SYNTHESIS OF 5-PHENYL-2(1*H*)-PYRIMIDINONE NUCLEOSIDES

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Reaction of 2-phenyltrimethinium salt **1** with thiourea and subsequent reaction with chloroacetic acid afforded 5-phenyl-2(1*H*)-pyrimidinone (**3**). Its silyl derivative **4** was condensed with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribofuranose under catalysis with tin tetrachloride or trimethylsilyl trifluoromethanesulfonate to give protected nucleoside **5** together with 5′,O^6-cyclo-5-phenyl-1,3-bis-(β-D-ribofuranosyl)-6-hydroxy-5,6-dihydro-2(1*H*,3*H*)-pyrimidinone (**7**). The greatest amounts of **7** were formed with the latter catalyst. Nucleosidation of the silyl derivative **4** with protected methyl 2-deoxy-D-ribofuranoside **8** or 2-deoxy-D-ribofuranosyl chloride **9** afforded 1-(2-deoxy-3,5-di-*O*-*p*-toluoyl-β-D-ribofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**10**) and its α-anomer **11**. Reaction of **10** and **11** with methanolic ammonia gave free 2′-deoxynucleosides **12** and **13**. Compound **13** was converted into 5′-*O*-*tert*-butyldiphenylsilyl-3′-*O*-mesyl derivative **14** which on heating with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and subsequent cleavage with tetrabutylammonium fluoride afforded 2′,3′-dideoxy-2′,3′-didehydronucleoside **15**. Reaction of the silyl derivative **4** with 1,2-di-*O*-acetyl-3,5-di-*O*-benzoylxylofuranose (**18**), catalyzed with tin tetrachloride, furnished 1-(2-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-xylofuranosyl)-2(1*H*)-pyrimidinone (**19**) which was deprotected to give the β-D-xylofuranosyl derivative **22**. As a side product, the nucleosidation afforded the β-D-xylopyranosyl derivative **23**. Deacetylation of compound **19** gave 1-(3,5-di-*O*-benzoyl-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**24**) which on reaction with thionyl chloride afforded 2′-chloro-2′-deoxynucleoside **25** and 2′,O^6-cyclonucleoside **26**. Heating of compound **25** with DBU in dimethylformamide furnished the *lyxo*-epoxide **27** which on reaction with methanolic ammonia was converted into free 1-(2,3-anhydro-β-D-lyxofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**28**). Reaction of 1,2-di-*O*-acetyl-5-*O*-benzoyl-3-*O*-methanesulfonyl-D-xylofuranose (**30**) with silyl derivative **4** gave the nucleoside **31** which by treatment with DBU was converted into an equilibrium mixture of 5′-benzoylated arabinofuranoside **33a** and its 2′,6-anhydro derivative **33b**.

Key words: Nucleosides; Deoxynucleosides; 5-Phenyl-2(1*H*)-pyrimidinone base-modified; Pyrimidines.

Nucleosides of 2(1*H*)-pyrimidinone and its 5-substituted derivatives play an important role among biologically active analogs of natural pyrimidine nucleosides. 1-(β-D-Ribofuranosyl)-2(1*H*)-pyrimidinone (zebularin) exhibits an antibacterial activity connected with its in vivo transformation into 1-(2-deoxy-β-D-ribofuranosyl)-2(1*H*)-pyrimidinone 5′-phosphate, a strong inhibitor of thymidylate synthetase[1]. Zebularin is also an effective cytidine deaminase inhibitor and can be therefore combined with some antitumor compounds of the cytosine nucleoside group that undergo in vitro deamination, e.g.

with araC (refs[2,3]). Moreover, zebularin itself, similarly as its 5-fluoro derivative, has antitumor effects (ref.[4] and references therein).

In connection with investigation of antiviral effects of 5-substituted 2-deoxyuridine derivatives, a series of 2′-deoxynucleosides with 5-substituted pyrimidinone ring has been prepared. Derivatives, substituted in the position 5 with a halogen atom (Br, I), an SCH_3 group[5,6] or an alkynyl (ethynyl, 1-propynyl) group[7] are active especially against herpesviruses. Other nucleosides, particularly with modified sugar moieties, were prepared by us already earlier[8].

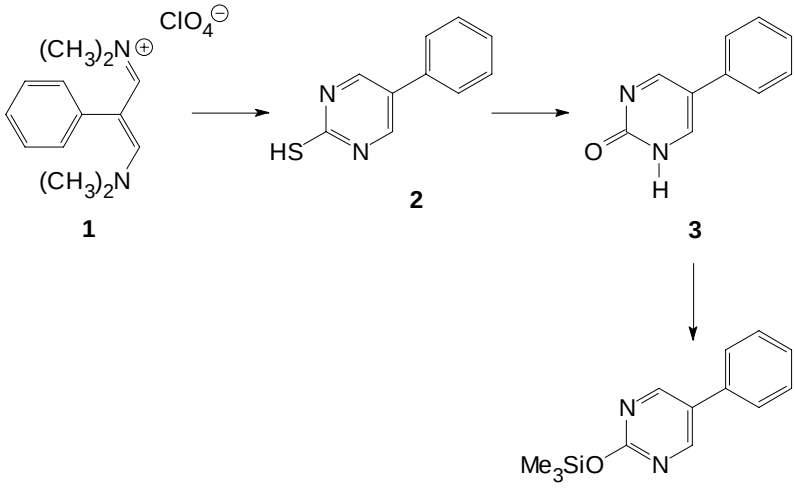
This communication concerns the preparation of pyrimidinone nucleosides substituted in position 5 with a phenyl group and is connected with investigations of uridine phosphorylase inhibitors[9]. The most effective inhibitors of this enzyme are pyrimidine nucleosides with a hydrophobic group (e.g. benzyl) in the position 5. It is also known that many C-5 alkylated pyrimidine nucleosides are potent antivirals or cytostatics.

All the compounds described in this study were prepared by nucleosidation reaction of silylated 2(1*H*)-pyrimidinone with the corresponding sugar derivative[8] and, where needed, by further transformations of the obtained nucleoside. The starting 5-phenyl-2(1*H*)-pyrimidinone (**3**) was prepared from 2-phenyltrimethinium salt (1-dimethylamino-3-dimethylimonio-2-phenyl perchlorate) (**1**) (ref.[10]) by cyclization with thiourea and subsequent conversion of the obtained 5-phenyl-2-mercaptopyrimidine (**2**) into 5-phenyl-2(1*H*)-pyrimidinone (**3**) by reaction with chloroacetic acid (Scheme 1). This pathway has been described by us already for the preparation of 5-substituted (5-ethyl-, 5-methyl- and 5-alkoxy-) 2(1*H*)-pyrimidinones[10,*].

Condensation of 5-phenyl-2(1*H*)-pyrimidinone (**3**) with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribofuranose was performed after conversion of the base into the silyl derivative **3** by reaction with hexamethyldisilazane. Nucleosidation in 1,2-dichloroethane or acetonitrile, catalyzed with tin tetrachloride, or in acetonitrile with trimethylsilyl trifluoromethanesulfonate as catalyst, afforded invariably the protected nucleoside **5** in low yield (about 40%). As a side product we isolated a compound containing further sugar unit in the molecule. After debenzoylation, the NMR spectrum has shown that the side product was 5′,O^6-anhydro-5-phenyl-1,3-bis(β-D-ribofuranosyl)-5,6-dihydro-6-hydroxy-2(1*H*,3*H*)-pyrimidinone (**7**). The highest ratio of the mono- to the bis(ribofuranosyl) derivative was achieved in the nucleosidation in acetonitrile with tin tetrachloride as catalyst. On the other hand, relatively the highest proportion of the side product **7** was obtained in reactions catalyzed with trimethylsilyl triflate. We did not find conditions suppressing entirely the formation of the compound **7**.

* Abbreviations: Ac, acetyl; Bz, benzoyl; *tert*-$BuPh_2Si$, *tert*-butyldiphenylsilyl; Ms, methanesulfonyl; TMS, trimethylsilyl; Tol, *p*-toluoyl.

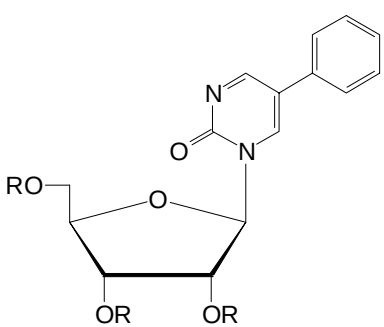
The reactivity in position 6 of the pyrimidinone ring is generally known and the formation of 5′,O^6-cyclo derivatives was observed also with other 5-substituted pyrimidinone nucleosides. The cyclization may take place e.g. during treatment with ammonia in removal of alkali-labile protecting groups. Such situation has been described



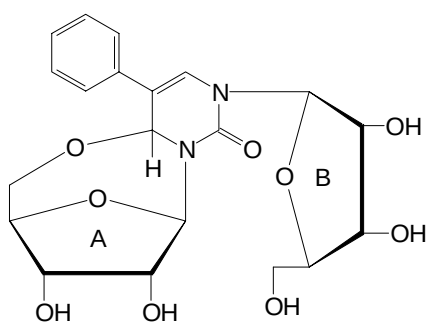
1 **2** **3** **4**

SCHEME 1

recently for 5-halogeno-2′,3′-dideoxy-3′-azidopyrimidinone nucleosides[12] and 2′-deoxynucleosides of 5-alkynylpyrimidinones[7]. The action of strong nucleophiles such as OH or F leads to complete destruction of the pyrimidinone ring, the attack by the nucleophilic anion taking place again in the position 6 (refs[4,7]). However, none of the cited papers has described such complications of the nucleosidation reaction that would lead



	R
5	Bz
6	H



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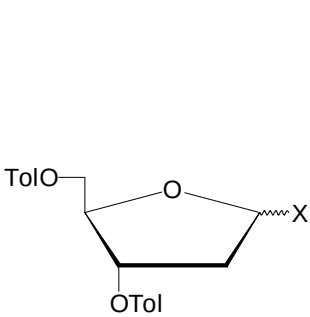
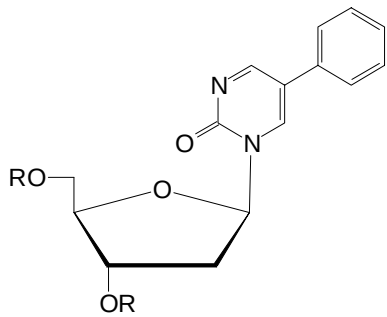
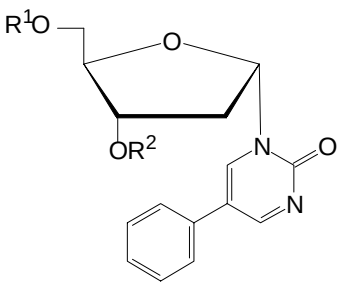
to products analogous to the bis(ribofuranosyl) derivative **7** isolated by us. On the contrary, most of the 5-phenylpyrimidinone nucleosides protected with acyl groups (ribofuranosyl derivative **5** and the 2′-deoxyribofuranosyl and xylofuranosyl derivatives described in this communication) were quantitatively deblocked with ammonia to give the free nucleosides (e.g. **6**) without any undesired cyclization to 5′,O^6-cyclo derivatives.



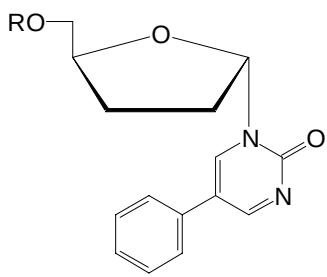
	X
8	OCH_3
9	Cl



	R
10	Tol
12	H



	R^1	R^2
11	Tol	Tol
13	H	H
14	*t*-$BuPh_2Si$	H
15	*t*-$BuPh_2Si$	Ms



	R
16	*t*-$BuPh_2Si$
17	H

Nucleosidation of compound **4** with protected methyl 2-deoxy-D-ribofuranoside (**8**) or 2-deoxy-D-ribofuranosyl chloride (**9**) afforded 1-(2-deoxy-3,5-bis(*O*-*p*-toluoyl)-β-D-ribofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**10**) together with its α-anomer **11**. The dependence of the anomer ratio on the reaction conditions is given in Table I. For the preparation of the β-anomer, the reaction with methyl glycoside **8** at low temperature in acetonitrile with trimethylsilyl triflate as catalyst is the method of choice. Treatment of bis(*O*-toluoyl) derivatives **10** and **11** with methanolic ammonia gave the free 2′-deoxynucleosides **12** and **13**. Both these nucleosides were utilized for the preparation of further 5-phenylpyrimidinone derivatives modified in the sugar part of the molecule.

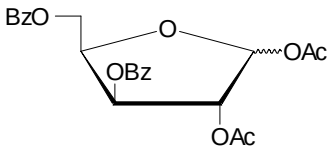
The free α-anomer **13** reacted with *tert*-butyldiphenylsilyl chloride in dimethylformamide in the presence of imidazole as base, affording in quantitative yield the 5′-*O*-*tert*-butyldiphenylsilyl derivative **14** which was converted into the mesyl derivative **15**. Heating of compound **15** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile gave 2′,3′-didehydronucleoside **16**. The 5′-silyl group was removed with tetrabutylammonium fluoride under neutral conditions (the reaction mixture was rendered at pH 7 by addition of acetic acid during the reaction) to suppress the nucleophilic attack in position 6 and opening the pyrimidinone ring. This procedure led to the free 2′,3′-dideoxy-2′,3′-didehydronucleoside **17**.

Preparation of the corresponding didehydro derivative from the β-anomer **10** using an analogous reaction pathway was not practical because the protection of the starting nucleoside was difficult. The silylation of compound **7** was not quantitative and afforded a mixture of the 5′-*O*-*tert*-butyldiphenylsilyl and 3′-*O*-*tert*-butyldiphenylsilyl derivatives, together with the 3′,5′-*O*-bis(*tert*-butyldiphenylsilyl) derivative, which arose in about the same ratios from the beginning of the reaction.

For the preparation of another group of modified nucleosides we carried out the nucleosidation of compound **4** with 1,2-di-*O*-acetyl-3,5-di-*O*-benzoylxylofuranose[13] in acetonitrile under catalysis with tin tetrachloride. The desired 1-(2-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-xylofuranosyl)-2(1*H*)-pyrimidinone (**19**) was obtained in 36% yield;

TABLE I
Nucleosidation reaction of 5-phenyl-2-trimethylsilyloxypyrimidine (**4**) with methyl 2-deoxy-3,5-di-*O*-*p*-toluoyl-D-ribofuranoside (**8**) and 2-deoxy-3,5-di-*O*-*p*-toluoyl-D-ribofuranosyl chloride (**9**)

Sugar	Solvent	Catalyst	Time	Temperature	Yield	β : α
8	acetonitrile	TMS-triflate	10 min	22	58	3 : 2
8	acetonitrile	TMS-triflate	20 min	–20	58	2 : 1
9	chloroform	–	overnight	22	86	1 : 3
9	chloroform	*p*-nitrophenol	overnight	22	56	1 : 3



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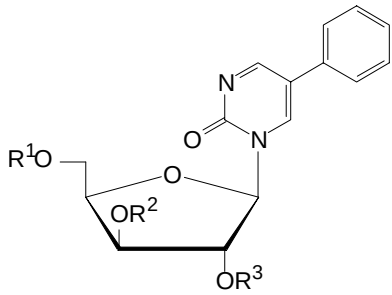
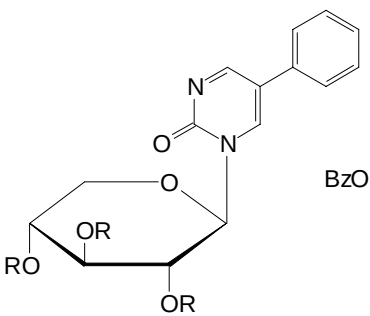
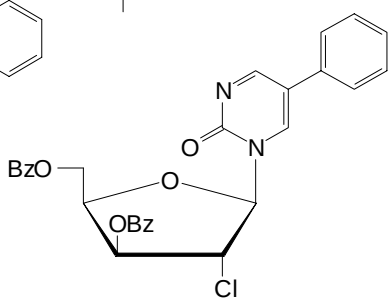


	R^1	R^2	R^3
19	Bz	Bz	Ac
20	Bz	Bz	Bz
22	H	H	H
24	Bz	Bz	H
29	Bz	Bz	Ms



	R
21	Bz
23	H



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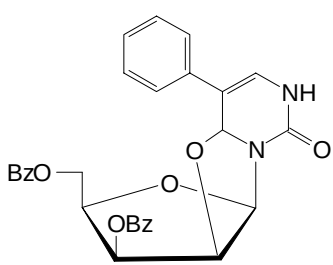

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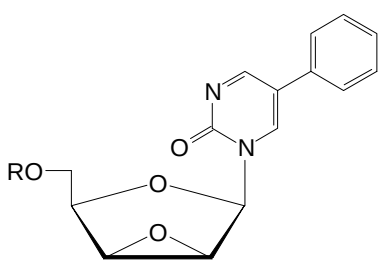
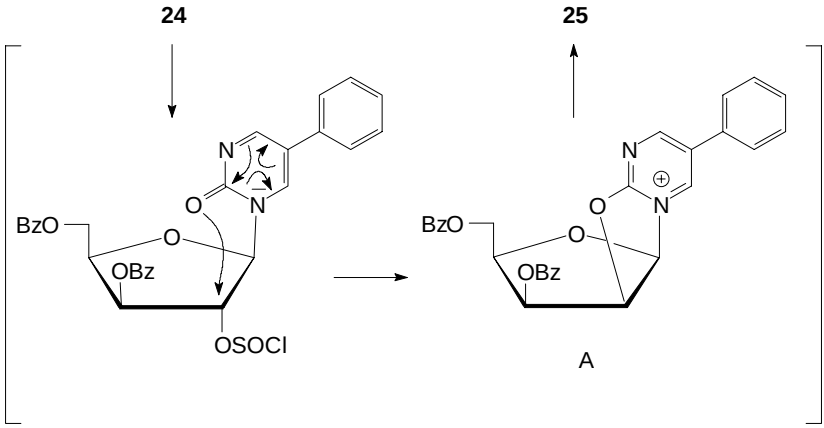


	R
27	Bz
28	H

together with this product we isolated a small amount of 2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl derivative **20** and 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl derivative **21**. The protected nucleosides **19** and **20** were converted into the free β-D-xylofuranosyl derivative **22** by reaction with methanolic ammonia. In the same way we also prepared free β-D-xylopyranosyl derivative **23** from tri-*O*-benzoyl derivative **21**. Deacetylation of compound **19** with hydrogen chloride in dioxane gave 1-(3,5-di-*O*-benzoyl-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**24**) in high yield. This compound was reacted with thionyl chloride in acetonitrile at 75 °C to give the desired 2′-chloro-2′-deoxynucleoside **25**. The reaction apparently proceeds via the 2′-*O*-chlorosulfinate which on nucleophilic attack by the carbonyl oxygen of the base gives rise to non-isolable pyrimidinium intermediate **A** (Scheme 2); analogously as in pyrimidine anhydronucleosides, the 2′,O^2 bond in the intermediate is cleaved with hydrogen chloride under formation of chloro derivative **25**. During the workup of the reaction mixture the pyrimidine base is attacked in the position 2 with water or hydroxyl anion to give the *lyxo* derivative. The cleavage of the anhydro bond in pyrimidine cyclonucleosides by alkali metal hydroxides proceeds in the same manner, however, the pyrimidinium derivative is much more reactive. Also in this case, there is a marked propensity of 2-pyrimidine analogs to add hydroxyl in the position "up" of the pentafuranose ring to the 5,6-double bond of the base. The reaction mixture afforded no *lyxo* derivative but only compound **26**. When the reaction was carried out at room temperature and for a relatively short time (6–7 h) in hexamethylphosphoramide, the cyclo derivative **26** was the principal product.

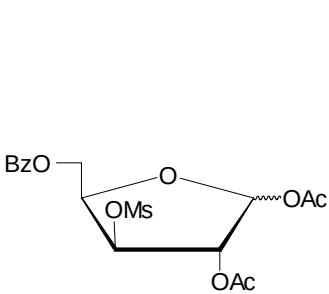
Heating of chloro derivative **25** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dimethylformamide in the presence of a catalytic amount of methanol afforded the *lyxo*-epoxide **27** which by reaction with methanolic ammonia was converted into free 1-(2,3-anhydro-β-D-lyxofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**28**). An alternative



SCHEME 2

preparation of this epoxide started from the 3′-*O*-mesyl derivative **29**, prepared by reaction of compound **24** with mesyl chloride in pyridine; the closure of the epoxide ring was realized by reaction with methanolic ammonia under simultaneous removal of the benzoyl group. The epoxide **28** was thus prepared from the mesylate **29** in one step and in high yield (higher than 80%).

Nucleosidation reaction of silyl derivative **3** with 1,2-di-*O*-acetyl-5-*O*-benzoyl-3-*O*-methanesulfonyl-D-xylofuranose (**30**) afforded the nucleoside **31**. The starting sugar was prepared from 5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-xylofuranose[14] by mesylation and subsequent acetolysis in a mixture of acetic anhydride, acetic acid and sulfuric acid. Originally, we intended to utilize 3′-*O*-mesylxylofuranoside **31** for the synthesis of 3′-substituted 2′,3′-dideoxy derivatives because the mesyl functionality in position 3′ can be easily substituted with inversion of configuration. It appeared, however, that such syntheses encounter deoxygenation in position 2′. Introduction of a halogen atom into position 2′ and its subsequent reduction invariably proceeds with simultaneous attack of the pyrimidinone ring. The easy reduction of this system under conditions of catalytic hydrogenation as well as radical deoxygenations with tributylstannane[15] is known. On the other hand, some mild reducing agents, such as tris(trimethylsilyl)silane with azobis(isobutyronitrile) (AIBN), do not reduce the pyrimidinone system[16]. We tried to reduce compound **25** with dimethyl phosphite under catalysis with AIBN or dibenzoyl peroxide[17]; however, in both cases the base was also reduced.



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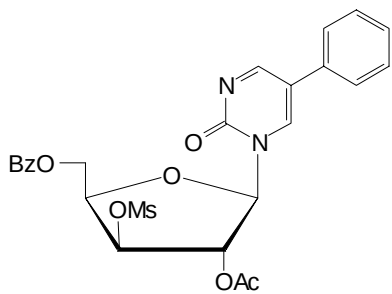

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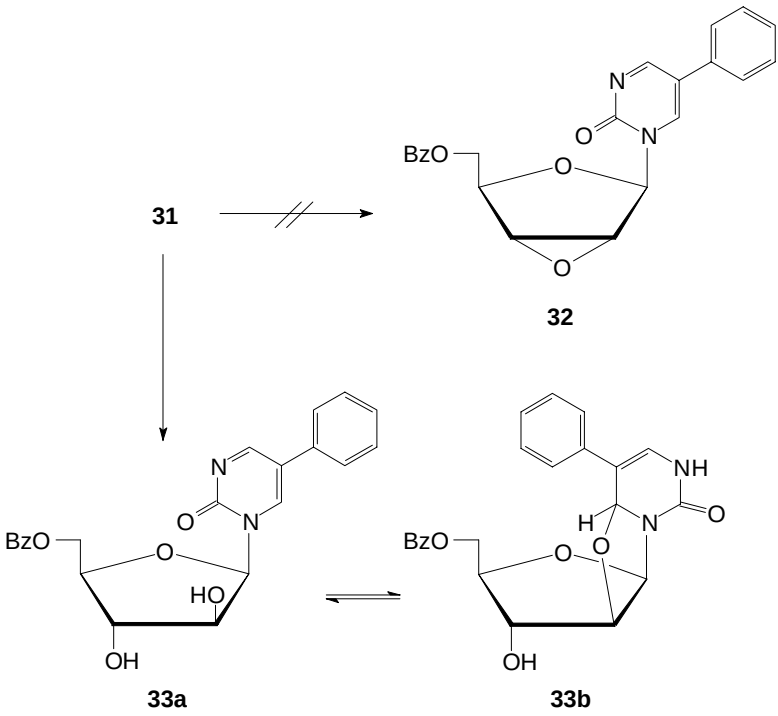
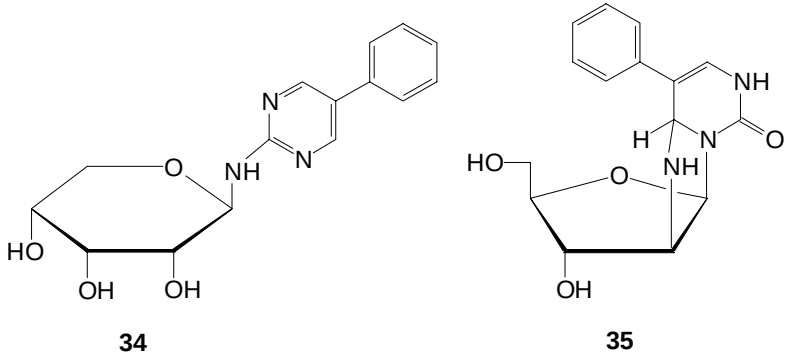
Reaction of the 3′-*O*-mesyl derivative **31** with DBU under conditions similar to those used for the preparation of epoxide **28** afforded, instead of the expected *ribo*-epoxide **32**, an equilibrium mixture of 5′-*O*-benzoylated arabinofuranosyl nucleoside **33a** and its 2′,6-anhydro derivative **33b** (Scheme 3). The reaction also gave rise to a chromatographically more mobile intermediate (probably **32**) which, however, could not be isolated. Obviously, the *ribo*-epoxide **32** also in this case gave the pyrimidinium intermediate. This was cleaved to the arabino derivative **33a** which then gave rise to the tricyclic analogue **33b**.

Attempts to obtain the free arabinofuranosyl derivative **33a** by reaction with methanolic ammonia resulted in total destruction of the pyrimidinone ring and from the complex reaction mixture we were able to isolate and characterize only compounds **34** and **35**.



SCHEME 3

The structure of the studied compounds was verified by their ^{1}H and ^{13}C NMR spectra. The individual carbon atoms were assigned on the basis of J-modulated spectra ("attached proton test pulse sequence", ref.[18]), enabling discrimination of the C, CH,



CH_2 and CH_3 type signals. The observed values of the NMR parameters are in accord with the literature data[19–22] for pentofuranose and pentopyranose derivatives.

In accord with the suggested structure of compound **7**, its ^{1}H NMR spectrum exhibited signals of two furanose rings one of which (sugar moiety A) does not contain the 5′-OH group and is characterized by small coupling constants $J(1',2')$ and $J(5',4')$ and in the ^{13}C NMR spectrum by a downfield shift (about 9 ppm) of the C-5′ signal. Due to the different structure of the base there are marked upfield shifts of the H-4 and H-6 proton signals (about 2.0 and 3.0 ppm, respectively) as well as C-4 and C-6 carbon signals (about 40 and 60 ppm, respectively). These differences correspond to the 5′,O^6-cyclo derivative structure[7]. Analogous results were obtained with the 2′,O^6-cyclonucleosides **26** and **33b**, where we confirmed identical structure of the base and found a downfield shift of the C-2′ carbon signal. The above structural conclusions were also confirmed by ^{1}H,^{13}C-heterocorrelated 2D NMR experiments.

The cytostatic activity of the free nucleoside analogs was tested on L1210, L929 and HeLa cell cultures. None of the studied compounds was active in these systems[23].

EXPERIMENTAL

Unless stated otherwise, solutions were evaporated at 40 °C/2 kPa and compounds were dried over phosphorus pentoxide at 13 Pa. Thin-layer chromatography was carried out on Silufol UV 254 sheets (Kavalier, Czech Republic). Compounds were detected by UV light at 254 nm. Preparative column chromatography was performed on silica gel (30–60 μm, Service Laboratories of the Institute). NMR spectra were measured on Varian UNITY-200 (^{1}H at 200 MHz) and Varian UNITY-500 (^{1}H at 500 MHz and ^{13}C at 125.7 MHz) in hexadeuteriodimethyl sulfoxide. Chemical shifts of protons were referenced to tetramethylsilane as internal standard whereas the carbon shifts to the solvent signal ($\delta(CD_3SOCD_3)$ = 39.7 ppm). Mass spectra were measured on a ZAB-EQ (VG Analytical) spectrometer by the FAB method (Xe, 8 kV) using glycerol (G) or thioglycerol (TG) as matrix.

5-Phenyl-2(1*H*)-pyrimidinone (**3**)

Methanolic sodium methoxide (1 M, 480 ml) was added to a suspension of 2-phenyltrimethinium perchlorate (**1**; 60.55 g, 200 mmol) and dry thiourea (20 g, 264 mmol) in absolute ethanol (400 ml). The mixture was stirred at room temperature for 30 min and then refluxed for 2 h. After cooling, the obtained solution was neutralized with acetic acid (precipitate formation) and the solvent was evaporated. Water (800 ml) was added, the solid was collected, washed with water and air-dried. Yield 37 g (98%) of 5-phenyl-2-mercaptopyrimidine (**2**).

This product (37 g, 197 mmol) was slurried in water (150 ml) and chloroacetic acid (20.8 g, 220 mmol) was added. After reflux for 2 h, 36% hydrochloric acid (60 ml) was added and reflux was continued for another 5 h. Azeotropic (20.2%) hydrochloric acid (1.15 l) was then added and the mixture was refluxed for 1 h. After cooling, the mixture was taken down and the residue codistilled with water (2 × 250 ml). Water (300 ml) was added to the residue, the mixture was neutralized with aqueous ammonia to pH 6 and the suspension was set aside in a refrigerator overnight. The deposited product was collected, washed with water, dissolved in hot ethanol and treated with charcoal. After filtration, the filtrate was concentrated and the residue crystallized from ethanol to give 20.2 g of compound **3** (60% from **2**). For $C_{10}H_8N_2O$ (172.2) calculated: 69.76% C, 4.68% H, 16.27% N; found: 69.49% C, 4.72% H, 16.07% N. ^{1}H NMR spectrum: 7.28–7.50 m, 3 H and 7.56–7.69 m, 2 H (H-arom.); 8.61 s, 2 H (H-4, H-6); 12.24

br s, 1 H (NH). ^{13}C NMR spectrum: 116.66 (C-5); 125.58, 2 C, 127.47, 129.19, 2 C and 133.67 (C-arom.); 155.0 br, 2 C (C-4 and C-6); 156.40 (C-2).

1-(2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl)-5-phenyl-2(1*H*)pyrimidinone (**5**)

A. A catalytic amount of ammonium sulfate was added to a suspension of compound **3** (1 g, 5.81 mmol) in hexamethyldisilazane and the mixture was heated at 150 °C to dissolution and then for another hour. After cooling, the solution was taken down and the residue was codistilled with xylene (2 × 25 ml). The obtained 5-phenyl-2-trimethylsilyloxypyrimidine (**4**) was added to a solution of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribose (2.93 g, 5.81 mmol) in 1,2-dichloroethane (30 ml). Tin tetrachloride (1 ml, 8.5 mmol) was added and the reaction mixture was stirred at room temperature for 4 h under exclusion of moisture. The reaction mixture was diluted with chloroform (100 ml) and poured into saturated solution of sodium hydrogen carbonate (250 ml). The formed emulsion was filtered through Celite, the organic layer was separated and washed with saturated solution of sodium hydrogen carbonate (3 × 150 ml). The combined organic extracts were dried over magnesium sulfate, the solvent was evaporated and the residue was chromatographed on silica gel (500 ml) in toluene–ethyl acetate (2 : 1). A side product (R_F 0.80) was eluted first, followed by the product **5** (R_F 0.35); yield 1.53 g (43%), m.p. 189.5 °C (toluene–ether). For $C_{36}H_{28}N_2O_8$ (616.6) calculated: 70.12% C, 4.58% H, 4.54% N; found: 69.54% C, 4.62% H, 4.15% N. ^{1}H NMR spectrum: 4.72 dd, 1 H, *J*(5′a,4′) = 5.4, *J*(gem) = 12.2 (H-5′a); 4.79 dd, 1 H, *J*(5′b,4′) = 3.4 (H-5′b); 4.89 td, 1 H (H-4′); 6.09 t, 1 H, *J*(3′,2′) = *J*(3′,4′) = 6.3 (H-3′); 6.11 dd, 1 H, *J*(2′,1′) = 3.0 (H-2′); 6.33 d, 1 H (H-1′); 7.30–7.50 m, 9 H, 7.55–7.70 m, 5 H, 7.90–8.00 m, 6 H (H-arom.); 8.60 d, 1 H and 9.07 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 63.75 (C-5′); 70.69 (C-3′); 74.12 (C-2′); 79.78 (C-4′); 92.66 (C-1′); 117.33 (C-5); 125.77, 2 C, 127.82 and 128.74–134.11, 21 C (C-arom.); 143.32 (C-6); 154.18 (C-2); 164.78, 2 C and 165.72 (C=O); 166.46 (C-4).

B. Tin tetrachloride (1 ml, 8.5 mmol) was added to a mixture of silyl derivative **4** (prepared from 1 g of compound **3** according to procedure *A*), 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribose (2.93 g, 5.81 mmol) and acetonitrile (30 ml) and the resulting solution was stirred at ambient temperature for 12 h. The workup was the same as described in procedure *A*. Yield 1.54 g (43%) of compound **5**.

C. To a mixture of silyl derivative **4**, 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribose (same amounts as in procedure *A*) and acetonitrile (50 ml) was added trimethylsilyl trifluoromethanesulfonate (1.6 ml, 8.5 mmol). The reaction mixture was stirred at room temperature for 12 h and worked up as described for procedure *A*. Yield 1.25 g (35%) of compound **5**.

5-Phenyl-1-(β-D-ribofuranosyl)-2(1*H*)-pyrimidinone (**6**)

Benzoyl derivative **5** (2.25 g, 3.65 mmol) was stirred with methanolic ammonia (100 ml) for 65 h at room temperature. After evaporation, the residue was mixed with light petroleum–ether (1 : 1, 100 ml), the mixture was set aside for 1 h and then decanted. The solid product was crystallized from methanol–ethanol (1 : 1) to give crystalline product **6** (626 mg, 56%), m.p. 188–191 °C. Further portion was obtained from the mother liquors by evaporation and chromatography on silica gel in ethyl acetate–acetone–ethanol–water (18 : 3 : 2 : 2), R_F 0.50. This afforded another 100 mg (9%) of compound **6**. For $C_{15}H_{16}N_2O_5$ (304.3) calculated: 59.20% C, 5.30% H, 9.21% N; found: 58.55% C, 5.35% H, 8.44% N. Mass spectrum (FAB, G + dimethyl sulfoxide): 305 (M^+ + H). ^{1}H NMR spectrum: 3.68 ddd, 1 H, *J*(5′a,4′) = 2.0, *J*(5′a,OH) = 4.4, *J*(gem) = 12.2 (H-5′a); 3.88 ddd, 1 H, *J*(5′b,4′) = 2.4, *J*(5′b,OH) = 4.6 (H-5′b); 4.00 dt, 1 H, *J*(4′,3′) = 7.6 (H-4′); 4.06 td, 1 H, *J*(2′,1′) = 1.7, *J*(2′,OH) = *J*(2′,3′) = 4.6 (H-2′); 4.10 ddd, 1 H (H-3′); 5.04 d, 1 H, *J*(OH,3′) = 6.6 (3′-OH); 5.50 t, 1 H, *J*(OH,5′) = 4.5 (5′-OH); 5.69 d, 1 H, *J*(OH,2′) = 4.6 (2′-OH); 5.80 d, 1 H (H-1′); 7.34 t, 1 H, 7.43 t, 2 H, 7.62 d, 2 H (H-arom.); 8.99 d, 1 H and 9.14 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 59.03 (C-5′); 67.72 (C-3′); 74.94

(C-2′); 83.98 (C-4′); 91.44 (C-1′); 116.72 (C-5); 125.43, 2 C, 127.52, 129.26, 2 C and 133.62 (C-arom.); 141.56 (C-6); 154.41 (C-2); 164.59 (C-4).

5′,O^6-Cyclo-5-phenyl-1,3-bis(β-D-ribofuranosyl)-2(1*H*,3*H*)-5,6-dihydropyrimidinone (**7**)

The chromatographically more mobile side product (2.06 g) from the preparation of compound **5** was stirred with methanolic ammonia (100 ml) for 72 h at room temperature. After evaporation of the solvent, the residue was mixed with ether (100 ml) and the mixture was set aside for 1 h. The ethereal layer was discarded and the solid residue was crystallized from ethanol. Yield 610 mg of pure crystalline compound **7**. For $C_{20}H_{24}N_2O_9$ (436.4) calculated: 55.04% C, 5.54% H, 6.42% N; found: 54.77% C, 5.52% H, 6.26% N. Mass spectrum (FAB, G + methanol): 437 (M^+ + H). ^{1}H NMR spectrum, sugar part A: 3.69 br d, 1 H, J(5′a,4′) ≥ 0, J(gem) = 12.4 (H-5′a); 3.75 dd, 1 H, J(5′b,4′) = 2.2 (H-5′b); 4.10 td, 1 H, J(3′,2′) = 6.1, J(3′,4′) = 2.2 (H-3′); 4.135 br t, 1 H (H-2′); 4.31 br t, 1 H (H-4′); 5.02 d, 1 H, J(OH,3′) = 5.9 (3′-OH); 5.25 d, 1 H, J(OH,2′) = 5.1 (2′-OH); 5.51 br s, 1 H, J(1′,2′) ≥ 0 (H-1′); sugar part B: 3.56 ddd, 1 H, J(5′a,4) = 3.4, J(5′a,OH) = 5.0, J(gem) = 11.7 (H-5′a); 3.64 ddd, 1 H, J(5′b,4′) = 3.2 (H-5′b); 3.79 br q, 1 H (H-4′); 3.97 dt, 1 H, J(3′,2′) = 5.0, J(3′,4′) = 3.6 (H-3′); 4.05 q, 1 H (H-2′); 5.00 d, 1 H, J(OH,3′) = 4.6 (3′-OH); 5.12 t, 1 H, J(OH,5′) = 5.0 (5′-OH); 5.16 d, 1 H, J(OH,2′) = 6.1 (2′-OH); 5.82 d, 1 H, J(1′,2′) = 6.1 (H-1′); base: 7.23 d, 1 H, J(4,6) = 1.4 (H-4); 7.20–7.40 m, 5 H (H-arom.); 5.99 d, 1 H (H-6). ^{13}C NMR spectrum: 61.48 (C-5′B); 70.34 (C-5′A); 70.49 (C-3′B); 71.13 (C-3′A); 72.54 (C-2′B); 76.62 (C-2′A); 83.07 (C-6); 84.41 (C-4′B); 87.50 (C-1′B); 89.54 (C-4′A); 94.42 (C-1′A); 109.94 (C-5); 123.05 (C-4), 124.78, 2 C, 126.45, 128.74, 2 C and 136.36 (C-arom.); 148.64 (C-2).

1-(2-Deoxy-3,5-di-*O*-*p*-toluoyl-β-D-ribofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**10**) and 1-(2-Deoxy-3,5-di-*O*-*p*-toluoyl-α-D-ribofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**11**)

Trimethylsilyl trifluoromethanesulfonate (1.6 ml, 8.5 mmol) was added at –20 °C to a mixture of silyl derivative **4** (prepared from compound **3**; 1 g, 5.81 mmol), methyl 2-deoxy-3,5-di-*O*-*p*-toluoyl-D-ribofuranoside (**8**; 2.23 g, 5.81 mmol) and acetonitrile (50 ml). The solution was stirred at –20 °C for 20 min and then poured into saturated solution of sodium hydrogen carbonate (300 ml). The product was taken up in chloroform (200 ml), the organic phase was dried over magnesium sulfate and the solvent was evaporated. Chromatography on silica gel (750 ml) in ethyl acetate–toluene (2 : 1) afforded the β-anomer **10** (R_F 0.49) as the first fraction (1.22 g, 40%); white foam. For $C_{31}H_{28}N_2O_6$ (524.6) calculated: 70.98% C, 5.38% H, 5.34% N; found: 70.20% C, 5.23% H, 5.09% N. ^{1}H NMR spectrum: 2.40 s, 3 H and 2.34 s, 3 H (CH_3); 2.66 dt, 1 H, J(2′a,3′) = 6.8, J(gem) = 14.4 (H-2′a); 2.86 ddd, 1 H, J(2′b,3′) = 2.4, J(2′b,1′) = 6.3 (H-2′b); 4.64 dd, 1 H, J(5′a,4′) = 6.6, J(gem) = 12.7 (H-5′a); 4.71 dd, 1 H, J(5′b,4′) = 3.4 (H-5′b); 4.72 br pent, 1 H (H-4′); 5.65 dt, 1 H, J(3′,2′b) = J(3′,4′) = 2.4 (H-3′); 6.31 dd, 1 H, J(1′,2′a) = 7.3, J(1′,2′b) = 6.3 (H-1′); 7.21 d, 2 H, 7.32 m, 3 H, 7.37 d, 2 H, 7.47 d, 2 H, 7.78 d, 2 H and 7.94 d, 2 H (H-arom.); 8.38 d, 1 H and 8.97 d, 1 H, J(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 21.32 and 21.40 (CH_3); 38.08 (C-2′); 64.37 (C-5′); 75.10 (C-3′); 83.01 (C-1′); 88.32 (C-4′); 117.15 (C-5); 125.65–129.65, 15 C and 133.31 (C-arom.); 140.58 (C-6); 144.01 and 144.28 (C-arom.); 154.15 (C-2); 165.36 (C-4); 165.46 and 165.71 (C=O).

Further chromatography afforded 0.56 g (18%) of amorphous α-anomer **11** (R_F 0.40). For $C_{31}H_{28}N_2O_6$ (524.6) calculated: 70.98% C, 5.38% H, 5.34% N; found: 69.89% C, 5.42% H, 5.26% N. ^{1}H NMR spectrum: 2.24 s, 3 H and 2.40 s, 3 H (CH_3); 2.55 dt, 1 H, J(2′a,1′) = J(2′a,3′) = 1.0, J(gem) = 14.4 (H-2′a); 3.05 dt, 1 H (H-2′b); 4.51 d, 2 H, J(5′,4′) = 4.9 (2 × H-5′); 5.37 br t, 1 H (H-4′); 5.59 br d, 1 H, J(3′,2′b) = 5.9, J(3′,4′) = 1.0 (H-3′); 6.26 dd, 1 H, J(1′,2′a) = 1.0, J(1′,2′b) = 6.8 (H-1′); 6.96 d, 2 H, 7.30–7.40 m, 5 H, 7.50 d, 2 H, 7.56 d, 2 H, 7.94 d, 2 H (H-arom.); 8.50 d, 1 H and 8.98 d, 1 H, J(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 21.24 and 21.37 (CH_3); 38.19 (C-2′); 64.15 (C-5′); 74.87 (C-3′);

85.11 (C-1′); 89.46 (C- 4′); 116.98 (C-5); 125.97–129.60, 15 C and 133.42 (C-arom.); 140.60 (C-6); 143.92 and 144.14 (C-arom.); 154.35 (C-2); 164.94 (C-4); 164.99 and 165.66 (C=O).

5-Phenyl-1-(2-deoxy-β-D-ribofuranosyl)-2(1*H*)-pyrimidinone (**12**)

A solution of compound **10** (2.2 g, 4.19 mmol) in methanolic ammonia (100 ml) was stirred at room temperature for 24 h. After evaporation of the solvent, the residue was crystallized from ethanol, yield 884 mg (73%) of compound **12**, m.p. 176–178 °C. For $C_{15}H_{16}N_2O_4$ (288.3) calculated: 62.49% C, 5.59% H, 9.72% N; found: 62.26% C, 5.58% H, 9.71% N. ^{1}H NMR spectrum: 2.20 dt, 1 H, *J*(2′a,1′) = *J*(2′a,3′) = 5.8, *J*(gem) = 13.4 (H-2′a); 2.42 ddd, 1 H, *J*(2′b,1′) = 6.1, *J*(2′b,3′) = 5.4 (H-2′b); 3.65 ddd, 1 H, *J*(5′a,4′) = 3.2, *J*(5′a,OH) = 4.9, *J*(gem) = 12.0 (H-5′a); 3.76 ddd, 1 H, *J*(5′b,4′) = 3.2, *J*(5′b,OH) = 4.9, *J*(gem) = 12.0 (H-5′b); 3.93 br q, 1 H (H-4′); 4.30 pent, 1 H (H-3′); 5.32 t, 1 H, *J*(OH,5′) = 4.9 (5′-OH); 5.32 d, 1 H, *J*(OH,3′) = 4.6 (3′- OH); 6.14 t, 1 H, *J*(1′,2′a) = *J*(1′,2′b) = 5.9 (H-1′); 7.34 t, 1 H, 7.44 t, 2 H and 7.61 d, 2 H (H-arom.); 8.94 d, 1 H and 8.98 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 41.35 (C-2′); 60.35 (C-5′); 69.10 (C-3′); 87.23 (C-1′); 88.19 (C-4′); 116.71 (C-5); 125.47, 2 C, 127.55, 129.28, 2 C and 133.69 (C-arom.); 141.25 (C-6); 154.30 (C-2); 164.48 (C-4).

5-Phenyl-1-(2-deoxy-α-D-ribofuranosyl)-2(1*H*)-pyrimidinone (**13**)

A solution of compound **11** (3.4 g, 6.48 mmol) in methanolic ammonia (100 ml) was stirred at room temperature for 24 h. After evaporation, the residue was crystallized from ethyl acetate–acetone–ethanol–water (18 : 3 : 1 : 1) mixture. Yield 1.4 g (73%), m.p. 103–105 °C. For $C_{15}H_{16}N_2O_4$. 1/2 H_2O (297.3) calculated: 60.06% C, 5.76% H, 9.42% N; found: 59.99% C, 5.77% H, 9.12% N. ^{1}H NMR spectrum: 2.07 dt, 1 H, *J*(2′a,1′) = *J*(2′a,3′) = 1.5, *J*(gem) = 12.7 (H-2′a); 2.63 ddd, 1 H, *J*(2′b,1′) = 7.3, *J*(2′b,3′) = 5.4 (H-2′b); 3.43 dd, 1 H, *J*(5′a,4′) = 5.4, *J*(gem) = 11.7 (H-5′a); 3.47 dd, 1 H, *J*(5′b,4′) = 4.4 (H-5′b); 4.27 dt, 1 H, *J*(3′,2′a) = *J*(3′,4′) = 1.0, *J*(3′,2′b) = 5.4 (H-3′); 4.44 br t, 1 H, *J*(4′,3′) ≤ 1.0, *J*(4′,5′a) ≈ *J*(4′,5′b) = 4.8 (H-4′); 4.90 br, 1 H and 5.20 br, 1 H (OH); 6.11 dd, 1 H, *J*(1′,2′a) = 1.5, *J*(1′,2′b) = 7.3 (H-1′); 7.36 t, 1 H, 7.46 t, 2 H and 7.58 d, 2 H (H-arom.); 8.45 d, 1 H and 8.95 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 40.67 (C-2′); 61.92 (C-5′); 70.96 (C-3′); 89.15 (C-1′); 91.07 (C-4′); 116.24 (C-5); 125.58, 2 C, 127.61, 129.36, 2 C and 133.88 (C-arom.); 141.91 (C-6); 154.44 (C-2); 164.40 (C-4).

1-(5-*O*-*tert*-Butyldiphenylsilyl-2-deoxy-α-D-ribofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**14**)

Prior to the reaction, compound **13** (1.82 g, 6.31 mmol) was codistilled with dry pyridine (30 ml). The residue was dissolved in dimethylformamide (30 ml), and imidazole (859 mg, 12.6 mmol), followed by *tert*-butyldiphenylsilyl chloride (1.64 ml, 6.31 mmol), was added. The reaction mixture was stirred at room temperature for 24 h, mixed with ethanol (1 ml) and the solvent was evaporated. The residue was twice codistilled with xylene. The deposited crystalline imidazole hydrochloride was removed by filtration, the filtrate was concentrated and the residue purified by chromatography on silica gel (400 ml) in toluene–acetone (1 : 1), R_F 0.33. Yield 3.04 g (92%) of white amorphous compound **14**. For $C_{31}H_{34}N_2O_4Si$ (526.7) calculated: 70.69% C, 6.51% H, 5.32% N; found: 70.33% C, 6.54% H, 5.23% N. ^{1}H NMR spectrum: 1.01 s, 9 H (CH_3); 2.12 br d, 1 H, *J*(gem) = 14.0 (H-2′a); 2.69 m, 1 H (H-2′b); 3.71 d, 2 H, *J*(5′,4′) = 4.0 (H-5′); 4.39 m, 1 H (H-4′); 4.58 t, 1 H, *J*(3′,4′) = 2.4 (H-3′); 5.31 d, 1 H, *J*(OH,3′) = 2.4 (OH); 6.15 d, 1 H, *J*(1′,2′b) = 6.3 (H-1′); 7.28–7.75 m, 15 H (H-arom.); 8.45 d, 1 H and 8.96 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4).

1-(5-*O*-*tert*-Butyldiphenylsilyl-2-deoxy-3-*O*-methanesulfonyl-α-D-ribofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**15**)

Methanesulfonyl chloride (0.21 ml, 2.78 mmol) was added at 0 °C to a solution of compound **14** (1.2 g, 2.28 mmol) in pyridine (15 ml) and the mixture was stirred overnight (about 16 h) at room temperature. The reaction was quenched with methanol (2 ml) and water (2 ml) and the solvent was evaporated. The residue was codistilled successively with ethanol (30 ml) and toluene (30 ml) and then partitioned between ethyl acetate (150 ml) and 1% hydrochloric acid (50 ml). The organic layer was washed with water (2 × 100 ml), dried over magnesium sulfate and taken down. The residue was chromatographed on silica gel (350 ml) in toluene–acetone (3 : 2), R_F 0.40. Yield 1.12 g (81%) of mesyl derivative **15**, white foam. For $C_{32}H_{36}N_2O_6SSi$ (604.8) calculated: 63.55% C, 6.00% H, 4.63% N, 5.30% S; found: 63.71% C, 6.05% H, 4.83% N, 5.09% S. ^{1}H NMR spectrum: 1.03 s, 9 H (CH_3); 2.53 br d, 1 H, *J*(gem) = 16.0 (H-2′a); 3.00 ddd, 1 H (H-2′b); 3.19 s, 3 H (CH_3); 3.80 d, 2 H, *J*(5′,4′) = 3.7 (H-5′); 5.06 t, 1 H (H-4′); 5.42 d, 1 H, *J*(3′,2′b) = 5.2 (H-3′); 6.20 d, 1 H, *J*(1′,2′b) = 5.8 (H-1′); 7.33–7.74 m, 15 H (H-arom.); 8.34 d, 1 H and 8.99 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4).

1-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-dideoxy-α-D-*glycero*-pent-2-enofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**16**)

To a solution of compound **15** (605 mg, 1 mmol) in acetonitrile was added DBU (0.22 ml, 1.5 mmol) and the solution was heated at 70 °C for 12 h. The reaction mixture was neutralized with acetic acid and taken down. The residue was partitioned between ethyl acetate and water (100 ml each) and the organic layer was dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel (100 ml) in toluene–acetone–triethylamine (25 : 8 : 1), R_F 0.45, to give 460 mg (90%) of pure amorphous compound **16**. For $C_{31}H_{32}N_2O_3Si$ (508.7) calculated: 73.20% C, 6.34% H, 5.51% N; found: 73.11% C, 6.38% H, 5.42% N. ^{1}H NMR spectrum: 1.00 s, 9 H (CH_3); 3.77 dd, 1 H, *J*(5′a,4′) = 4.0, *J*(gem) = 11.0 (H-5′a); 3.86 dd, 1 H, *J*(5′b,4′) = 3.7 (H-5′b); 5.47 m, 1 H (H-4′); 6.17 dt, 1 H *J*(3′,4′) = 1.8, *J*(3′,2′) = 6.1 (H-3′); 6.50 dt, 1 H, *J*(2′,3′) = 6.1, *J*(2′,4′) = 1.5 (H-2′); 6.99 dt, 1 H, *J*(1′,4′) = 5.2, *J*(1′,2′) = *J*(1′,3′) = 1.5 (H-1′); 7.30–7.73 m, 15 H (H-arom.); 8.07 d, 1 H and 8.99 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4).

1-(2,3-Dideoxy-α-D-*glycero*-pent-2-enofuranosyl)-5-phenyl-2(1*H*)pyrimidinone (**17**)

To a solution of compound **16** (440 mg, 0.86 mmol) in tetrahydrofuran (50 ml) was added 1 M tetrabutylammonium fluoride in tetrahydrofuran (0.86 ml) and the solution was stirred for 2 h at room temperature. During the reaction the mixture was kept neutral by dropwise addition of acetic acid. After evaporation of the solvent, the residue was chromatographed on silica gel in ethyl acetate–ethanol–triethylamine (25 : 2 : 1), R_F 0.33. Yield 147 mg (63%) of white foam. ^{1}H NMR spectrum: 3.55 m, 2 H (H-5′); 4.90 t, 1 H, *J*(OH,5′) = 6.0 (OH); 5.33 m, 1 H (H-4′); 6.11 d, 1 H, *J*(3′,2′) = 6.1 (H-3′); 6.46 d, 1 H, *J*(2′,3′) = 6.1 (H-2′); 6.93 d, 1 H, *J*(1′,4′) = 4.9 (H-1′); 7.26–7.72 m, 5 H (H-arom.); 8.04 d, 1 H and 8.97 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4).

Reaction of Compound **12** with *tert*-Butyldiphenylsilyl Chloride

Nucleoside **12** (100 mg, 0.35 mmol) was codistilled with pyridine (20 ml) and then dissolved in dimethylformamide (1.6 ml). Imidazole (48 mg, 0.7 mmol) and *tert*-butyldiphenylsilyl chloride (0.1 ml, 0.38 mmol) were added and the solution was stirred at room temperature overnight. After addition of ethanol (0.2 ml), the solution was taken down, the residue was codistilled with xylene and partitioned between ethyl acetate and water (50 ml each). The organic phase was dried over magnesium sulfate, the solvent was evaporated and the residue was chromatographed on silica gel (40 ml) in toluene–

ethyl acetate (2 : 1). First eluted was the 3′,5′-bis(*tert*-butyldiphenylsilyl) derivative, R_F 0.80 (70 mg, 26%), then the 3′-*O*-*tert*-butyldiphenylsilyl derivative, R_F 0.45 (20 mg, 11%), and finally the desired 5′-*O*-*tert*-butyldiphenylsilyl derivative, R_F 0.40 (74 mg, 40%) as a white foam. ^{1}H NMR spectrum: 0.96 s 9 H (CH_3); 2.20 ddd, 1 H, *J*(2′a,3′) = 6.1, *J*(2′a,1′) = 7.1, *J*(gem) = 13.2 (H-2′a); 2.51 ddd, 1 H, *J*(2′b,3′) = 2.9, *J*(2′b,1′) = 6.1 (H-2′b); 3.79 dd, 1 H, *J*(5′a,4′) = 5.1, *J*(gem) = 11.7 (H-5′a); 3.94 dd, 1 H, *J*(5′b,4′) = 3.2 (H-5′b); 4.08 dt, 1 H, *J*(4′,3′) = 3.0 (H-4′); 4.24 m, 1 H (H-3′); 5.37 d, 1 H, *J*(OH,3′) = 4.1 (OH); 6.16 br t, 1 H (H-1′); 7.25–7.48 and 7.54 m, 15 H (H-arom.); 8.39 d, 1 H and 8.95 d 1 H, *J*(4,6) = 3.4 (H-6 and H-4).

1-(2-*O*-Acetyl-3,5-di-*O*-benzoyl-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**19**)

The silyl derivative **4**, prepared from 5-phenyl-2(1*H*)-pyrimidinone (**3**; 12.54 g, 72.8 mmol) as described in the preparation of compound **5**, was added to a solution of 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-D-xylose (32.23 g, 72.8 mmol) in acetonitrile (500 ml). To this mixture was added tin tetrachloride (13 ml, 111 mmol). The reaction mixture was stirred at room temperature overnight, poured into saturated solution of sodium hydrogen carbonate (2 l) and shaken with ethyl acetate (2 l). The formed suspension was filtered through Celite, the organic layer in the filtrate was separated and washed with a solution of sodium hydrogen carbonate (2 × 750 ml). The organic phase was dried over magnesium sulfate, the solvent was evaporated and the residue chromatographed on silica gel (2.5 l).

Elution with ethyl acetate–toluene (1 : 1) afforded 1.313 g (3%) of 1-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**21**) as a white solid, R_F 0.43. For $C_{36}H_{28}N_2O_8$ (616.6) calculated: 70.12% C, 4.58% H, 4.54% N; found: 69.83% C, 4.72% H, 4.66% N. Mass spectrum (FAB, T + G, dimethyl sulfoxide): 617 (M^+ + H). ^{1}H NMR spectrum: 4.22 t, 1 H, *J*(5′a,4′) = *J*(gem) = 11.0 (H-5′a); 4.36 dd, 1 H, *J*(5′b,4′) = 5.8 (H-5′b); 5.81 br td, 1 H, Σ*J* = 25.3 (H-4′); 6.20 br t, 1 H, *J*(2′,3′) = 9.5 (H-2′); 6.23 br t, 1 H, *J*(3′,4′) = 8.5 (H-3′); 6.58 d, 1 H, *J*(1′,2′) = 8.6 (H-1′); 7.40–7.65 m, 12 H and 7.75–7.90 m, 8 H (H-arom.); 9.00 d, 1 H and 9.01 d, 1 H, *J*(4,6) = 3.35 (H-6 and H-4).

Further elution with ethyl acetate–toluene (1 : 1) afforded 1-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**20**; 820 mg, 2%) as a white foam, R_F 0.35. For $C_{36}H_{28}N_2O_8$ (616.6) calculated: 70.12% C, 4.58% H, 4.54% N; found: 69.80% C, 4.85% H, 4.86% N. Mass spectrum (FAB, T + G, dimethyl sulfoxide): 617 (M^+ + H). ^{1}H NMR spectrum: 4.74 dd, 1 H, *J*(4′,5′a) = 3.7, *J*(gem) = 12.2 (H-5′a); 4.96 dd, 1 H, *J*(4′5′b) = 7.0 (H-5′b); 5.13 m, 1 H (H-4′); 5.85 m, 1 H (H-2′); 5.91 dd, 1 H, *J*(3′,2′) = 1.2, *J*(3′,4′) = 3.7 (H-3′); 6.29 d, 1 H, *J*(1′,2′) = 1.8 (H-1′); 7.12–8.18 m, 20 H (H-arom.); 8.61 d, 1 H and 9.06 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 64.65 (C-5′); 68.96 (C-4′); 71.10 (C-2′); 73.17 (C-3′); 81.94 (C-1′); 117.51 (C-5); 125.88, 2 C, 128.02, 129.42, 14 C, 132.95, 133.98, 134.05 a 134.16 (C-arom.); 142.43 (C-6); 154.11 (C-2); 164.91, 165.13 and 165.33 (C=O); 166.52 (C-4).

Elution with ethyl acetate–toluene (3 : 1) finally gave 14.6 g (36%) of the product **19**, R_F 0.35, as a white foam. For $C_{31}H_{26}N_2O_8$ (554.6) calculated: 67.14% C, 4.73% H, 5.05% N; found: 66.94% C, 4.87% H, 5.14% N. ^{1}H NMR spectrum: 2.19 s, 3 H (CH_3); 4.69 dd, 1 H, *J*(5′a,4′) = 3.7, *J*(gem) = 12.0 (H-5′a); 4.91 dd, 1 H, *J*(5′b,4′) = 6.8 (H-5′b); 4.97 dt, 1 H (H-4′); 5.78 dd, 1 H, *J*(3′,2′) = 1.5, *J*(3′,4′) = 3.7 (H-3′); 5.80 t, 1 H (H-2′); 6.10 d, 1 H, *J*(1′,2′) = 1.7 (H-1′); 7.18 t, 2 H, 7.40 m, 5 H, 7.55 t, 1 H, 7.60 t, 1 H, 7.62 d, 2 H, 7.70 d, 2 H and 7.88 d, 2 H (H-arom.); 8.55 d, 1 H and 9.04 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 20.74 (CH_3); 61.78 (C-5′); 74.74 (C-3′); 79.04 (C-2′); 80.15 (C-4′); 90.67 (C-1′); 117.26 (C-5); 125.80, 2 C, 127.80, 128.40–129.40, 12 C, 133.22, 133.66 and 133.93 (C-arom.); 140.20 (C-6); 154.18 (C-2); 164.24 and 165.67 (C=O); 165.83 (C-4); 168.99 (C=O).

5-Phenyl-1-(β-D-xylofuranosyl)-2(1*H*)-pyrimidinone (**22**)

Compound **20** (600 mg, 0.97 mmol) was stirred with methanolic ammonia (20 ml) at room temperature for 48 h. The solvent was evaporated and the residue was crystallized from ethyl acetate–acetone–ethanol–water (18 : 3 : 2 : 1). Evaporation of the mother liquors and chromatography of the residue in the mentioned solvent system gave further amount of the product, R_F 0.41. Total yield 262 mg (89%) of crystalline compound **22**, m.p. 199.5–202 °C. For $C_{15}H_{16}N_2O_5$ (304.3) calculated: 59.20% C, 5.30% H, 9.21% N; found: 58.87% C, 5.26% H, 8.94% N. ^{1}H NMR spectrum: 3.84 t, 2 H J(5′,4′) = 5.8 (H-5′); 3.97 t, 1 H, J(3′,4′) = 3.1 (H-3′); 4.09 br d, 1 H (H-2′); 4.34 m, 1 H (H-4′); 4.91 t, 1 H, J(OH,5′) = 5.8 (OH); 5.35 d, 1 H, J(OH,3′) = 3.1 (OH); 5.71 s, 1 H (H-1′); 5.98 d, 1 H, J(2′,OH) = 4.3 (OH); 7.30–7.60 m, 5 H (H-arom.); 8.51 d, 1 H and 8.96 d, 1 H, J(4,6) = 3.4 (H-6 and H-4).

5-Phenyl-1-(β-D-xylopyranosyl)-2(1*H*)-pyrimidinone (**23**)

A suspension of compound **21** (1.3 g, 2.1 mmol) in methanolic ammonia (150 ml) was stirred at room temperature for 72 h. After evaporation of the solvent, the residue was adsorbed on silica gel (25 ml) and chromatographed on a silica gel column (100 ml) in ethyl acetate–acetone–ethanol–water (18 : 3 : 1 : 1), R_F 0.20. The chromatographically pure product **23** was crystallized from ethanol, yield 475 mg (74%), m.p. 225–227 °C. For $C_{15}H_{16}N_2O_5$ (304.3) calculated: 59.20% C, 5.30% H, 9.21% N; found: 58.80% C, 5.26% H, 9.11% N. ^{1}H NMR spectrum: 3.28 dd, 1 H, J(5′a,4′) = 10.4, J(gem) = 11.3 (H-5′a); 3.33 td, 1 H, J(3′,2′) = J(3′,4′) = 8.9, J(3′,OH) = 4.3 (H-3′); 3.55 ddt, 1 H (H-4′); 3.79 td, 1 H, J(2′,1′) = 9.4, J(2′,OH) = 5.8 (H-2′); 3.86 dd, 1 H, J(5′b,4′) = 5.5 (H-5′b); 5.14 d, 1 H, J(OH,4′) = 5.2 (4′-OH); 5.31 d, 1 H (3′-OH); 5.39 d, 1 H (2′-OH); 5.57 d, 1 H, J(1′,2′) = 9.4 (H-1′); 7.36 t, 1 H, 7.45 t, 2 H and 7.68 d, 2 H (H-arom.); 8.45 d, 1 H, 9.00 d, 1 H, J(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 69.04 (C-5′); 69.13 (C-4′); 71.20 (C-2′); 77.32 (C-3′); 85.64 (C-1′); 125.94, 2 C, 127.80, 129.16, 2 C and 133.20 (C-arom.); 142.36 (C-6); 154.82 (C-2); 165.69 (C-4).

1-(3,5-Di-*O*-benzoyl-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**24**)

Hydrochloric acid (36%, 0.8 ml) was added to a solution of compound **19** (1.14 g, 2.06 mmol) in dioxane (12 ml). The reaction mixture was stirred at room temperature for 48 h and then diluted with methanol to dissolution of the product. The solution was neutralized with triethylamine and the solvent evaporated. The residue was partitioned between water and ethyl acetate (130 ml each), the organic layer was dried over magnesium sulfate and the solvent was evaporated to give 878 mg (83%) of compound **24** as a white foam. ^{1}H NMR spectrum: 4.50 br d, 1 H, J(2′,OH) = 4.6 (H-2′); 4.69 dd, 1 H, J(5′a,4′) = 2.0, J(gem) = 12.0 (H-5′a); 5.02 m, 1 H (H-4′); 5.04 dd, 1 H, J(5′b, 4′) = 7.6 (H-5′b); 5.47 dd, 1 H, J(3′,2′) = 1.0, J(3′,4′) = 3.2 (H-3′); 5.86 br s, 1 H, J(1′,2′) ≤ 1 (H-1′); 6.68 d, 1 H (2′-OH); 7.05 t, 2 H, 7.40–7.55 m, 6 H, 7.70 m, 5 H and 7.95 d, 2 H (H-arom.); 8.62 d, 1 H and 8.99 d, 1 H, J(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 62.08 (C-5′); 77.43 (C-3′); 78.21 (C-2′); 80.73 (C-4′); 93.79 (C-1′); 116.78 (C-5); 125.60, 2 C, 127.74, 128.56–129.42, 12 C, 133.34, 133.69 and 133.77 (C-arom.); 140.04 (C-6); 154.36 (C-2); 164.42 (C=0); 165.12 (C-4); 165.83 (C=O).

1-(3,5-Di-*O*-benzoyl-2-chloro-2-deoxy-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**25**) and 2′,6-Anhydro-1-(3,5-di-*O*-benzoyl-β-D-lyxofuranosyl)-1,6-dihydro-5-phenyl-6-hydroxy-2(3*H*)-pyrimidinone (**26**)

Thionyl chloride (3 ml, 41 mmol) was added to a solution of compound **24** (5 g, 9.76 mmol) in acetonitrile (30 ml). The reaction mixture was heated at 75 °C for 6 h, cooled to room temperature, poured into saturated solution of sodium hydrogen carbonate (300 ml) and the product was taken up in ethyl acetate (500 ml). The organic layer was separated, again washed with a sodium hydrogen

carbonate solution (3 × 200 ml), dried over magnesium sulfate and the solvent was evaporated. Chromatography on silica gel (750 ml) in toluene–acetone (5 : 2) gave 3.3 g (64%) of the product **25**, R_F 0.37, as a yellowish foam. For $C_{29}H_{23}ClN_2O_6$ (531.0) calculated: 65.60% C, 4.37% H, 5.28% N, 6.68% Cl; found: 65.89% C, 4.56% H, 5.27% N, 6.73% Cl. Mass spectrum (FAB, T + G, dimethyl sulfoxide): 531 (M^+ + H). ^{1}H NMR spectrum: 4.74 dd, 1 H, *J*(5′a,4′) = 3.4, *J*(gem) = 12.0 (H-5′a); 5.06 br t, 1 H (H-2′); 5.08 dd, 1 H, *J*(5′b,4′) = 7.6 (H-5′b); 5.16 dt, 1 H (H-4′); 5.75 dd, 1 H, *J*(3′,2′) = 1.0, *J*(3′,4′) = 3.4 (H-3′); 6.19 d, 1 H, *J*(1′,2′) = 1.4 (H-1′); 7.11 t, 2 H, 7.40–7.55 m, 6 H, 7.60–7.70 m, 5 H and 7.98 d, 2 H (H-arom.); 8.57 d, 1 H and 9.02 d, 1 H, *J*(6,4) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 61.89 (C-5′); 61.97 (C-2′); 77.41 (C-3′); 80.34 (C-4′); 93.48 (C-1′); 117.02 (C-5); 125.69, 2 C, 127.82, 128.56–129.46, 12 C, 133.24, 133.73 and 133.85 (C-arom.); 139.47 (C-6); 154.25 (C-2); 164.14 (C=0); 165.60 (C-4); 165.79 (C=O).

Further elution afforded 2′,6-anhydro-1-(3,5-di-*O*-benzoyl-β-D-lyxofuranosyl)-1,6-dihydro-5-phenyl-6-hydroxy-2(3*H*)-pyrimidinone (**26**), R_F 0.36 (ethyl acetate–toluene, 3 : 1). Yield 1.25 g (25%) of white solid. Mass spectrum (FAB, T + G, methanol): 513 (M^+ + H). ^{1}H NMR spectrum: 4.48 dt, 1 H, *J*(4′,3′) = *J*(4′,5′b) = 4.4, *J*(4′,5′a) = 7.1 (H-4′); 4.72 dd, 1 H, *J*(5′a,4′) = 7.1, *J*(gem) = 11.7 (H-5′a); 4.77 dd, 1 H, *J*(5′b,4′) = 4.4 (H-5′b); 4.80 dd, 1 H, *J*(2′,1′) = 5.4, *J*(2′,3′) = 6.3 (H-2′); 5.67 dd, 1 H, *J*(3′,4′) = 4.4 (H-3′); 5.79 s, 1 H (H-6); 6.27 d, 1 H, *J*(1′,2′) = 5.4 (H-1′); 6.89 d, 1 H, *J*(NH,4) = 5.4 (H-4); 6.89–8.23 m, 15 H (H-arom.); 9.70 d, 1 H (NH). ^{13}C NMR spectrum: 62.57 (C-5′); 73.17 (C-3′); 76.00 (C-2′); 76.34 (C-4′); 86.54 (C-6); 90.16 (C-1′); 106.67 (C-5); 123.97, 2 C (C-arom.); 124.36 (C-4); 126.05, 127.96, 2 C, 128.97–129.80, 10 C, 133.69, 133.93 and 134.50 (C-arom.); 148.95 (C-2); 164.66 and 165.63 (C=O).

1-(2,3-Anhydro-β-D-lyxofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**28**)

A. DBU (1 ml) and methanol (0.3 ml) were added at 80 °C to a solution of compound **25** (2.35 g, 4.4 mmol) in dimethylformamide (30 ml). The reaction mixture was heated at 80 °C for 2 h, cooled, neutralized with acetic acid and the solvent was evaporated. The residue was codistilled with toluene (100 ml) and partitioned between ethyl acetate (200 ml) and water (150 ml). The organic layer was dried over magnesium sulfate, the solvent was evaporated and the remaining compound **27** was stirred with methanolic ammonia (100 ml) for 48 h at room temperature. After evaporation of the solvent, the product was chromatographed on silica gel (400 ml) in ethyl acetate–acetone–ethanol–water (36 : 6 : 1 : 1), R_F 0.20, to give 600 mg (48%) of compound **28** as a white foam. Mass spectrum (FAB): 287 (M^+ + H). ^{1}H NMR spectrum: 3.71 t, 2 H, *J*(5′,4′) = *J*(5′,OH) = 5.8 (H-5′); 4.11 dd, 1 H, *J*(3′,2′) = 3.2, *J*(3′,4′) = 1.0 (H-3′); 4.23 td, 1 H (H-4′); 4.27 dd, 1 H, *J*(2′,1′) = 1.O (H-2′); 5.14 t, 1 H (5′-OH); 6.20 d, 1 H (H-1′); 7.38 t, 1 H, 7.48 t, 2 H and 7.56 d, 2 H (H-arom.); 8.29 d, 1 H and 9.025 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 56.30 (C-2′); 57.41 (C-3′); 59.84 (C-5′); 79.13 (C-4′); 84.03 (C-1′); 116.86 (C-5); 125.60, 2 C, 127.84, 129.45, 2 C and 133.39 (C-arom.); 141.52 (C-6); 154.28 (C-2); 165.53 (C-4).

B. Mesyl derivative **29** (750 mg, 1.27 mmol) was stirred with methanolic ammonia (60 ml) for 30 h at room temperature. Evaporation of the solvent and chromatography on silica gel (120 ml) in ethyl acetate–acetone–ethanol–water (36 : 6 : 1 : 1) gave 300 mg (83%) of compound **28**.

1-(3,5-Di-*O*-benzoyl-2-*O*-methanesulfonyl-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**29**)

Methanesulfonyl chloride (0.18 ml, 2.34 mmol) was added at 0 °C to a solution of compound **24** (1 g, 1.95 mmol) in pyridine (10 ml) and the mixture was stirred at 0 °C for 30 min and then at room temperature overnight. The reaction was quenched with methanol (1 ml) and the solvent was evaporated. The residue was partitioned between ethyl acetate and 1% hydrochloric acid (150 ml each), the organic layer was washed several times with water to neutral reaction and dried over magnesium

sulfate. Evaporation of the solvent and chromatography on silica gel (200 ml) in toluene–acetone (2 : 1, R_F 0.34) gave 867 mg (75%) of compound **29** as a white foam. For $C_{30}H_{26}N_2O_9S$ (590.6) calculated: 61.01% C, 4.44% H, 4.74% N, 5.43% S; found: 60.82% C, 4.59% H, 4.44% N, 4.99% S. Mass spectrum (FAB, TG + dimethyl sulfoxide): 591 (M^+ + H). ^{1}H NMR spectrum: 3.51 s, 3 H (CH_3); 4.74 dd, 1 H, *J*(5′a,4′) = 7.1, *J*(gem) = 14.7 (H-5′a); 4.97–5.02 m, 2 H (H-4′and H-5′b); 5.67 br t, 1 H, *J* = 1.5 (H-2′); 5.85 dd, 1 H, *J*(3′,2′) = 1.5, *J*(3′,4′) = 3.0 (H-3′); 6.20 d, 1 H, *J*(1′,2′) = 1.5 (H-1′); 7.13 t, 2 H, 7.40–7.50 m, 5 H, 7.53 t, 1 H, 7.62 t, 1 H, 7.64 t, 2 H, 7.68 d, 2 H and 7.89 d, 2 H (H-arom.); 8.56 d, 1 H and 9.05 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 38.22 (CH_3); 61.66 (C-5′); 75.04 (C-3′); 80.32 (C-2′); 83.88 (C-4′); 90.78 (C-1′); 117.38 (C-5); 125.79, 2 C, 127.86, 128.50–129.47, 12 C, 133.20, 133.70 and 133.88 (C-arom.); 140.11 (C-6); 154.25 (C-2); 165.12 and 165.74 (C=O); 165.78 (C-4).

1-(2-*O*-Acetyl-5-*O*-benzoyl-3-*O*-methanesulfonyl-β-D-xylofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**31**)

Silyl derivative **4**, prepared from 5-phenyl-2(1*H*)-pyrimidinone (**3**; 1.72 g, 10 mmol) as described for compound **5**, was added to a solution of 1,2-di-*O*-acetyl-5-*O*-benzoyl-3-*O*-methanesulfonyl-D-xylofuranose (**18**; 3.37 g, 9 mmol) in acetonitrile (50 ml). Tin tetrachloride (1.5 ml) was added and the reaction mixture was stirred at room temperature overnight, poured into saturated solution of sodium hydrogen carbonate (1 l) and the product was taken up in ethyl acetate (1 l). The organic layer was filtered through Celite and washed with a solution of sodium hydrogen carbonate (3 × 300 ml). After drying over magnesium sulfate, the solvent was evaporated to give 4.22 g (89%) of chromatographically pure product **31** as a foam. To obtain an analytically pure sample, a part of the product (200 ml) was chromatographed on silica gel in toluene–acetone (1 : 1), R_F 0.40. For $C_{25}H_{24}N_2O_9S$ (528.5) calculated: 56.81% C, 4.58% H, 5.30% N, 6.07% S; found: 56.61% C, 4.62% H, 5.54% N, 5.94% S. Mass spectrum (FAB, TG + dimethyl sulfoxide): 529 (M^+ + H). ^{1}H NMR spectrum: 2.19 s, 3 H (acetyl); 3.33 s, 3 H (CH_3); 4.67 dd, 1 H, *J*(5′a,4′) = 7.1, *J*(gem) = 14.7 (H-5′a); 4.83–4.88 m, 2 H (H-5′b and H-4′); 5.52 dd, 1 H, *J*(3′,2′) = 1.5, *J*(3′,4′) = 3.2 (H-3′); 5.58 br t, 1 H, (H-2′); 6.08 d, 1 H, *J*(1′,2′) = 1.7 (H-1′); 7.37 t, 1 H, 7.44 t, 2 H, 7.49 t, 2 H, 7.60 d, 2 H, 7.65 t, 1 H and 8.00 d, 2 H (H-arom.); 8.33 d, 1 H and 9.03 d, 1 H, *J*(4,6) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 20.79 and 37.63 (CH_3); 61.73 (C-5′); 78.91 (C-3′); 79.78 and 79.79 (C-4′ and C-2′); 90.01 (C-1′); 117.32 (C-5); 125.86, 2 C; 127.84; 128.90, 2 C, 129.27, 129.30, 2 C, 129.55, 2 C, 133.38 and 133.78 (C-arom.); 140.08 (C-6); 154.19 (C-2); 165.64 (C=O); 165.83 (C-4); 169.39 (C=O).

1-(5-*O*-Benzoyl-β-D-arabinofuranosyl)-5-phenyl-2(1*H*)-pyrimidinone (**33a**)
and 2′,6-Anhydro-1-(5-*O*-benzoyl-β-D-arabinofuranosyl)-1,6-dihydro-
5-phenyl-6-hydroxy-2(3*H*)-pyrimidinone (**33b**)

Methanol (0.2 ml) and DBU (0.2 ml) were added to a solution of compound **31** (500 mg, 0.946 mmol) in dimethylformamide (7 ml) and the reaction mixture was stirred at room temperature for 90 min. The solution was diluted with ethyl acetate (35 ml), neutralized with acetic acid and washed with water (15 ml). The organic layer was dried over magnesium sulfate, the solvent was evaporated and the residue chromatographed on silica gel (100 ml), first in toluene–acetone (3 : 2) to remove nonpolar impurities and then in acetone–toluene (2 : 1). The product fractions (R_F 0.23) were evaporated and the residue was crystallized from methanol to give 116 mg (30%) of the product. According to NMR spectrum, the product was an equilibrium mixture of compounds **33a** and **33b** in which the cyclic form **33b** predominated in the ratio 5 : 2.

^{1}H NMR spectrum: Compound **33a**: 4.13 m, 1 H (H-3′); 4.24 td, 1 H, *J*(2′,3′) = 1.5, (H-2′); 4.35 ddd, *J*(4′,3′) = 1.5 (H-4′); 4.48 dd, 1 H, *J*(5′a,4′) = 3.4, *J*(gem) = 12.0 (H-5′a); 4.81 dd, 1 H, *J*(5′b,4′) = 8.3 (H-5′b); 5.79 d, 1 H, *J*(OH,3′) = 3.7 (3′-OH); 5.83 d, 1 H, *J*(OH,2′) = 4.6 (2′-OH); 6.18 d, 1 H,

J(1′,2′) = 3.2 (H-1′); 7.34 m, 3 H, 7.50 m, 4 H, 7.65 t, 1 H and 8.01 d, 2 H (H-arom.); 8.26 d, 1 H and 8.98 d, 1 H, *J*(6,4) = 3.4 (H-6 and H-4). ^{13}C NMR spectrum: 64.28 (C-5′); 74.15 (C-2′); 76.97 (C-3′); 84.13 (C-4′); 88.86 (C-1′); 116.03 (C-5); 125.36, 2 C, 127.59, 128.97, 2 C, 129.24, 2 C, 129.46, 2 C, 129.60, 133.50 and 133.73 (C-arom.); 142.11 (C-6); 154.18 (C-2); 164.68 (C-4); 165.92 (C=O).

Compound **33b**: 3.84 ddd, 1 H, *J*(4′,3′) = 8.3 (H-4′); 4.44 dd, 1 H, *J*(5′a,4′) = 6.4, *J*(gem) = 12.2 (H-5′a); 4.22 br pent, 1 H (H-3′); 4.40 dd, 1 H, *J*(2′,3′) = 4.2 (H-2′); 4.63 dd, 1 H, *J*(5′b,4′) = 2.2 (H-5′b); 5.82 s, 1 H (H-6); 5.86 d, 1 H, *J*(OH,3′) = 5.4 (3′-OH); 6.16 d, 1 H, *J*(1′,2′) = 5.5 (H-1′); 6.90 d, 1 H, *J*(4,NH) = 5.4 (H-4); 7.22 t, 7.35 m, 7.40–7.55 m, 7.62 t and 7.96 d, 10 H (H-arom.); 9.61 d, 1 H (NH). ^{13}C NMR spectrum: 64.20 (C-5′); 73.91 (C-3′); 78.52 (C-4′); 83.88 (C-6); 83.98 (C-2′); 88.05 (C-1′); 106.53 (C-5); 124.39, 2 C (C-arom.); 124.49 (C-4); 126.49, 128.65, 2 C, 128.93, 2 C, 129.30, 2 C, 129.60, 133.62 and 135.13 (C-arom.); 149.06 (C-2); 165.67 (C=O).

Reaction of Compound **31** with DBU and Methanolic Ammonia

Methanol (0.5 ml) and DBU (0.5 ml) were added to a solution of compound **31** (1.25 g, 2.35 mmol) in dimethylformamide (15 ml). After stirring for 6 h at room temperature, a further amount of methanol (0.5 ml) was added and stirring was continued for 30 min. The solution was neutralized with acetic acid, diluted with ethyl acetate (80 ml) and washed with water (35 ml). The organic layer was dried over magnesium sulfate, the solvent was evaporated and the residue was stirred with methanolic ammonia (40 ml) at room temperature for 40 h. After evaporation, the residue was chromatographed on silica gel in ethyl acetate–acetone–ethanol–water (36 : 6 : 1 : 1). The chromatography afforded:

6-Amino-2′,N^6-anhydro-1-(β-D-arabinofuranosyl)-1,6-dihydro-5-phenyl-2(3H)-pyrimidinone (**35**) as white crystalline solid (80 mg), m.p. 227–229.5 °C (methanol), R_F 0.15. Mass spectrum (FAB, T + G, methanol + trifluoroacetic acid): 304 (M^+ + H). ^{1}H NMR spectrum: 3.25 dd, 1 H, *J*(NH,2′) = 7.3, *J*(NH,6) = 13.2 (NH); 3.39 ddd, 1 H, *J*(4′,5′b) = 2.2, *J*(4′,5′a) = 5.4, *J*(4′,3′) = 8.0 (H-4′); 3.44 br pent, 1 H, *J*(5′a,4′) = *J*(5′a,OH) = 5.9, *J*(gem) = 11.7 (H-5′a); 3.52 dt, 1 H (H-2′); 3.63 ddd, 1 H, *J*(5′b,4′) = 2.2, *J*(5′b,OH) = 5.4 (H-5′b); 3.77 dt, 1 H, *J*(3′,OH) = 5.9, *J*(3′,2′) = 5.6, *J*(3′,4′) = 8.0 (H-3′); 4.67 brt, 1 H, *J* = 5.9 (5′-OH); 5.10 d, 1 H, *J*(6,NH) = 13.2 (H-6); 5.34 d, 1 H, *J* = 5.9 (3′-OH); 5.85 d, 1 H, *J*(1′,2′) = 6.4 (H-1′); 6.73 d, 1 H, *J*(4,NH) = 5.4 (H-4); 7.16 t, 1 H, 7.29 t, 2 H and 7.57 d, 2 H (H-arom.); 9.04 d, 1 H (NH). ^{13}C NMR spectrum: 61.15 (C-5′); 67.21 (C-2′); 71.37 (C-6); 74.36 (C-3′); 82.13 (C-4′); 88.52 (C-1′); 108.13 (C-5); 123.45 (C-4); 124.90, 2 C, 126.43, 128.70, 2 C and 136.21 (C-arom.); 149.91 (C-2).

5-Phenyl-2-[(β-D-ribopyranosyl)amino]pyrimidine (**34**; 60 mg), white crystalline compound, R_F 0.13. Mass spectrum (FAB, T + G, methanol): 304 (M^+ + H). ^{1}H NMR spectrum: 3.44 br d, 1 H (H-5′a); 3.50 m, 1 H (H-3′); 3.63 m, 1 H (H-2′); 3.65 br dd, 1 H, *J*(5′b,4′) = 3.6, *J*(gem) = 12.2 (H-5′b); 3.72 m, 1 H (H-4′); 4.57 br d, 1 H, *J* = 4.0 (OH); 4.85 d, 1 H, *J* = 4.6 (OH); 4.95 d, 1 H, *J* = 4.4 (OH); 5.04 br t, 1 H, *J* = 8.2 (H-1′); 7.34 t, 1 H, 7.45 t, 2 H and 7.64 d, 2 H (H-arom.); 7.66 d, 1 H (NH); 8.68 s, 2 H (H-4 and H-6). ^{13}C NMR spectrum: 66.50 (C-5′); 68.24 (C-3′); 70.35 (C-2′); 73.87 (C-4′); 82.93 (C-1′); 124.58 (C-5); 126.31, 2 C, 127.92, 129.71, 2 C and 135.70 (C-arom.); 156.56, 2 C (C-4 and C-6); 161.74 (C-2).

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