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Preparation of selenoanhydro- and telluroanhydroglycofuranosides and some corresponding nucleosides☆

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Dedicated to Professor Wolfgang Walter on the occasion of his 80th birthday

Abstract

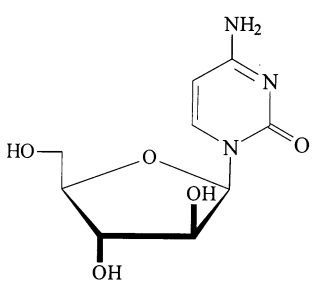
Methyl 2,3-anhydro-α-D-ribofuranoside (**3a**) was transformed into methyl 2-seleno-2,5-anhydro-α-D-arabinofuranoside (**5a**) and methyl 3-seleno-3,5-anhydro-α-D-xylofuranoside (**6a**) in two steps via the reaction of the C-5 mesylate of **3a**, methyl 2,3-anhydro-5-*O*-mesyl-α-D-ribofuranoside (**4a**), with sodium hydrogen selenide. The corresponding β anomer of **3a** yielded methyl 3-seleno-3,5-anhydro-β-D-xylofuranoside as the main product and only traces of methyl 2-seleno-2,5-anhydro-β-D-arabinofuranoside. Sodium hydrogen telluride transformed **4a** into methyl 2-telluro-2,5-anhydro-α-D-arabinofuranoside. Starting from **5a** we prepared 1-(2-seleno-2,5-anhydro-α-D-arabinofuranosyl)uracil and the analogous thymidine nucleoside. Compound **6a** could not be transformed into nucleosides.

Keywords: 2-Seleno-2,5-anhydro-D-arabinofuranosides; 3-Seleno-3,5-anhydro-D-xylofuranosides; 2-Telluro-2,5-anhydro-α-D-arabinofuranoside; X-ray structural analysis; 2-Seleno-2,5-anhydro-α-D-arabinofuranosyl nucleosides

1. Introduction

1-β-D-Arabinofuranosylcytosine (araC, **1**) is an effective agent in the therapy of acute myeloblastic leukaemia [2,3]. Some derivatives have proved to behave similarly, but are more slowly metabolised than araC. For example, 1-(2,5-anhydro-β-D-arabinofuranosyl)cytosine (**2**) [4,5] is a highly potent araC derivative.

Also 3′-thio-3′,5′-anhydro-D-xylofuranosyl nucleosides have been prepared and examined but did not display appreciable cytotoxicity or antiviral activity [6–9]. Carbohydrates and nucleosides of this type containing higher chalcogene homologues have not been reported so far. Our interest, therefore, was to find a pathway to selenoanhydro carbohydrates and their corresponding nucleosides. In



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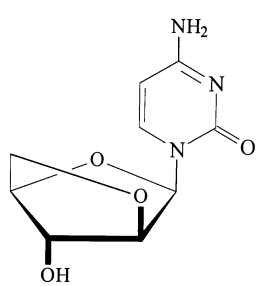

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☆ Part 4 of the series: Thiosugars. For Part 3 see Ref. [1].

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contrast to the above-mentioned reports, we started with the preparation of the bicyclic sugar before linking it with the nucleobase. En route to the bicyclic sugar, we also discovered a possibility for the introduction of tellurium into the sugar moiety.

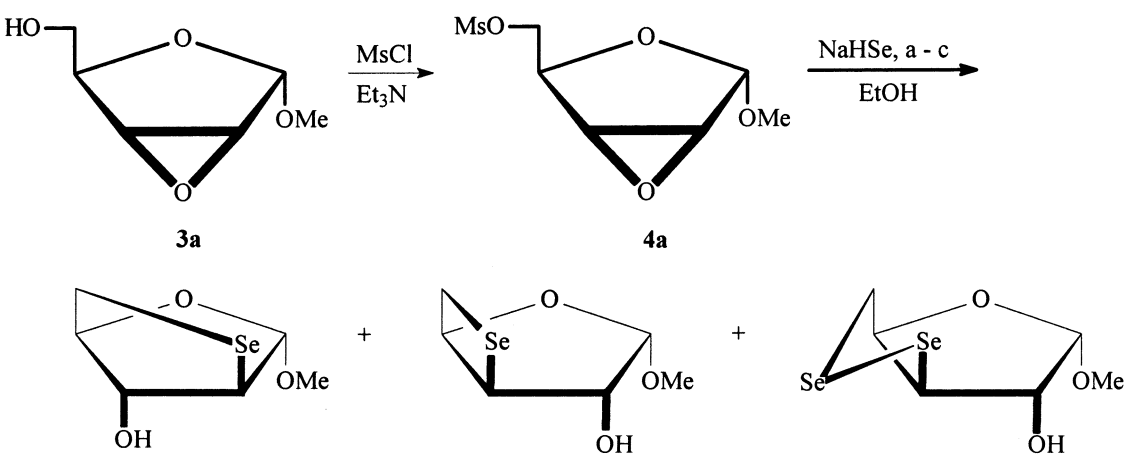
2. Results and discussion

Starting from methyl 2,3-anhydro-α-D-ribofuranoside (**3a**) [10] (we recommend preparing methyl 3,5-*O*-isopropylidene-D-xylofuranoside according to [10b]), bicyclic carbohydrate derivatives containing selenium or tellurium were prepared via the mesylate **4a**. In situ-generated sodium hydrogen selenide [11] proved to be a useful nucleophile for reaction with **4a**. Since it could attack different positions in **4a**, it was necessary to investigate the regioselectivity and its dependence on the reaction conditions. We found that the formation of the 3-seleno-3,5-anhydro compound **6a** was favoured at elevated temperature (60 °C), whereas the formation of the 2-seleno-2,5-anhydro compound **5a** required a lower temperature (40 °C; see Scheme 1).

In principle, the first nucleophilic attack of hydrogen selenide can occur at the oxirane substructure (C-2 or C-3) or at the C-5 position. The postulated intermediates are shown in Scheme 2. A decision about the reaction pathway was not possible. Entropy effects should be the reason for the preferred formation of the selenetane derivative **6a** at higher temperatures. If the temperature is too low, the intramolecular reaction of the selenolate is to slow, which enables a second hydrogen selenide anion to attack the epoxide moiety under formation of a bis-selenol, and eventually during workup, the diselenide **7a** (Scheme 2) is produced. The diselenide **7a** could be crystallised from ethanol as orange needles, which were suitable for an X-ray structural analysis (Fig. 1). The corresponding diselenide **8** was not observed.

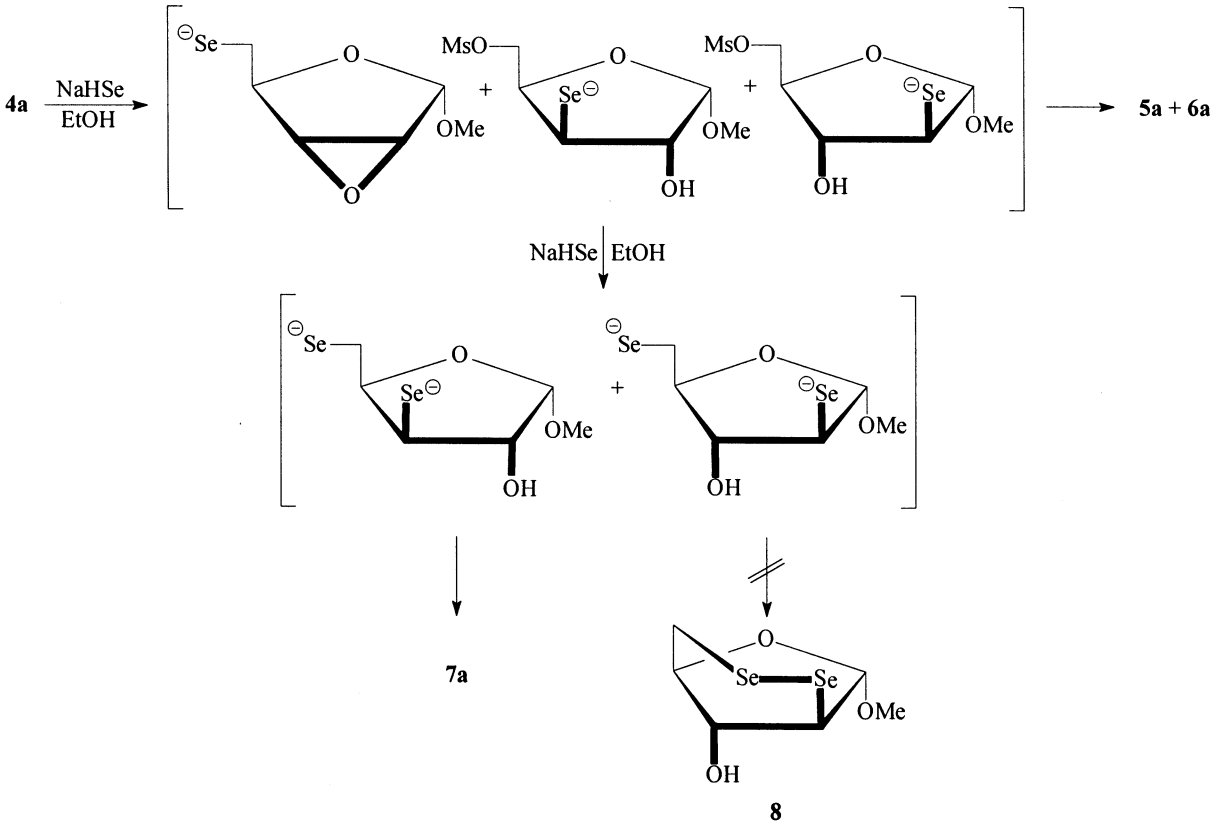
We also performed this synthesis with the analogous β anomer **4b**. In this case the corresponding β anomers **6b** and **7b** were formed as the main products. Only traces of the selenolane derivative **5b** could be isolated. This can be explained by steric hindrance at the 2-position of **4b** by the anomeric methoxy group (Scheme 3).

We also used in situ-generated sodium hydrogen telluride [12] instead of sodium hydrogen selenide. The workup was difficult because the crude product decomposed rapidly by getting in contact with silica gel. Nevertheless, the 2-telluro-2,5-anhydro compound **9** could be isolated with a yield of 24% (Scheme 4). To the best of our knowledge compound **9** represents the first telluroanhydro carbohydrate reported in the literature.



	5a	6a	7a
a: 60 °C	33%	56%	--
b: 40 °C	25%	31%	5%
c: −10 °C	25%	19%	14%

Scheme 1.



Scheme 2.

The structure and configuration, e.g., α or β anomer, of the bicyclic selenium and tellurium derivatives could be unequivocally assigned on the basis of their ^{1}H and ^{13}C NMR spectra. The selenolane sugar **5a** exhibits small $^{3}J_{H,H}$ coupling constants, whereas the corresponding splittings in the thietanes **6a** and **6b** are large due to the special conformation of the ring. In general, the ^{1}H chemical shifts of the seleno- and tellurosugars are very similar to the shifts of the corresponding thiosugars. However, the signals of the ^{13}C nuclei adjacent to the chalcogen nuclei are significantly high-field shifted in the order S < Se < Te. Moreover the NMR spectra of selenium- and tellurium-containing organic compounds are of special interest, since the isotopes ^{77}Se (natural abundance, 7.6%) and ^{125}Te (natural abundance, 7.0%) have a spin of 1/2. Therefore, they are coupling with ^{1}H and ^{13}C, leading to small satellite signals. These satellite peaks can be detected easily in the ^{13}C NMR spectra (Fig. 2). Usually spin–spin coupling constants between ^{125}Te and ^{13}C are about two to three times larger than the corresponding $^{77}Se-^{13}C$ splittings [13]. We observed that the coupling constants of the 2-telluro-2,5-anhydrofuranoside **9** were about 2.5 times larger than the constants for the corresponding 2-seleno-2,5-anhydrofuranoside **5a**. Due to the fact that the satellites have the same shape as the parent signal they can only be observed in the ^{1}H

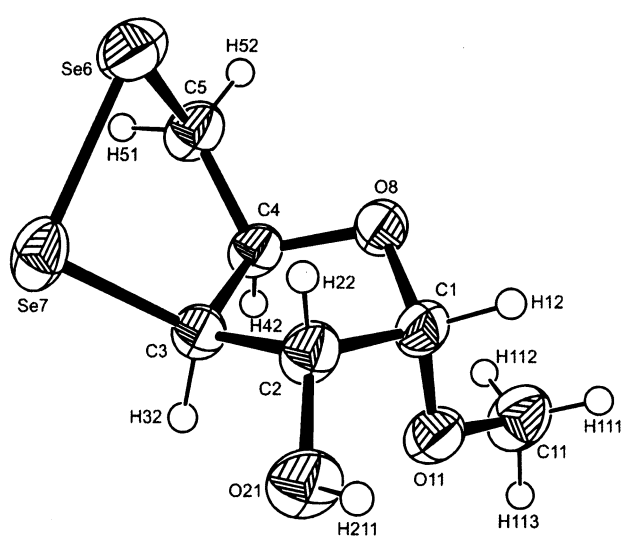
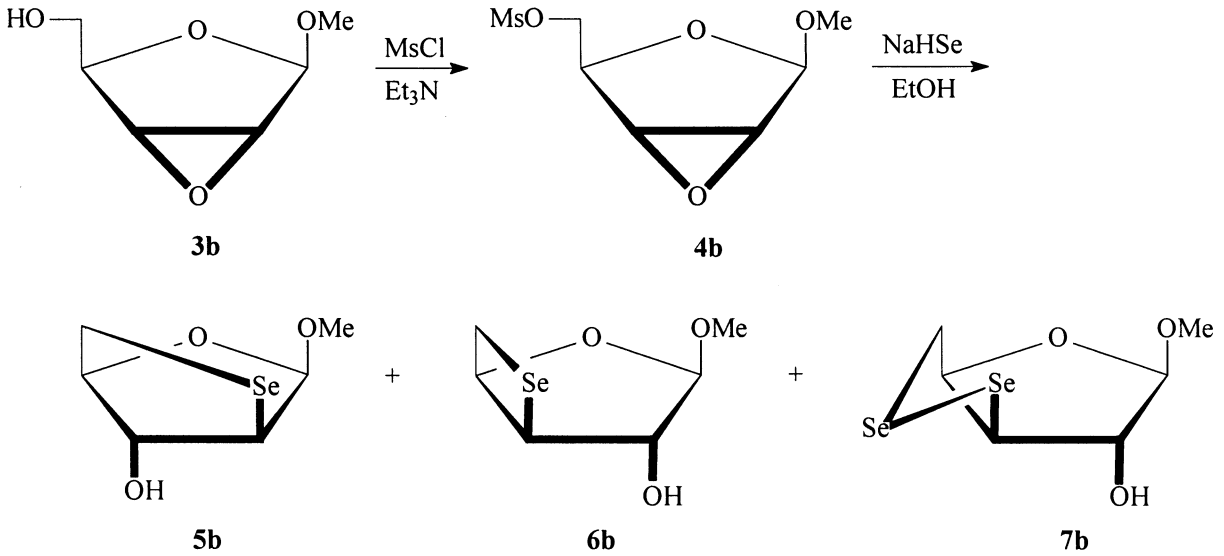


Fig. 1. ORTEP view of the X-ray diffraction structure of diselenide **7a** with atom numbering. Thermal ellipsoids are drawn at the 50% probability level.



Scheme 3.

NMR spectra if the parent signal is narrow and intense, e.g., if it is a singlet. Broad signals of low intensity are usually not detected because they overlap with the main lines.

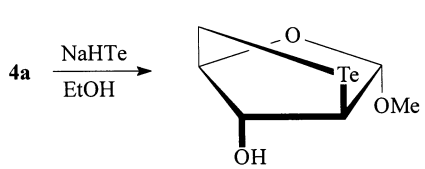
In principle, it is also possible to use sulfur instead of selenium or tellurium, but the yields of bicyclic products are much lower because of the lower nucleophilicity as compared with its higher homologues. A more suitable strategy for the preparation of the corresponding thioanhydro carbohydrates is, therefore, to use the thio-Mitsunobu reaction [14].

Methyl 2-seleno-2,5-anhydro-α-D-arabinofuranoside (**5a**) turned out to be a useful starting material for the synthesis of nucleosides. First, the free hydroxyl group of **5a** was silylated with trimethylsilyl azide. The protected selenosugar **10** needed no further purification. It was coupled with *O*,*O*′-bis(trimethylsilyl)uracil and the corresponding thymine derivative [15] in the presence of trimethylsilyl trifluoromethanesulfonate [16,17] to give the crude protected pyrimidine nucleosides **11** and **12** with yields of about 80%. Both the uridine **11** and thymidine **12** nucleoside analogues were formed as anomeric mixtures. The NMR spectra of the crude products revealed anomeric ratios of 10:1 for **11** and 4:1 for **12**. In both cases the α anomer was the main product. Furthermore the NMR spectra indicated a high purity of both nucleosides. The final step of the synthesis was deprotection of the 3′-position. This was achieved by stirring the protected nucleosides **11** and **12** in a suspension of silica gel in chloroform in the presence of tetrabutylammonium fluoride [18]. In the case of 1-(2-seleno-2,5-anhydro-α-D-arabinofuranosyl)-uracil (**13**), a 44% yield was obtained; the analogous thymidine **14** was obtained in 74% yield. Only the α anomers of both nucleosides were isolated (Scheme 5). The uracil nucleoside **13** could be crystallised from ethanol–acetone to give colourless crystals that were suitable for an X-ray structural analysis (Fig. 3).

Attempts at preparing 1-(3-seleno-3,5-anhydro-D-xylofuranosyl)uracil **15** from **6a** failed in a similar way (Scheme 6).

3. Experimental

General procedures.—Melting points were determined by the use of an electrothermal apparatus (values are corrected). IR spectra were measured with an ATI Mattson Genesis spectrometer. NMR spectra were recorded



Scheme 4.

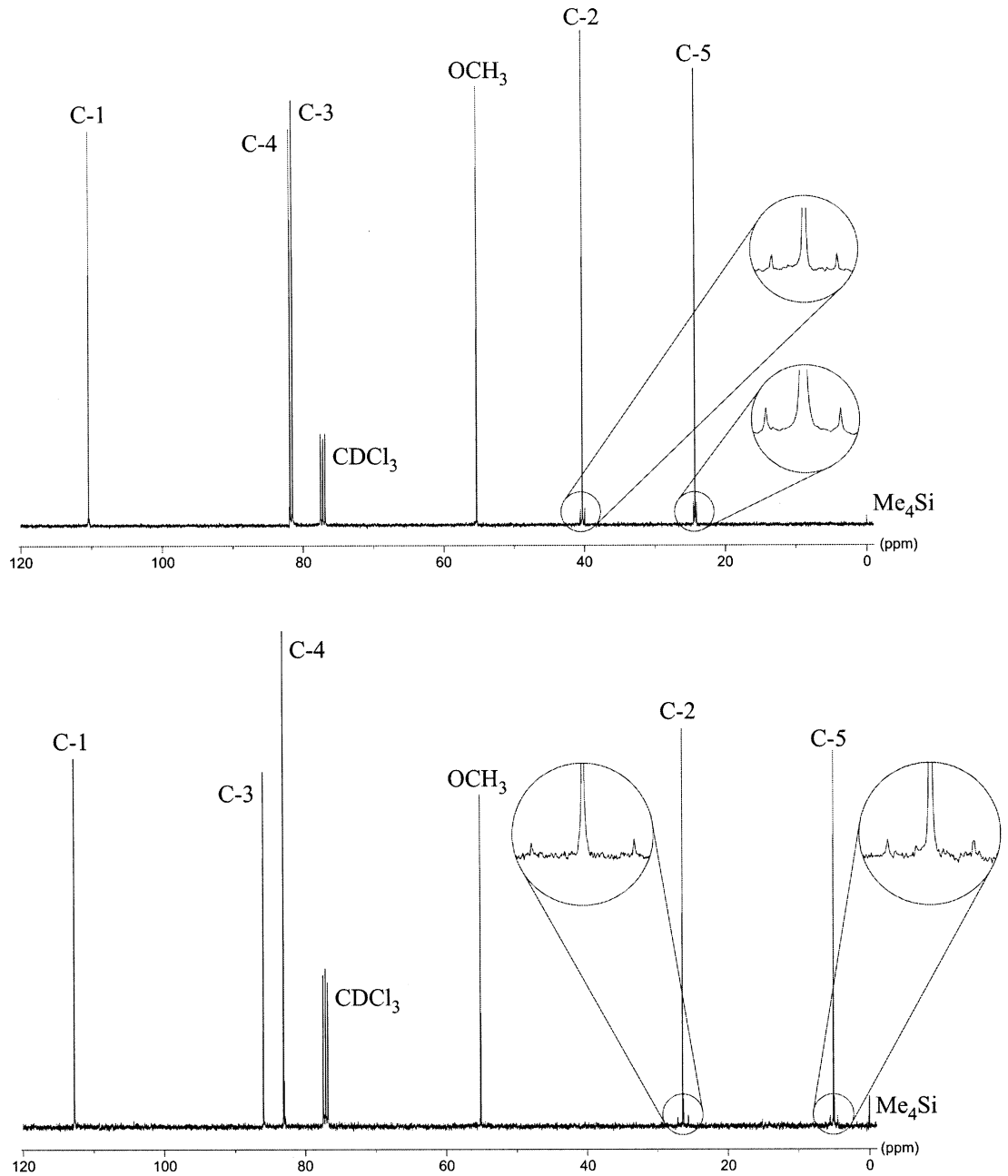
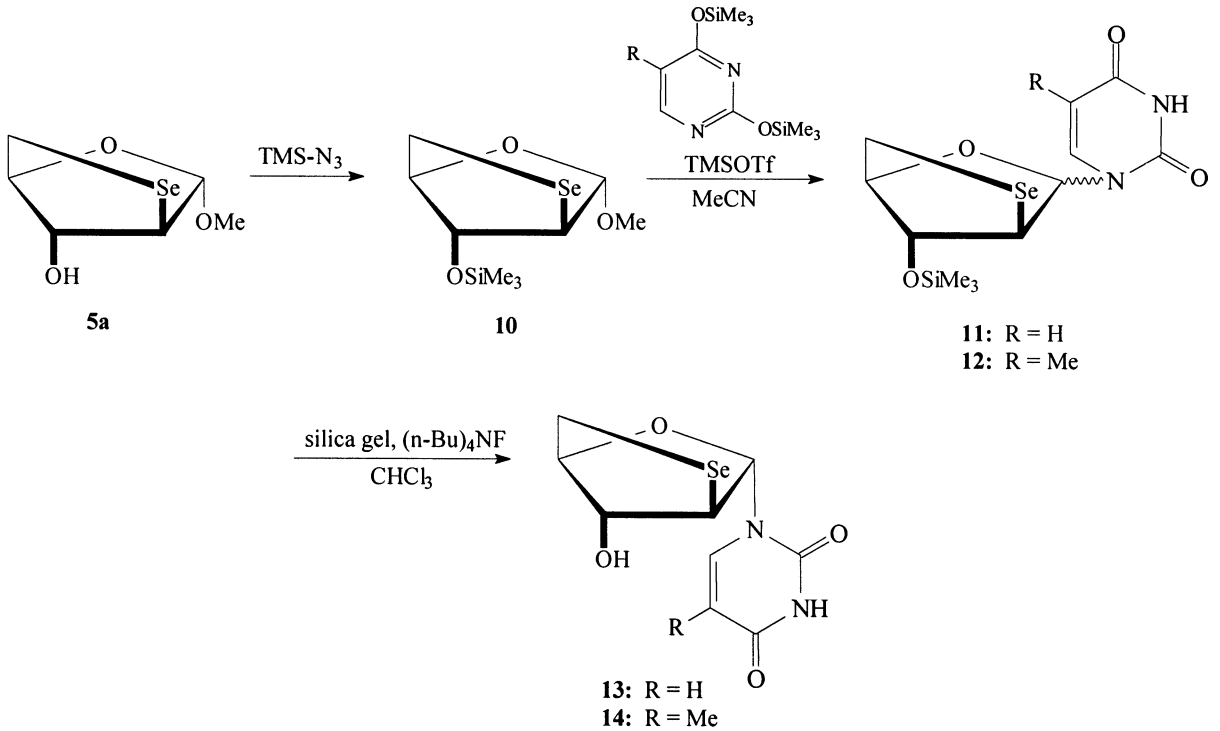


Fig. 2. ^{13}C NMR spectra of 2-seleno-2,5-anhydrofuranoside **5a** (top) and 2-telluro-2,5-anhydrofuranoside **9** (bottom).

with Bruker AMX 400 and DRX 500 spectrometers. Chemical shifts (ppm) are related to Me_4Si (^1H and ^{13}C). Standard correlation techniques were used for assignments. Mass spectra were measured on a Varian CH 7 (EI, 70 eV) and VG Analytical 70–250 S (HRMS) apparatus. HRMS for selenium-containing compounds is calculated for the isotope ^{80}Se. Optical rotations were measured on a Perkin–Elmer polarimeter 341. Thin-layer chromatography (TLC) was carried out on E. Merck PF_{254} foils (detection: UV light, iodine vapour, EtOH–H_2SO_4 spray/200 °C), and column chromatography on E. Merck Kieselgel 60 (70–230 mesh). Solvents were purified and dried according to standard laboratory procedures [19].

X-ray structure analysis.—The crystal data and a summary of experimental details for the diselenide **7a** and the selenonucleoside **13** are given in Tables 1 and 2, respectively. In case of compound **7a** data collection was performed on a CAD4 Nonius diffractometer, with graphite-monochromated Cu K_α radia-



Scheme 5.

tion in the θ–2θ scan mode. In the case of compound **13** data collection was performed on a KappaCCD Nonius diffractometer, with graphite-monochromated Mo K_α radiation in the rotation Φ scan mode. In both cases cell parameters were determined by least-squares refinement of the angular settings of 25 centred reflections with $\theta = 21.5$–47.4 (compound **7a**) and of 180 reflections with $\theta = 9$–27 (compound **13**). The structures were solved by direct methods using the SIR-97 [20] program, and refined by full-matrix-block least-squares on F^2 using all data and the SHELXL-97 [21] program. Hydrogen positions were obtained by difference Fourier synthesis. Cremer–Pople puckering parameter calculations (Tables 3 and 4) and H-bond parameter calculations (Table 5) were performed with the PLATON [22] program.

*Methyl 2,3-anhydro-5-*O*-mesyl-α-*D*-ribofuranoside* (**4a**).—A soln of **3a** (1.57 g, 10.74 mmol) in CH_2Cl_2 (50 mL) was cooled to −16 °C. Then Et_3N (2.8 mL, 2.04 g, 20.20 mmol) and methanesulfonyl chloride (1.4 mL, 2.07 g, 18.09 mmol) were added and the mixture was allowed to warm to room temperature (rt). After evaporation of most of the solvent the reaction mixture was diluted with EtOAc, followed by filtration and evaporation. The crude product was filtered through silica gel (EtOAc, R_f 0.61) to yield **4a** (2.21 g, 92%) as a colourless syrup: $[\alpha]_D^{20}$ +20° (*c* 1.0, $CHCl_3$); IR (film): *v* 3023, 2940, 2845, 1451, 1355, 1248, 1208, 1176, 1131, 1090, 1040, 963, 926, 890, 867, 821, 782, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.08 (s, 3 H, OMs), 3.52

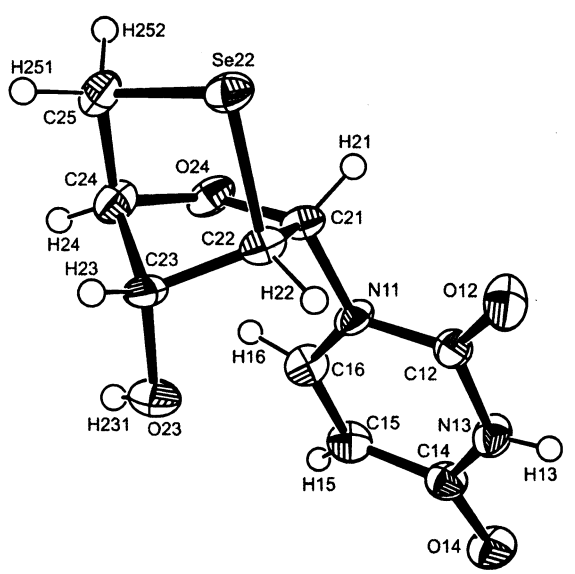
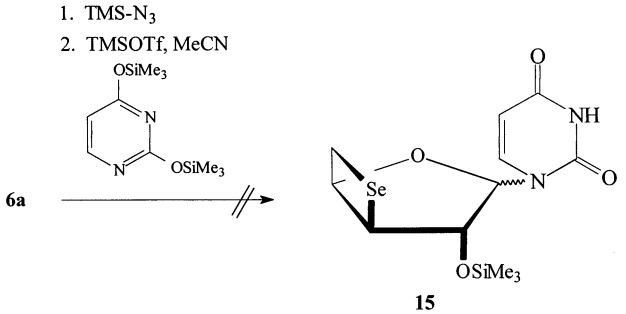


Fig. 3. ORTEP view of the X-ray diffraction structure of selenonucleoside **13**. Thermal ellipsoids are drawn at the 50% probability level.



Scheme 6.

Table 1
Crystal data and structure refinement for **7a**

Diffractometer	CAD4 Nonius
Molecular formula	$C_6H_{10}O_3Se_2$
Molecular weight	288.06
Temperature (K)	293(2)
Wavelength (Å)	1.54184, Cu K_α, graphite monochromated
Scan mode	θ–2θ scan
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	5.296(1)
b (Å)	8.370(1)
c (Å)	19.941(2)
$\alpha=\beta=\gamma$ (°)	90
Volume (Å^3)	883.9(2)
Z (molecules per cell)	4
D_{calcd} (g cm^{-3})	2.165
Absorption coefficient (mm^{-1})	10.163
$F(000)$	552
Crystal size (mm)	$0.37\times0.25\times0.22$
θ Range for data collection (°)	4.43–74.93
Index ranges	$0\le h\le6$, $-10\le k\le8$, $0\le l\le24$
Reflections collected	1893
Independent reflections	1696
Reflections with $[I\ge2\sigma(I)]$	1696
Refinement method	full-matrix-block least-squares on F^2
Function minimized	$\Sigma w(F_o^2-F_c^2)^2$ [a]
H-atom refinement	difmap
Data/restraints/parameters	1696/0/141
Goodness-of-fit on F^2	1.125
Final R indices $[I\ge2\sigma(I)]$	$R_1=0.0282$, $wR_2=0.0777$
R indices (all data)	$R_1=0.0282$, $wR_2=0.0777$
Absolute structure parameter	−0.04(5)
Largest difference peak and hole (e Å^{-3})	0.465 and −0.473

[a] Weighting scheme calcd $w=1/[\sigma^2(F_o^2)+(0.0322P)^2+1.4996P]$, where $P=(F_o^2+2F_c^2)/3$.

(s, 3 H, OMe), 3.78 (d, 1 H, H-2 or H-3), 3.84 (d, 1 H, H-2 or H-3), 4.30 (dd, 1 H, H-5$_a$), 4.33 (dd, 1 H, H-5$_b$), 4.51 (dd, 1 H, H-4), 5.21 (s, 1 H, H-1) ppm. $J_{1,2}$ 0, $J_{2,3}$ 2.8, $J_{3,4}$ 0, $J_{4,5a}$ 3.7, $J_{4,5b}$ 3.4, $J_{5a,5b}$ 11.3 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): δ 37.55 (SO_2CH_3), 55.92 (C-2 or C-3), 56.11 (C-2 or C-3), 57.14 (OCH_3), 69.24 (C-5), 75.77 (C-4), 102.84 (C-1) ppm; EIMS: m/z (%) 224 (0.5) [$M^{+\cdot}$], 193 (7) [$M^{+\cdot}-OCH_3$], 151 (3), 135 (5), 129 (7) [$M^{+\cdot}-OSO_2CH_3$], 115 (91), 101 (36), 97 (26)

Table 2
Crystal data and structure refinement for **13**

Diffractometer	KappaCCD Nonius
Molecular formula	$C_9H_{10}N_2O_4Se$
Molecular weight	289.15
Temperature (K)	293(2)
Wavelength (Å)	0.71070, Mo K_α, graphite monochromated
Scan mode	rotation Φ
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	7.217(1)
b (Å)	5.329(1)
c (Å)	13.089(1)
$\alpha=\gamma$ (°)	90
β (°)	95.45(1)
Volume (Å^3)	501.12(12)
Z (molecules per cell)	2
D_{calcd} (g cm^{-3})	1.916
Absorption coefficient (mm^{-1})	3.747
$F(000)$	288
Crystal size (mm)	$0.42\times0.36\times0.32$
θ Range for data collection (°)	4.02–25.03
Index ranges	$0\le h\le8$, $-6\le k\le5$, $-15\le l\le15$
Reflections collected	7022
Independent reflections	1638
Reflections with $[I\ge2\sigma(I)]$	1619
Refinement method	full-matrix-block least-squares on F^2
Function minimized	$\Sigma w(F_o^2-F_c^2)^2$ [a]
H-atom refinement	difmap
Data/restraints/parameters	1638/1/176
Goodness-of-fit on F^2	1.725
Final R indices $[I\ge2\sigma(I)]$	$R_1=0.0319$, $wR_2=0.0818$
R indices (all data)	$R_1=0.0322$, $wR_2=0.0819$
Absolute structure parameter	0.103(18)
Largest difference peak and hole (e Å^{-3})	1.138 and −0.758

[a] $w=1/[\sigma^2(F_o^2)+(0.0300P)^2+0.2000P]$, where $P=(F_o^2+2F_c^2)/3$.

Table 3
Cremer–Pople puckering parameters Q (pm) and Φ (°) for **7a**

Atom sequence	Se(7)–Se(6)–C(5)–C(4)–C(3) [a]	O(8)–C(1)–C(2)–C(3)–C(4)
Puckering Parameter	$Q(2) = 71.2(4)$ $\Phi(2) = 208.7(4)$	$Q(2) = 40.3(5)$ $\Phi(2) = 36.5(7)$
Closest pucker descriptor	envelope Se(6)	envelope C(3)–exo

[a] Puckering analysis may be dubious as % (bond distance range/average) > 25%.

$[M^{+\cdot} - OSO_2CH_3, -OCH_3]$, 85 (69), 79 (90), 71 (49), 69 (51), 68 (100), 61 (67), 59 (78), 57 (84), 45 (79), 41 (64); HRMS Calcd for $C_7H_{12}O_6S$: 224.0354. Found: 224.0320.

*Methyl 2,3-anhydro-5-*O*-mesyl-β-*D*-ribo-furanoside* (**4b**).—Preparation of **4b** was carried out as described for **4a**, using **3b** (3.94 g, 26.96 mmol), Et_3N (7.1 mL, 5.18 g, 51.22 mmol), methanesulfonyl chloride (3.5 mL, 5.18 g, 45.22 mmol) and CH_2Cl_2 (85 mL). Filtration through silica gel (EtOAc, R_f 0.78) yielded **4b** (5.59 g, 93%) as a colourless syrup; $[\alpha]_D^{20}$ −89° (*c* 1.0, $CHCl_3$); IR (film): ν 3025, 2941, 2838, 1458, 1412, 1357, 1249, 1215, 1177, 1123, 1103, 1075, 1048, 967, 925, 893, 836, 780, 762, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.02 (s, 3 H, OMs), 3.35 (s, 3 H, OMe), 3.65 (d, 1 H, H-2 or H-3), 3.77 (d, 1 H, H-2 or H-3), 4.14 (dd, 1 H, H-5_a), 4.19 (dd, 1 H, H-5_b), 4.31 (dd, 1 H, H-4), 4.92 (s, 1 H, H-1) ppm. $J_{1,2}$ 0, $J_{2,3}$ 2.7, $J_{3,4}$ 0, $J_{4,5a}$ 6.7, $J_{4,5b}$ 6.0, $J_{5a,5b}$ 10.5 Hz; ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.80 (SO_2CH_3), 54.75 (C-2 or C-3 or OCH_3), 56.10 (C-2 or C-3 or OCH_3), 56.21 (C-2 or C-3 or OCH_3), 68.60 (C-5), 75.69 (C-4), 103.04 (C-1) ppm; EIMS: m/z (%) 224 (1) $[M^{+\cdot}]$, 193 (14) $[M^{+\cdot} - OCH_3]$, 151 (2), 135 (4), 129 (10) $[M^{+\cdot} - OSO_2CH_3]$, 115 (100), 97 (26) $[M^{+\cdot} - OSO_2CH_3, -OCH_3]$, 85 (67), 79 (77), 71 (29), 69 (50), 68 (91), 61 (54), 59 (82), 57 (68), 45 (78), 41 (55); HRMS Calcd for $C_7H_{13}O_6S$: 225.0388; $C_7H_{11}O_6S$: 223.0276; $C_6H_9O_5S$: 193.0171. Found: 224.9931; 223.0267; 193.0168; The M^+ peak was covered by the matrix.

Reaction of **4a** *with sodium hydrogen selenide.*—Under nitrogen, a soln of sodium hydrogen selenide prepared from black sele-

Table 4
Cremer–Pople puckering parameters Q (pm) and Φ, Θ (°) for **13**

Atom sequence	Se(22)–C(22)–C(23)–C(24)–C(25) [a]	O(24)–C(21)–C(22)–C(23)–C(24)	Se(22)–C(22)–C(21)–O(24)–C(24)–C(25)
Puckering	$Q(2) = 65.1(5)$	$Q(2) = 49.2(5)$	$Q(2) = 105.0(5)$ $Q(3) = -10.7(5)$
Parameter	$\Phi(2) = 70.1(4)$	$\Phi(2) = 106.5(6)$	$\Phi(2) = 233.3(2)$
Closest pucker descriptor	envelope C(23)	envelope C(23)–exo	
Total puckering amplitude			$Q = 161.2(3)$ $\Theta = 95.8(3)$ $\Phi = 233.2(2)$

[a] Puckering analysis may be dubious as % (bond distance range/average) > 25%.

Table 5
Intermolecular H-bond parameters for **7a** and **13**

	Donor	Acceptor	Distance (pm)			Angle (°)	Symmetry equivalence of A
	(D–H)	(A)	D–H	H···A	D···A	D–H···A	
7a	O(21)–H	O(11)	95(8)	192(8)	282.2(5)	156(7)	$-1/2+x, 1/2-y, -z$
12	N(13)–H	O(14)	78(8)	235(8)	308.1(6)	155(8)	$-x, 1/2+y, 1-z$
	O(23)–H	O(14)	71(9)	213(8)	282.5(5)	169(9)	$1-x, -1/2+y, 1-z$

nium (0.88 g, 11.14 mmol), $NaBH_4$ (0.45 g, 11.90 mmol) and EtOH (20 mL) [11] was poured into a soln of **4a** (2.09 g, 9.32 mmol) in abs EtOH (500 mL) stirred at 60 °C. After raising the temperature to 80 °C the reaction mixture was kept under reflux for 1 h and then cooled to rt. The solvent was evaporated under diminished pressure and the residue was resolved in EtOAc. After filtration, the products were purified by silica gel chromatography (3:2 petroleum ether–EtOAc) to yield **5a** (0.65 g, 33%) as a pale yellow oil (R_f 0.43) and **6a** (1.09 g, 56%) as colourless crystals (R_f 0.36). Adding the sodium hydrogen selenide soln at 40 °C, stirring for 1 h and raising the temperature to 60 °C for 1 h yielded **5a** (25%), **6a** (31%) and the diselenide **7a** (5%) as orange needles (R_f 0.29), which were recrystallised from EtOH. Adding the sodium hydrogen selenide soln at −10 °C, warming to rt within 3 h, stirring for 12 h and finally heating to reflux for 2 h yielded **5a** (25%), **6a** (19%) and **7a** (14%).

*Methyl 2-seleno-2,5-anhydro-α-*D*-arabino-furanoside* (**5a**). $[\alpha]_D^{20}$ +174° (*c* 1.0, $CHCl_3$); IR (film): *ν* 3490, 2957, 2832, 1465, 1429, 1359, 1335, 1306, 1277, 1259, 1241, 1203, 1194, 1119, 1077, 1020, 1006, 969, 960, 936, 904, 842, 814, 765, 722, 647 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 2.75 (ddd, 1 H, H-5_a), 2.87 (ddd, 1 H, H-5_b), 3.35 (dd, 1 H, H-2), 3.44 (s, 3 H, OCH_3), 3.70 (d, 1 H, OH), 4.29 (d, 1 H, H-3), 4.63 (dd, 1 H, H-4), 5.29 (s, 1 H, H-1) ppm. $J_{1,2}$ 0, $J_{2,3}$ 1.7, $J_{2,Se}$ 29.7, $J_{3,OH}$ 11.2, $J_{3,4}$ 0, $J_{4,5a}$ 1.6, $J_{4,5b}$ 2.1, $J_{5a,5b}$ 9.9, $J_{5a,Se}$ 15.0, $J_{5b,Se}$ 11.6 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 24.26 (C-5), 40.26 (C-2), 52.29 (OCH_3), 81.49 (C-3), 81.87 (C-4), 110.36 (C-1) ppm. $J_{2,Se}$ 61.8, $J_{5,Se}$ 43.7; EIMS: *m/z* (%) 212 (8)/210 (50)/208 (25)/207 (9)/206 (10); [$M^{+\bullet}$], 179 (17) [$M^{+\bullet} - OCH_3$], 150 (38) [$M^{+\bullet} - O - CH - OCH_3$], 148 (20), 121 (19), 108 (17), 93 (27), 87 (80), 69 (31), 68 (27), 57 (55), 55 (100), 43 (60), 41 (50); HRMS Calcd for $C_6H_{10}O_3Se$: 209.9795. Found: 209.9792.

*Methyl 3-seleno-3,5-anhydro-α-*D*-xylofuranoside* (**6a**). Mp 51 °C; $[\alpha]_D^{20}$ +196° (*c* 1.0, $CHCl_3$); IR (KBr): *ν* 3449, 3008, 2984, 2941, 2835, 1471, 1454, 1441, 1426, 1372, 1326, 1316, 1283, 1268, 1221, 1185, 1162, 1140, 1106, 1086, 1059, 1026, 992, 948, 902, 863, 844, 767, 716, 695, 602, 565, 519 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.80 (d, 1 H, OH), 2.93 (dd, 1 H, H-5_a), 3.43 (dd, 1 H, H-5_b), 3.52 (s, 3 H, OCH_3), 3.68 (dd, 1 H, H-3), 4.65 (ddd, 1 H, H-2), 5.33 (d, 1 H, H-1), 5.40 (ddd, 1 H, H-4) ppm. $J_{1,2}$ 4.1, $J_{2,3}$ 3.4, $J_{2,OH}$ 7.3, $J_{3,4}$ 6.6, $J_{4,5a}$ 3.3, $J_{4,5b}$ 6.4, $J_{5a,5b}$ 9.7 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 18.43 (C-5), 34.62 (C-3), 55.98 (OCH_3), 80.19 (C-2), 81.42 (C-4), 103.20 (C-1) ppm. $J_{3,Se}$ 19.0, $J_{5,Se}$ 12.8 Hz; EIMS: *m/z* (%) 212 (5)/210 (25)/208 (13)/207 (4)/206 (5) [$M^{+\bullet}$], 179 (3) [$M^{+\bullet} - OCH_3$], 150 (100) [$M^{+\bullet} - O - CH - OCH_3$], 148 (46), 121 (33), 119 (20), 108 (17), 93 (17), 87 (30), 69 (70), 68 (63), 41 (92); HRMS Calcd for $C_6H_{10}O_3Se$: 209.9795. Found: 209.9753; Anal. Calcd for $C_6H_{10}O_3Se$: C, 34.46; H, 4.82; O, 22.95; Se, 37.76. Found: C, 34.77; H, 4.94; O, 22.73; Se, 35.70.

*Methyl 3,5-diseleno-3,5-anhydro-α-*D*-xylofuranoside* (**7a**). Mp 84 °C; $[\alpha]_D^{20}$ +746° (*c* 1.0, $CHCl_3$); IR (KBr): *ν* 3434, 3001, 2939, 2904, 2876, 2830, 1450, 1422, 1391, 1353, 1316, 1277, 1193, 1162, 1148, 1113, 1096, 1027, 994, 956, 899, 872, 773, 749, 702, 606, 579, 520, 461 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 2.48 (bs, 1 H, OH), 3.26 (dd, 1 H, H-5_a), 3.48 (s, 3 H, OCH_3), 3.68 (dd, 1 H, H-5_b), 3.98 (dd, 1 H, H-3), 4.29 (dd, 1 H, H-2), 4.89 (d, 1 H, H-1), 5.35 (ddd, 1 H, H-4) ppm. $J_{1,2}$ 4.4, $J_{2,3}$ 6.4, $J_{3,4}$ 6.7, $J_{4,5a}$ 4.0, $J_{4,5b}$ 1.3, $J_{5a,5b}$ 12.3 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 42.21 (C-5), 55.26 (OCH_3), 56.64 (C-3), 80.65 (C-2), 87.23 (C-4), 102.56 (C-1) ppm. $J_{3,Se}$ 77.9, $J_{5,Se}$ 67.8 Hz; EIMS: *m/z* (%) 294 (0.2)/293 (0.2)/292 (2.2)/291 (0.3)/290 (5.7)/289 (0.7)/288 (4.9)/287 (1.9)/286 (2.9)/285 (0.6)/284 (1.1)/283 (0.3)/282 (0.2); [$M^{+\bullet}$], 258 (1), 199 (2), 160 (5), 130 (2 [$M^{+\bullet} - 2$ Se]), 93 (5), 87 (7), 71 (9), 70 (100), 69 (36); HRMS Calcd for $C_6H_{10}O_3Se_2$: 289.8960. Found: 289.8972; Anal. Calcd for $C_6H_{10}O_3Se_2$: C, 25.02; H, 3.50; O, 16.66; Se, 54.82. Found: C, 25.24; H, 3.59; O, 16.55; Se, 51.40.

Reaction of **4b** *with sodium hydrogen selenide.*—A soln of sodium hydrogen selenide prepared from black selenium (0.63 g, 7.98 mmol), $NaBH_4$ (0.50 g, 13.22 mmol) and EtOH (15 mL) [11] was reacted with a soln of **4b** (1.15 g, 5.13 mmol) in abs EtOH (350 mL) stirred at 70 °C. After raising the temperature and refluxing for 2 h, the reaction mixture was

worked up as described for the corresponding α anomers **5a**, **6a** and **7a** to yield **6b** (0.56 g, 52%) as a yellow syrup (1:1 petroleum ether–EtOAc, R_f 0.40) and the diselenide **7b** (0.15 g, 10%) as a red oil (1:1 petroleum ether–EtOAc, R_f 0.38), which was still contaminated with traces of **6b**. Only traces of **5b** could be identified by GC–MS coupling.

*Methyl 2-seleno-2,5-anhydro-β-*D*-arabino-furanoside* (**5b**). EIMS: *m/z* (%) 212 (3)/210 (10)/208 (5)/207 (2)/206 (3); [$M^{+\bullet}$], 179 (2) [$M^{+\bullet} - OCH_3$], 150 (60) [$M^{+\bullet} - O - CH - OCH_3$], 148 (28), 133 (12), 121 (23), 108 (17), 93 (20), 87 (25), 69 (71), 68 (64), 61 (31), 57 (18), 55 (22), 43 (44), 41 (100); HRMS Calcd for $C_6H_{10}O_3Se$: 209.9795. Found: 209.9778.

*Methyl 3-seleno-3,5-anhydro-β-*D*-xylofuranoside* (**6b**). IR (KBr): *ν* 3391, 2988, 2923, 2830, 1466, 1449, 1416, 1372, 1312, 1302, 1249, 1200, 1174, 1109, 1046, 1000, 967, 936, 817, 786, 760, 740, 684, 652, 591, 573, 473 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 1 H, OH), 3.16 (dd, 1 H, H-5_a), 3.39 (dd, 1 H, H-5_b), 3.56 (s, 3 H, OCH_3), 3.71 (d, 1 H, H-3), 4.68 (s, 1 H, H-2), 5.17 (s, 1 H, H-1), 5.59 (ddd, 1 H, H-4) ppm. $J_{1,2}$ 0, $J_{2,3}$ 0, $J_{3,4}$ 7.0, $J_{4,5a}$ 4.1, $J_{4,5b}$ 7.4, $J_{5a,5b}$ 9.5 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.66 (C-5), 35.97 (C-3), 56.10 (OCH_3), 81.74 (C-2), 83.99 (C-4), 114.17 (C-1) ppm. $J_{3,Se}$ 21.1, $J_{5,Se}$ 12.1 Hz; EIMS: *m/z* (%) 212 (3)/210 (17)/208 (9)/207 (3)/206 (4) [$M^{+\bullet}$], 179 (3) [$M^{+\bullet} - OCH_3$], 150 (78) [$M^{+\bullet} - O - CH - OCH_3$], 148 (38), 133 (17), 121 (35), 108 (20), 93 (37), 87 (83), 69 (100), 67 (90), 61 (61), 55 (33), 41 (99); HRMS Calcd for $C_6H_{10}O_3Se$: 209.9795; $C_5H_7O_2Se$: 178.9795; C_4H_6OSe: 149.9584. Found: 209.9801; 178.9618; 149.9557.

*Methyl 3,5-diseleno-3,5-anhydro-β-*D*-xylofuranoside* (**7b**). ^1H NMR (400 MHz, $CDCl_3$): δ 3.39 (dd, 1 H, H-5_a), 3.46 (s, 3 H, OCH_3), 3.74 (dd, 1 H, H-5_b), 4.08 (dd, 1 H, H-3), 4.24 (dd, 1 H, H-2), 4.79 (d, 1 H, H-1), 5.44 (ddd, 1 H, H-4) ppm. $J_{1,2}$ 3.5, $J_{2,3}$ 4.3, $J_{3,4}$ 6.5, $J_{4,5a}$ 3.9, $J_{4,5b}$ 3.3, $J_{5a,5b}$ 12.4 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): δ 41.89 (C-5), 55.29 (C-3), 56.68 (OCH_3), 82.05 (C-2), 88.55 (C-4), 109.02 (C-1) ppm. $J_{3,Se}$ 78.3, $J_{5,Se}$ 67.8 Hz.

Reaction of **4a** *with sodium hydrogen telluride.*—Under nitrogen a soln of sodium hydrogen telluride, prepared by refluxing tellurium (680 mg, 5.33 mmol) and $NaBH_4$ (540 mg, 14.27 mmol) in EtOH (10 mL) [12], was poured at 60 °C into a stirred soln of **4a** (1.00 g, 4.46 mmol) in abs EtOH (250 mL). After raising the temperature and refluxing for 1 h, the workup was carried out as described for the reaction of **4a** with sodium hydrogen selenide. Purification by silica gel chromatography (EtOAc, R_f 0.75) yielded **9** (270 mg, 24%) as a yellow oil.

*Methyl 2-telluro-2,5-anhydro-α-*D*-arabino-furanoside* (**9**). IR (film): *ν* 3483, 2944, 2831, 1440, 1422, 1358, 1335, 1304, 1275, 1257, 1241, 1189, 1145, 1111, 1073, 1035, 1016, 1004, 971, 944, 936, 908, 881, 808, 757, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.01 (dd, 1 H, H-5_a), 3.13 (dd, 1 H, H-5_b), 3.44 (s, 3 H, OCH_3), 3.64 (d, 1 H, H-2), 3.77 (d, 1 H, OH), 4.41 (dd, 1 H, H-3), 4.71 (dd, 1 H, H-4), 5.67 (s, 1 H, H-1) ppm. $J_{1,2}$ 0, $J_{2,3}$ 1.2, $J_{3,4}$ 0, $J_{4,OH}$ 11.3, $J_{4,5a}$ 1.9, $J_{4,5b}$ 2.3, $J_{5a,5b}$ 10.1; ^{13}C NMR (101, $CDCl_3$): δ 4.98 (C-5), 26.34 (C-2), 55.10 (OCH_3), 83.06 (C-4), 85.93 (C-3), 112.75 (C-1) ppm. $J_{2,Te}$ 152.1, $J_{5,Te}$ 101.6 Hz.

*1-(2-Seleno-2,5-anhydro-3-*O*-trimethylsilyl-*D*-arabinofuranosyl)uracil* (**11**).—To the bicyclic carbohydrate **5a** (240 mg, 1.15 mmol) was added trimethylsilyl azide (0.6 mL, 528 mg, 4.58 mmol). After 3 h, all **5a** was dissolved and the soln was stirred at rt for 24 h. After addition of satd aq $NaHCO_3$ soln (20 mL) and extraction with $CHCl_3$, the organic phase was evaporated to yield the crude silyl protected carbohydrate **10** (302 mg, 94%). This was dissolved in dry MeCN (10 mL), *O,O′*-bis(trimethylsilyl)uracil [15] (1.10 g, 4.29 mmol) and molecular sieves A4 (50 mg) were added and the soln cooled to −18 °C. Then Me_3SiOTf (1.2 mL, 1.48 g, 6.64 mmol) was added and the reaction mixture was stirred for 1.5 h, while the mixture was allowed to warm to 0 °C. The reaction was stopped by quenching with satd aq $NaHCO_3$ soln (50 mL). The aq phase was extracted with $CHCl_3$, dried with $MgSO_4$ and evaporated to yield the solid, protected nucleoside **11** (356 mg, 86%). The ^1H NMR of the crude product indicated that **11** was formed as an anomeric mixture with an α:β ratio of 10:1: IR (KBr): *ν* 3134, 3026, 2956, 2924, 2854, 2805, 1681, 1464, 1394, 1279, 1258, 1207, 1131, 1112, 1089, 1046,

1009, 911, 886, 842, 749, 641, 559, 545, 430 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): α anomer: δ 0.07 (s, 9 H, CH_3), 2.86 (dd, 1 H, H-5′a), 2.90 (dd, 1 H, H-5′b), 3.64 (d, 0.9 H, H-2′), 3.64 (dd, 0.1 H, H-2′), 4.46 (d, 1 H, H-3′), 4.73 (dd, 1 H, H-4′), 5.61 (dd, 1 H, H-5), 6.19 (s, 1 H, H-1′), 7.70 (d, 1 H, H-6), 8.63 (bs, 1 H, NH) ppm. $J_{1',2'}$ 0, $J_{2',3'}$ 1.2, $J_{2',Se}$ 28.7, $J_{3',4'}$ 0, $J_{4',5'a}$ 1.5, $J_{4',5'b}$ 1.9, $J_{5'a,5'b}$ 10.3, $J_{5,6}$ 8.2, $J_{5,NH}$ 1.9 Hz. β Anomer: δ 0.07 (s, 9 H, CH_3), 2.87–2.90 (m, 1 H, H-5′a), 2.94 (dd, 1 H, H-5′b), 4.09 (d, 1 H, H-2′), 4.63 (d, 1 H, H-3′), 4.89 (dd, 1 H, H-4′), 5.42 (dd, 1 H, H-5), 6.19 (s, 1 H, H-1′), 7.80 (d, 1 H, H-6), 10.65 (bs, 1 H, NH) ppm. $J_{1',2'}$ 0, $J_{2',3'}$ 1.1, $J_{3',4'}$ 0, $J_{4',5'a}$ 1.4, $J_{4',5'b}$ 2.0, $J_{5'a,5'b}$ 10.1, $J_{5,6}$ 8.1, $J_{5,NH}$ 1.5 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): α anomer: δ 2.19 (CH_3), 23.76 (C-5′), 43.07 (C-2′), 80.40 (C-3′), 84.26 (C-4′), 93.08 (C-1′), 99.48 (C-5), 141.73 (C-6), 150.56 (2-CO), 164.19 (4-CO) ppm. β Anomer: because of the fast decomposition of the β anomer, its carbon atoms could not be detected by NMR spectroscopy.

*1-(2-Seleno-2,5-anhydro-3-*O*-trimethylsilyl-*D*-arabinofuranosyl)thymine* (**12**).—The reaction was carried out as described for **11** by using carbohydrate **5a** (200 mg, 0.96 mmol) and trimethylsilyl azide (0.6 mL, 528 mg, 4.58 mmol) to yield the crude silyl-protected carbohydrate **7** (217 mg, 81%). This was transformed into the protected thymine nucleoside **12** by using *O*,*O*′-bis(trimethylsilyl)thymine [15] (830 mg, 3.07 mmol), Me_3SiOTf (0.86 mL, 1.06 g, 4.76 mmol), 4 Å molecular sieves (50 mg) and dry MeCN (10 mL) to yield the solid, crude nucleoside **12** (255 mg, 88%) as an anomeric mixture with an α:β ratio of 4:1: IR (KBr): *v* 3192, 3030, 2966, 2926, 2853, 1691, 1663, 1459, 1388, 1341, 1331, 1279, 1256, 1202, 1178, 1127, 1108, 1087, 1051, 1009, 941, 915, 879, 855, 838, 766, 749, 570, 478 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): α anomer: δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.91 (s, 3 H, CH_3), 2.90 (dd, 1 H, H-5′a), 2.95 (dd, 1 H, H-5′b), 3.63 (d, 0.9 H, H-2′), 3.63 (dd, 0.1 H, H-2′), 4.46 (d, 1 H, H-3′), 4.74 (dd, 1 H, H-4′), 6.19 (s, 1 H, H-1′), 7.53 (q, 1 H, H-6), 9.09 (bs, 1 H, NH) ppm. $J_{1',2'}$ 0, $J_{2',3'}$ 1.1, $J_{2',Se}$ 28.7, $J_{3',4'}$ 0, $J_{4',5'a}$ 1.4, $J_{4',5'b}$ 2.1, $J_{5'a,5'b}$ 11.1, $J_{6,Me}$ 1.2 Hz. β Anomer: δ 0.07 (s, 9 H, $Si(CH_3)_3$), 1.73 (s, 3 H, CH_3), 2.94–2.96 (m, 1 H, H-5′a), 3.01 (dd, 1 H, H-5′b), 4.10 (d, 0.9 H, H-2′), 4.10 (dd, 0.1 H, H-2′), 4.65 (d, 1 H, H-3′), 4.90 (dd, 1 H, H-4′), 6.25 (s, 1 H, H-1′), 7.69 (q, 1 H, H-6), 11.24 (bs, 1 H, NH) ppm. $J_{1',2'}$ 0, $J_{2',3'}$ 1.1, $J_{2',Se}$ 29.2, $J_{3',4'}$ 0, $J_{4',5'a}$ 2.1, $J_{4',5'b}$ 2.1, $J_{5'a,5'b}$ 10.1, $J_{6,Me}$ 1.2 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): α anomer: δ 1.94 ($Si(CH_3)_3$), 12.22 (CH_3), 23.47 (C-5′), 42.98 (C-2′), 80.13 (C-3′), 83.93 (C-4′), 92.75 (C-1′), 106.52 (C-5), 138.80 (C-6), 152.28 (2-CO), 165.45 (4-CO) ppm. β Anomer: δ −0.34 ($Si(CH_3)_3$), 12.59 (CH_3), 24.49 (C-5′), 43.69 (C-2′), 79.86 (C-3′), 83.84 (C-4′), 92.61 (C-1′), 107.21 (C-5), 137.44 (C-6), 150.17 (2-CO), 164.17 (4-CO) ppm.

*1-(2-Seleno-2,5-anhydro-α-*D*-arabinofuranosyl)uracil* (**13**).—The protected nucleoside **11** (356 mg, 0.99 mmol, α:β 10:1) was dissolved in $CHCl_3$ (200 mL) and silica gel (50 g) was added. After 2 h tetrabutylammonium fluoride (0.4 mL, 1 M soln in THF) was added and the mixture was stirred for another 2 h. Then the silica gel was filtered, washed with $CHCl_3$ and MeOH, the organic phase evaporated and the crude deprotected nucleoside purified by silica gel chromatography (7:1 $CHCl_3$–MeOH, R_f 0.52) to yield **13** (126 mg, 44%). Only the α anomer could be isolated as a white solid. This was recrystallised from EtOH–acetone to give 88 mg (31%) as colourless crystals: mp 194–196 °C (under decomposition); $[\alpha]_D^{20}$ + 77° (*c* 0.8, MeOH); IR (KBr): *v* 3393, 3231, 3087, 3050, 2959, 2926, 1704, 1667, 1466, 1399, 1354, 1325, 1277, 1256, 1199, 1134, 1086, 1050, 1009, 981, 943, 903, 835, 808, 778, 652, 620, 552 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.94 (dd, 1 H, H-5′a), 3.01 (dd, 1 H, H-5′b), 3.67 (d, 0.9 H, H-2′), 3.67 (dd, 0.1 H, H-2′), 4.51 (d, 1 H, H-3′), 4.84 (dd, 1 H, H-4′), 5.59 (dd, 1 H, H-5), 6.18 (s, 1 H, H-1′), 7.83 (d, 1 H, H-6) ppm. $J_{1',2'}$ 0, $J_{2',3'}$ 1.3, $J_{2',Se}$ 28.7, $J_{3',4'}$ 0, $J_{4',5'a}$ 1.5, $J_{4',5'b}$ 2.0, $J_{5'a,5'b}$ 10.2, $J_{5,6}$ 8.2 Hz; ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.26 (C-5′), 43.18 (C-2′), 79.65 (C-3′), 83.97 (C-4′), 93.07 (C-1′), 99.10 (C-5), 142.16 (C-6), 150.96 (2-CO), 165.42 (4-CO) ppm; EIMS: *m*/*z* (%) 292 (0.3) [$M^{+\bullet}$; ^{82}Se], 290 (1.6) [$M^{+\bullet}$; ^{80}Se], 288 (1.1) [$M^{+\bullet}$; ^{78}Se], 287 (0.3) [$M^{+\bullet}$; ^{77}Se], 286 (0.2) [$M^{+\bullet}$; ^{76}Se], 180 (1.5) [$C_5H_8O_2{}^{82}Se^{+\bullet}$], 178 (5.4) [$C_5H_8O_2{}^{80}Se^{+\bullet}$], 176 (3.8) [$C_5H_8O_2{}^{78}Se^{+\bullet}$], 175 (1.8) [$C_5H_8O_2{}^{77}Se^{+\bullet}$], 174 (1.4) [$C_5H_8O_2{}^{76}Se^{+\bullet}$], 149 (5), 113 (8), 112

(100) [$C_4H_4N_2O_2^{+\bullet}$], 81 (8), 69 (42), 68 (11), 57 (5), 55 (5), 44 (65), 42 (20), 41 (16), 40 (12). HRMS Calcd for $C_9H_{10}N_2O_4^{82}Se$: 291.9808; $C_9H_{10}N_2O_4^{80}Se$: 289.9806; $C_9H_{10}N_2O_4^{78}Se$: 287.9814; $C_9H_{10}N_2O_4^{77}Se$: 286.9840; $C_9H_{10}N_2O_4^{76}Se$: 285.9833. Found: 291.9801; 289.9813; 287.9824; 286.9866; 285.9838. Anal. Calcd for $C_9H_{10}N_2O_4Se$: C, 37.39; H, 3.49; N, 9.69. Found: C, 37.27; H, 3.66; S, 9.56.

1-(2-Seleno-2,5-anhydro-α-D-arabinofuranosyl)thymine (**14**).—Deprotection of **12** was carried out according to the same procedure as described for **13** by using **12** (255 mg, 0.68 mmol, α:β 4:1), silica gel (25 g), $CHCl_3$ (150 mL) and tetrabutylammonium fluoride (0.4 mL, 1 M soln in THF). After column chromatography (silica gel; 7:1 $CHCl_3$–MeOH, R_f 0.46) the unprotected nucleoside **14** was obtained (153 mg, 74%). Only the α anomer could be isolated as a white solid. Crystallisation from MeOH–EtOAc–petroleum ether yielded **14** as colourless needles (75 mg, 36%): mp 199–200 °C (under decomposition); $[\alpha]_D^{20}$ + 81° (*c* 1.0, $CHCl_3$); IR (KBr): *ν* 3394, 3208, 3030, 2953, 2839, 1671, 1471, 1427, 1404, 1347, 1272, 1200, 1130, 1097, 1050, 1013, 978, 943, 914, 830, 778, 770, 746, 687, 657, 575, 490, 432 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.73 (d, 3 H, CH_3), 2.94 (dd, 1 H, H-5′$_a$), 3.00 (dd, 1 H, H-5′$_b$), 4.03 (d, 0.9 H, H-2′), 4.03 (dd, 0.1 H, H-2′), 4.85 (d, 1 H, H-3′), 4.90 (dd, 1 H, H-4′), 5.31 (bs, 1 H, OH), 6.25 (s, 1 H, H-1′), 7.69 (q, 1 H, H-6), 11.12 (bs, 1 H, NH) ppm. $J_{1',2'}$ 0, $J_{2',3'}$ 1.2, $J_{2',Se}$ 29.3, $J_{3',4'}$ 0, $J_{4',5'a}$ 1.6, $J_{4',5'b}$ 1.9, $J_{5'a,5'b}$ 10.2, $J_{6,Me}$ 1.2 Hz; ^{13}C NMR (126 MHz, $CDCl_3$): δ 12.22 (CH_3), 24.49 (C-5′), 43.71 (C-2′), 79.88 (C-3′), 83.87 (C-4′), 92.64 (C-1′), 106.54 (C-5), 138.85 (C-6), 151.31 (2-CO), 165.48 (4-CO) ppm; EIMS: *m*/*z* (%) 306 (1.3) [$M^{+\bullet}$; ^{82}Se], 304 (6.0) [$M^{+\bullet}$; ^{80}Se], 302 (3.1) [$M^{+\bullet}$; ^{78}Se], 301 (1.0) [$M^{+\bullet}$; ^{77}Se], 300 (1.1) [$M^{+\bullet}$; ^{76}Se], 181 (18) [$M^{+\bullet}$ − base; ^{82}Se], 179 (100) [$M^{+\bullet}$ − base; ^{80}Se], 177 (48) [$M^{+\bullet}$ − base; ^{78}Se], 176 (20) [$M^{+\bullet}$ − base; ^{77}Se], 175 (20) [$M^{+\bullet}$ − base; ^{76}Se], 173 (20) [$M^{+\bullet}$ − base; ^{74}Se], 160 (5), 151 (25), 149 (22), 147 (10), 135 (10), 133 (19), 131 (10), 127 (9), 126 (58) [$C_5H_6N_2O_2^+$], 123 (17), 121 (11), 119 (6), 105 (5), 97 (7), 95 (10), 93 (16), 91 (9), 83 (15), 82 (12), 81 (17), 71 (10), 69 (14), 68 (9), 57 (16), 56 (11), 55 (90), 54 (32), 52 (11), 43 (25), 42 (16), 41 (27), 40 (15), 39 (26). HRMS Calcd for $C_{10}H_{12}N_2O_4^{82}Se$: 305.9964; $C_{10}H_{12}N_2O_4^{80}Se$: 303.9962; $C_{10}H_{12}N_2O_4^{78}Se$: 301.9970; $C_{10}H_{12}N_2O_4^{77}Se$: 300.9996; $C_{10}H_{12}N_2O_4^{76}Se$: 299.9989. Found: 305.9946; 303.9951; 301.9949; 286.9988; 285.9989. Anal. Calcd for $C_{10}H_{12}N_2O_4Se$: C, 39.62; H, 3.99; N, 9.24. Found: C, 39.35; H, 4.25; N, 9.28.

Supplementary material

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 135209 for **7a** and 135210 for **13**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: + 44-1223-336408, fax: + 44-1223-336033, e-mail deposit@ccdc.cam.ac.uk).

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