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Synthesis of 2'-Deoxy-2'-Phenylselenenyl-Furanosyl Nucleosides from Glycals using Electrophilic Selenium Reagents. Conversion into 2'-Deoxynucleosides.

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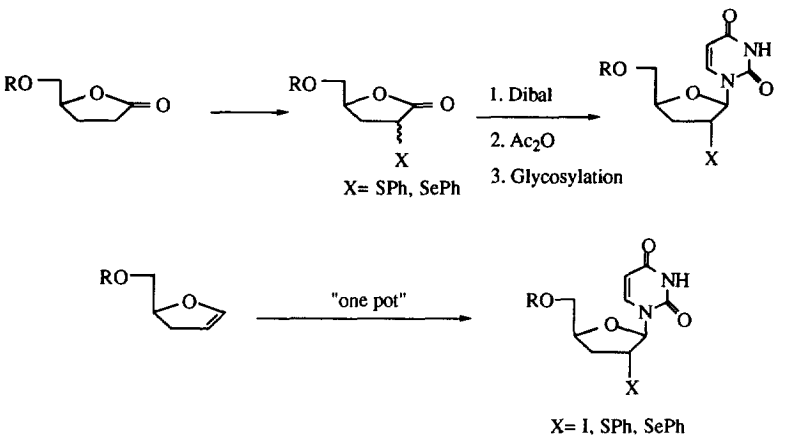
Abstract: 2'-Deoxy-2'-phenylselenenyl-furanosyl nucleosides have been synthesized stereoselectively from glycals using selenium reagents, and converted into 2'-deoxynucleosides by treatment with tributyltin hydride. Some of the factors which affect the stereoselectivity of the reaction are the stereochemistry at position 3, the nature of the protecting groups, the phenylselenenyl reagent and the solvent. © 1997 Elsevier Science Ltd.

2'-Deoxynucleosides such as AZT, ddI, D4T and related analogues are some of the most active agents against HIV viruses, and the synthesis of this type of compounds and their analogues is at the moment an active field of research.[1] Glycosylation of the carbohydrate and the base is the most useful and versatile way of synthesizing nucleoside analogues, as it enables either of the two fragments to be modified. In this context, a classical synthetic problem is to control the stereoselectivity in the absence of substituents at position 2 in the sugar ring. 2'-Deoxynucleosides are usually prepared from naturally occurring nucleosides by deoxygenation at the 2'-position or direct glycosylation reactions. Deoxygenation is often performed by way of a Barton type reaction starting from the appropriatly protected nucleoside;[2] successful conversions have also been obtained by treating unprotected nucleosides with acetyl bromide to give the 3',5'-diacetyl-2'-bromo derivative followed by reduction.[3]

A variety of glycosylation methods starting from 2-deoxyfuranosides have been described but most of the conventional ones, which involve the formation of a carbocation intermediate, give α/ß equimolar mixtures of nucleosides. Reasonably high stereoselectivities have been achieved for the preparation of ß-nucleosides starting from 1-α-chloro-2-deoxy-3,5-di-tolyl-D-*erythro*-pentofuranose,[4] but S_N2-like pathways must be strictly guaranteed in order for this to occur. ß-Nucleosides have also been obtained from phenyl 1-thio-furanosides using NBS as an activator.[5] Recently, methodologies have also been described in which stereoselective control in the glycosylation reaction is determined by anchimeric assistance. In two outstanding reports, long distance anchimeric assistance is provided by a sulphoxide group attached to position 3 of the sugar,[6] or, in the synthesis of oxothiolanyl and dioxolanyl derivatives,[7] by a glycosylation catalyst



Scheme 1

coordinated stereoselectively to the second ring heteroatom. The use of easily removable heteroatoms, such as sulphur or selenium, attached to position 2 for controlling the stereoselectivity has also been widely studied. The reported preparation of 2'-sulphenyl[8] or 2'-selenenyl[9] nucleosides, by a glycosylation reaction usually involves four steps, starting from the corresponding lactones, and the stereoselectivity of the process is determined at the step where sulphur or selenium is introduced (Scheme 1).

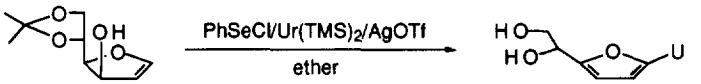
In the glycoside field, high levels of stereoselectivity in the synthesis of 2'-deoxyglycosides have been obtained via sulphur-,[10] selenium-[11] and iodine-[12-14] mediated glycosylation reactions starting from glycals. We have recently shown that 2'-deoxy-2'-phenylselenenyl-pyranosyl nucleosides can be stereoselectively prepared from pyranoid glycals by addition of PhSeCl followed by glycosylation, and can finally be converted into 2'-deoxynucleosides by treatment with Bu_3SnH.[15] 2',3'-Dideoxy nucleosides[16] have been obtained from glycals by NIS[17]-, PhSCl[18]- and PhSeCl[19]-induced glycosylation (Scheme 1). In this paper, we report that 2'-deoxy-2'-phenylselenenyl nucleosides can also be stereoselectively obtained from furanoid glycals in a "one pot" reaction and efficiently converted into 2'-deoxynucleosides.[20] 2'-Deoxy-2'-phenylselenenyl nucleosides have also been obtained from naturally occurring nucleosides by nucleophilic ring opening of anhydronucleosides or by S_N2 reactions,[21] and have been shown to be useful intermediates in intramolecular radical reactions.[22]

2'-Deoxy-2'-phenyselenenyl-furanosyl nucleosides

The glycal with a *threo* configuration **1** (Scheme 2) was prepared from D-mannose[23] by Ireland's[24] method and was transformed into **3**[25] and **4**[26] (Table 1) by treatment with NaH/BnBr in THF and *t*-$BuMe_2SiCl/DBU/CH_2Cl_2$, respectively. Glycal **5**[27] was prepared from D-mannose by degradation of the side chain, in a similar way to **1**, or from 2-deoxyribose.[28] Glycals **9**, **10**, **11**, **12**, and **16** (Table 2) were synthesized from ribonolactone[24] and glycals **13, 14, 15 and 17** from 2-deoxyribose.[28]

In a previous report[15], we showed that the reaction of pyranoid glycals with PhSeCl in the presence of uracil$(TMS)_2$ only gave PhSeCl addition products, and a halogen scavenger had to be used to obtain 2'-deoxy-2'-phenylselenenyl nucleosides. Thus, when glycal **3** was treated in ether at room temperature with PhSeCl and uracil$(TMS)_2$ and with AgOTf as the halogen scavenger (ratio 1:1.5:2:1.7), nucleosides **6ß-gluco** and **6α-gluco** were obtained in 81% yield (ratio **6ß-gluco/6α-gluco**=90:10) (Table 1).

When the reaction was run at -20°C, the yield was similar, but the stereoselectivity decreased. When a

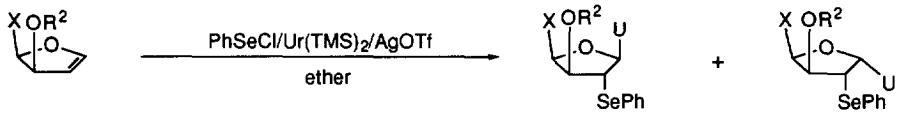


1 2

Scheme 2

solution of glycal and PhSeCl was heated to reflux for 15 minutes, prior to the addition of uracil and AgOTf, the yield decreased and no stereoselectivity was observed. Using benzene as a solvent, the yield increased but the stereoselectivity decreased slightly.

Table 1. Stereoselectivity in the Synthesis of 2'-Phenylselenenylnucleosides Derived from *Threo* Glycals.[a]



Starting Glycal	Time(h)	Yield(%)[b]	2'-selenenylnucleosides(Diastereoisomeric Ratio)[c]	
3 R^2=Bn, X=	1	81	**6β-gluco** (90)	**6α-gluco** (10)
4 R^2=TBDMS, X=	1	95	**7β-gluco** (86)	**7α-gluco** (14)
5 R^2=Bn, X=$BnOCH_2$	0.5	90	**8β-xylo** (91)	**8α-xylo** (9)

[a] Reactions were carried out using the molar ratio glycal/PhSeCl/AgOTf/Uracil(TMS)$_2$= 1/1.5/1.7/2. [b] Expressed as a percentage of recovered mixture of products after chromatography. [c] Determined by integration of the H-1' protons in the ^{1}H NMR spectrum of the reaction mixture.

As observed for pyranoid glycals,[15] the use of PhSeBr or PhSeI gave lower stereoselectivity than PhSeCl, and AgOTf also had to be used. Treatment of glycal **4** with PhSeCl, uracil(TMS)$_2$ and AgOTf in ether gave an 86:14 mixture of 2'-deoxy-2'-phenylselenenyl nucleosides **7ß-gluco** and **7α-gluco** in 95% yield.

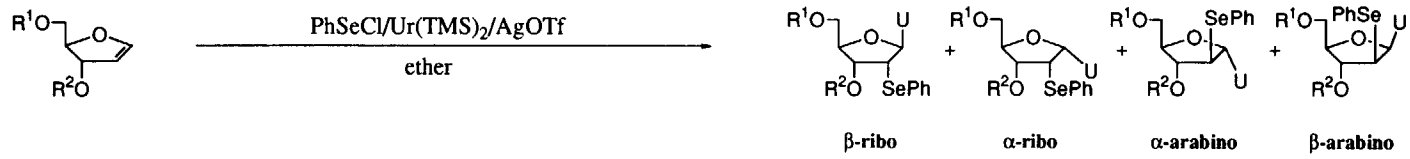
The reaction of glycal **5** in standard conditions afforded 2'-deoxy-2'-phenylselenenyl nucleosides **8ß-xylo** and **8α-xylo** (91:9) in good yields and selectivities, which were similar to the other glycals with a *threo* configuration (Table 1). ß-Nucleosides were the principal products, when starting from glycals with a *threo* configuration. Nevertheless, starting from the unprotected glycal **1**, only the furan derivative **2** was obtained in 70% yield, as a result of the sugar ring being aromatized and the ketal deprotected (Scheme 2).

In the case of glycals with *erythro* configuration, with substituents on both faces of the almost flat dihydrofuran ring, the stereoselectivity is uncertain. In order to better understand the influence of substituent groups on the control of the stereoselectivity, we studied the reaction of selenium-mediated glycosylation with a variety of protected glycals (**9**-**17**) (Table 2).

Treatment of glycal **9** in the standard conditions gave an inseparable mixture of three nucleosides **19ß-ribo**, **19α-arabino** and its corresponding 5'-deprotected nucleoside **19aα-arabino** in a ratio **19ß-ribo**:**19α-arabino**:**19aα-arabino**= 14:49:37. Total **ß-ribo**: **α-arabino** ratio= 14:86 (Table 2).

Glycal **10** also gave a mixture of six nucleosides, which was separable by chromatography into two fractions containing the nucleosides **20ß-ribo**, **20α-ribo** and **20α-arabino** and the 5'-unprotected derivatives

Table 2. Stereoselectivity in the synthesis of 2'-phenylselenenylnucleosides derived from *erythro* glycals[a].



Starting Glycal	Time(h)	Yield(%)[b]	2'-Selenenylnucleosides	Diastereoisomeric Ratio[c]			
			18 R^1=R^2=H				-
9 R^1=MEM, R^2=Bn	2	82	**19** R^1=MEM, R^2=Bn	14	-	49	-
			19a R^1=OH, R^2=Bn	-	-	37	-
10 R^1=TBDMS, R^2=Bn	1.5	87	**20** R^1=TBDMS, R^2=Bn	32	16	16	-
			20a R^1=OH, R^2=Bn	18	5	13	-
11 R^1=TBDMS, R^2=TBDMS	1.5	88	**21** R^1=TBDMS, R^2=TBDMS	28	21	15	-
			21a R^1=OH, R^2=TBDMS	22	8	6	-
12 R^1=Bn, R^2=Bn	1	89	**22** R^1=Bn, R^2=Bn	30	-	70	-
13 R^1=TBDPS, R^2=Bn	2	58	**23** R^1=TBDPS, R^2=Bn	44	9	-	-
			23b R^1=TBDPS, R^2=Bn, R=SePh[d]	19	8	6	14
14 R^1=Bn, R^2=TBDPS	2	85	**24** R^1=Bn, R^2=TBDPS	43	11	32	14
15 R^1=TBDPS, R^2=MEM	2	83	**25** R^1=TBDPS, R^2=MEM	54	18	15	4
			25b R^1=TBDPS, R^2=MEM, R=SePh[d]	9	-	-	-
16 R^1=Ac, R^2=TBDPS	2	84	**26** R^1=Ac, R^2=TBDPS	23	14	16	6
			26b R^1=Ac, R^2=TBDPS, R=SePh[d]	26	5	5	5
17 R^1=TBDPS, R^2=TBDMS	2	87	**27** R^1=TBDPS, R^2=TBDMS	66	20	14	-

[a] Reactions were carried out at r. t. using the molar ratio glycal/PhSeCl/AgOTf/Uracil(TMS)$_2$= 1/1.5/1.7/2. [b] Expressed as a percentage of recovered mixture of products after chromatography. [c] Determined by integration of the H-1' protons in the ^{1}H NMR of the reaction mixture. [d] R=SePh stands for selenenylation of nucleosides at position 5.

20aß-ribo, **20aα-ribo** and **20aα-arabino** (ratio 32:16:16:18:5:13). The total **20ß-ribo**: **20α-ribo**: **20α-arabino** ratio was 50:21:29. The percentage of ß-ribo was higher than the percentage of α-ribo, but this was balanced by the significant amount of α-arabino derivative obtained.

Although no acid is present in the reaction medium to catalyze the deprotection of the MEM and $^{t}BuMe_2Si$ groups, the "in situ" formation of TMSOTf from AgOTf and the TMS protecting groups of uracil may well explain this reaction. It has been shown that it is possible to selectively deprotect the primary silyl group in 3',5'-di-$^{t}BuMe_2Si$ nucleosides, or an $^{t}BuMe_2Si$ group in the presence of an $^{t}BuPh_2Si$ group by treatment with Me_3SiOTf.[29]

To verify the extent of deprotection of the $^{t}BuMe_2Si$ group, the glycosylation was performed starting from the 3,5-di-*tert*-butyldimethylsilyl derivative **11**. The presence of 6 nucleosides in the reaction crude and the ^{t}Bu group integration in ^1H NMR suggests that only position 5' was partially deprotected. Treatment of the reaction mixture with $Bu_4N^+F^-$ gave a mixture of unprotected nucleosides **18ß-ribo**, **18α-ribo** and **18α-arabino** in a ratio 50:29:21.

The stability of the $^{t}BuPh_2Si$ group at position 5' under the reaction conditions was also tested. Thus, glycosylation from glycal **17** afforded a mixture of nucleosides **27ß-ribo**, **27α-ribo** and **27α-arabino** in a ratio of 66:20:14. In this case, no deprotection was observed. Subsequent treatment of this mixture with $Bu_4N^+F^-$ afforded a mixture of nucleosides, the data of which were identical to the data of **18ß-ribo**, **18α-ribo** and **20α-arabino** nucleosides.

The 3,5-di-O-benzyl glycal **12** gave a 30:70 mixture of nucleosides **22ß-ribo** and **22α-arabino** in 89% yield, when it was treated in the standard reaction conditions. These data suggested that an increase in the ß-stereoselectivity would be expected when there are bulky substituents at position 5. To confirm this assumption, we performed a series of glycosylation experiments starting from differently protected glycals at positions 3 and 5. Hence, glycal **13**, which has a $^{t}BuPh_2Si$ group at position 5, gave a complex mixture of nucleosides in 58% yield, which was separated by chromatography into two fractions. The low Rf fraction contained two nucleosides. The ^1H spectrum of the high Rf fraction showed four nucleosides, none of which had H-5 proton, which is a sign that 5-selenenylation had taken place. Substitution of uracil at position 5 by reaction with electrophilic selenium reagents has, in fact, been reported.[30] All these nucleosides were **23ß-ribo**, **23α-ribo**, **23bß-ribo**, **23bα-ribo**, **23bα-arabino**, **23bß-arabino** in a ratio 44:9:19:8:6:14 (Table 2). The ß-ribo nucleoside is the major one, but the fact that almost half of this derivative was selenenylated at position 5 makes the problem more complex and the synthesis less efficient.

Glycal **14** also afforded a complex mixture of nucleosides in 85% yield. Spectroscopical analysis of the mixture identified nucleosides **24ß-ribo**, **24α-ribo**, **24α-arabino**, **24ß-arabino** in a ratio 43:11:32:14. In this case, no 5-selenenylation occurred.

In an earlier report, we showed that ester type protecting groups direct the attack of the PhSe group to the double bond.[15] It has also been demonstrated that electronegative substituents on the lower face of the furanose ring are determinant in the control of the stereoselectivity.[6] With these facts in mind, glycals **15** and **16** were submitted to the standard glycosylation reaction conditions. With glycal **15**, the ^1H NMR spectrum of the reaction crude showed five different anomeric protons but only four H-5 signals. A spectroscopical study of the crude identified nucleosides **25ß-ribo**, **25α-ribo**, **25α-arabino**, **25ß-arabino and 25bß-ribo** in a ratio of 54:18:15:4:9, respectively. The major compound of this mixture, **25ß-ribo**, was isolated in 45% yield, and its structure confirmed. For glycal **16**, which has an acetyl group at position 5, the ^1H NMR of the reaction crude indicated a complex mixture of eight nucleosides, which were partially separated by chromatography into several fractions. The structure of each of the nucleosides was found by analysing the ^1H spectra of the fractions. They were **26ß-ribo**, **26α-ribo**, **26α-arabino**, **26ß-arabino**, **26bß-ribo**, **26bα-ribo**, **26bα-arabino**,

26bß-arabino in a ratio of 23:14:16:6:26:5:5:5. Several nucleosides were isolated and their structure confirmed.

Two factors should be taken into account, as far as the stereoselectivity is concerned, when the results from glycals **9-17** were compared. On one hand, the stereoselectivity of the selenium reagent addition cannot be accounted for only by the steric hindrance of the substituents at positions 3 and 5; the presence of TMDPS and TBDMS groups at position 5 appear to determine the preferred attack of selenium from the α face side and consequently the ß-nucleoside is the major product; nevertheless, when the ß-face was deblocked by small protecting groups at position 5, the stereoselectivity was inverted for glycals **9** and **12**, but was surprisingly null in glycals **14** and **16**. In a previous report[15], we pointed out that the addition of PhSeCl to a double bond is a reversible process that leads to the most stable adduct. Hence, it can be stated that the diastereoisomeric ratio observed in each case is due to the relative stability of the selenonium cations, and in some cases, may be very different from the ratios which should be expected only from steric factors. Somehow, substituents must be involved in a stereoelectronic stabilization/destabilization of the two possible selenonium cations. On the other hand, the relative configurations of positions 1' and 2' in the nucleosides that were synthesized reveal that the selenonium cation is not responsible for the stereoselectivity in the nucleophilic attack of the base, or at least is not the only intermediate involved in the process. The most plausible mechanism is that the selenonium is in equilibrium with the flat oxonium cation. This has already been discussed by Liotta, in relation to sulfur analogues[31] and would explain the formation of nucleosides where the base is *cis* to the phenylselenenyl residue.

Structure assignment

The structure of the phenylselenenyl nucleosides was elucidated by taking into account the following facts: 1) The presence of the pyrimidine base was confirmed by a broad singlet at low field which is characteristic of amidic NH in ^1H spectra and double bond signals in the ^1H and in the ^{13}C spectra. In cases where 5-selenenylation took place no H-5 proton was observed in the ^1H spectrum and H-6 appeared as a singlet. 2) The introduction of a phenylselenenyl residue in the sugar ring was confirmed by the integration of the aromatic protons in the ^1H spectra and by the presence of a ^{13}C NMR signal at 49-52 ppm assigned to C2', typical of carbon bonded to selenium.

The configuration of position 1' and 2' in the nucleosides synthesized was established by taking the following facts into account: **1**) The coupling constants of the protons in the sugar ring taking as a basis that some puckering modes are preferred when five-membered rings are asymmetrically substituted. Moreover, if electronegative substituents are present at positions 2' or 3', the puckering mode of the lowest potential energy is the one where electronegative substituents adopt an axial orientation, effect that is known as gauche effect. Bearing this in mind, the preferred conformation of the sugar ring in the nucleosides should predominantly be in C-3'-endo conformation range (N form) for the derivatives of the *threo* glycals and in the C-3'-exo conformation range (S form) for the derivatives of the *erythro* glycals. The coupling constants of the nucleosides isolated agree with this assumption (Table 3). One exception to this assumption is the case of the deprotected nucleoside **18α-arabino**. Its coupling constants suggest that the preferred conformation is the N form, for it allows the stabilizing hydrogen bonds to form between the hydroxylic functions.

2) Some general trends were observed in the chemical shifts of the proton signals in the ^1H spectra: H-4' protons of the ß-anomers were upfield from the ones observed for the α-anomer; H-2' protons *cis* to the bases were upfield of the ones with a *trans* arrangement (up to 0.7 ppm) (Table 3). H-5 protons of the α-anomers were downfield from the ones observed for ß-anomers. Furthermore, H-5 protons *cis* to the PhSe residue shift

S N

Figure 1

Table 3. Selected Spectral Parameters, δ (ppm) and J (Hertzs), for 2-Phenylselenenylnucleosides.

Compound/ Parameter	$H_{1'}$	$H_{2'}$	$H_{3'}$	$H_{4'}$	H_5	$J_{1',2'}$	$J_{2',3'}$	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$
6β-gluco	6.12	(d)3.56	3.97	4.08	5.54	2.5	0	89.5	49.5	82.8	82.9
6α–gluco	6.27	(d)4.43	4.19	4.58	5.72	4.5	0	88.0	50.5	82.2	82.9
7β-gluco	6.10	(d)3.46	4.24	4.11	5.64	1.9	0	90.0	53.2	76.7	84.1
7α-gluco	6.24				5.70	4.4	0				
8β-xilo	6.07	(dd)3.64	3.93	4.42	5.44	3.2	2.11	90.9	49.2	81.1	82.3
8α-xilo	6.23	(d)4.36	4.09	4.65	5.62	4.9	0	87.7	50.6	80.9	83.1
18β-ribo	6.47	(dd)3.82	4.47	4.02	5.35	9.4	5.5	91.9	51.9	74.9	88.6
18α-ribo	6.58	(dd)4.38	4.50	4.31	5.68	7.2	5.7	89.6	54.0	73.9	88.8
18α-ara	6.12	(t)3.85	4.15	4.09	5.55	8.1	8.1	91.7	51.7	74.1	86.5
22β-ribo	6.51	(dd)3.77	4.30	4.31	5.05	8.8	5.5	90.8	49.4	81.1	82.2
22α-ara	6.24	(dd)3.68	4.09	4.39	5.66	4.5	3.4	90.9	49.0	83.2	84.7
25β-ribo	6.53	(dd)3.73	4.56	4.21	5.02	9.3	5.6	89.8	49.7	79.5	84.3
26β-ribo	6.47	(dd)3.62	4.55	3.99	5.37	8.7	5.4	91.7	50.7	75.2	83.4
26bβ-ribo	6.52	(dd)3.57	4.55	3.95	-	8.8	5.3	91.5	51.0	75.5	83.6
26bα-ribo	6.26	(t)4.28	4.60	4.26	-	5.8	5.8	86.4	52.8	73.9	82.6
26bα-ara	5.97	(t)3.84	4.23	4.34	-	4.0	4.0	92.8	51.6	76.5	86.3
27β-ribo	6.56	(dd)3.64	4.53	3.99	5.13	9.3	5.1	90.2	52.0	75.3	87.1
27α-ribo	6.63	(dd)4.20	4.48	4.29	5.68	7.5	5.3	88.0	52.8	75.1	87.7

downfield. As far as the ^{13}C spectra are concerned, anomeric carbon signals from α-xylo, α-gluco and α-ribonucleosides appear at lower chemical shifts than those from the rest of the nucleosides (up to 5 ppm).

3) All these observations were ultimately confirmed by NOE experiments (Figure 2).When H-1' and H-2' protons were in a *cis* arrangement, big enhancements were observed in one of the protons when irradiation took place in the other one (ca. 10-20%). In the nucleosides where PhSe residue and the base were in a trans arrangement, small or no appreciable enhancements were observed in either case. Increase in the H-4' proton signal when H-1' was irradiated confirmed the anomeric configuration in ß-nucleosides. No effect was observed in the α-anomers.

Whenever the different diastereoisomers could not be separated from the reaction crude, their configuration was determined by taking into account the general trends described above (chemical shifts and

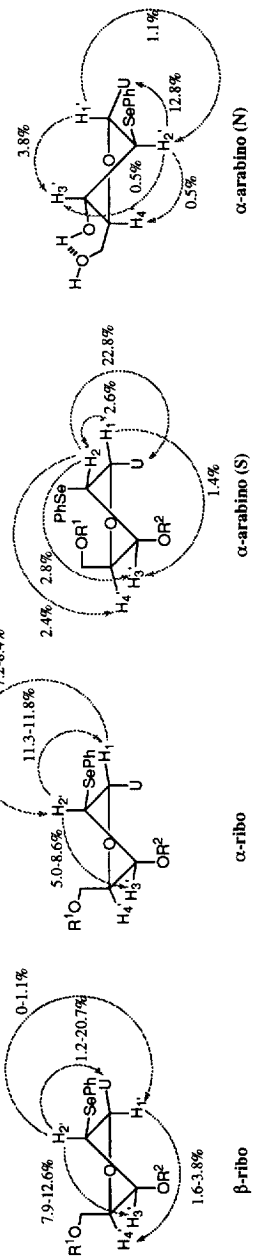


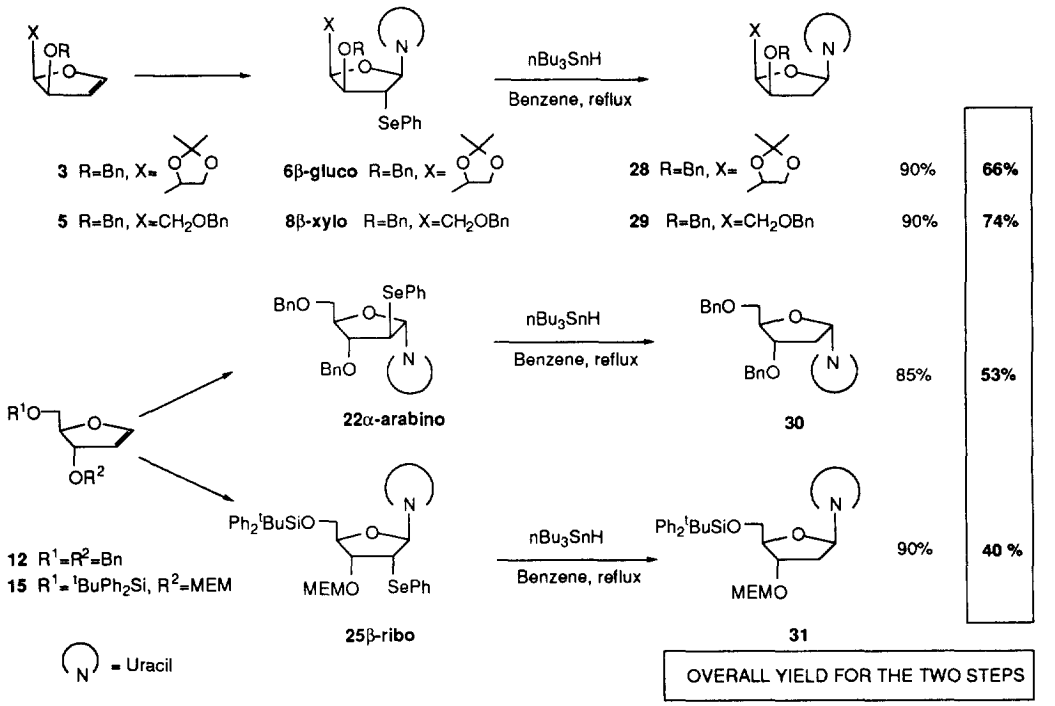
Figure 2. Selected NOE enhancements for 2'-phenylselenenylnucleosides derived from furanoid glycals.

coupling constants of the anomeric protons, chemical shift of H-5 signals, etc). Besides, irradiation of the fairly isolated anomeric signals enabled the H-2 protons to be identified.

2'-Deoxyfuranosyl Nucleosides

Some representative examples of the 2'deoxy-2'phenylselenenylnucleosides which were obtained in fairly good stereoselectivity, such as **6ß-gluco**, **8ß-xylo**, **22α-arabino** and **25ß-ribo**, were treated with tributyltin hydride and AIBN in benzene and heated to reflux to give the 2'-deoxy-furanosyl nucleosides **28–31** respectively, in yields over 85%.

In conclusion, 2'-deoxy-2'-phenylselenenyl-ß-furanosyl nucleosides were stereoselectively obtained from glycals **3-5** with a *threo* configuration. For the glycals with an *erythro* configuration, stereoselectivity was seen to depend on the protecting groups at positions 3 and 5.



Scheme 3

EXPERIMENTAL SECTION

General Procedures: Melting points were measured in a Büchi 510 apparatus and are uncorrected. Optical rotations were measured at room temperature in 10 cm cells in a Perkin-Elmer 241 polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded in a Varian Gemini 300 MHz (300 and 75.4 MHz resp.) apparatus, with $CDCl_3$ as solvent and using Me_4Si (δ=0) and the reference solvent peak at ∂ 77.0 ppm respectively as an internal reference, unless otherwise specified. Elemental analyses were determined using a Carlo-Erba Microanalysis. Flash column chromatography was performed using silica gel 60 A CC (230-400 mesh). TLC plates were prepared by using Kieselgel 60 PF_{254} (E. Merk). HPLC was performed with a C-18 silicagel column (25mm x 10 cm) using acetonitrile/water 60:40 as eluent. Solvents for chromatography were distilled at atmospheric pressure prior to use. Dichloromethane was distilled from P_2O_5. Benzene was dried by distillation from Na ribbon and stored over 4Å molecular sieves under argon. Anhydrous ether was obtained by distillation, under nitrogen, from sodium benzophenone ketyl. Other solvents were purified and dried by using standard procedures. All the reactions were carried out in an argon atmosphere using standard syringe techniques.

General Procedure for the synthesis of 2'-phenylselenenyl-furanosyl nucleosides from glycals. 0.37 mmol of the phenylselenenyl chloride was added at room temperature to a solution of furanoid glycal (0.25 mmol) in 1 ml of ether, kept under argon and protected from light. After 5 minutes, 0.5 mmol of bis-(trimethylsilyl)uracil and finally 0.42 mmol of silver trifluoromethanesulphonate were added to the reaction flask. After the reaction had finished, the reaction mixture was poured into ethyl acetate and saturated $NaHCO_3$ while stirring. The layers were separated, and the organic layer washed once with saturated $NaHCO_3$, water and saturated NaCl solution, dried, filtered and concentrated. The crude obtained was subsequently purified by column chromatographic techniques.

1-[3-O-benzyl-5,6-O-isopropyliden-2-*Se*-phenyl-2-seleno-ß-D-*gluco*-hexofuranosyl]uracil (6ß-gluco) and **1-[3-O-benzyl-5,6-O-isopropyiden-2-*Se*-phenyl-2-seleno-α-D-*gluco*-hexofuranosyl]uracil (6α-gluco).**
The general procedure for glycosylation involved a reaction mixture containing glycal **3**, phenylselenenyl chloride, silver triflate and bis-(trimethylsilyl)uracil in ether. The mixture was stirred at room temperature for 1.5 h. Flash chromatography of the crude reaction product in ethyl acetate/hexane= 1:2 afforded 0.108 g (81%) of a diastereoisomeric mixture of **6ß-gluco/6α-gluco** (90:10). The isomers were separated by TLC using the same solvent mixture.
(6ß-gluco): $[\alpha]^{25}_D$ +38.1° (c = 0.54, $CHCl_3$). **^{1}H NMR:** 8.65 (bs, 1H, NH); 7.55 (d, 1H, $J_{6,5}$=8.6 Hz, H_6); 7.50-7.00 (Ph); 6.12 (d, 1H, $J_{1',2'}$=2.5 Hz, $H_{1'}$); 5.54 (dd, 1H, $J_{5,NH}$=2.2 Hz, H_5); 4.36 (dt, 1H, $J_{5',6'}$=5.4 Hz, $J_{5',6''}$=8.6 Hz, $H_{5'}$); 4.26 (s, 2H, C$\underline{H_2}$Ph); 4.08 (dd, 1H, $J_{4',5'}$=5.4 Hz, $H_{4'}$); 4.04 (dd, 1H, $J_{6',6''}$=8.7 Hz, $H_{6'}$); 3.97 (d, 1H, $J_{3',4'}$=3.1 Hz, $H_{3'}$); 3.90 (dd, 1H, $H_{6''}$); 3.56 (d, 1H, $H_{2'}$); 1.34 (Me); 1.30 (Me). **^{13}C NMR:** 163.0 (C_4); 149.5 (C_2); 140.3 (C_6); 136.8-127.8 (Ph); 102.4 (C_5); 89.5 ($C_{1'}$); 82.9 ($C_{4'}$); 82.9 ($C_{3'}$); 72.3 (C$\underline{H_2}$Ph); 71.8 ($C_{6'}$); 67.2 ($C_{5'}$); 49.5 ($C_{2'}$); 26.8 (Me); 25.4 (Me). **IR:** 1694 cm^{-1}($\sqrt{}_{CO}$); 1634 cm^{-1}($\sqrt{}_{CH=CH}$). Anal. Calcd. for $C_{26}H_{28}O_6N_2Se$ C, 57.46; H, 5.19; N, 5.15 . Found: C, 57.39; H, 5.17; N, 5.12.
(6α-gluco): **^{1}H NMR:** 8.17 (bs 1H, NH); 7.58 (d, 1H, $J_{6,5}$=8.2 Hz, H_6); 7.40-7.15 (Ph); 6.27 (d, 1H, $J_{1',2'}$=4.5 Hz, $H_{1'}$); 5.72 (dd, 1H, $J_{5,NH}$=2.2 Hz, H_5); 4.59 (d, 1H, J_{gem}=12.1 Hz, C$\underline{H_2}$Ph); 4.58 (dd, 1H, $J_{4',5'}$=6.1, $H_{4'}$); 4.43 (d, 1H, $H_{2'}$); 4.36 (m, 1H, $H_{5'}$); 4.35 (d, 1H, C$\underline{H_2}$Ph); 4.19 (d, 1H, $J_{3',4'}$=3.2 Hz, $H_{3'}$); 4.11 (dd, 1H, $J_{6',5'}$=6.2 Hz, $J_{6',6''}$=8.6 Hz, $H_{6'}$); 4.02 (dd, 1H, $J_{6'',5'}$=5.5 Hz, $H_{6''}$); 1.44 (Me); 1.37 (Me). **^{13}C NMR:**163.0 (C_4); 149.5 (C_2); 137.0-127.9 (Ph); 139.3 (C_6); 100.8 (C_5); 88.0 ($C_{1'}$); 82.9 ($C_{4'}$); 82.2 ($C_{3'}$); 73.5 (C$\underline{H_2}$Ph); 72.0

($C_{6'}$); 66.5 ($C_{5'}$); 50.5 ($C_{2'}$); 26.7 (Me); 25.2 (Me). **IR**: 1691 cm^{-1} (ν_{CO}); 1600 cm^{-1} ($\nu_{CH=CH}$). Anal. Calcd. for $C_{26}H_{28}O_6N_2Se$ C, 57.46; H, 5.19; N, 5.15. Found: C, 57.35; H, 5.20; N, 5.11.

1-[3-O-(*tert*-butyldimethylsilyl)-5,6-O-isopropyiden-2-*Se*-phenyl-2-seleno-ß-D-*gluco*-hexofuranosyl) uracil (7ß-gluco): Following the general procedure described above, glycal **4** was allowed to react with phenylselenenyl chloride, silver triflate and bis-(trimethylsilyl)uracil in ether for 1.5 h. The reaction crude was chromatographed in hexane/ethyl acetate to afford 0.134 g (95%) of a mixture of **7ß-gluco/7α-gluco** (86/14), from which only **7ß-gluco** was isolable as a pure compound.

(7ß-gluco): $[\alpha]^{25}_D$ +20.3° (*c* = 0.77, $CHCl_3$). **^{1}H NMR:** 8.08(bs 1H, NH); 7.72 (d,1H, $J_{6,5}$= 8.2 Hz, H_6), 7.71-7.29 (m, 5H, Ph); 6.10 (d, 1H, $J_{1',2'}$=1.9 Hz, $H_{1'}$); 5.64 (dd, 1H, $J_{5,NH}$=1.8 Hz, $J_{5,6}$=8.2 Hz, H_5); 4.28 (dt, 1H, dd, 1H, $J_{5',6'} = J_{5',6''}$ = 5.3 Hz, $J_{5',4'}$ = 8.9 Hz, $H_{5'}$); 4.24 (d,1H, $J_{3',4'}$ = 2.7 Hz, $H_{3'}$); 4.13 (dd, 1H, $J_{6',5'}$ = 5.3 Hz, $J_{6',6''}$ = 8.5 Hz, $H_{6'}$); 4.11 (dd, 1H, $J_{4',3'}$ = 2.7 Hz, $J_{4',5'}$ = 9.2 Hz, $H_{4'}$); 4.13 (dd, 1H, $J_{6'',5'}$ = 5.3 Hz, $J_{6'',6'}$ = 8.5 Hz, $H_{6''}$); 3.46 (d, 1H, $J_{2',1'}$ = 1.9 Hz, $H_{2'}$); 1.40 (s, 3H, CH_3); 1.31 (s, 3H, CH_3); 1(Me); 0.75 (s, 9H, $(CH_3)_3CSi$); -0.11 (s, 3H, CH_3Si); -0.28 (s, 3H, CH_3Si);**^{13}C NMR:** 162.7 (C_4); 149.8 (C_2); 140.6-126.9 (C_6, Ph); 109,4 ($\underline{C}(CH_3)_2$); 101.9 (C_5); 90.0 ($C_{1'}$); 84.1 ($C_{4'}$); 76.7 ($C_{3'}$); 72.0 ($C_{6'}$); 67.6 ($C_{5'}$); 53.2 ($C_{2'}$); 26.9 (CH_3); 25.5 ($(C\underline{H}_3)_3CSi$); 25.3 (CH_3); 17.9 ($(CH_3)_3\underline{C}Si$); -4.6 (CH_3Si); -4.9 (CH_3Si). Anal. Calcd. for $C_{25}H_{36}O_6N_2SiSe$: C, 52.90 H, 6.39; N, 4.93. Found: C, 52.98; H, 6.41; N, 4.95 .

1-[3,5-di-O-benzyl-2-*Se*-phenyl-2-seleno-ß-D-*xylo*-pentofuranosyl]uracil (8ß-xylo) and 1-[3',5'-di-O-benzyl-2-*Se*-phenyl-2-seleno-α-D-*xylo*-pentofuranosyl]uracil (8α-xylo). Using the general procedure described above, the glycosylation was performed starting from glycal **5**, phenylselenenyl chloride, silver triflate and bis-(trimethylsilyl)uracil in ether for 0.5 h. The reaction crude was purified by flash chromatography in hexane / ethyl acetate= 2:1 to give 0.101 g (90%) of a mixture of **8ß-xylo/8α-xylo** (91: 9) which were separated by preparative TLC using ethyl acetate/hexane = 1: 3.

(8ß-xylo): $[\alpha]^{25}_D$ +32.1° (*c* = 0.52, $CHCl_3$). **^{1}H NMR** : δ 8.62-8.47 (m, 1H, NH), 7.55 (d, 1H, $J_{6,5}$ = 8.23 Hz, H_6), 7.35-6.90 (m, 15H, Ph, SePh), 6.07 (d, 1H, $J_{1',2'}$ = 3.18 Hz, $H_{1'}$), 5.44 (dd, 1H, $J_{5,NH}$ = 2.20 Hz, H_5), 4.53 (d, 1H, J_{gem} = 11.75 Hz, $H_{OCH_2Ph(1)}$), 4.45 (d, 1H, $H_{OCH_2Ph(1)}$), 4.42 (m, 1H, $H_{4'}$), 4.29 (d, 1H, J_{gem} = 11.85 Hz, $H_{OCH_2Ph(2)}$), 4.10 (d, 1H, $H_{OCH_2Ph(2)}$), 3.93 (dd, 1H, $J_{3',4'}$ = 4.08 Hz, $J_{3',2'}$ = 2.11 Hz, $H_{3'}$), 3.73 (m, 2H, $H_{5'}$, $H_{5''}$), 3.64 (dd, 1H, $H_{2'}$). **^{13}C NMR** : δ 160.57 (C_4), 150.04 (C_2), 140.35 (C_6), 135.79-127.90 (Ph, SePh), 101.93 (C_5), 89.98 ($C_{1'}$), 82.26 ($C_{4'}$), 81.08 ($C_{3'}$), 73.60(C_{OCH_2Ph}), 71.70 (C_{OCH_2Ph}), 67.99 ($C_{5'}$), 49.21 ($C_{2'}$). Anal. Calcd. for $C_{29}H_{28}O_5N_2Se$: C, 61.81 H, 5.01; N, 4.97. Found: C, 61.59; H, 5.02; N, 4.96 .

(8α-xylo): $[\alpha]^{25}_D$ -81.5° (*c* = 1.09, $CHCl_3$). **^{1}H NMR** : δ 7.70 (bs, 1H, NH), 7.51 (d, 1H, $J_{6,5}$ = 8.01 Hz, H_6), 7.40-6.98 (m, 15H, Ph, SePh), 6.23 (d, 1H, $J_{1',2'}$ = 4.88 Hz, $H_{1'}$), 5.62 (dd, 1H, $J_{5,NH}$ = 2.34 Hz, H_5), 4.65 (ddd, 1H, $J_{4',5'}$ = 6.89 Hz, $J_{4',5''}$ = 4.22 Hz, $H_{4'}$), 4.55 (d, 1H, J_{gem} = 11.87 Hz, $H_{OCH_2Ph(1)}$), 4.50 (d, 1H, J_{gem} = 12.35 Hz, $H_{OCH_2Ph(2)}$), 4.45 (d, 1H, $H_{OCH_2Ph(2)}$), 4.36 (d, 1H, $H_{2'}$), 4.16 (d, 1H, $H_{OCH_2Ph(1)}$), 4.09 (d, 1H, $H_{3'}$), 3.71 (dd, 1H, $J_{5',5''}$ = 10.59 Hz, $J_{5',4'}$ = 6.96 Hz, $H_{5'}$), 3.62 (dd, 1H, $J_{5'',4'}$ = 4.41 Hz, $H_{5''}$). **^{13}C NMR** : δ 160.57 (C_4), 150.04 (C_2), 139.60 (C_6), 134.02-127.86 (Ph, SePh), 100.70 (C_5), 87.73 ($C_{1'}$), 83.10 ($C_{4'}$), 80.93 ($C_{3'}$), 73.71 (C_{OCH_2Ph}), 71.70 (C_{OCH_2Ph}), 68.85 ($C_{5'}$), 50.62 ($C_{2'}$). Anal. Calcd. for $C_{29}H_{28}O_5N_2Se$: C, 61.81 H, 5.01; N, 4.97. Found: C, 61.99; H, 5.03; N, 4.95 .

1-[2-*Se*-phenyl-2-seleno-ß-D-*ribo*-pentofuranosyl]uracil (18ß-ribo), 1-[2-*Se*-phenyl-2-seleno-α-D-*ribo*-pentofuranosyl]uracil (18α-ribo) and 1-[2-*Se*-phenyl-2-seleno-α-D-*arabino*-pentofuranosyl]uracil (18α-arabino). Glycal **11** was coupled with bis-(trimethylsilyl)uracil in ether as a solvent using the general procedure described above. The suspension was stirred for 90 mins until TLC in ethyl acetate/ hexane= 1:2

indicated that the reaction was complete. The resulting reaction crude was chromatographed to afford a mixture of 4 nucleosides that were submitted to the deprotection reaction of the TBDMSi group. Thus, a solution of the resulting mixture in THF in an inert atmosphere was cooled to 0°C and treated with a 1M solution of tetrabutylammonium fluoride in THF. After 10 min, the deprotection was complete as shown by TLC in ethyl acetate/hexane= 2:1. Treatment of the reaction mixture gave 0.092 g (81%) of a mixture of nucleosides **18ß-ribo**, **18α-ribo** and **18α-arabino**, that were subsequently separated by TLC in ether/acetone=7:1

(**18ß-ribo**): **^{1}H NMR (CD$_3$OD)**: 7.55 (d,1H, $J_{6,5}$= 8.1 Hz, H_6); 7.54-7.17 (m, 5H, Ph); 6.47 (d, 1H, $J_{1',2'}$= 9.4 Hz, $H_{1'}$); 5.35 (d, 1H, $J_{5,6}$= 8.1 Hz, H_5); 4.47 (dd, 1H, $J_{3',4'}$= 1.1 Hz, $J_{3',2'}$= 5.5 Hz, $H_{3'}$); 4.02 (td, 1H, $J_{4',3'}$= 1.1 Hz, $J_{4',5'}$= 3.2 Hz, $J_{4',5''}$= 3.2 Hz, $H_{4'}$); 3.82 (dd, 1H, $J_{2',3'}$ = 5.5 Hz, $J_{2',1'}$ = 9.4 Hz, $H_{2'}$); 3.73 (d, 2H, $J_{5',4'}$ = 3.2 Hz, $H_{5'}$, $H_{5''}$). **^{13}C NMR** 165.6 (C_4); 151.7 (C_2); 141.9 (C_6); 136.9-129.0 (Ph); 103.2 (C_5); 91.9 ($C_{1'}$); 88.6 ($C_{4'}$); 74.9 ($C_{3'}$); 63.3 ($C_{5'}$); 51.9 ($C_{2'}$). Anal. Calcd. for $C_{15}H_{16}O_5N_2Se$: C, 47.01 H, 4.21; N, 7.31. Found: C, 47.15; H, 4.19; N, 7.33.

(**18α-ribo**): $[\alpha]^{25}_D$ +117.3° (*c* = 0.075, CH_3OH). **^{1}H NMR ((CD$_3$OD)**: 8.05 (d, 1H, $J_{6,5}$= 8.2 Hz, H_6); 7.54-7.21 (m, 5H, Ph); 6.58 (d, 1H, $J_{1',2'}$=7.2 Hz, $H_{1'}$); 5.68 (d, 1H, $J_{5,6}$=8.2 Hz, H_5); 4.50 (dd, 1H, $J_{3',4'}$= 2.0 Hz, $J_{3',2'}$= 5.7 Hz, $H_{3'}$); 4.38 (dd, 1H, $J_{2',3'}$ = 5.7 Hz, $J_{2',1'}$ = 7.2 Hz, $H_{2'}$); 3.65 (dd, 1H, $J_{5',4'}$= 3.9 Hz, $J_{5',5''}$= 12.1 Hz, $H_{5'}$); 3.59 (dd, 1H, $J_{5'',4'}$=6.6 Hz, $J_{5'',5}$= 12.1 Hz, $H_{5''}$). **^{13}C NMR** 166.3 (C_4); 152.4 (C_2); 144.3 (C_6); 134.3-128.5 (Ph); 101.6 (C_5); 89.6 ($C_{1'}$); 88.8 ($C_{4'}$); 73.9 ($C_{3'}$); 63.5 ($C_{5'}$); 54.0 ($C_{2'}$). Anal. Calcd. for $C_{15}H_{16}O_5N_2Se$: C, 47.01 H, 4.21; N, 7.31. Found: C, 47.11; H, 4.20; N, 7.28.

(**18α-arabino**): **^{1}H NMR (CD$_3$OD)**: 7.65-7.25 (m, 5H, Ph); 7.58 (d,1H, $J_{6,5}$= 8.1 Hz, H_6); 6.12 (d, 1H, $J_{1',2'}$= 8.1 Hz, $H_{1'}$); 5.55 (d, 1H, $J_{5,6}$= 8.1 Hz, H_5); 4.15 (dd, 1H, $J_{3',4'}$= 6.9 Hz, $J_{3',2'}$= 8.1 Hz, $H_{3'}$); 4.09 (ddd, 1H, $J_{4',5'}$= 2.8 Hz, $J_{4',5''}$= 4.3 Hz, $J_{4',3'}$= 6.9 Hz, $H_{4'}$); 3.85 (t, 1H, $J_{2',1'}$ = 8.1 Hz, $J_{2',3'}$ = 8.1 Hz, $H_{2'}$); 3.74 (dd, 1H, $J_{5',4'}$= 2.8 Hz, $J_{5',5''}$= 12.3 Hz, $H_{5'}$); 3.59 (dd, 1H, $J_{5'',4'}$=4.3 Hz, $J_{5'',5}$= 12.3 Hz, $H_{5''}$). **^{13}C NMR** 165.2 (C_4); 152.7 (C_2); 142.6 (C_6); 136.8-129.6 (Ph); 103.2 (C_5); 91.7 ($C_{1'}$); 86.5 ($C_{4'}$); 74.1 ($C_{3'}$); 62.3 ($C_{5'}$); 51.7 ($C_{2'}$). Anal. Calcd. for $C_{15}H_{16}O_5N_2Se$: C, 47.01 H, 4.21; N, 7.31. Found: C, 47.13; H, 4.22; N, 7.34.

1-[3,5-di-O-benzyl-2-*Se*-phenyl-2-seleno-ß-D-*ribo*-pentofuranosyl]uracil (**22ß-ribo**) and **1-[3,5-di-O-benzyl-2-*Se*-phenyl-2-seleno-α-D-*arabino*-pentofuranosyl]uracil** (**22α-arabino**). Glycosylation was carried out using glycal **12**, phenylselenenyl chloride, silver triflate and bis-(trimethylsilyl)uracil in ether as a solvent in standard conditions. The mixture was stirred at room temperature for 1 h. The crude reaction mixture was purified by flash chromatography to afford 0.125 g (89%) of a diastereoisomeric mixture of **22ß-ribo/22α-arabino** (30:70). Preparative TLC in ethyl acetate/hexane= 1: 3 separated both isomers.

(**22ß-ribo**): $[\alpha]^{25}_D$ +43.3° (*c* = 0.43, $CHCl_3$). **^{1}H NMR**: 7.97 (bs, 1H, NH); 7.46-7.08 (m, 16H, H_6, Ph); 6.51 (d, 1H, $J_{1',2'}$=8.8 Hz, $H_{1'}$); 5.05 (dd, 1H, $J_{5,NH}$=2.2 Hz, $J_{5,6}$=8.1 Hz, H_5); 4.64 (s, 2H, C$\underline{H_2}$Ph); 4.56 (d, 1H, J_{gem}=11.0 Hz, C$\underline{H_2}$Ph); 4.46 (d, 1H, J_{gem}=11.0 Hz, C$\underline{H_2}$Ph); 4.32-4.29 (m, 2H, $H_{3'}$, $H_{4'}$); 3.77 (dd, 1H, $J_{2',3'}$=5.5 Hz, $J_{2',1'}$=8.8 Hz, $H_{2'}$); 3.75 (dd, 1H, $J_{5',4'}$=2.5 Hz, $J_{5',5''}$=10.3 Hz, $H_{5'}$); 3.57 (dd, 1H, $J_{5'',4'}$=1.9 Hz, $J_{5'',5'}$=10.3 Hz, $H_{5''}$). **^{13}C NMR**162.3 (C_4); 149.8 (C_2); 139.6 (C_6); 137.0-127.1 (Ph); 102.3 (C_5); 90.8 ($C_{1'}$); 82.2 ($C_{4'}$); 81.2 ($C_{3'}$); 73.9 (C$\underline{H_2}$Ph); 72.2 (C$\underline{H_2}$Ph); 70.8 ($C_{5'}$); 49.4 ($C_{2'}$). **IR**: 1706, 1680 cm^{-1} ($\sqrt{}_{CO}$); 1600 cm^{-1} ($\sqrt{}_{CH=CH}$). Anal. Calcd. for $C_{29}H_{28}O_5N_2Se$: C, 61.81 H, 5.01; N, 4.97. Found: C, 61.91; H, 5.03; N, 5.00 .

(**22α-arabino**): **^{1}H NMR**: 8.33 (bs, 1H, NH); 7.60-7.10 (H_6, Ph); 6.24 (d, 1H, $J_{1',2'}$=4.5 Hz, $H_{1'}$); 5.66 (dd, 1H, $J_{5,NH}$=2.2 Hz, $J_{5,6}$=8.1 Hz, H_5); 4.53 (s, 2H, C$\underline{H_2}$Ph); 4.41 (d, 1H, J_{gem}= 11.9 Hz, C$\underline{H_2}$Ph); 4.39 (td, 1H, $J_{4',3'}$=3.4 Hz, $J_{4',5'}$= 5.5 Hz, $H_{4'}$); 4.34 (d, 1H, J_{gem}= 11.9 Hz, C$\underline{H_2}$Ph); 4.09 (t, 1H, $J_{3',2'}$=3.4 Hz, $J_{3',4'}$=3.4 Hz, $H_{3'}$); 3.68 (dd, 1H, $J_{2',3'}$= 3.4 Hz, $J_{2',1'}$= 4.5 Hz, $H_{2'}$); 3.50 (dd, 1H, $J_{5',4'}$=5.4 Hz, $J_{5',5''}$=10.2 Hz, $H_{5'}$); 345 (dd,

1H, $J_{5'',4'}$=5.4 Hz, $J_{5'',5'}$=10.2 Hz, $H_{5''}$). **^{13}C NMR** 163.4 (C_4); 150.2 (C_2); 139.9 (C_6); 135.6-127.8 (Ph); 102.4 (C_5); 90.9 ($C_{1'}$); 84.7 ($C_{4'}$); 83.2 ($C_{3'}$); 73.3 ($\underline{C}H_2Ph$); 71.9 ($\underline{C}H_2Ph$); 68.7 ($C_{5'}$); 49.0 ($C_{2'}$). **IR**: 1690 cm^{-1} ($\sqrt{}_{CO}$); 1620 cm^{-1}($\sqrt{}_{CH=CH}$). Anal. Calcd. for $C_{29}H_{28}N_2O_5Se$: C, 61.81; H, 5.01; N, 4.97. Found: C, 61.73; H, 5.02; N, 4.96.

1-[5-O-(*tert*-butyldiphenylsilyl)-3-O-(methoxy-ethoxy-methylen)-2-*Se*-phenyl-2-seleno-ß-D-*ribo*-pentofuranosyl]uracil (25ß-ribo): Glycal **15** was allowed to react with phenylselenenyl chloride, silver triflate and bis-(trimethylsilyl)uracil for 1 h in the standard conditions. Flash chromatography provided a mixture of 5 nucleosides, which were purified by preparative TLC in ethyl acetate/hexane=1:4. Compound **25ß-ribo** (0.062 g, 45%) was isolated in a pure form. **^{1}H NMR** : δ 8.41 (bs, 1H, NH), 7.70-7.10 (16H, Ph, H_6), 6.53 (d, 1H, $J_{1',2'}$ = 9.3 Hz, $H_{1'}$); 5.02 (dd, 1H, $J_{5,NH}$ = 2.1 Hz, $J_{5,6}$ = 8.1 Hz, H_5), 4.82 (s, 2H, O-C$\underline{H}$2-O); 4.56 (d, 1H, $J_{3',2'}$ = 5.6 Hz, $H_{3'}$), 4.24-4.18 (m, 1H, $H_{4'}$); 3.97 (dd, 1H, $J_{5',4'}$ = 2.4 Hz, $J_{5',5''}$ = 11.6 Hz, $H_{5'}$); 3.85 (dd, 1H, $J_{5'',4'}$ = 1.8 Hz, $H_{5''}$); 3.83-3.76 (m, 2H, O-C$\underline{H}_2$-CH_2-O); 3.73 (dd, 1H, $H_{2'}$); 3.62-3.48 (m, 2H, O-CH_2-C$\underline{H}_2$-O); 3.36 (s, 3H, C$\underline{H}_3$O); 1.08 (s, 9H, (C$\underline{H}_3$)$_3$CSi) . **^{13}C NMR** : δ 162.4 (C_4), 150.0 (C_2), 139.3-128.0 (C_6, Ph), 102.4 (C_5), 95.2 (O-$\underline{C}$H2-O), 89.8 ($C_{1'}$), 84.3 ($C_{4'}$), 79.5 ($C_{3'}$), 71.5 (O-$\underline{C}H_2$-CH_2-O), 67.6 (O-CH_2-$\underline{C}H_2$-O), 64.6 ($C_{5'}$), 59.0 (CH_3O), 49.7 ($C_{2'}$), 27.1 .((C$\underline{H}_3$)$_3$CSi), 19.4 ((CH_3)$_3\underline{C}$Si). Anal. Calcd. for $C_{35}H_{42}O_7N_2SeSi$: C, 59.23; H, 5.96;N, 3.95. Found: C, 59.01; H, 5.93; N, 3.94.

1-[5-O-acetyl-3-O-(*tert*-butyldiphenylsilyl)-2-*Se*-phenyl-2-seleno-ß-D-*ribo*-pentofuranosyl]uracil (26ß-ribo); **1-[5-O-acetyl-3-O-(*tert*-butyldiphenylsilyl)-2-*Se*-phenyl-2-seleno-ß-D-*ribo*-pentofuranosyl]-5-phenylselenenyluracil (26bß-ribo)**; **1-[5-O-acetyl-3-O-(*tert*-butyldiphenylsilyl)-2-*Se*-phenyl-2-seleno-α-D-*arabino*-pentofuranosyl]-5-phenylselenenyluracil (26bα-arabino)** and **1-[5-O-acetyl-3-O-(*tert*-butyldiphenylsilyl)-2-*Se*-phenyl-2-seleno-α-D-*ribo*-pentofuranosyl]-5-phenylselenenyluracil (26bα-ribo)**: The general procedure was applied starting from glycal **16**, phenylselenenyl chloride, silver triflate and bis-(trimethylsilyl)uracil. The mixture was stirred in ether for 2 h at room temperature. After flash chromatography (ethyl acetate/hexane = 1:2) of the reaction crude and preparative TLC, only compounds **26ß-ribo** (0.033 g, 20%), **26bß-ribo** (0.033 g, 16%), **26bα-arabino** (0.008 g, 4%)and **26bα-ribo** (0.008 g, 4%) proved to be isolable.

(26ß-ribo): **^{1}H NMR** : δ 8.18 (bs, 1H, NH), 7.83-7.13 (Ph), 6.90 (d, 1H, $J_{6,5}$ = 8.1 Hz, H_6), 6.47 (d, 1H, $J_{1',2'}$ = 8.7 Hz, $H_{1'}$); 5.37 (dd, 1H, $J_{5,NH}$ = 2.1 Hz, $J_{5,6}$ = 8.1 Hz, H_5), 4.55 (dd, 1H, $J_{3',2'}$ = 5.4 Hz, $J_{3',4'}$ = 2.0 Hz, $H_{3'}$); 3.99 (ddd, 1H, $J_{4',5'}$ = 4.6 Hz, $J_{4',5''}$ = 3.3 Hz, $H_{4'}$); 3.62 (dd, 1H, $H_{2'}$); 3.58 (dd, 1H, $J_{5',5''}$ = 12.2 Hz, $H_{5'}$); 3.46 (dd, 1H, $H_{5''}$); 2.05 (s, 3H, C$\underline{H}_3$COO); 1.16 (s, 9H, (C$\underline{H}_3$)$_3$CSi) . **^{13}C NMR** : δ 169.8 (C$H_3\underline{C}$OO); 162.1 (C_4), 149.6 (C_2), 139.2-127.0 (C_6, Ph), 102.6 (C_5), 91.7 ($C_{1'}$), 83.4 ($C_{4'}$), 75.2 (C_3), 63.4 ($C_{5'}$), 50.7 ($C_{2'}$), 26.9 .((C$\underline{H}_3$)$_3$CSi), 20.7 (C$\underline{H}_3$COO); 19.5 ((CH_3)$_3\underline{C}$Si). Anal. Calcd. for $C_{33}H_{36}N_2O_6SeSi$: C, 59.72; H, 5.47;N, 3.95. Found: C, 59.60; H, 5.46; N, 3.95.

(26bß-ribo): **^{1}H NMR** : δ 8.10 (bs, 1H, NH), 7.90-7.10 (m, 21H, Ph, H_6), 6.52 (d, 1H, $J_{1',2'}$ = 8.8 Hz, $H_{1'}$); 4.55 (dd, 1H, $J_{3',2'}$ = 5.3 Hz, $J_{3',4'}$ = 1.7 Hz, $H_{3'}$), 3.95 (ddd, 1H, $J_{4',5'}$ = 3.1 Hz, $J_{4',5''}$ = 3.8 Hz, $H_{4'}$); 3.58 (dd, 1H, $J_{5',5''}$ = 12.2 Hz, $H_{5'}$); 3.57 (dd, 1H, $H_{2'}$), 3.31 (dd, 1H, $H_{5''}$); 1.95 (s, 3H, C$\underline{H}_3$COO); 1.17 (s, 9H, (C$\underline{H}_3$)$_3$CSi) . **^{13}C NMR** : δ 169.8 (C$H_3\underline{C}$OO); 160.4 (C_4), 149.5 (C_2), 143.7-126.9 (C_6, Ph), 104.2 (C_5), 91.5 ($C_{1'}$), 83.6 ($C_{4'}$), 75.5 (C_3), 63.5 ($C_{5'}$), 51.0 ($C_{2'}$), 26.9 .((C$\underline{H}_3$)$_3$CSi), 20.8 (C$\underline{H}_3$COO); 19.5 ((CH_3)$_3\underline{C}$Si). Anal. Calcd. for $C_{39}H_{40}N_2O_6Se_2Si$: C, 57.21; H, 4.92;N, 3.42. Found: C, 57.31; H, 4.95; N, 3.40.

(26bα-arabino): $[\alpha]^{25}_D$ +60.3° (*c* = 0.39, $CHCl_3$). **^{1}H NMR** : δ 8.18 (bs, 1H, NH), 7.65-7.14 (m, 21H, H_6, Ph), ; 5.97 ((d, 1H, $J_{1',2'}$ = 4.2 Hz, $H_{1'}$); 4.34 (dt, 1H, $J_{4',3'}$ = 4.0 Hz, $J_{4',5'}$ = 4.0 Hz, $J_{4',5''}$ = 6.0 Hz, $H_{4'}$); 4.23 (t, 1H, $J_{3',2'}$ = 4.0 Hz, $J_{3',4'}$ = 4.0 Hz, $H_{3'}$); 3.89 (dd, 1H, $J_{5',4'}$ = 4.0 Hz, $J_{5',5''}$ = 12.1 Hz, $H_{5'}$); 3.84 (dd, 1H, $J_{2',1'}$ =

4.0 Hz, $J_{2',3'}$ = 4.0 Hz, $H_{2'}$); 3.82 (dd, 1H, $J_{5'',4'}$ = 6.0 Hz, $J_{5'',5'}$ = 12.1 Hz, $H_{5'}$); 1.94 (s, 3H, $C\underline{H}_3COO$); 1.08 (s, 9H, $(C\underline{H}_3)_3CSi$) . **^{13}C NMR** : δ 170.2 ($CH_3\underline{C}OO$); 160.9 (C_4), 149.5 (C_2), 143.4 (C_6), 135.9-128.0 (Ph), 104.2 (C_5), 92.8 ($C_{1'}$), 86.3 ($C_{4'}$), 76.5 ($C_{3'}$), 63.4 ($C_{5'}$), 51.6 ($C_{2'}$), 26.8 .($(\underline{C}H_3)_3CSi$), 20.7 ($\underline{C}H_3COO$); 19.0 ($(CH_3)_3\underline{C}Si$). Anal. Calcd. for $C_{39}H_{40}N_2O_6Se_2Si$: C, 57.21; H, 4.92;N, 3.42. Found: C, 57.37; H, 4.89; N, 3.40.

(26bα-ribo): $[\alpha]^{25}_D$ +108.5° (*c* = 0.41, $CHCl_3$). **^{1}H NMR** : δ 8.50 (bs, 1H, NH), 8.20 (s, 1H, H_6); 7.84-7.06 (m, 20H, Ph), 6.26 (d, 1H, $J_{1',2'}$ = 5.8 Hz, $H_{1'}$); 4.60 (dd, 1H, $J_{3',4'}$ = 4.6 Hz, $J_{3',2'}$ =5.8 Hz, $H_{3'}$); 4.28 (t, 1H, $J_{2',1'}$ = 5.8 Hz, $J_{2',3'}$ = 5.8 Hz, $H_{2'}$); 4.26 (td, 1H, $J_{4',5'}$ = 3.5 Hz, $J_{4',5''}$ = 4.6 Hz, $J_{4',3'}$ = 4.6 Hz, $H_{4'}$); 3.92 (dd, 1H, $J_{5',4''}$ = 3.5 Hz, $J_{5',5''}$ = 12.2 Hz, $H_{5'}$); 3.46 (dd, 1H, $J_{5'',4''}$ = 4.6 Hz, $J_{5'',5'}$ = 12.2 Hz, $H_{5''}$); 1.89 (s, 3H, $C\underline{H}_3COO$); 1.14 (s, 9H, $(C\underline{H}_3)_3CSi$) . **^{13}C NMR** : δ 170.2 ($CH_3\underline{C}OO$); 160.9 (C_4), 149.4 (C_2), 145.5 (C_6), 136.3-127.7 (Ph), 102.2 (C_5), 86.4 ($C_{1'}$), 82.6 ($C_{4'}$), 73.9 ($C_{3'}$), 62.6 ($C_{5'}$), 52.8 ($C_{2'}$), 26.9 .($(\underline{C}H_3)_3CSi$), 20.7 ($\underline{C}H_3COO$); 19.3 ($(CH_3)_3\underline{C}Si$). Anal. Calcd. for $C_{39}H_{40}N_2O_6Se_2Si$: C, 57.21; H, 4.92;N, 3.42. Found: C, 57.08; H, 4.90; N, 3.43.

1-[3-O-(tert-butyldimethylsilyl)-5-O-(*tert*-butyldiphenylsilyl)-2-*Se*-phenyl-2-seleno-ß-D-*ribo*-pentofuranosyl]uracil (27ß-ribo) and **1-[3-O-(tert-butyldimethylsilyl)-5-O-(*tert*-butyldiphenylsilyl)-2-*Se*-phenyl-2-seleno-α-D-*ribo*-pentofuranosyl]uracil (27α-ribo)**: Glycal **17** was treated with phenylselenenyl chloride, silver triflate and bis-(trimethylsilyl)uracil in ether for 2 h using the general procedure described above in the standard conditions. After workup, the reaction crude was chromatographed over silica gel to afford 0.160 g (87%) of a mixture of nucleosides **27ß-ribo, 27α-ribo** and **27α-arabino** that was submitted to MPLC using linear gradient (from hexane to ethylacetate/hexane= 1:2) to afford nucleosides **27ß-ribo** and **27α-ribo.**

(27ß-ribo): **^{1}H NMR:** 8.05 (bs, 1H, NH); 7.67-7.14 (m, 16H, H_6, Ph); 6.56 (d, 1H, $J_{1',2'}$=9.3 Hz, $H_{1'}$); 5.13 (dd, 1H, $J_{5,NH}$=2.2 Hz, $J_{5,6}$=8.2 Hz, H_5); 4.53 (d, 1H, $J_{3',2'}$=5.1 Hz, $H_{3'}$); 3.99 (bs, 1H, $H_{4'}$); 3.93 (dd, 1H, $J_{5',4'}$=2.2 Hz, $J_{5',5''}$=11.6 Hz, $H_{5'}$); 3.74 (dd, 1H, $J_{5'',4'}$=1.8 Hz, $J_{5'',5'}$=11.6 Hz, $H_{5''}$); 3.64 (dd, 1H, $J_{2',3'}$=5.1 Hz, $J_{2',1'}$=9.3 Hz, $H_{2'}$); 1.07 (s, 9H, $(C\underline{H}_3)_3CSi$); 0.91 (s, 9H, $(C\underline{H}_3)_3CSi$); 0.13 (s, 3H, CH_3Si); 0.01 (s, 3H, CH_3Si).
^{13}C NMR 162.2 (C_4); 149.9 (C_2); 140.3-128.0 (C_6, Ph); 102.4 (C_5); 90.2 ($C_{1'}$); 87.1 ($C_{4'}$); 75.3 ($C_{3'}$); 64.3 ($C_{5'}$); 52.0 ($C_{2'}$); 27.0 ($(C\underline{H}_3)_3CSi$)); 25.7 ($(C\underline{H}_3)_3CSi$); 19.3 ($(CH_3)_3\underline{C}Si$); -4.6 (CH_3Si); -4.9 (CH_3Si). Anal. Calcd. for $C_{37}H_{48}N_2O_5SeSi_2$: C, 60.39; H, 6.57; N, 3.80. Found: C, 60.18; H, 6.55; N, 3.79.
(27α-ribo): $[\alpha]^{25}_D$ +46.3° (*c* = 1.08, $CHCl_3$). **^{1}H NMR:** 8.42 (bs, 1H, NH); 7.84 (d, 1H, $J_{6,5}$=8.2 Hz, H_6); 7.62-7.22 (m, 15H, Ph); 6.63 (d, 1H, $J_{1',2'}$=7.5 Hz, $H_{1'}$); 5.68 (dd, 1H, $J_{5,NH}$=2.4 Hz, $J_{5,6}$=8.2 Hz, H_5); 4.48 (t, 1H, $J_{3',4'}$=0.8 Hz, $J_{3',2'}$=5.3 Hz, $H_{3'}$); 4.29 (td, 1H, $J_{4',3'}$=0.8 Hz, $J_{4',5'}$= 3.9 Hz, $J_{4',5''}$= 3.9 Hz, $H_{4'}$); 4.20 (dd, 1H, $J_{2',3'}$= 5.3 Hz, $J_{2',1'}$= 7.5 Hz, $H_{2'}$); 364 (d, 2H, $J_{5',4'}$=3.9, $H_{5'}$, $H_{5''}$); 0.97 (s, 9H, $(C\underline{H}_3)_3CSi$); 0.93 (s, 9H, $(C\underline{H}_3)_3CSi$); 0.21 (s, 3H, CH_3Si); 0.11 (s, 3H, CH_3Si). **^{13}C NMR** 163.0 (C_4); 150.5 (C_2); 142.1 (C_6); 135.6-127.7 (Ph); 101.2 (C_5); 88.0 ($C_{1'}$); 87.4 ($C_{4'}$); 75.1 ($C_{3'}$); 64.5 ($C_{5'}$); 52.8 ($C_{2'}$); 26.7 ($(C\underline{H}_3)_3CSi$)); 25.7 ($(C\underline{H}_3)_3CSi$); 19.0 ($(CH_3)_3\underline{C}Si$); 18.1 ($(CH_3)_3\underline{C}Si$); -4.5 (CH_3Si); -4.9 (CH_3Si). Anal. Calcd. for $C_{37}H_{48}N_2O_5SeSi_2$: C, 60.39; H, 6.57; N, 3.80. Found: C, 60.54; H, 6.60; N, 3.78.

General procedure for the reduction of the 2'-phenylselenenylfuranosyl nucleosides with tributyltin hydride. 0.33 mmol (1 mL) of tributyltin hydride and 3 mg of 2,2'-azoisobutyronitrile (AIBN) were added at room temperature to a solution of 0.15 mmol of 2'-phenylselenyl nucleoside in 2 mL of anhydrous benzene at room temperature. The reaction was then heated to reflux and when the starting material had disappeared (0.5-2 hours), the reaction mixture was cooled and evaporated to dryness. The resulting crude reaction mixture was purified by flash chromatography.

1-(3'-O-benzyl-2'-deoxy-5',6'-O-isopropyliden-ß-D-*arabino*-furanosy)-uracil (28): 2'-Deoxy-2'-phenylselenenyl nucleoside **6ß-gluco** was converted into 2'-deoxynucleoside **28** in standard reaction conditions. The reaction was monitored by TLC in ethyl acetate/ hexane= 1:1. After 35 min the reaction was interrupted by flash evaporation of the solvent. The crude reaction mixture was then chromatographed to afford 0.046 g (90%) of nucleoside **28**. $[\alpha]^{25}_D$ -0.2° (c 5, $CHCl_3$). **^{1}H NMR:** 9.14 (bs, 1H, NH); 7.67 (d, 1H, $J_{6,5}$=8.2 Hz, H_6); 7.35-7.15 (Ph); 6.20 (dd, 1H, $J_{1',2'b}$=8.3 Hz, $J_{1',2'a}$=1.9 Hz, $H_{1'}$); 5.54 (dd, 1H, $J_{5,NH}$=2.0 Hz, H_5); 4.55 (d, 1H, J_{gem}=11.8 Hz, $C\underline{H}_2Ph$); 4.50 (d, 1H, $C\underline{H}_2Ph$); 4.42 (m, 1H, $H_{5'}$); 4.13-4.04 (m, 2H, $H_{3'}$, $H_{4'}$); 3.91 (dd, 1H, $J_{6',6''}$=8.6 Hz, $J_{6',5'}$=5.5 Hz, $H_{6'}$); 3.74 (dd, 1H, $J_{6'',5'}$=3.0 Hz, $H_{6''}$); 2.46 (ddd, 1H, $J_{2',2''}$=15.2 Hz, $J_{2'',3'}$=5.0 Hz, $H_{2''}$); 2.11 (d, 1H, $H_{2'}$); 1.35 (Me); 1.33 (Me). **^{13}C NMR:** 163.3 (C_4); 150.4 (C_2); 140.2 (C_6); 137.2-127.6 (Ph); 102.1 (C_5); 84.9 ($C_{1'}$); 84.4 ($C_{4'}$); 76.6 ($C_{3'}$); 72.3 ($\underline{C}H_2Ph$); 71.9 ($C_{6'}$); 67.4 ($C_{5'}$); 38.8 ($C_{2'}$); 26.8 (Me); 25.4 (Me). **IR**: 1702, 1690 cm^{-1}($\sqrt{}_{CO}$); 1630 cm^{-1}($\sqrt{}_{CH=CH}$).

1-(3',5'-di-O-benzyl-2'-deoxy-ß-D-*threo*-pentofuranosyl)-uracil (29): Nucleoside **8ß-xylo** was converted into **29** using the general procedure described above. After 30 mins, TLC in ethyl acetate/ hexane= 2:1 indicated that the reaction was complete. The solvent was then removed by flash evaporation, and the crude reaction mixture was chromatographed to give 0.061 g (90%) of nucleoside **29**. **^{1}H NMR** : δ 8.41 (bs, 1H, NH), 7.66 (d, 1H, $J_{6,5}$ = 8.23 Hz, H_6), 7.30-7.09 (m, 10H, Ph), 6.15 (dd, 1H, $J_{1',2''}$ = 7.76 Hz, $J_{1',2'}$ = 2.25 Hz, $H_{1'}$), 5.49 (dd, 1H, $J_{5,NH}$ = 2.07 Hz, H_5), 4.56 (d, 1H, J_{gem} = 11.96 Hz, $H_{OCH_2Ph(1)}$), 4.49 (d, 1H, $H_{OCH_2Ph(1)}$), 4.44 (d, 1H, J_{gem} = 11.72 Hz, $H_{OCH_2Ph(2)}$), 4.34 (d, 1H, $H_{OCH_2Ph(2)}$), 4.15-4.05 (m, 2H, $H_{3'}$,$H_{4'}$), 3.81 (dd, 1H, $J_{5',5''}$ = 10.34 Hz, $J_{5',4'}$ = 5.10 Hz, $H_{5'}$), 3.76 (dd, 1H, $H_{5''}$,$_{4'}$ = 6.36 Hz, $H_{5''}$), 2.41 (ddd, 1H, $J_{2'',2'}$ = 15.00 Hz, $J_{2'',3'}$ = 4.91 Hz, $H_{2''}$), 2.17 (dd, 1H, $H_{2'}$). **^{13}C NMR** : δ 160.03 (C_4), 150.22 (C_2), 140.88 (C_6), 128.57-127.68 (Ph, SePh), 101.63 (C_5), 84.87 ($C_{1'}$), 83.15 ($C_{4'}$), 76.70 ($C_{3'}$), 73.60 (C_{OCH_2Ph}), 71.48 (C_{OCH_2Ph}), 67.76 ($C_{5'}$), 38.09 ($C_{2'}$).

1-(3',5'-di-O-benzyl-2'-deoxy-α-D-*erythro*-pentofuranosyl)-uracil (30): As described above, nucleoside **22α-arabino** was reduced with tributyltin hydride. When the reaction was complete (30 min), the solvent was removed by flash evaporation. Chromatography of the crude mixture afforded 0.054g (90%) of nucleoside **30**. $[\alpha]^{25}_D$+0.04° (c 2.9, $CHCl_3$). **^{1}H NMR:** 8.23 (bs 1H, NH); 7.62 (d, 1H, $J_{6,5}$ =8.2 Hz, H_6); 7.35-7.10 (Ph); 6.22 (dd, 1H, $J_{1',2'b}$=1.9 Hz, $J_{1',2'a}$=7.59 Hz, $H_{1'}$); 5.56 (dd, 1H, $J_{5,NH}$=2.4 Hz, H_5); 4.46 (s, 2H, $C\underline{H}_2Ph$); 4.50 (dd, 1H, $H_{4'}$); 4.40 (s, 2H, $C\underline{H}_2Ph$); 4.10 (d, 1H, $H_{3'}$); 3.44 (dd, 1H, $J_{5',5''}$=10.5 Hz, $J_{5',4'}$=3.9 Hz, $H_{5'}$); 3.39 (dd, 1H, $J_{5'',4'}$=4.7 Hz, $H_{5''}$); 2.59 (ddd, 1H, $J_{2',2''}$=15.0 Hz, $J_{2',3'}$=6.2 Hz, $H_{2'}$); 2.14 (dd, 1H, $H_{2''}$). **^{13}C NMR:** 63.1 (C_4); 150.2 (C_2); 140.8 (C_6); 137.5-127.6 (Ph); 103.4 (C_5); 87.0 ($C_{1'}$); 85.9 ($C_{4'}$); 79.4 ($C_{3'}$); 73.6 ($\underline{C}H_2Ph$); 71.3 ($\underline{C}H_2Ph$); 70.5 ($C_{5'}$); 38.3 ($C_{2'}$). **IR**: 1685 cm^{-1}($\sqrt{}_{CO}$); 1600 cm^{-1}($\sqrt{}_{CH=CH}$).

1-(5'-O-(*tert*-butyldiphenylsilyl)-2'-deoxy-3'-O-(methoxy-ethoxy-methylen)-ß-D-*erythro*-furanosyl)-uracil (31): Nucleoside **25ß-ribo** was treated with tributyltin hydride in benzene. After 0.5 h, TLC in ethyl acetate/hexane= 2:1 revealed that the reaction had finished. The solvent was then removed by flash evaporation and the resulting crude mixture was chromatographed in ethyl acetate/hexane= 1/2 to give 0.075 g (90 %) of nucleoside **31**. $[\alpha]^{25}_D$ +31.2° (*c* = 0.47, $CHCl_3$). **^{1}H NMR** : δ 8.30 (bs, 1H, NH), 7.75 (d, 1H, $J_{6,5}$= 8.2 Hz, H_6); 7.67-7.32 (15H, Ph), 6.27 (t, 1H, 9$J_{1',2a'}$ = $J_{1',2b'}$ = 6.4 Hz, $H_{1'}$); 5.35 (d, 1H, H_5), 4.72 (s, 2H, O-$C\underline{H}_2$-O); 4.42 (ddd, 1H, $J_{3',2a'}$ = 6.6 Hz, $J_{3',2b'}$ = 3.6 Hz, $J_{3',4'}$ = 3.3 Hz, $H_{3'}$), 4.08-4.02 (m, 1H, $H_{4'}$); 3.98 (dd, 1H, $J_{5',4'}$ = 2.6Hz, $J_{5',5''}$ = 11.6 Hz, $H_{5'}$); 3.80 (dd, 1H, $J_{5'',4'}$ = 2.4Hz, $H_{5''}$); 3.72-3.60 (m, 2H, O-$C\underline{H}_2$-CH_2-O); 3.53-3.48 (m, 2H, O-CH_2-$C\underline{H}_2$-O); 3.34 (s, 3H, $C\underline{H}_3$O); 2.47 (ddd, 1H, $J_{2b',2a'}$= 13.6 Hz, $H_{2b'}$); 2.14 (ddd, 1H, $H_{2a'}$); 1.06 (s, 9H, $(C\underline{H}_3)_3$CSi). **^{13}C NMR** : δ 162.7 (C_4), 149.9 (C_2), 139.9-128.0 (Ph), 102.3 (C_5), 94.9 (O-

$\underline{C}H_2$-O), 85.2 ($C_{1'}$), 84.9 ($C_{4'}$), 76.6 ($C_{3'}$), 71.5 (O-$\underline{C}H_2$-CH_2-O), 67.3 (O-CH_2-$\underline{C}H_2$-O), 63.6 ($C_{5'}$), 59.0 (CH_3O), 39.0 ($C_{2'}$), 26.9 (($\underline{C}H_3)_3CSi$), 19.3 (($CH_3)_3\underline{C}Si$).

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