57.46%, H, 5.49%; N, 9.20%.

2',3',5'-Tri-*O*-acetyl-arabinofuranosyl-N^4-[2',6'-dimethylphenyl]-cytidine **14e**- (382 mg, 81%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [$CDCl_3$, 200 MHz] 1.91 (3H, s, CH_3), 1.99 (3H, s, CH_3), 2.07 (6H, s, CH_3), 2.18 (6H, s, CH_3), 4.10-4.45 (3H, m, H-4', 5', 5''), 4.96 (1H, m, H-2'), 5.24 (1H, d, J 7.7 Hz, H-5), 5.40 (1H, m, H-3'), 6.35 (1H, d, J 3.6 Hz, H-1'), 7.10 (3H, m, Ph-H), 7.49 (1H, d, J 7.7 Hz, H-6); δ_C [$CDCl_3$, 200 MHz] 18.17 (CH_3), 20.38 (CH_3), 20.61 (CH_3), 20.70 (CH_3), 62.80 (CH_2), 74.16 (CH), 77.07 (CH), 80.73 (CH), 85.24 (CH), 90.59 (CH), 128.17 (CH), 128.59 (CH), 133.87 (CH), 136.59 (C), 142.71 (C), 153.10 (C), 163.15 (C), 168.70 (C), 169.58 (C), 170.48 (C); m/z 473 (M^+, 13%). Anal. Calcd. for $C_{23}H_{27}N_3O_8$: C, 58.34%; H, 5.75%; N, 8.87%. Found. C, 58.40%, H, 6.79 %; N, 8.90%.

2',3',5'-Tri-*O*-acetyl-adenosine **22a**- (747 mg, 95%), m.p. 173-174 °C (from EtOH) [lit.[38], m.p. 174 °C]. I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1730 cm^{-1} (C=O); δ_H [$CDCl_3$, 200 MHz] 2.01 (6H, s, CH_3), 2.10 (3H, s, CH_3), 4.45 (3H, m, H-4', 5', 5''), 5.70 (1H, m, H-2'), 5.95 (1H, m, H-3'), 6.31 (1H, d, J 4.5 Hz, H-1'), 8.80 (1H, s, H-8), 8.98 (1H, s, H-2) ; m/z 393 (M^+, 22%). Anal. Calcd. for $C_{16}H_{19}N_5O_7$: C, 48.86%; H, 4.87%; N, 17.80%. Found. C, 48.90%, H, 4.84%; N, 17.89%.

2',3',5'-Tri-*O*-acetyl-N^6-methyl-adenosine **22b**- (223 mg, 55%). I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1730 cm^{-1} (C=O); δ_H [$CDCl_3$, 200 MHz] 2.05 (6H, s, CH_3), 2.10 (3H, s, CH_3), 3.15 (3H, b. s., CH_3), 4.30 (3H, m, H-4', 5', 5''), 5.55 (1H, m, H-2'), 5.85 (1H, m, H-3'), 6.10 (1H, d, J 7.2 Hz, H-1'), 7.90 (1H, s, H-8), 8.35 (1H, s, H-2) ; δ_C [$CDCl_3$, 200 MHz] 20.15 (CH_3), 20.28 (CH_3), 20.53 (CH_3), 28.10 (CH_3), 62.91 (CH_2), 70.54 (CH), 73.03 (CH), 80.49 (CH), 86.13 (CH), 138.04 (CH), 142.44 (CH), 152.90 (C), 153.68 (C), 155.72 (C), 169.60 (C), 169.81 (C), 170.58 (C); m/z 407 (M^+, 31%). Anal. Calcd. for $C_{17}H_{21}N_5O_7$: C, 50.12%; H, 5.20%; N, 17.19%. Found. C, 50.22%, H, 5.11%; N, 17.27%.

2-Acetamido-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)adenine **23a**- (292 mg, 65%), 148-150 °C (from EtOH); I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [$CDCl_3$, 200 MHz] 1.95 (3H, s, CH_3), 2.10 (3H, s, CH_3), 2.15 (3H, s, CH_3), 2.35 (3H, s, CH_3), 4.50 (3H, m, H-4', 5', 5''), 5.95 (3H, m, H-1', 2', 3'), 6.65 (2H, b.s., NH_2), 7.75 (1H, s, H-8), 9.70 (1H, b.s., NH); δ_C [$CDCl_3$, 200 MHz] 20.34 (CH_3), 20.55 (CH_3), 25.0 (CH_3), 29.52 (CH_3), 63.29 (CH_2), 70.68 (CH), 73.91 (CH), 79.98 (CH), 87.33 (CH), 116.90 (CH), 138.30 (C), 149.96 (C), 153.44 (C), 156.52 (C), 170.10 (C), 170.68 (C); m/z 450 (M^+, 22%). Anal. Calcd. for $C_{18}H_{22}N_6O_8$: C, 48.00%; H, 4.92%; N, 18.66%. Found. C, 48.12%, H, 4.85%; N, 18.77%.

2-Acetamido-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)-N^6-methyl-adenine **23b**- (292 mg, 63%). I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [$CDCl_3$, 200 MHz] 2.05 (3H, s, CH_3), 2.12 (3H, s, CH_3), 3.28 (3H, s, CH_3), 4.40 (3H, m, H-4', 5', 5''), 5.65 (1H, m, H-3'), 5.91 (1H, m, H-2'), 6.18 (1H, d, J 3.8 Hz, H-1'), 7.90 (1H, s, H-8); m/z 464 (M^+, 9%). Anal. Calcd. for $C_{19}H_{24}N_6O_8$: C, 49.14%; H, 5.21%; N, 18.10%. Found. C, 48.97%, H, 5.23%; N, 18.23%.

2-Acetamido-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)-N^6-ethyl-adenine **23c**- (320 mg, 67%). I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [$CDCl_3$, 200 MHz] 1.23 (3H, m, CH_3), 2.07 (3H, s, CH_3), 2.12 (6H, s, CH_3), 3.50 (2H, m, CH_2), 4.31 (3H, m, H-4', 5', 5''), 5.38 (1H, m, H-3'), 5.70 (1H, m, H-2'), 5.82

(1H, d, J 4.1 Hz, H-1'), 7.77 (1H, s, H-8), 8.40 (1H, s, H-8); m/z 478 (M^+, 9%). Anal. Calcd. for $C_{20}H_{26}N_6O_8$: C, 50.21%; H, 5.48%; N, 17.56%. Found. C, 50.34%, H, 5.53%; N, 17.42%.

2-Acetamido-9-(2',3',5'-tri-*O*-acetyl-β-D-ribosyl)-N^6-p-tolyl-adenine **23d**- (410 mg, 76%). I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [$CDCl_3$, 200 MHz] 2.05 (3H, s, CH_3), 2.07 (3H, s, CH_3), 2.12 (3H, s, CH_3), 2.31 (3H, s, CH_3), 2.40 (3H, s, CH_3), 4.25 (3H, m, H-4', 5', 5''), 5.70 (1H, m, H-3'), 5.94 (1H, m, H-2'), 5.99 (1H, d, J 4.52 Hz, H-1'), 7.15 (2H, d, J= 8.44 Hz, Ph-H), 7.58 (2H, d, J= 8.44 Hz, Ph-H), 7.81 (1H, s, H-8); δ_C [$CDCl_3$, 200 MHz] 20.23 (CH_3), 20.30 (CH_3), 20.71 (CH_3), 24.93 (CH_3), 63.02 (CH_2), 70.45 (CH), 73.16 (CH), 79.92 (CH), 86.79 (CH), 117.63 (CH), 121.18 (CH), 129.62 (CH), 133.99 (C), 135.53 (C), 138.46 (C), 150.04 (C), 152.75 (C), 153.06 (C), 169.62 (C), 169.78 (C), 170.68 (C); m/z 540 (M^+, 33%). Anal. Calcd. for $C_{25}H_{28}N_6O_8$: C, 55.55%; H, 5.22%; N, 15.55%. Found. C, 55.53%, H, 5.31%; N, 15.67%.

8-Methylamino-N^6, 2',3',5'-tetra-*O*-acetyl-adenosine **26**- (385 mg, 83%). I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1730 cm^{-1} (C=O); δ_H [$CDCl_3$, 200 MHz] 2.01 (3H, s, CH_3), 2.10 (6H, s, CH_3), 2.25 (3H, s, CH_3), 3.45 (3H, s, CH_3), 4.30 (3H, m, H-4', 5', 5''), 5.75 (1H, m, H-2'), 6.05 (1H, d, J 3.8 Hz, H-1'), 6.21 (1H, m, H-3'), 8.30 (1H, s, H-8); δ_C [$CDCl_3$, 200 MHz] 20.25 (CH_3), 20.38 (CH_3), 20.48 (CH_3), 23.57 (CH_3), 63.18 (CH_2), 70.49 (CH), 72.10 (CH), 79.15 (CH), 84.56 (CH), 108.58 (CH), 137.94 (CH), 150.60 (CH), 137.94 (C), 150.60 (C), 150.93 (C), 169.87 (C), 170.24 (C), 170.41 (C), 170.88 (C); m/z 464 (M^+, 15%). Anal. Calcd. for $C_{19}H_{24}N_6O_8$: C, 49.13%; H, 5.20%; N, 18.09%. Found. C, 49.16%, H, 5.25%; N, 18.13%.

Deacetylation of nucleoside derivatives. General procedure- The reactions were carried out by adding an excess of ammonia (15 equiv./mol., 2N methanol solution) to solutions of the required substrate (1 mmol) in CH_2Cl_2 (5 ml) at 25°, until the substrate disappeared (TLC solvent CH_2Cl_2/CH_3OH = 9.0/1.0 or CH_2Cl_2/CH_3OH = 8.0/2.0). The reaction mixture was evaporated and the residue was purified by flash-chromatography using a gradient CH_2Cl_2/CH_3OH as eluent.

N^4-Methyl-cytidine **4b**-[39] (229 mg, 90%), m.p. 61-63 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 3.40-3.63 (3H, m, H-4', 5', 5''), 3.81 (3H, s, CH_3), 4.93 (2H, m, H-2', 3'), 5.80 (1H, d, J 3.34 Hz, H-1'), 6.36 (1H, d, J 7.62 Hz, H-5), 7.73 (1H, d, J 7.62 Hz, H-6); δ_C [CD_3OD, 200 MHz] 48.43 (CH_3), 60.45 (CH_2), 69.19 (CH), 74.45 (CH), 84.82 (CH), 88.80 (CH), 90.41 (CH), 113.27 (CH), 135.55 (CH), 148.48 (C), 190.51 (C); m/z 257 (M^+, 37%). Anal. Calcd. for $C_{10}H_{15}N_3O_5$: C, 46.69%; H, 5.88%; N, 16.33%. Found. C, 46.77%, H, 5.97%; N, 16.50%.

N^4-Ethyl-cytidine **4c**- (220 mg, 82%), m.p. 48-50 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 1.18 (3H, m, CH_3), 3.30 (2H, m, CH_2), 3.50-3.80 (3H, m, H-4', 5', 5''), 4.10 (2H, m, H-2', 3'), 5.73 (2H, m, H-1', 5), 7.88 (1H, d, J 8.98 Hz, H-6); δ_C [CD_3OD, 200 MHz] 20.71(CH_3), 36.49 (CH_2), 64.61 (CH_2), 71.05 (CH), 75.75 (CH), 82.40 (CH), 92.75

(CH), 97.07 (CH), 140.64 (CH), 158.71 (C), 165.22 (C); m/z 271 (M^+, 18%). Anal. Calcd. for $C_{11}H_{17}N_3O_5$: C, 48.70%; H, 6.32%; N, 15.49%. Found. C, 48.56%, H, 6.31%; N, 15.56%.

N^4-n-Propyl-cytidine **4d**- (246 mg, 82%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 0.86 (3H, m, CH_3), 1.50 (2H, m, CH_2), 3.25 (3H, m, H-4', 5', 5"), 3.70 (2H, m, CH_2), 4.05 (2H, m, H-2', 3'), 5.71 (2H, m, H-1', 5), 7.78 (1H, d, J 5.0 Hz, H-6); δ_C [CD_3OD, 200 MHz] 10.27 (CH_3), 21.41 (CH_2), 41.69 (CH_2), 60.12 (CH_2), 62.54 (CH), 68.69 (CH), 74.27 (CH), 83.88 (CH), 90.83 (CH), 95.37 (CH), 139.23 (CH), 156.99 (C), 163.51 (C); m/z 285 (M^+, 21%). Anal. Calcd. for $C_{12}H_{19}N_3O_5$: C, 50.52%; H, 6.71%; N, 14.73%. Found. C, 50.42%, H, 6.62%; N, 14.75%.

N^4-n-Butyl-cytidine **4e**- (214 mg, 72%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3/CD_3OD$, 200 MHz] 0.76 (3H, m, CH_3), 1.25 (4H, m, CH_2), 3.20 (3H, m, H-4', 5', 5"), 3.67 (2H, m, CH_2), 3.70-4.10 (2H, m, H-2', 3'), 5.60 (2H, m, H-1', 5), 7.58 (1H, d, J 8.5 Hz, H-6); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 14.11 (CH_3), 19.45 (CH_2), 32.16 (CH_2), 41.39 (CH_2), 62.10 (CH_2), 64.32 (CH), 70.87 (CH), 76.08 (CH), 85.82 (CH), 92.34 (CH), 96.96 (CH), 141.35 (CH), 158.96 (C), 165.49 (C); m/z 299 (M^+, 43%). Anal. Calcd. for $C_{13}H_{21}N_3O_5$: C, 52.16%; H, 7.07%; N, 14.04%. Found. C, 52.21%, H, 7.09%; N, 14.00%.

N^4-p-Tolyl-cytidine **4f**- (291 mg, 88%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [$CDCl_3$,CD_3OD, 200 MHz] 2.18 (3H, s, CH_3), 3.76 (3H, m, H-4', 5', 5"), 3.90 (2H, m, H-2', 3'), 5.61 (1H, d, J 2.1 Hz, H-1'), 5.85 (1H, d, J 5.10 Hz, H-5), 7.0 (4H, m, Ph-H), 7.90 (1H, d, J 5.10 Hz, H-6); δ_C [$CDCl_3/CD_3OD$, 200 MHz] 21.73 (CH_3), 60.43 (CH_2), 63.16 (CH), 68.89 (CH), 74.62 (CH), 84.43 (CH), 91.85 (CH), 121.0 (CH), 124.39 (CH), 128.57 (C), 129.45 (CH), 130.86 (C), 156.74 (C), 232.48 (C); m/z 333 (M^+, 37%). Anal. Calcd. for $C_{16}H_{19}N_3O_5$: C, 57.65%; H, 5.75%; N, 12.61%. Found. C, 57.73%, H, 5.77%; N, 12.56%.

2'-Deoxy-cytidine **15a**- (228 mg, 93%), m.p. 208-210 °C [lit.[40], 209-211 °C].

2'-Deoxy-N^4-methyl-cytidine **15b**- (140 mg, 58%), m.p. 160-162 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 2.17 (2H, m, CH_2), 2.94 (3H, s, CH_3), 3.30 (1H, m, H-4'), 3.77 (2H, m, H-5', 5"), 4.37 (1H, m, H-3'), 5.86 (1H, d, J 7.6 Hz, H-5), 6.24 (1H, m, H-1'), 7.98 (1H, d, J 7.6 Hz, H-6); δ_C [CD_3OD, 200 MHz] 28.21 (CH_2), 41.89 (CH_3), 62.74 (CH_2), 72.0 (CH), 87.54 (CH), 88.97 (CH), 96.52 (CH), 141.61 (CH), 164.38 (C), 171.25(C); m/z 241 (M^+, 34%). Anal. Calcd. for $C_{10}H_{15}N_3O_4$: C, 49.79%; H, 6.27%; N, 17.42%. Found. C, 49.81%, H, 6.33%; N, 17.45%.

2'-Deoxy-N^4-ethyl-cytidine **15c**- (160 mg, 63%), m.p. 58-60 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 1.07 (3H, s, CH_3), 2.22 (2H, m, CH_2), 3.27 (2H, m, CH_2), 3.57 (3H, m, H-4', 5', 5"), 4.20 (1H, m, H-3'), 5.62 (1H, d, J 7.5 Hz, H-5), 6.03 (1H, t, J= 6.3 Hz, H-1'), 7.57 (1H, d, J 7.5 Hz, H-6); δ_C [CD_3OD, 200 MHz] 13.68 (CH_3), 40.38 (CH_2), 61.37 (CH_2), 70.19 (CH), 86.42 (CH), 86.88 (CH), 95.81 (CH), 139.43 (CH), 156.87 (C), 163.42 (C); m/z

255 (M^+, 7%). Anal. Calcd. for $C_{11}H_{17}N_3O_4$: C, 51.76%; H, 6.71%; N, 16.46%. Found. C, 51.89%, H, 6.75%; N, 16.54%.

2'-Deoxy-N^4-p-tolyl-cytidine **15d**- (140 mg, 58%), m.p. 42-44 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [DMSO, 200 MHz] 2.10 (2H, m, CH_2), 2.35 (3H, s, CH_3), 3.50 (3H, m, H-4', 5', 5"), 3.70 (1H, m, H-3'), 5.95 (1H, d, J 8.95 Hz, H-5), 6.13 (1H, t, J= 6.1 Hz, H-1'), 7.10 (2H, d, J= 12.0 Hz, Ph-H), 7.60 (2H, d, J= 12.0 Hz, Ph-H), 7.95 (1H, d, J 8.95 Hz, H-6); m/z 317 (M^+, 18%). Anal. Calcd. for $C_{16}H_{19}N_3O_4$: C, 60.56%; H, 6.03%; N, 13.24%. Found. C, 60.63%, H, 6.08%; N, 13.12%.

5-Methyl-2'-deoxy-cytidine **16a**- (205 mg, 85%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 1.93 (3H, s, CH_3), 2.23 (2H, m, CH_2), 3.79 (3H, m, H-4', 5', 5"), 4.40 (1H, m, H-3'), 6.22 (1H, m, H-1'), 7.79 (1H, s, H-6); δ_C [CD_3OD, 200 MHz] 13.86 (CH_2), 42.24 (CH_3), 62.96 (CH_2), 71.99 (CH), 87.73 (CH), 88.64 (CH), 104.50 (CH), 140.69 (C), 158.54 (C), 167.53 (C); m/z 241 (M^+, 23%). Anal. Calcd. for $C_{10}H_{15}N_3O_4$: C, 49.79%; H, 6.27%; N, 17.42%. Found. C, 49.85%, H, 6.33%; N, 17.35%.

5-Methyl-2'-deoxy-N^4-methyl-cytidine **16b**- (153 mg, 60%), m.p. 188-90 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 1.94 (3H, s, CH_3), 2.34 (2H, m, CH_2), 2.95 (3H, s, CH_3), 3.91 (2H, m, H-5', 5"), 4.06 (1H, m, H-4'), 4.46 (1H, m, H-3'), 6.32 (1H, t, J= 6.66 Hz, H-1'), 7.55 (1H, s, H-6); δ_C [CD_3OD, 200 MHz] 13.22 (CH_2), 28.45 (CH_3), 41.97 (CH_3), 62.97 (CH_2), 72.16 (CH), 87.43 (CH), 88.83 (CH), 105.25 (CH), 138.64 (C), 159.03 (C), 165.81 (C); m/z 255 (M^+, 16%). Anal. Calcd. for $C_{11}H_{17}N_3O_4$: C, 51.76%; H, 6.71%; N, 16.46%. Found. C, 51.87%, H, 6.63%; N, 16.59%.

5-Methyl-2'-deoxy-N^4-ethyl-cytidine **16c**- (150 mg, 56%), m.p. 100-102 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 1.16 (3H, m, CH_3), 2.12 (3H, s, CH_3), 2.39 (2H, m, CH_2), 3.48 (2H, m, CH_2), 3.98 (3H, m, H-4', 5', 5"), 4.15 (1H, m, H-3'), 6.20 (1H, m, H-1'), 7.19 (1H, s, H-6); m/z 269 (M^+, 13%). Anal. Calcd. for $C_{12}H_{19}N_3O_4$: C, 53.52%; H, 7.11%; N, 15.60%. Found. C, 53.58%, H, 7.03%; N, 15.48%.

5-Methyl-2'-deoxy-N^4-p-tolyl-cytidine **16d**- (245 mg, 74%), m.p. 80-82 °C (from EtOAc); I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1740 (C=O) and 1645 cm^{-1} (C=C); δ_H [CD_3OD, 200 MHz] 2.10 (3H, s, CH_3), 2.23 (2H, m, CH_2), 2.35 (3H, s, CH_3), 3.88 (3H, m, H-4', 5', 5"), 4.41 (1H, m, H-3'), 6.25 (1H, t, J= 7.2 Hz, H-1'), 7.15 (2H, d, J= 12.0 Hz, Ph-H), 7.53 (2H, d, J= 12.0 Hz, Ph-H), 7.95 (1H, s, H-6); δ_C [CD_3OD, 200 MHz] 13.74 (CH_2), 21.0 (CH_3), 42.0 (CH_2), 62.73 (CH), 71.91 (CH), 87.34 (CH), 88.84 (CH), 105.25 (C), 124.57 (CH), 124.63 (C), 130.06 (CH), 137.10 (C), 139.03 (C), 139.90 (C); m/z 331 (M^+, 9%). Anal. Calcd. for $C_{17}H_{21}N_3O_5$: C, 58.78%; H, 6.09%; N, 12.09%. Found. C, 58.83%, H, 6.11%; N, 12.13%.

Arabinofuranosyl-cytidine **17a**- (245 mg, 88%), m.p. 198-199 °C [lit.[41], 197-198 °C].

N^4-Methyl-arabinofuranosyl-cytidine **17b**- (203 mg, 79%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [DMSO, 200 MHz] 2.75 (3H, s, CH_3), 3.53 (3H, m, H-4', 5', 5''), 3.93 (2H, m, H-2', 3'), 5.77 (1H, d, J 8.1 Hz, H-5), 6.05 (1H, d, J 4.2 Hz, H-1'), 7.50 (1H, d, J 8.1 Hz, H-6), 7.65 (1H, b. s., NH); δ_C [DMSO, 200 MHz] 26.83 (CH_3), 61.28 (CH_2), 75.02 (CH), 76.53 (CH), 84.98 (CH), 85.98 (CH), 93.27 (CH), 141.88 (CH), 155.67 (C), 164.30 (C); m/z 257 (M^+, 34%). Anal. Calcd. for $C_{10}H_{15}N_3O_5$: C, 46.69%; H, 5.88%; N, 16.33%. Found. C, 46.77%, H, 5.77%; N, 16.41%.

N^4-Ethyl-arabinofuranosyl-cytidine **17c**- (249 mg, 92%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [DMSO, 200 MHz] 1.05 (3H, m, CH_3), 3.25 (2H, m, CH_2), 3.70 (3H, m, H-4', 5', 5''), 3.92 (2H, m, H-2', 3'), 5.68 (1H, d, J 5.8 Hz, H-5), 6.05 (1H, d, J 4.1 Hz, H-1'), 7.51 (1H, d, J 5.8 Hz, H-6), 7.70 (1H, b. s., NH); δ_C [DMSO, 200 MHz] 14.26 (CH_3), 34.56 (CH_2), 61.29 (CH_2), 75.03 (CH), 76.57 (CH), 85.01 (CH), 86.03 (CH), 93.34 (CH), 141.95 (CH), 155.71 (C), 163.62 (C); m/z 271 (M^+, 8%). Anal. Calcd. for $C_{11}H_{17}N_3O_5$: C, 48.70%; H, 6.32%; N, 19.49%. Found. C, 47.99%, H, 6.28%; N, 19.52%.

N^4-p-Tolyl-arabinofuranosyl-cytidine **17d**- (243 mg, 79%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [DMSO, 200 MHz] 2.24 (3H, s, CH_3), 3.58 (2H, m, H-5', 5''), 3.60 (1H, m, H-4'), 3.90-4.0 (2H, m, H-2', 3'), 5.93 (1H, d, J 4.9 Hz, H-5), 6.06 (1H, d, J 2.6 Hz, H-1'), 7.09 (2H, d, J= 5.5 Hz, Ph-H), 7.69 (1H, d, J 4.9 Hz, H-6), 7.72 (2H, d, J= 5.5 Hz, Ph-H), 9.60 (1H, b. s., NH); δ_C [DMSO, 200 MHz] 30.75 (CH_3), 61.19 (CH_2), 66.40 (CH), 74.81 (CH), 76.32 (CH), 79.24 (CH), 85.19 (CH), 86.31(CH), 94.01 (CH), 120.31 (CH), 129.07 (CH), 132.01 (C), 136.93 (C), 142.79 (C), 154.92 (C); m/z 333 (M^+, 14%). Anal. Calcd. for $C_{16}H_{19}N_3O_5$: C, 57.65%; H, 5.75%; N, 12.61%. Found. C, 57.69%, H, 5.83%; N, 12.74%.

N^4-(2',6'-Dimethylphenyl)-arabinofuranosyl-cytidine **17e**- (271 mg, 78%), oil; I.R. ($CHCl_3$) ν_{max} 3400 (NH), 1745 (C=O) and 1638 cm^{-1} (C=C); δ_H [DMSO, 200 MHz] 2.12 (6H, s, CH_3), 3.58 (2H, m, H-5', 5''), 3.62 (1H, m, H-4'), 3.89 (2H, m, H-2', 3'), 5.03 (1H, d, J 7.4 Hz, H-5), 6.0 (1H, m, H-1'), 7.07 (3H, s, Ph-H), 7.69 (1H, d, J 4.9 Hz, H-6), 7.72 (2H, d, J= 5.5 Hz, Ph-H), 7.67 (1H, d, J= 7.4 Hz, H-6), 8.98 (1H, b. s., NH); δ_C [DMSO, 200 MHz] 18.23 (CH_3), 48.61 (CH_2), 60.70 (CH), 75.51 (CH), 76.46 (CH), 85.07 (CH), 86.04 (CH), 92.82 (CH), 126.49 (CH), 127.26 (CH), 128.31 (C), 135.67 (CH), 142.94 (C), 150.46 (C), 154.74 (C), 163.34 (C); m/z 347 (M^+, 14%). Anal. Calcd. for $C_{17}H_{21}N_3O_5$: C, 58.78%; H, 6.09%; N, 12.10%. Found. C, 58.66%, H, 6.11%; N, 12.20%.

2-Amino-adenosine **25a**- (228 mg, 65%), oil; I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [DMSO, 200 MHz] 3.54 (2H, m, H-5', 5''), 3.90 (1H, m, H-4'), 4.15 (1H, m, H-3'), 4.54 (1H, m, H-2'), 5.80 (1H, d, J= 4.0 Hz, H-1'), 8.21 (1H, s, H-8); δ_C [DMSO, 200 MHz] 61.58 (CH_2), 70.62 (CH), 73.68 (CH), 85.71 (CH), 87.37 (CH), 116.31 (CH), 139.10 (C), 150.43 (C), 152.91 (C), 156.21 (C); m/z 282 (M^+, 33%). Anal. Calcd. for $C_{10}H_{14}N_6O_4$: C, 42.55%; H, 5.00%; N, 29.77%. Found. C, 42.61%, H, 5.11%; N, 29.81%.

2-Amino-N^6-methyl-adenosine **25b**- (245 mg, 83%), m.p. 105-107 °C; I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [DMSO, 200 MHz] 2.90 (3H, s, CH_3), 4.10-4.20 (4H, m, H-3', 4', 5', 5''), 4.55 (1H,

m, H-2'), 5.75 (1H, d, J= 5.4 Hz, H-1'), 7.84 (1H, s, H-8). m/z 296 (M^+, 18%). Anal. Calcd. for $C_{11}H_{16}N_6O_4$: C, 44.59%; H, 5.44%; N, 28.36%. Found. C, 44.43%, H, 5.33%; N, 28.30%.

2-Amino-N^6-ethyl-adenosine **25c**- (242 mg, 78%), m.p. 148-150 °C; I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [DMSO, 200 MHz] 1.23 (3H, m, CH_3), 3.25 (2H, m, CH_2), 4.10-4.40 (5H, m, H-2', 3', 4', 5', 5''), 5.93 (1H, d, J= 5.6 Hz, H-1'), 7.81 (1H, s, H-8). m/z 310 (M^+, 9%). Anal. Calcd. for $C_{12}H_{18}N_6O_4$: C, 46.45%; H, 5.85%; N, 27.08%. Found. C, 46.56%; H, 5.97%; N, 27.13%.

2-Amino-N^6-p-tolyl-adenosine **25d**- (227 mg, 61%), oil; I.R. ($CHCl_3$) ν_{max} 3200 (NH) and 1750 cm^{-1} (C=O); δ_H [DMSO, 200 MHz] 3.70 (2H, m, H-5', 5''), 3.90 (1H, m, H-4'), 4.15 (1H, m, H-3'), 4.53 (1H, m, H-2'), 5.85 (1H, d, J= 5.0 Hz, H-1'), 7.05 (2H, d, J= 12.5 Hz, Ph-H), 7.93 (2H, d, J= 12.5 Hz, Ph-H), 8.40 (1H, s, H-8); δ_C [DMSO, 200 MHz] 28.98 (CH_3), 61.56 (CH_2), 70.58 (CH), 73.80 (CH), 85.72 (CH), 87.28 (CH), 117.05 (CH), 120.94 (CH), 129.10 (CH), 131.68 (C), 137.40 (C), 139.59 (C), 150.66 (C), 152.26 (C), 152.70 (C); m/z 372 (M^+, 13%). Anal. Calcd. for $C_{17}H_{20}N_6O_4$: C, 54.83%; H, 5.41%; N, 22.56%. Found. C, 54.85%; H, 5.42%; N, 22.58%.

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