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Carbohydrate Research 339 (2004) 1787–1802
Carbohydrate RESEARCH

The thio-Mitsunobu reaction: a useful tool for the preparation of 2,5-anhydro-2-thio- and 3,5-anhydro-3-thiopentofuranosides ☆

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Received 9 October 2003; accepted 12 April 2004
Available online 7 June 2004

Abstract—The unprotected methyl L-arabinofuranosides, D-ribofuranosides and D-xylofuranosides are transformed into the corresponding *S*-acetyl-5-thio derivatives by the thio-Mitsunobu reaction. Mesylation and subsequent reaction with sodium hydrogen carbonate led, depending on the configuration of the intermediate, to 2,5-anhydro-2-thio- or 3,5-anhydro-3-thiopentofuranosides. Due to inversion at C-3 or C-2 during the intramolecular nucleophilic displacement the products exhibit L-*lyxo*-, D-*arabino*- or D-*lyxo*-configuration. Analogously, the methyl 2,3-anhydro-D-ribofuranosides yielded 5-thio-*S*-acetates with intact 2,3-oxirane groups, which were cyclised with sodium hydrogen carbonate by epoxide ring opening and concomitant ring closure to form exclusively 3,5-anhydro-3-thio-D-xylofuranosides. A related 3,5-anhydro-3-seleno-D-lyxofuranoside was obtained by reaction of a 3,5-di-*O*-mesyl-D-arabinofuranoside with sodium hydrogen selenide. Several X-ray diffraction analyses proved the structures of the products.

Keywords: Thio-Mitsunobu reaction; 5-*S*-Acetyl-5-thiopentofuranosides; Methyl 2,3-anhydro-D-ribofuranosides; Methyl 2,5-anhydro-2-thiopentofuranosides; Methyl 3,5-anhydro-3-thiopentofuranosides; Methyl 3,5-anhydro-3-seleno-α-D-lyxofuranoside; X-ray structural analysis

1. Introduction

The thio-Mitsunobu reaction[1] represents a versatile method for the substitution of hydroxy groups by sulfur nucleophiles. We have applied thioacetic acid as the reagent of choice for the synthesis of thiopentoses,[2] thiohexoses[3] and thiohexitols,[4] and have with this reagent observed total chemoselectivity: primary hydroxy groups could be selectively replaced by acetylthio groups in the presence of unprotected secondary hydroxy groups. We took further advantage of this and present here our comprehensive[5] results on the regioselective and stereocontrolled preparation of anhydrothiopentofuranosides from the 5-*S*-acetyl-5-thiopentofuranosides.

The anhydrothiosugars are compounds with interesting stereochemical properties. Due to their bicyclic molecular skeleton, they exhibit a fixed ring conformation and, consequently, a fixed disposition of the substituents in contrast to the flexible five-membered ring of the monocyclic thiofuranoses. Since they are also highly functionalised compounds, they represent useful intermediates for the synthesis of additional sulfur-containing heterobicycles. They have therefore found interest as building blocks for the preparation of compounds with potential biological activity[6] such as thionucleosides.[7] Furthermore, they are useful precursors for oligohydroxythiolanes.[7b] Compounds of this type represent

☆ Thiosugars, Part 11. For Part 10 see Wirsching, J.; Voss, J.; Giesler, A.; Kopf, J.; Adiwidjaja, G.; Balzarini, J.; De Clercq, E. *Nucleos. Nucleot.*, **2003**, *22*, 1867–1897.

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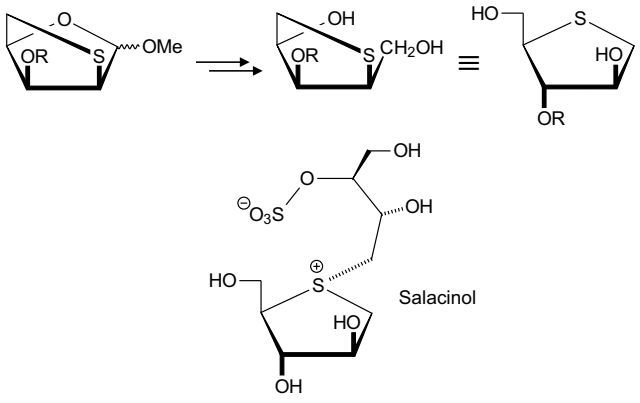
doi:10.1016/j.carres.2004.04.020



Scheme 1.

building blocks for the synthesis of potent natural glycosidase inhibitors such as salacinol[8] (Scheme 1).

2. Results and discussion

We have chosen the methyl furanosides of the three inexpensive aldopentoses, L-arabinose, D-ribose and D-xylose, as starting compounds for our syntheses. Two types of precursors were applied for the cyclisations. We used either 5-*S*-acetyl-5-thio-furanosides with a mesylate leaving group in the appropriate position for the preparation of 3,5-anhydro-3-thio-(*thietano*-) and 2,5-anhydro-2-thio-(*thiolano*-) furanosides or, in the D-*ribo* series, 5-*S*-acetyl-2,3-anhydro-5-thiofuranosides for the transformation into 3,5-anhydro-3-thio-(*thietano*-) furanosides by a ring opening–ring closing reaction.

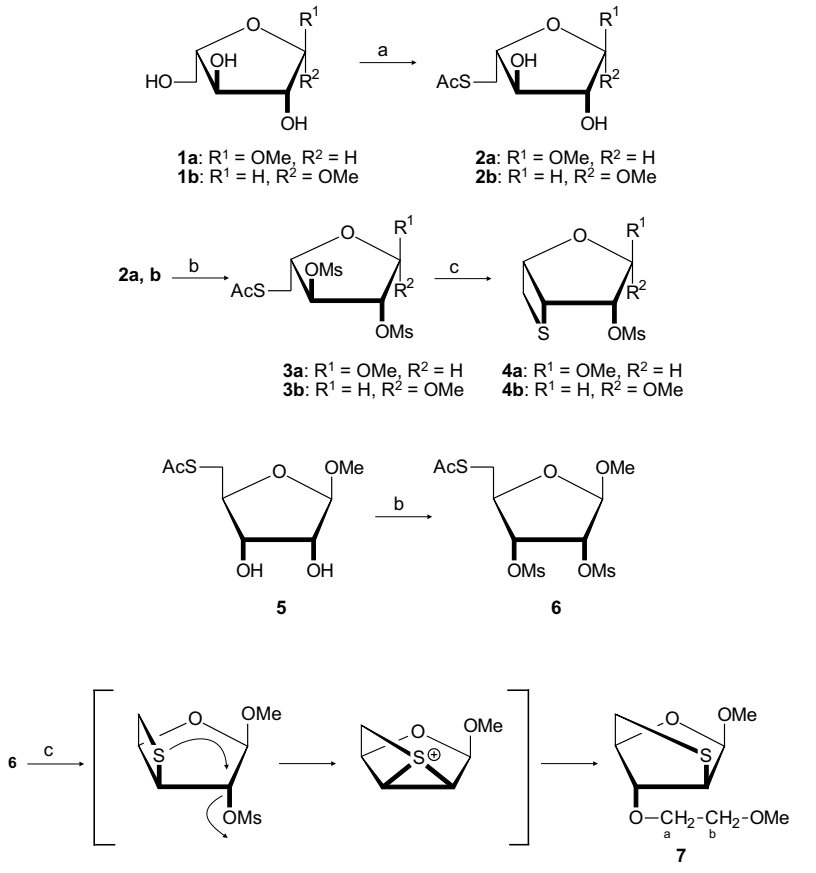
In all cases, the acetylthio group was introduced into the sugar by the thio-Mitsunobu reaction. Colourless thioacetic acid, which had to be carefully purified by repeated low-temperature vacuum distillation and maintenance of an inert atmosphere during the reaction are prerequisites for a successful synthesis. In accordance with our previous experiences,[2,3] the reaction took place exclusively at the primary 5-hydroxy groups. The synthesis was quite straightforward in the L-*arabino* series (Scheme 2). Both the methyl α-(**1a**) and the methyl β-arabinoside **1b**[2] gave the corresponding 5-*S*-acetyl derivatives **2a** and **2b** in high yields of 91% (from **1a**) and 87% (from **1b**), respectively. Subsequent mesylation led to the 2,3-di-*O*-mesylarabinosides **3a** (≈100% from **2a**) and **3b** (85% from **2b**). Finally, the deacetylation with sodium hydrogen carbonate[†] in refluxing methanol under a strictly inert atmosphere and concomitant cyclisation by intramolecular nucleophilic attack of the thiolate anion afforded the 3,5-anhydro-3-thio-α-furanoside **4a** (81% from **3a**). The corresponding reaction of the β anomer **3b** was performed in 2-methoxyethanol at 100 °C because significant amounts of byproducts besides the desired **4b** were formed in methanol at 65 °C (see Experimental). Probably these ring-closure reactions take place as S_N2 displacements under inversion of configuration, which can only occur at the 3-position and, consequently, leads to the thietanes with L-*lyxo*-configuration.

The structure and configuration of **4a** and **4b** were proved by their ^1H and ^{13}C NMR spectra. In particular, the large proton–proton coupling constants $J_{4,5exo}$ 6.3/7.2 Hz as compared with $J_{4,5endo}$ 3.0/3.2 Hz, as well as the large coupling constants $J_{2,3}$ 8.0 Hz and $J_{3,4}$ 6.9 Hz, are in agreement with the approximately ecliptic arrangement of H-2, H-3, H-4 and H-5_{exo} in the L-*lyxo*-configuration. Furthermore, the ^{13}C chemical shifts for C-3: δ 43.9 and 43.2 in **4a** and **4b** are characteristic of an anellated thietane but not of a thiolane ring ($\delta \approx 50$, see below), whereas the ^{13}C chemical shifts for C-2: δ 82.1 and 76.3, respectively, are in agreement with oxygen-substituted carbon centres. The structural assignment was finally corroborated by the X-ray structural analyses of both anomers (Fig. 1).

Mesylation of methyl 5-*S*-acetyl-5-thio-β-D-ribofuranoside (**5**)[2] readily gave the dimesylate **6** (78%), which was treated with sodium hydrogen carbonate in 2-methoxyethanol. In contrast to the arabino derivatives **3**, in this case an intramolecular displacement either of the 2-mesyloxy group to form a thiolane ring or of the 3-mesyloxy group to form a thietane ring was possible. However, only one product, the 2,5-anhydro-2-thio (thiolane) derivative **7** was obtained with 72% yield (Scheme 2). Under the rather harsh reaction conditions (3 h refluxing at 124 °C), not only the intramolecular ring closure, but also a displacement of the 3-mesyloxy group by methoxyethanolate had taken place. In methanol the related methyl 2,5-anhydro-3-*O*-methyl-2-thio-β-D-arabinofuranoside (50%), besides several byproducts, was isolated. The structure and the α-D-*arabino*-configuration of **7** was proved by NMR spectroscopic means. The coupling constants $J_{2,3}$ 1.7 Hz and especially $J_{3,4} \sim 0.0$ Hz are too small as compared with other 2,5-anhydro-2-thio-β-D-lyxofuranosides. For instance, $J_{2,3}$ 2.4 Hz, $J_{3,4}$ 3.0 Hz is found for **11b** and $J_{2,3}$ 2.4 Hz, $J_{3,4}$ 2.5 Hz is found for **17b**. The configuration is also evident from the X-ray structural analysis of two follow-up products, 1-[2,5-anhydro-3-*O*-(2-methoxyethyl)-2-thio-α-D-arabinofuranosyl]uracil and -thymine, which we have prepared from **7**.[9]

This rather unexpected outcome of the reaction can be rationalised as follows. First the 5-thioacetate group of **6** is cleaved. Then an intramolecular nucleophilic displacement of the mesylate group at C-3 by the 5-thiolate under formation of an intermediate thietane with inversion of the configuration at C-3 occurs. This attack is favoured over the substitution at the much less

[†] Sodium hydrogen carbonate is transformed into the stronger base sodium carbonate in boiling alcoholic solvents.[3]



Scheme 2. Reagents and conditions: (a) AcSH, DIAD, PPh_3; (b) MsCl, NEt_3; (c) $NaHCO_3$, MeOH (for **3a**) or 2-methoxyethanol (for **3b** and **6**).

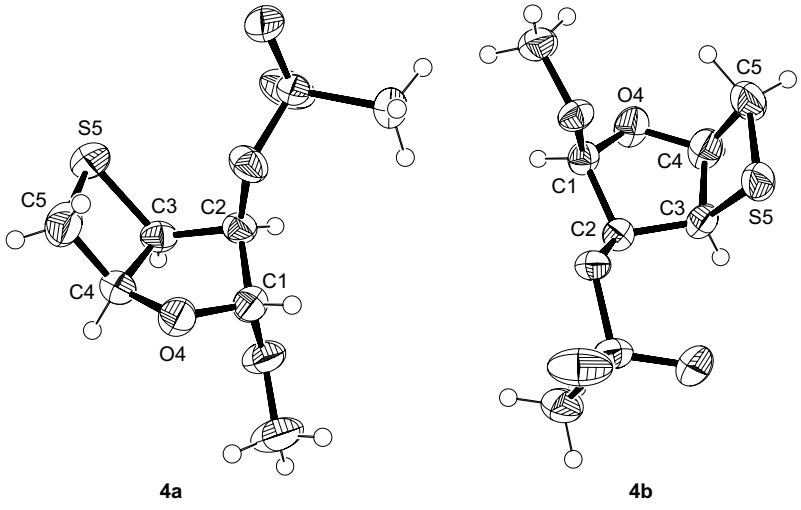
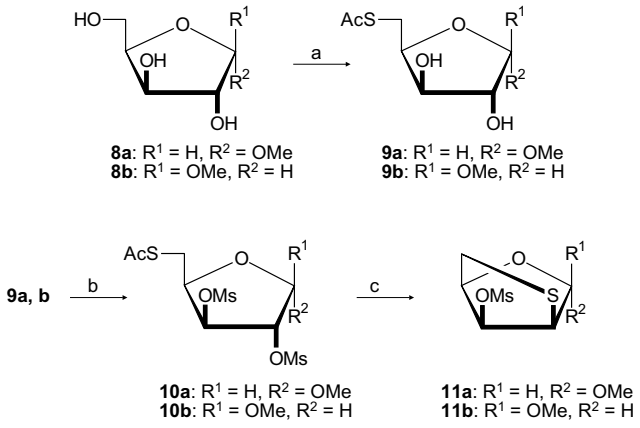


Figure 1. ORTEP views of the X-ray diffraction structure of **4a** and **4b** with common carbohydrate atomic numbering that differs from the CCDC files. Only one of the two conformers in the asymmetric unit of **4a** (cf. Table 3) is shown. Thermal ellipsoids are drawn on the 50% probability level.

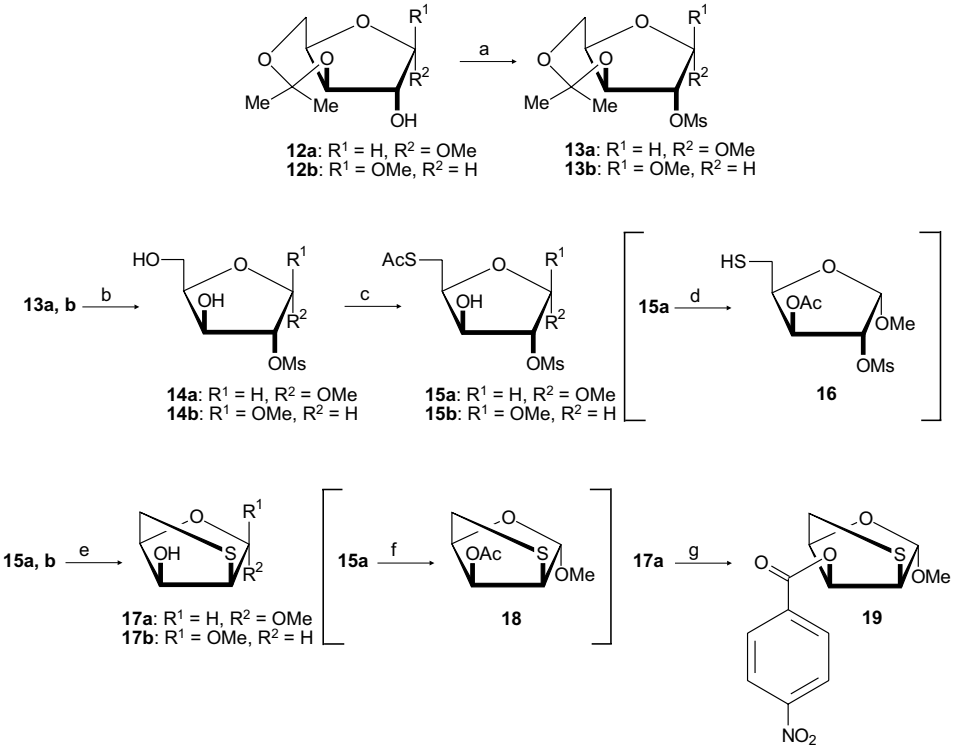
reactive 2-position.[10] However, in a further step another intramolecular nucleophilic attack of the thietane sulfur atom at C-2 under formation of an episulfonium cation takes place. Finally, the solvent, 2-methoxyethanol, reacts with the episulfonium cation at the more reactive 3-position to form **7** (Scheme 2). Thiiranium cations are known to occur as intermediates in related reactions of other thiosugars.[6c,11]



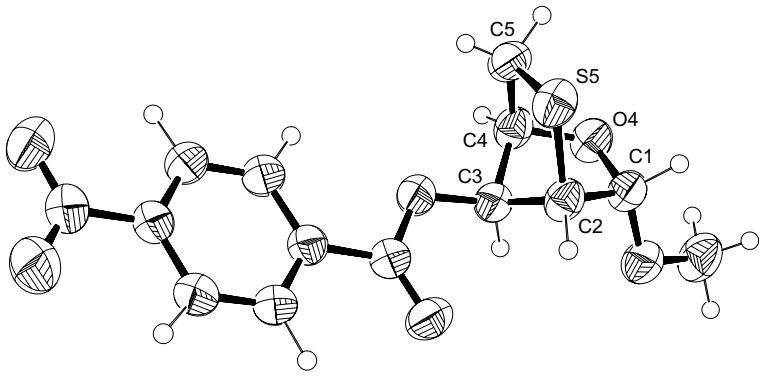
Scheme 3. Reagents and conditions: (a) AcSH, DIAD, PPh_3; (b) MsCl, NEt_3; (c) $NaHCO_3$, 2-methoxyethanol.

The thio-Mitsunobu reaction of an anomeric mixture of methyl α-D-(**8a**)[12] and methyl β-D-xylofuranoside **8b**[12] led to the corresponding thioacetates **9a** and **9b** with 52% yield (α/β = 3:2) (Scheme 3). The anomers were not separated. Mesylation of [**9a**+**9b**] gave a mixture of the two dimesylates **10a** and **10b** in 86% yield. The two anomers were then treated with sodium hydrogen carbonate in boiling 2-methoxyethanol (10 h, 124 °C). On stereochemical reasons an intramolecular nucleophilic cyclisation of the 5-thiolate anion is only possible at C-2, although this position is less reactive.[10] As the result, the 3-*O*-mesyl group remained unaffected, and the 2,5-anhydro-D-*lyxo*-derivatives **11a** and **11b** were formed. The two anomers could be separated by column chromatography and were isolated with yields (as referred to the content of **10a** and **10b** in the starting material) of 73% (**11a**) and 69% (**11b**). The β anomer **11b** turned out to be unstable. It decomposed in a few days at room temperature. Interestingly, in chloroform solution it rearranged to the α anomer **11a**, possibly by acid catalysis due to traces of hydrogen chloride present in this solvent.

Acid-catalysed reaction of the methyl xylofuranosides **8a** and **8b**[12] with 2-methoxypropene yielded the protected 3,5-*O*-isopropylidene derivatives **12a** and **12b** (Scheme 4).[12] These were easily mesylated at the 3-hydroxy group to give nearly quantitative yields of **13a** and **13b**. Subsequent deprotection led to 89% and 98% of the monomesylates **14a** and **14b**. In the following step the thioacetates **15** were prepared by the thio-Mitsunobu reaction of **14**. When **15a** was chromatographed on silica gel partial acetyl migration took place. Besides 57% of the pure **15a**, 7% of the 3-*O*-acetyl-5-thio-D-xylofuranoside **16** was obtained. We have observed a rearrangement of the same type in the thiohexitol series.[2] It is thermodynamically favoured because thioacetates are activated esters, but obviously it occurs only if the two functional groups are located in a *cis*-position to each other. In order to avoid this rearrangement, **15b** was not



Scheme 4. Reagents and conditions: (a) MsCl, NEt_3; (b) HCl, MeOH; (c) AcSH, DIAD, PPh_3; (d) SiO_2, H^+; (e) $NaHCO_3$, MeOH; (f) NaOAc, 2-methoxyethanol; (g) 4-nitrobenzoyl chloride, pyridine.



19

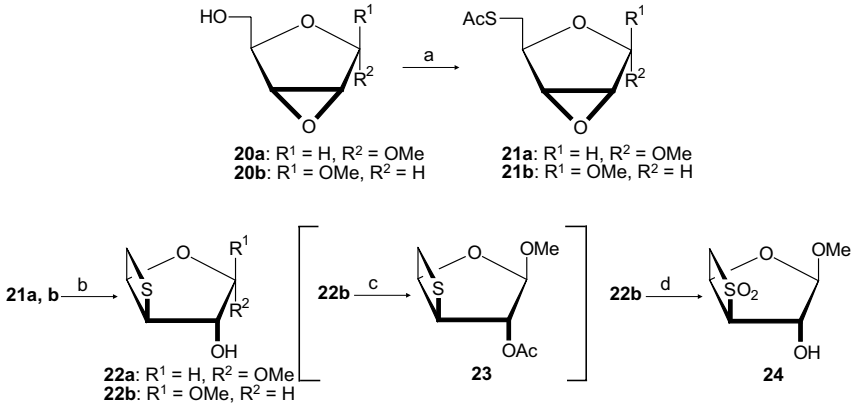
Figure 2. ORTEP view of the X-ray diffraction structure of **19** with common carbohydrate atomic numbering, which differs from the CCDC files. Thermal ellipsoids are drawn on the 50% probability level.

purified by chromatography. Reaction of **15a** with sodium hydrogen carbonate in refluxing methanol finally gave 94% of methyl 2,5-anhydro-2-thio-α-D-lyxofuranoside (**17a)**. When we used sodium acetate as the nucleophile instead of the hydrogen carbonate, the yield dropped to 55%, and 13% of methyl 3-*O*-acetyl-2,5-anhydro-2-thio-α-D-lyxofuranoside (**18)** was formed by acetyl migration. Only 17% of the β anomer **17b** could be isolated after the cyclisation of **15b** because anomerisation to form 33% of **17a** occurred during the chromatography on (acidic) silica gel.

The structures of **17a** and **17b** are in agreement with their NMR spectra. This was confirmed by the mesylation of **17a**, which led to **11a** in 81% yield. Furthermore, the 4-nitrobenzoate **19** of **17a** formed suitable crystals for an X-ray structural analysis (see Fig. 2), which left no doubt on the structure.

Epoxides easily react with nucleophiles under ring opening. Accordingly, we could successfully apply methyl 2,3-anhydrofuranosides as precursors for anhydroseleno- and tellurofuranosides.[13] They represent, therefore, promising candidates for cyclisations by intramolecular thiolate attacks, too. We have performed the thio-Mitsunobu reaction with methyl 2,3-anhydro-α-D-ribofuranoside (**20a**)[2] and -β-D-ribofuranoside (**20b**)[2] and obtained the thioacetates **21a** and **21b** in 73% and 85% yield (Scheme 5). No ring opening of the oxirane ring by nucleophilic attack of the thioacetic acid was observed. Both thioacetates were cyclised with sodium acetate in refluxing methoxyethanol, and the 3,5-anhydro-3-thio-D-xylofuranosides **22a** and **22b** were obtained in 89% and 82% yield. During the column chromatography of **22b**, 18% of the 2-*O*-acetate **23** was formed by re-esterification with the eluent, ethyl acetate.

The thietane structures of **22a** and **22b** and their D-*xylo*-configurations are unequivocal since X-ray structural analyses of both the anomers could be performed (see Fig. 3). Also, the NMR spectra unobjectionably agree with the structures. None of the corresponding 2,5-anhydro-2-thio derivatives was detected. The intramolecular attack of the thiolate anion exclusively occurs at the 3-position. Ring opening at the 2-position is not observed since the nucleophilic attack adjacent to the anomeric centre is disfavoured.[10] In contrast to the



Scheme 5. Reagents and conditions: (a) AcSH, DIAD, PPh_3; (b) NaOAc, 2-methoxyethanol; (c) EtOAc, SiO_2, H^+; (d) H_2O_2, MeOH.

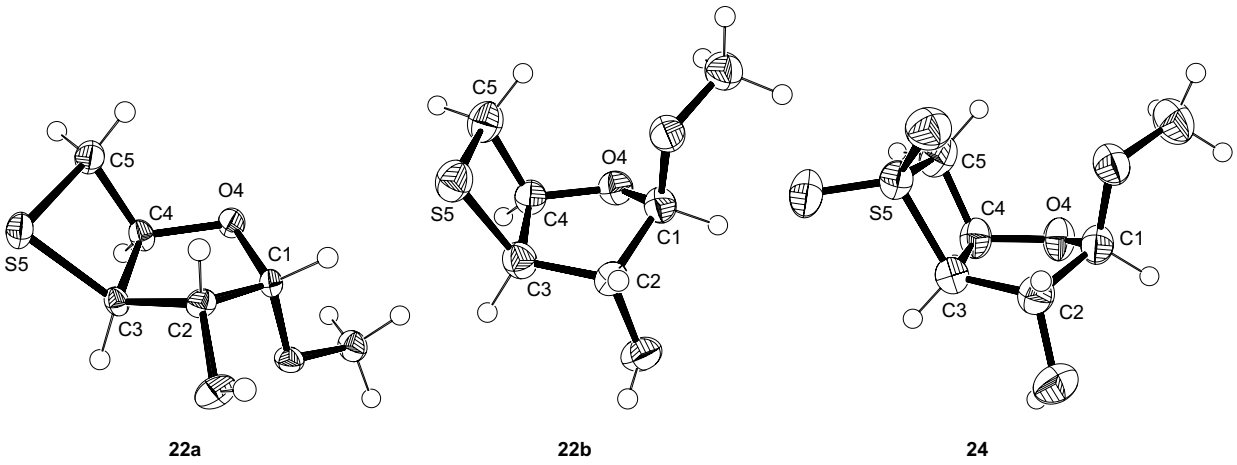


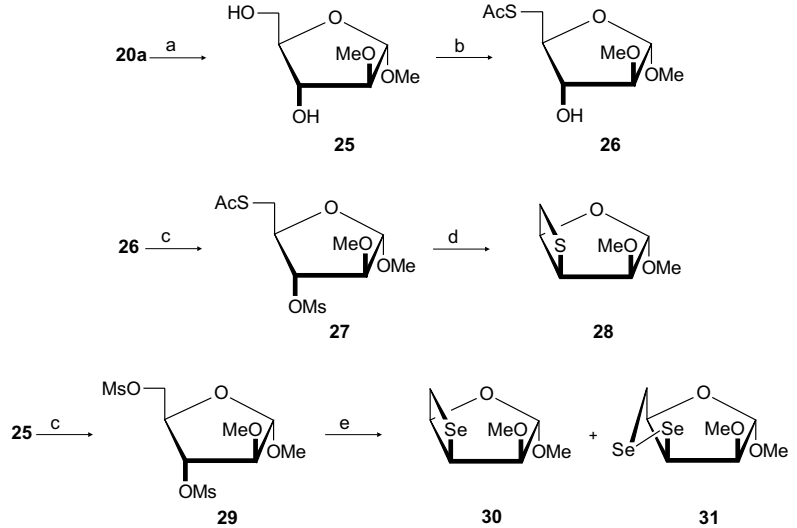
Figure 3. ORTEP views of the X-ray diffraction structure of **22a**, **22b** and **24** with common carbohydrate atomic numbering, which differs from the CCDC files. Thermal ellipsoids are drawn on the 50% probability level.

follow-up reaction of the thietane to **7** in Scheme 2, **22** does not exhibit another leaving group at C-2. Thus an episulfonium cation cannot be formed in a further step, and **22** remains as the stable final product. We have observed a similar selectivity for the formation of the corresponding 3,5-anhydro-3-seleno-D-xylofuranosides.[13]

In preliminary experiments the thietanes **22a** and **22b** were oxidised with hydrogen peroxide. In both cases mixtures of the *endo*-sulfoxide, the *exo*-sulfoxide and the sulfone were obtained. Only the sulfone **24** (34%) could be isolated from the mixture by column chromatography in the pure crystalline form. X-ray structural analysis confirmed its structure, which shows a remarkably flat thietane ring with a folding angle of only 2° (Fig. 3).

The oxirane ring of **20a** also reacted with sodium methoxide under nucleophilic ring opening. Inversion at C-2 during the reaction selectively led to the 2-*O*-methylfuranoside **25** with the D-*arabino*-configuration (Scheme 6). Apparently, in this case an attack upon C-3 is disfavoured due to steric hindrance. The thio-Mitsunobu reaction of **25** expectedly gave the thioacetate **26** (99%). Also the subsequent mesylation achieved a virtually quantitative yield of the mesylate **27**. Eventually, deacetylation and concomitant ring closure with sodium bicarbonate in refluxing methanol led to methyl 3,5-anhydro-2-*O*-methyl-3-thio-α-D-lyxofuranoside (**28**) (80%), which was the only product for the same reasons as in the case of **22**.

We were also interested in the preparation of selenetano sugars. However, a different approach was necessary for the introduction of selenium into the sugar molecule since a seleno-Mitsunobu reaction by use of selenoacetic acid is not possible.[13] Therefore, we used in situ generated sodium hydrogen selenide as the reagent of choice, which we had already successfully applied in the D-*xylo*-series.[13] It reacted in refluxing ethanol with the dimesyl-



Scheme 6. Reagents and conditions: (a) NaOMe, MeOH; (b) AcSH, DIAD, PPh_3; (c) MsCl, NEt_3; (d) $NaHCO_3$, MeOH; (e) NaSeH, EtOH.

ate **29** prepared from **25**. X-ray diffraction analysis revealed the configuration of **29** and hence of **25**. A yield of 77% methyl 3,5-anhydro-3-seleno-α-D-lyxofuranoside (**30**) besides 6% of the corresponding 3,5-diseleno(1,2-diselenolane) derivative **31** was obtained. In this reaction one of the two mesyloxy groups of **29** is first displaced by the strong nucleophilic hydrogen selenide anion. Then either ring closure under formation of the selenetane **30** occurs or, to a lesser extent, hydrogen selenide substitutes the second leaving group, and the resulting bis-selenolate is oxidised to the 1,2-diselenolane **31** (Scheme 5). The NMR spectra of the selenosugars **30** and **31** are in agreement with their structures. In particular, the expected ^{13}C–^{77}Se couplings $^{1}J_{C\text{-}3,Se}$ 21.3 Hz, and $^{1}J_{C\text{-}5,Se}$ 12.9 Hz of **27** are indicative of the selenetane ring.

3. Experimental

3.1. General methods

Melting points were determined by the use of an electrothermal apparatus (values are corrected). IR spectra (KBr pellets or films) were measured with an ATI Mattson Genesis spectrometer. NMR spectra were recorded 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 a VG Analytical 70–250 S (HRMS) apparatus. The HRMS for the selenium compounds were calculated for the ^{80}Se isotope. Optical rotations were measured on a Perkin–Elmer polarimeter 341. Thin-layer chromatography 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 Merck Kieselgel 60 (70–230 mesh). Solvents were purified and dried according to standard laboratory procedures.[14]

3.2. X-ray structural analyses

The crystal data and a summary of experimental details are given in Tables 1 and 2. In case of **19**, **22a**, **22b** and **24**, data collection was performed on a CAD4 Enraf-Nonius diffractometer, with graphite-monochromated Cu Kα radiation (wavelength 1.54184 Å) in the Θ–2Θ scan mode. In case of **4a**, **4b** and **29**, data collection was performed on a Kappa CCD Nonius diffractometer, with graphite-monochromated Mo Kα radiation (wavelength 0.71073 Å) in the rotation Φ scan mode. In all cases the refinement method was full-matrix-block

Table 1. Crystal data and structure refinement for **4a**, **4b** and **19**

	4a	**4b**	**19**
Molecular formula	$C_7H_{12}O_5S_2$	$C_7H_{12}O_5S_2$	$C_{13}H_{13}NO_6S$
Molecular weight ($g\,mol^{-1}$)	240.29	240.29	311.30
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
Unit cell dimensions			
a (pm)	738.7(1)	544.0(1)	567.1(1)
b (pm)	1271.5(1)	769.9(1)	1622.8(1)
c (pm)	2241.3(1)	2378.6(1)	772.5(1)
β (°)			102.69(1)
Volume (10^6 pm)	2105.2(3)	996.2(2)	693.6(2)
Z (molecules per cell)	8	4	2
D_{calcd} ($g\,cm^{-3}$)	1.516	1.602	1.491
Absorption coefficient (mm^{-1})	0.500	0.528	2.349
$F(0\,0\,0)$	1008	504	324
Crystal size (mm)	$0.38\times0.31\times0.27$	$0.31\times0.26\times0.13$	$0.54\times0.48\times0.38$
θ range for data collection (°)	1.84–27.46	2.78–27.49	5.45–74.98
Index ranges	$-9\leqslant h\leqslant 9$; $-16\leqslant k\leqslant 16$; $-29\leqslant l\leqslant 28$	$-7\leqslant h\leqslant 6$; $-9\leqslant k\leqslant 9$; $-30\leqslant l\leqslant 30$	$-7\leqslant h\leqslant 0$; $-20\leqslant k\leqslant 20$; $-9\leqslant l\leqslant 9$
Reflections collected	4344	4180	3165
Independent reflections	4344	1807	2862
Reflections with $[I\geqslant 2\sigma(I)]$	4129	1671	2804
Function minimized[a]	$x = 0.0551$, $y = 0.4919$	$x = 0.0500$, $y = 0.4685$	$x = 0.0820$, $y = 0.0822$
Data/restraints/parameters	4344/0/303	1807/0/153	2862/1/243
Goodness-of-fit on F^2	1.094	1.112	1.132
Final R indices $[I\geqslant 2\sigma(I)]$	$R_1 = 0.0297$, $wR_2 = 0.0838$	$R_1 = 0.0350$, $wR_2 = 0.0965$	$R_1 = 0.0418$, $wR_2 = 0.1181$
R indices (all data)	$R_1 = 0.0331$, $wR_2 = 0.0937$	$R_1 = 0.0395$, $wR_2 = 0.1006$	$R_1 = 0.0427$, $wR_2 = 0.1218$
Largest difference peak and hole ($e\,Å^3$)	0.222 and −0.304	0.254 and −0.242	0.205 and −0.558
Absolute structure parameter	0.00(6)	0.00(12)	0.00(2)

[a] $\sum w\left(F_o^2 - F_c^2\right)^2$, $w = 1/\left[\sigma^2\left(F_o^2\right) + x^2 + yP\right]$, where $P = \left(F_o^2 + 2F_c^2\right)/3$.

Table 2. Crystal data and structure refinement for **22a**, **22b**, **24** and **29**

	22a	**22b**	**24**	**29**
Molecular formula	$C_6H_{10}O_3S$	$C_6H_{10}O_3S$	$C_6H_{10}O_5S$	$C_9H_{18}O_9S_2$
Molecular weight ($g\,mol^{-1}$)	162.20	162.20	194.20	334.35
Temperature (K)	173(2)	173(2)	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P1$
Unit cell dimensions				
a (pm)	543.8(1)	529(4)	562.3(1)	565.6(1)
b (pm)	979.2(2)	1019(11)	564.8(1)	730.0(1)
c (pm)	1355.0(2)	1296(12)	2496.2(1)	935.1(1)
α (°)				71.79(1)
β (°)				78.02(1)
γ (°)				85.54(1)
Volume ($10^6\,pm^3$)	721.5(2)	699(11)	792.8(2)	358.73(9)
Z (molecules per cell)	4	4	4	1
D_{calcd} ($g\,cm^{-3}$)	1.493	1.542	1.627	1.548
Absorption coefficient (mm^{-1})	3.564	3.680	3.550	0.410
$F(0\,0\,0)$	344	344	408	176
Crystal size (mm)	$0.40\times0.30\times0.20$	$0.40\times0.30\times0.30$	$0.35\times0.30\times0.21$	$0.45\times0.19\times0.12$
θ range for data collection (°)	5.57–76.44	6.83–69.84	3.54–74.67	2.3427.54
Index ranges	$-6\leqslant h\leqslant 2$; $-12\leqslant k\leqslant 3$; $0\leqslant l\leqslant 17$	$-6\leqslant h\leqslant 6$; $-12\leqslant k\leqslant 12$; $-3\leqslant l\leqslant 16$	$0\leqslant h\leqslant 7$; $0\leqslant k\leqslant 7$; $-30\leqslant l\leqslant 31$	$-7\leqslant h\leqslant 7$; $-9\leqslant k\leqslant 9$; $-12\leqslant l\leqslant 12$
Reflections collected	922	2752	1601	4506
Independent reflections	911	1320	1601	3263
Reflections with $[I\leqslant 2\sigma(I)]$	908	1099	1557	3203
Function minimized[a]	$x = 0.1118$, $y = 0.2693$	$x = 0.1517$, $y = 0.4204$	$x = 0.0382$, $y = 0.1657$	$x = 0.1323$, $y = 0.1496$
Data/restraints/parameters	911/1/106	1318/0/104	1601/0/150	3263/3/206
Goodness-of-fit on F^2	1.198	1.030	1.094	1.044
Final R indices $[I\leqslant 2\sigma(I)]$	$R_1 = 0.0584$, $wR_2 = 0.1463$	$R_1 = 0.0948$, $wR_2 = 0.2382$	$R_1 = 0.0251$, $wR_2 = 0.0699$	$R_1 = 0.0544$, $wR_2 = 0.1646$
R indices (all data)	$R_1 = 0.0584$, $wR_2 = 0.1468$	$R_1 = 0.1031$, $wR_2 = 0.2513$	$R_1 = 0.0263$, $wR_2 = 0.0709$	$R_1 = 0.0552$, $wR_2 = 0.1660$
Largest difference peak and hole ($e\,Å^3$)	1.000 and −0.613	1.111 and −1.172	0.176 and −0.360	0.784 and −0.538
Absolute structure factor	0.06(5)	0.06(7)	0.01(2)	0.02(9)

[a] $\sum w\left(F_o^2 - F_c^2\right)^2$, $w = 1/\left[\sigma^2\left(F_o^2\right) + x^2 + yP\right]$, where $P = \left(F_o^2 + 2F_c^2\right)/3$.

least-squares on F^2. Hydrogen positions were obtained by difference-Fourier synthesis. The H-atom refinement method was geometrical in case of **19**, **22a** and **22b**, difmap in case of **24**, and a mixed in case of **4a**, **4b** and **29**. All absolute structure parameters (flack values) were in accordance with the expected structure. The structures were solved by direct methods using the SIR-97 program[15] and the SHELXL-97 program.[16] The calculation of Cremer–Pople puckering parameters (Table 3) was performed with the PLATON program.[17]

3.3. Starting materials

The methyl furanosides **1a**, **1b**, **8a** and **8b**, as well as the *S*-acetyl derivative **5** and the methyl 2,3-anhydrofuranosides **20a** and **20b**, were synthesised as previously described.[2] The isopropylidene derivatives **12a** and **12b** were prepared as described in Ref. 12. They could be easily separated by vacuum distillation.[18]

3.4. Thio-Mitsunobu reaction (typical procedure)

The reaction was carried out under Ar or N_2. Thioacetic acid (AcSH) was purified prior to use by repeated low-temperature distillation. A cooled (0 °C) solution of the substrate and AcSH (ca. 1.3 equiv) in dry THF was added to a cooled (0 °C) solution of triphenylphosphine (ca. 1.2 equiv) and diisopropyl azodicarboxylate (DIAD, ca. 1.2 equiv) in dry THF. The reaction mixture was allowed to warm to room temperature and stirred overnight. After evaporation a concd solution of the residue in EtOAc was filtered through silica gel in order to remove most of the triphenylphosphine oxide and diisopropyl hydrazodicarboxylate. The crude product was purified by column chromatography to yield methyl 5-*S*-acetyl-5-thio-α-L-arabinofuranoside (**2a**), methyl 5-*S*-acetyl-5-thio-β-L-arabinofuranoside (**2b**), methyl 5-*S*-acetyl-5-thio-α-D-xylofuranoside (**9a**), methyl 5-*S*-acetyl-5-thio-β-D-xylofuranoside (**9b**), methyl 5-*S*-acetyl-2-*O*-mesyl-5-thio-α-D-xylofuranoside (**15a**), methyl

Table 3. Cremer–Pople puckering parameters

	Atom sequence (ORTEP plots)	Puckering parameters		Closest pucker descriptor
		$Q(2)$ (pm)	$\Phi(2)$ (°)	
4a[a]	O(4)–C(1)–C(2)–C(3)–C(4)	37.9(2)	230.3(4)	Twist C(1)-*endo*, C(2)-*exo*
4a[b]	O(4)–C(1)–C(2)–C(3)–C(4)	31.6(2)	196.3(5)	Twist O(4)-*exo*, C(1)-*endo*
4b	O(4)–C(1)–C(2)–C(3)–C(4)	32.1(3)	36.0(6)	Envelope C(1)-*exo*
19	S(5)–C(2)–C(3)–C(4)–C(5)	60.3(3)	72.1(2)	Envelope C(3)
	O(4)–C(1)–C(2)–C(3)–C(4)	56.4(3)	101.3(3)	Envelope C(3)-*exo*
22a	O(4)–C(1)–C(2)–C(3)–C(4)	37.0(3)	62.7(5)	Twist C(1)-*exo*, C(2)-*endo*
22b	O(4)–C(1)–C(2)–C(3)–C(4)	32.1(6)	210.3(12)	Envelope C(1)-*endo*
24	O(4)–C(1)–C(2)–C(3)–C(4)	27.1(2)	212.1(4)	Envelope C(1)-*endo*
29	O(4)–C(1)–C(2)–C(3)–C(4)	33.4(4)	38.0(6)	Envelope C(1)-*exo*

[a] First conformer.
[b] Second conformer.

5-*S*-acetyl-2-*O*-mesyl-5-thio-β-D-xylofuranoside (**15b**), methyl 5-*S*-acetyl-2,3-anhydro-5-thio-α-D-ribofuranoside (**21a**), methyl 5-*S*-acetyl-2,3-anhydro-5-thio-β-D-ribofuranoside (**21b**) and methyl 5-*S*-acetyl-2-*O*-methyl-5-thio-β-D-arabinofuranoside (**26**). Experimental details for the individual compounds are given in Table 4. ^{1}H and ^{13}C NMR data are given in Tables 5–7. When **15a** was purified by column chromatography, an acetyl group migration from *S*-5 to O-3 under formation of the mercaptosugar **16** was observed. This rearrangement was possibly catalyzed by the contact with silica gel. In order to avoid a similar migration, compound **15b** was not purified by column chromatography. Instead, the crude product was used directly in the next step.

3.5. Methyl 3-*O*-acetyl-2-*O*-mesyl-5-thio-α-D-xylofuranoside (16)

IR: ν 2583 (SH), 1743 (C=O), 1365 (SO_2), 1184 (SO_2) cm^{-1}; H NMR (400 MHz, $CDCl_3$): δ 1.58 (dd, 1H, SH), 2.14 (s, 3H, OAc), 2.61 (ddd, 1H, H-5), 2.68 (ddd, 1H, H-5′), 3.06 (s, 3H, OMs), 3.47 (s, 3H, OMe), 4.41 (ddd, 1H,

Table 4. Preparative experimental details, physical properties and IR absorptions [ν (C=O)] of methyl 5-*S*-acetyl-5-thiopentofuranosides

Starting compd (mmol)		AcSH (mmol)	THF (mL)	PPh_3 (mmol)	DIAD (mmol)	THF (mL)	Product[a] (mmol)		Yield (%)	R_f (eluent)	IR [ν] (cm^{-1})
1a	19.9	25.3	60	23.7	23.7	70	**2a**	18.1	91	0.57 (EtOAc)	1691
1b	7.01	9.20	30	8.39	8.21	30	**2b**	6.12	87	0.41 (EtOAc)	1691
8a+	38.9	104.1	400	97.0	95.6	280	**9a**+	24.0	61	0.67 (EtOAc)	1690
8b[b]	42.4						**9b**[b]	17.8	42	0.62 (EtOAc)	
14a	5.94	8.41	15	7.09	7.22	20	**15a**	3.40	57	0.47 (Et_2O)	1690
14b	26.5	33.8	125	31.6	31.4	125	**15b**	[c]	[c]	[c]	
20a	6.16	7.75	15	7.36	7.22	20	**21a**	4.50	73	0.24 (1:1 Et_2O–hexane)	1693
20b	5.95	7.49	15	7.13	7.22	20	**21b**	5.04	85	0.46 (1:1 Et_2O–hexane)	1694
25	2.02	2.50	10	2.40	2.57	10	**26**	1.99	99	0.74 (EtOAc)	1694

[a] Yellow or colourless (**21**) syrups.
[b] Mixture of the anomers.
[c] The crude product was not purified in order to avoid an acetyl group migration.

Table 5. Chemical shifts δ in the ^{1}H NMR spectra (400 MHz) of methyl 5-*S*-acetyl-5-thiopentofuranosides

Compd	Solvent	H-1	H-2	H-3	H-4	H-5	H-5′	OMe	SAc	Additional signals
2a	$CDCl_3$[a]	4.84	4.04–4.09	3.75–3.82	4.04–4.09	3.20	3.25	3.39	2.39	OH-2: 3.98, OH-3: 3.79
2a	D_2O	4.91	4.05	3.87	4.09	3.20	3.30	3.39	2.42	HDO: 4.75
2b	$CDCl_3$	4.78	4.07	4.00	3.92	3.12	3.24	3.42	2.35	OH-2: 3.57, OH-3: 4.20
5	$CDCl_3$	4.81	4.01–4.05	4.01–4.05	4.01–4.05	3.10	3.27	3.36	2.38	OH: 3.70, OH′: 3.78
5	D_2O	4.84	4.04	4.05–4.15	4.05–4.15	3.13	3.30	3.36	2.40	
9a	D_2O	4.89	4.04–4.09	4.15–4.23	4.15–4.23	2.96	3.09–3.17	3.29	2.32	
9b	D_2O	4.77	4.27	4.04–4.09	4.04–4.09	3.09–3.17	3.09–3.17	3.35	2.33	
15a	$CDCl_3$	5.06	4.85	4.50	4.27	3.05	3.32	3.45	2.37	OMs: 3.13, OH-3: 3.87
21a	$CDCl_3$	5.18	3.75	3.62	4.42	3.02	3.14	3.50	2.38	
21b	$CDCl_3$[a]	4.94	3.70[b]	3.68[b]	4.14	3.00	3.08	3.40	2.37	
26	$CDCl_3$	4.87	3.69	3.81	4.06	3.17	3.21	3.42	2.38	OH: 3.31, OMe′: 3.38

[a] Measurement at 500 MHz.
[b] Assignment may be inverted.

Table 6. ^1H–^1H coupling constants J (Hz)[a] of methyl 5-*S*-acetyl-5-thiopentofuranosides

Compd	Solvent[b]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	Additional couplings
2a	$CDCl_3$[c]	1.7	m	m	6.1	5.3	14.1	$J_{2,OH-2}$: 4.0
2a	D_2O	1.6	3.3	5.7	6.7	5.1	14.2	
2b	$CDCl_3$	4.6	7.3	6.7	6.8	5.0	13.8	$J_{2,OH-2}$: 7.7, $J_{3,OH-3}$: 2.9
5	$CDCl_3$	0.0	m	m	6.5	5.0	13.9	
5	D_2O	0.0	4.2	m	6.3	4.4	14.3	
9a	D_2O	5.6	m	m	7.2	m	14.0	
9b	D_2O	1.0	4.9	m	m	m	m	
15a	$CDCl_3$	4.2	4.6	5.9	6.6	6.4	14.1	$J_{3,OH-3}$: 4.7
21a	$CDCl_3$	0.6	2.8	0.0	6.5	5.2	13.8	
21b	$CDCl_3$[c]	0.0	2.8	0.0	7.4	7.2	14.0	
26	$CDCl_3$	1.1	3.3	5.4	5.9	5.5		

[a] m (unresolved multiplet): J could not be determined.
[b] Measurement at 400 MHz if not stated otherwise.
[c] Measurement at 500 MHz.

Table 7. Chemical shifts δ in the ^{13}C NMR spectra (101 MHz) of methyl 5-*S*-acetyl-5-thiopentofuranosides

Compd	Solvent	C-1	C-2	C-3	C-4	C-5	OMe	SAc	C=O	Additional signals
2a	$CDCl_3$	108.58	81.27	79.69	82.26	31.42	55.21	30.58	196.68	
2a	D_2O	108.79	81.19	79.47	82.45	31.34	55.39	30.38	200.47	
2b	$CDCl_3$[a]	102.13	78.04	78.87	80.42	33.39	55.30	30.57	195.76	
5	$CDCl_3$	108.32	74.78	73.69[b]	81.07[b]	32.40	55.54	30.36	200.62	
9a	D_2O	102.20	81.47	77.46	75.06	29.22	56.14	30.40	200.51	
9b	D_2O	109.15	84.59	76.97	75.06	29.44	56.22	30.40	200.51	
15a	$CDCl_3$	100.44	83.68	73.56	77.32	28.11	55.88	30.52	196.76	OMs: 38.56
21a	$CDCl_3$	102.37	56.19	57.25	77.11	31.13	56.93	30.55	194.65	
21b	$CDCl_3$	102.51	56.04	55.69	77.01	31.18	55.44	30.48	194.57	
26	$CDCl_3$	106.80	90.31	77.71	82.44	31.27	55.03	30.52	196.14	OMe′: 57.73

[a] Measurement at 126 MHz.
[b] Assignments may be inverted.

H-4), 5.02 (dd, 1H, H-2), 5.09 (d, 1H, H-1), 5.50 (dd, 1H, H-3) ppm; $J_{1,2}$ 4.5, $J_{2,3}$ 5.4, $J_{3,4}$ 6.5, $J_{4,5}$ 5.6, $J_{4,5'}$ 6.6, $J_{5,5'}$ 14.0, $J_{5,SH}$ 9.4, $J_{5',SH}$ 7.5 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.67 (OAc), 23.94 (C-5), 38.74 (OMs), 55.60 (OMe), 75.10 (C-3), 76.81 (C-4), 80.95 (C-2), 99.73 (C-1), 170.13 (C=O) ppm.

3.6. Mesylation (typical procedure)

A solution of the substrate in CH_2Cl_2 was cooled to −20 °C. Then Et_3N (ca. 1.7 equiv) and methanesulfonyl chloride (ca. 1.7 equiv) were added, and the mixture was allowed to warm to room temperature. After evaporation of half of the solvent, the reaction mixture was diluted with EtOAc to its original volume. This was repeated two more times. The solution was filtered and evaporated to dryness. The crude product was crystallised or purified by column chromatography to yield methyl 5-*S*-acetyl-2,3-di-*O*-mesyl-5-thio-α-L-arabinofuranoside (**3a**), methyl 5-*S*-acetyl-2,3-di-*O*-mesyl-5-thio-β-L-arabinofuranoside (**3b**), methyl 5-*S*-acetyl-2,3-di-*O*-mesyl-5-thio-β-D-ribofuranoside (**6**), methyl 5-*S*-acetyl-2,3-di-*O*-mesyl-5-thio-α-D-xylofuranoside (**10a**), methyl 5-*S*-acetyl-2,3-di-*O*-mesyl-5-thio-β-D-xylofuranoside (**10b**), methyl 3,5-*O*-isopropylidene-2-*O*-mesyl-α-D-xylofuranoside (**13a**), methyl 3,5-*O*-isopropylidene-2-*O*-mesyl-β-D-xylofuranoside (**13b**), methyl 5-*S*-acetyl-3-*O*-mesyl-2-*O*-methyl-5-thio-α-D-arabinofuranoside (**27**) and methyl 3,5-di-*O*-mesyl-2-*O*-methyl-α-D-arabinofuranoside (**29**). Experimental details for the individual compounds are given in Table 8. ^1H NMR and ^{13}C NMR data are given in Tables 9–11.

3.7. Methyl 2-*O*-mesyl-α-D-xylofuranoside (14a)

AcCl (0.77 g, 0.70 mL, 9.81 mmol) was added to MeOH (90 mL). Methyl 3,5-*O*-isopropylidene-2-*O*-mesyl-α-D-xylofuranoside (**13a**) (12.79 g, 45.30 mmol), and after 4 h, K_2CO_3 (1.34 g, 9.70 mmol) were added at room temperature. After filtration and evaporation the residue was crystallised from EtOAc–Et_2O. Colourless crystals (9.78 g, 40.37 mmol, 89%): R_f 0.30 (15:1 CH_2Cl_2–MeOH); mp 89 °C; IR: ν 3360 (OH), 1354 (SO_2), 1177 (SO_2) cm^{-1}; NMR spectra cf. Tables 9–11.

3.8. Methyl 2-*O*-mesyl-β-D-xylofuranoside (14b)

Compound **14b** was prepared as described for **14a** from **13b** (7.62 g, 27.0 mmol), AcCl (0.40 mL, 0.44 g, 5.61 mmol), MeOH (50 mL) and K_2CO_3 (0.80 g, 5.79 mmol).

Table 8. Preparative experimental details, physical properties and IR absorptions of mesylates and dimesylates

Starting compd (mmol)		CH_2Cl_2 (mL)	NEt_3 (mmol)	MsCl (mmol)	Product (mmol)		Yield (%)	Mp (°C)	R_f (eluent)	IR ν (cm^{-1})
2a	17.2	150	65.6	58.1	**3a**[a]	17.2	100	Colourless syrup	0.82 (EtOAc)	1694 (C=O), 1365 (SO_2), 1179 (SO_2)
2b	6.12	60	13.3	23.9	**3b**	5.95	97	87 (MeOH)	0.81 (EtOAc)	1700 (C=O), 1368 (SO_2), 1349 (SO_2), 1179 (SO_2)
5	2.92	14.5	9.39	9.78	**6**	2.27	78	82 (EtOAc)	0.85 (EtOAc)	1689 (C=O), 1366 (SO_2), 1341 (SO_2), 1178 (SO_2)
9a+	23.8	200	142.1	137.0	**10a+**	20.6	86	Colourless solid	0.83 (EtOAc)	
9b[b]	17.7				**10b**[b]	14.9	84			
12a	199.6	385	304.5	222.3	**13a**	195.7	98	86 (MeOH)	0.81 (15:1 CH_2Cl_2–MeOH)	1353 (SO_2), 1180 (SO_2)
12b	31.1	60	47.6	34.9	**13b**	30.9	99	Colourless syrup	0.80 (15:1 CH_2Cl_2–MeOH)	1365 (SO_2), 1179 (SO_2)
26	1.99	8	3.66	3.84	**27**	1.94	98	Yellow syrup	0.82 (EtOAc)	1693 (C=O), 1364 (SO_2), 1178 (SO_2)
25	1.85	10	7.21	6.46	**29**[c]	1.79	97	92 (MeOH)	0.72 (EtOAc)	1355 (SO_2), 1340 (SO_2), 1176 (SO_2)

[a] EIMS of **3a**: m/z (%) 347 (0.3) [$M^{+\cdot}$–OMe], 225 (18), 193 (8), 165 (13), 135 (5), 115 (16), 101 (47), 97 (15), 95 (27), 79 (32), 73 (24), 45 (25), 43 (100).
[b] Mixture of the anomers.
[c] EIMS of **29**: m/z (%) 225 (6), 179 (56), 178 (8), 135 (36), 129 (15), 111 (32), 101 (29), 100 (18), 99 (100), 87 (35), 85 (11), 83 (16), 79 (37), 73 (10), 71 (65), 69 (14), 54 (13), 45 (21), 41 (14); optical rotation of **29**: $[\alpha]_{20}^{D}$ +86.4 (c 1.0, $CHCl_3$). Anal. of **29**. Calcd for $C_9H_{18}O_9S_2$ (334.4): C, 32.33; H, 5.43; S, 19.18. Found: C, 32.45; H, 5.41; S, 18.85.

Pale yellow syrup (6.41 g, 26.5 mmol, 98%): R_f 0.34 (15:1 CH_2Cl_2–MeOH); NMR spectra cf. Tables 9–11.

3.9. Nucleophile-promoted cyclisation of thioacetates (typical procedure)

The reactions were carried out under N_2 or Ar. A solution of the thioacetate in oxygen-free MeOH or 2-methoxyethanol was heated to a temperature of ca. 10 °C below the boiling point. The nucleophile ($NaHCO_3$ or NaOAc) was added, and the solution was refluxed. After completion of the reaction (TLC control), the solvent was evaporated to dryness, and the residue was redissolved in EtOAc. After filtration and evaporation of the solvent, column chromatography led to methyl 3,5-anhydro-2-*O*-mesyl-3-thio-α-L-lyxofuranoside (**4a**), methyl 3,5-anhydro-2-*O*-mesyl-3-thio-β-L-lyxofuranoside (**4b**), methyl 2,5-anhydro-3-*O*-(2-methoxyethyl)-2-thio-β-D-arabinofuranoside (**7**), methyl 2,5-anhydro-3-*O*-mesyl-2-thio-α-D-lyxofuranoside (**11a**), methyl 2,5-anhydro-3-*O*-mesyl-2-thio-β-D-lyxofuranoside (**11b**), methyl 2,5-anhydro-2-thio-α-D-lyxofuranoside (**17a**) [together with methyl 3-*O*-acetyl-2,5-anhydro-2-thio-α-D-lyxofuranoside (**18**) when NaOAc in 2-methoxyethanol was used], methyl 2,5-anhydro-2-thio-β-D-lyxofuranoside (**17b**), methyl 3,5-anhydro-3-thio-α-D-xylofuranoside (**22a**), methyl 3,5-anhydro-3-thio-β-D-xylofuranoside (**22b**) and methyl 3,5-anhydro-2-*O*-methyl-3-thio-α-D-lyxofurano-

Table 9. Chemical shifts δ in the ^1H NMR spectra (400 MHz) of mesylates and dimesylates

Compd	Solvent	H-1	H-2	H-3	H-4	H-5	H-5′	OMe	OMs	OMs′	Additional signals
3a	$CDCl_3$	5.08	5.01	4.79	4.29	3.28	3.36	3.39	3.16	3.17	SAc: 2.39
3b	$CDCl_3$	5.05	5.03	5.18	4.17	3.12	3.42	3.47	3.14	3.18	SAc: 2.38
6	$CDCl_3$	5.05	4.97–5.01	4.97–5.01	4.33–4.39	3.22	3.30	3.41	3.15	3.18	SAc: 2.39
10a	$CDCl_3$	5.10	5.07	5.28	4.42	3.16	3.28	3.45	3.14	3.17	SAc: 2.37
10a	C_6D_6	4.73	4.92	5.17	4.14	3.05	3.17	2.97	2.41	2.41	SAc: 1.78
10b	$CDCl_3$	5.04–5.12	5.04–5.12	5.16	4.47	3.10–3.25	3.10–3.25	3.42	3.16	3.19	SAc: 2.37
10b	C_6D_6	4.86	5.12	4.98	4.30	3.18	3.18	3.00	2.34	2.40	SAc: 1.80
13a	$CDCl_3$	5.24	4.93	4.44	4.16	3.86	4.01	3.50	3.10		Me: 1.38, Me′: 1.40
13b	$CDCl_3$	5.08	4.89	4.40	4.20	3.86	4.00	3.44	3.10		Me: 1.38, Me′: 1.41
14a	Acetone-d_6[a]	5.07	4.87	4.63	4.22	3.80	3.85	3.44	3.21		OH-5: 3.90, OH-3: 4.79
14a	D_2O	4.95	4.71	4.35	4.03	3.47	3.53	3.20	3.02		
14b	D_2O	4.92	4.68	4.30	4.13	3.51	3.60	3.19	3.05		
27	$CDCl_3$[a]	4.90	3.91	4.67	4.23	3.19	3.34	3.37	3.13		SAc: 2.38, OMe′: 3.44
29	$CDCl_3$	4.95	3.94	4.86	4.35	4.43	4.50	3.40	3.08	3.12	OMe′: 3.45

[a] Measurement at 500 MHz.

Table 10. ^1H–^1H coupling constants J (Hz)[a] of mesylates and dimesylates

Compd	Solvent[b]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$
3a	$CDCl_3$	0.4	1.9	5.7	5.5	5.4	14.3
3b	$CDCl_3$	3.2	4.3	5.4	7.8	5.3	14.0
6	$CDCl_3$	0.0	m	m	5.7	5.3	14.3
10a	$CDCl_3$	4.5	4.8	6.4	6.7	5.7	14.1
10a	C_6D_6	4.6	4.9	6.2	6.7	5.9	13.9
10b	$CDCl_3$	m	1.7	5.6	7.7	6.1	m
10b	C_6D_6	0.8	1.6	5.6	7.1	7.1	7.1 (vd[c])
13a	$CDCl_3$	4.1	2.3	3.9	4.3	4.0	12.6
13b	$CDCl_3$	0.0	0.0	4.2	4.9	4.6	12.3
14a	Acetone-d_6[d]	4.3	6.7	7.3	3.9	3.8	12.6
14a	D_2O	4.5	6.2	7.0	5.3	3.7	12.4
14b	D_2O	0.8	2.3	5.5	7.4	4.3	12.1
27	$CDCl_3$[d]	0.0	2.3	5.5	6.3	5.3	14.1
29	$CDCl_3$	0.0	2.3	5.5	4.5	3.7	11.5

[a] m (unresolved multiplet): J could not be determined.
[b] Measurement at 400 MHz if not stated otherwise.
[c] vd: virtual doublet.
[d] Measurement at 500 MHz.

Table 11. Chemical shifts δ in the ^{13}C NMR spectra (101 MHz) of mesylates and dimesylates

Compd	Solvent	C-1	C-2	C-3	C-4	C-5	OMe	OMs	OMs′	Additional signals
3a	$CDCl_3$	106.21	85.91	82.85	79.59	29.99	55.02	38.30	38.38	SAc: 30.50, C=O: 194.84
3b	$CDCl_3$	100.75	80.26	82.78	78.03	33.01	55.72	38.91	39.02	SAc: 30.52, C=O: 194.61
6	$CDCl_3$	105.69	77.45[a]	79.87[a]	78.64	31.55	55.64	38.49	38.53	SAc: 30.56, C=O: 194.95
10a	$CDCl_3$	99.79	81.20	80.49	74.47	28.10	55.71	38.48	38.64	SAc: 30.46, C=O: 194.43
10a	C_6D_6	100.30	81.34	80.94	75.02	28.69	55.49	37.73	38.05	SAc: 30.16, C=O: 193.80
10b	$CDCl_3$	106.56	84.83	79.73	79.09	29.05	55.80	38.24	38.46	SAc: 30.46, C=O: 194.61
10b	C_6D_6	107.25	85.50	79.93	79.75	29.54	55.69	37.93	38.25	SAc: 31.12, C=O: 193.98
13a	$CDCl_3$	101.92	82.91	73.74	71.20	60.13	56.34	38.64		CMe_2: 98.72, Me: 27.65, Me′: 20.70
13b	$CDCl_3$	107.60	86.14	73.22	74.53	60.44	55.50	38.28		CMe_2: 98.73, Me: 20.90, Me′: 27.11
14a	Acetone	100.04	84.84	73.75	77.57	61.44	54.83	38.06		
14a	D_2O	100.11	83.73	72.74	77.90	60.45	55.91	37.99		
14b	D_2O	106.46	87.09	73.42	82.67	61.12	55.98	38.01		
27	$CDCl_3$	106.61	89.10	83.46	79.73	30.69	54.91	38.53		SAc: 30.50, C=O: 194.85, OMe′: 57.95
29	$CDCl_3$	106.61	88.72	80.57	78.93	67.43	55.14	37.71	38.32	OMe′: 57.96

[a] Assignments may be inverted.

side (**28**). During the column chromatography on SiO_2 with EtOAc, **22b** gave 18% of methyl 2-*O*-acetyl-3,5-anhydro-3-thio-β-D-xylofuranoside (**23**) by re-esterification. Experimental details for the individual compounds are given in Tables 12 and 13. MS, ^1H NMR and ^{13}C NMR data are given in Tables 14–17.

3.10. Methyl 2,5-anhydro-3-*O*-(4-nitrobenzoyl)-2-thio-α-D-lyxofuranoside (19)

To a solution of **17a** (0.44 g, 2.71 mmol) in pyridine (25 mL) a concd solution of 4-nitrobenzoyl chloride (0.63 g, 3.39 mmol) in pyridine was slowly added at 0 °C. The resulting mixture was allowed to warm up to room temperature. The solvent was evaporated in vacuum. The residue was dissolved in $CHCl_3$ (200 mL) and washed three times with water (75 mL each), with aq 3 M $NaHSO_4$ solution and finally with satd aq $NaHCO_3$ solution (75 mL each). After drying over $MgSO_4 \cdot H_2O$, filtration and evaporation of most of the solvent, the hot concd solution was allowed to cool down slowly overnight to yield **19** as yellow crystals that were suitable for X-ray structural analysis. The mother liquor was purified by column chromatography to give further **19** (total yield 0.24 g, 0.77 mmol, 28%): R_f 0.59 (2:1 petroleum ether–EtOAc); mp 124 °C; $[\alpha]_D^{20}$ 49.4 (c 1.0, $CHCl_3$); IR: ν 1729 (C=O), 1526 (NO_2), 1343 (NO_2) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.95 (dd, 1H, H-5_{endo}), 3.04 (dd, 1H, H-5_{exo}), 3.42 (s, 3H, OMe), 3.62 (d, 1H, H-2), 4.76 (ddd, 1H, H-4), 5.00 (s, 1H, H-1), 5.63 (dd, 1H, H-3), 8.20 (ddd, 2H, H-b, H-b′), 8.31 (ddd, 2H, H-c, H-c′) ppm; $J_{1,2}$ 0, $J_{2,3}$ 2.3, $J_{3,4}$ 2.9, $J_{4,5\text{-}endo}$ 0.8, $J_{4,5\text{-}exo}$ 1.2, $J_{5\text{-}endo,5\text{-}exo}$ 10.6, $J_{b,c}$ 9.0, $J_{b,b'}$ ca. 2.1, $J_{b,c'}$ ca. 2.1, $J_{c,c'}$ ca. 2.1 Hz; ^{13}C NMR (126 MHz, $CDCl_3$): δ 34.63 (C-5), 48.60 (C-2), 55.11 (OMe), 75.49 (C-4), 75.73 (C-3), 109.33 (C-1), 123.67 (C-c, C-c′), 130.90 (C-b, C-b′), 134.67 (C-a), 150.76 (C-d), 163.70 (C=O) ppm; EIMS: m/z (%) 311 (1) [$M^{+\cdot}$], 280 (7) [$M^{+\cdot}-OMe$], 251 (1) [$M^{+\cdot}-HCO_2Me$], 150 (86) [4-nitrobenzoyl]; HRMS Calcd for $C_{13}H_{13}NO_6S$: m/z 311.0464. Found: m/z

Table 12. Preparation of methyl 2,5-anhydro-2-thio- and 3,5-anhydro-3-thiopentofuranosides

Substrate (mmol)		Solvent (mL)	Nucleophile (mmol)	Time (min)	Product (mmol)		Yield (%)	
3a	17.2	MeOH (720)	$NaHCO_3$ (43.1)	60	**4a**	13.9	80.6	Colourless crystals
3b	5.55	Glyme (210)	$NaHCO_3$ (14.1)	60	**4b**	4.58	82.5	Colourless crystals
6	8.11	Glyme (280)	$NaHCO_3$ (19.1)	180	**7**	5.90	72.7	Yellow oil
10a+	17.5+	Glyme (3000)	$NaHCO_3$ (57.1)	600	**11a**[a]	12.8	73.0	Yellow solid
10b	12.7				**11b**[a]	8.78	69.2	Yellow oil
15a	20.7	MeOH (800)	$NaHCO_3$ (44.0)	240	**17a**	19.5	94.4	Yellow syrup
15a	2.70	Glyme (100)+H_2O (5.5)	NaOAc (4.85)	360	**17a**[a]	1.48	54.8	Yellow syrup
					18[a]	0.34	12.6	Yellow oil
15b	26.5	MeOH (880)	$NaHCO_3$ (47.6)	780	**17b**[a]	4.50	17.0	Yellow syrup
					17a[a,b]	8.69	32.8	Yellow syrup
21a	4.11	Glyme (150)+H_2O (8)	NaOAc (7.35)	180	**22a**	3.64	88.6	Colourless crystals
21b	8.47	Glyme (310)+H_2O (17)	NaOAc (15.1)	720	**22b**	6.90	81.5	Colourless crystals
21b	4.94	MeOH (170)	$NaHCO_3$ (9.28)	60	**22b**[a]	3.58	72.5	Colourless crystals
					23[a]	0.88	17.8	Yellow oil
27	1.84	MeOH (70)	$NaHCO_3$ (3.57)	240	**28**	1.48	80.4	Yellow syrup

[a]Separation by column chromatography.
[b]Compound **17a** was formed by anomerization during the column chromatography.

Table 13. Physical, IR and analytical data of methyl 2,5-anhydro-2-thio- and 3,5-anhydro-3-thiopentofuranosides

	R_f (eluent)	Mp (°C) (solvent)	$[\alpha]_D^{20}$ (*c* 1.0, $CHCl_3$)	*v* (SO_2) (cm^{-1})	Elemental analysis	
					Calcd	Found
4a	0.56 (1:1 EtOAc–PE)	74 (MeOH)	−241.7	1355, 1178	C, 34.99; H, 5.03; S, 26.69	C, 35.34; H, 5.06; S, 26.41
4b	0.45 (1:1 EtOAc–PE)	159 (EtOH)	−10.9	1359, 1170	C, 34.99; H, 5.03; S, 26.69	C, 34.65; H, 4.98; S, 26.35
7	0.59 (Et_2O)					
11a	0.66 (Et_2O)	81 (Et_2O)		1354, 1174		
11b	0.33 (Et_2O)			1359, 1178		
17a	0.75 (2:1 EtOAc–PE)			3435 (OH)		
17b	0.30 (2:1 EtOAc–PE)					
18	0.72 (1:1 EtOAc–PE)			1745 (C=O)		
22a	0.27 (1:1 EtOAc–PE)	38 (1:1 Et_2O–PE)	+233.6	3447 (OH)	C, 44.43; H, 6.21; S, 19.77	C, 44.22; H, 6.24; S, 19.75
22b	0.25 (1:1 Et_2O–PE)	52 (1:1 Et_2O–PE)	−67.1	3420 (OH)	C, 44.43; H, 6.21; S, 19.77	C, 44.52; H, 6.25; S, 19.62
23	0.47 (1:1 Et_2O–PE)					
28	0.82 (EtOAc)		+126.8			

311.0423. Anal. Calcd for $C_{13}H_{13}NO_6S$: C, 50.16; H, 4.21; N, 4.50; S, 10.30. Found: C, 50.05; H, 4.14; N, 4.37; S, 10.32.

3.11. Methyl 3,5-anhydro-3-thio-β-D-xylofuranoside *S*-dioxide (24)

A solution of **22b** (0.51 g, 3.14 mmol) and H_2O_2 (30%, 0.70 mL, 0.78 g, 6.84 mmol) in MeOH (15 mL) was left at room temperature for 2 days. The solution was poured on to water and extracted intensively with $CHCl_3$. After drying the extract over $MgSO_4 \cdot H_2O$, filtration and evaporation of the solvent, the residue was purified by column chromatography (2-butanone, R_f 0.96) to yield **24** (0.21 g, 1.08 mmol, 34%) as a colourless solid: mp 140 °C (colourless blocks from acetone); $[\alpha_D^{20}]$ −76.2 (*c* 1.0, acetone); IR (KBr): *v* 3511 (OH), 1316 (SO_2) 1140 (SO_2) cm^{-1}; ^1H NMR (400 MHz, D_2O): δ 3.36 (s, 3H, OMe), 4.14 (ddd, 1H, H-5$_{endo}$), 4.44 (ddd, 1H, H-5$_{exo}$), 4.64 (d, 1H, H-2), 4.90 (dddd, 1H, H-3), 5.09 (ddd, 1H, H-4), 5.10 (s, 1H, H-3) ppm; $J_{1,2}$ 0.0, $J_{2,3}$ 1.1, $J_{3,4}$ 7.2, $J_{3,5\text{-}endo}$ 1.5, $J_{3,5\text{-}exo}$ 2.9, $J_{4,5\text{-}endo}$ 3.0, $J_{4,5\text{-}exo}$ 7.4, $J_{5\text{-}endo,5\text{-}exo}$ 15.2 Hz; ^1H NMR (500 MHz, acetone-d_6): δ 3.30 (s, 3H, OMe), 3.96 (ddd, 1H, H-5$_{endo}$), 4.22 (ddd, 1H, H-5$_{exo}$), 4.66–4.70 (m, 2H, H-2, H-3), 4.81 (d, 1H, OH), 4.95 (d, 1H, H-1), 4.98 (ddd, 1H, H-4) ppm; $J_{1,2}$ 1.4, $J_{2,OH}$ 5.2, $J_{3,4}$ 6.9, $J_{3,5\text{-}endo}$ 1.3, $J_{3,5\text{-}exo}$ 2.8, $J_{4,5\text{-}endo}$ 3.2, $J_{4,5\text{-}exo}$ 7.3, $J_{5\text{-}endo,5\text{-}exo}$ 14.5 Hz; ^{13}C NMR (101 MHz, D_2O): 55.94 (OMe), 65.73 (C-4), 73.74 (C-5), 75.99 (C-2), 88.32 (C-3), 113.65 (C-1) ppm; ^{13}C NMR (101 MHz, acetone-d_6): δ 55.41 (OMe), 64.98 (C-4), 73.03 (C-5), 76.80 (C-2), 88.91 (C-3), 114.70 (C-1) ppm; EIMS: *m*/*z* (%) 163 (0.3) [$M^{+\cdot}$−OMe], 116 (4), 97 (8), 87 (19), 70 (100), 69 (59), 51 (27), 55 (19), 45 (24), 43 (33), 42 (56), 41 (59), 39 (45); FABMS (*m*-NBA): *m*/*z* (%) 195 [$M^{+\cdot}$+H]; HRMSFAB Calcd for $C_6H_{10}O_5S$: *m*/*z* 195.0327. Found: *m*/*z* 195.0403. Anal. Calcd for

Table 14. Mass spectrometric data of methyl 2,5-anhydro-2-thio- and 3,5-anhydro-3-thiopentofuranosides

	EIMS m/z (%)	HRMS m/z	
		Calcd	Found
4a	240 (1) [$M^{+\cdot}$], 209 (5) [$M^{+\cdot}-OMe$], 194 (5) [$M^{+\cdot}-CH_2{=}S$], 180 (15) [$M^{+\cdot}-HCO_2Me$], 165 (8), 145 (15) [$M^{+\cdot}-OMs$], 115 (85), 101 (86), 87 (51), 85 (100), 84 (67), 79 (36), 73 (43), 71 (30), 61 (28), 45 (83), 41 (39)	240.0126 208.9905	240.0089 208.9905
4b	240 (9) [$M^{+\cdot}$], 208 (26) [$M^{+\cdot}-MeOH$], 194 (6) [$M^{+\cdot}-CH_2{=}S$], 175 (15), 165 (9), 145 (14) [$M^{+\cdot}-OMs$], 144 (11), 115 (100), 101 (66), 99 (37), 87 (51), 85 (72), 84 (52), 79 (30), 73 (38), 71 (45), 69 (21), 61 (24), 45 (74), 41 (34)	240.0126 207.9864	240.0096 207.9846
18	204 (0.3) [$M^{+\cdot}$], 173 (2) [$M^{+\cdot}-OMe$], 145 (4), 130 (21) [$M^{+\cdot}-OMe$, –Ac], 112 (6), 111 (8), 102 (10), 101 (23), 87 (19), 85 (21), 84 (22), 75 (58), 73 (9), 50 (8), 45 (22), 43 (100) [Ac]		
22a	162 (2) [$M^{+\cdot}$], 131 (4) [$M^{+\cdot}-OMe$], 116 (16) [$M^{+\cdot}-CH_2{=}S$], 104 (5), 103 (7), 102 (100) [$M^{+\cdot}-HCO_2Me$], 101 (21), 87 (55), 85 (32), 84 (10), 75 (5), 74 (18), 73 (55), 72 (9), 71 (16), 69 (21), 68 (18), 61 (38)		
22b	162 (5) [$M^{+\cdot}$], 131 (3) [$M^{+\cdot}-OMe$], 130 (3) [$M^{+\cdot}-MeOH$], 116 (28) [$M^{+\cdot}-CH_2{=}S$], 103 (5), 102 (76) [$M^{+\cdot}-HCO_2Me$], 101 (12), 87 (14), 60 (40), 59 (71), 58 (30), 57 (75), 56 (63), 55 (72), 48 (6), 47 (33), 46 (26), 45 (100)		
23	204 (2) [$M^{+\cdot}$], 173 (1) [$M^{+\cdot}-OMe$], 158 (2) [$M^{+\cdot}-CH_2{=}S$], 145 (3) [$M^{+\cdot}-OAc$], 144 (3), 126 (15), 116 (7), 103 (6), 102 (8), 101 (6), 98 (4), 87 (26), 85 (19), 84 (33), 68 (8), 43 (100) [Ac]; FAB-MS: 205 [$M^{+\cdot}+1$]	FAB-HRMS: 205.0535	FAB-HRMS: 205.0520
28	176 (1) [$M^{+\cdot}$], 145 (3) [$M^{+\cdot}-OMe$], 130 (9), 116 (29) [$M^{+\cdot}-HCO_2Me$], 101 (17), 85 (100), 70 (16), 59 (4), 45 (18), 43 (12), 41 (17)	145.0323 116.0296	145.0333 116.0300

Table 15. Chemical shifts δ in the ^1H NMR spectra (400 MHz) of methyl 2,5-anhydro-2-thio- and 3,5-anhydro-3-thiopentofuranosides

Compd	Solvent	H-1	H-2	H-3	H-4	H-5 (*endo*)	H-5′ (*exo*)	OMe	Further signals
4a	$CDCl_3$	5.39	4.91	4.21	5.12	3.05	3.45	3.42	OMs: 3.15
4b	$CDCl_3$	5.29	5.07	4.23	5.14	3.27	3.50	3.63	OMs: 3.16
7	$CDCl_3$	5.50	3.34	4.31	4.44	2.95	2.92	3.39 3.56	H_a, $H_{a'}$: 3.56–3.59[b] H_b, $H_{b'}$: 3.71–3.74[b]
11a	$CDCl_3$[a]	4.94	3.50	5.31	4.67	2.88	3.05	3.37	OMs: 3.13
11b	$CDCl_3$	5.25	3.74	5.16	4.62	3.04	3.04	3.41	OMs: 3.16
17a	$CDCl_3$	4.89	3.25	4.66	4.36	2.78	2.93	3.36	OH-3: 2.56
17b	$CDCl_3$	5.21	3.46	4.49	4.33	2.95	2.90	3.48	
18	$CDCl_3$	4.92	3.49	5.31	4.58	2.83	2.94	3.37	OAc: 2.10
19	$CDCl_3$[a]	5.00	3.62	5.63	4.76	2.95	3.04	3.42	ArH: 8.20, 8.31
22a	$CDCl_3$	5.42	4.43	3.74	5.11	2.98	3.45	3.55	OH: 2.75
22b	$CDCl_3$	5.21	4.47	3.75	5.37	3.20	3.44	3.55	OH: 2.55
23	$CDCl_3$	5.25	5.29	3.80	5.35	3.25	3.44	3.56	OAc: 2.05
24	D_2O	5.10	4.64	4.90	5.09	4.14	4.44	3.36	
24	Acetone-d_6[a]	4.95	4.66–4.70	4.66–4.70	4.98	3.96	4.22	3.30	OH: 4.81
28	$CDCl_3$	5.28	3.74	4.17	5.09	3.02	3.47	3.39	OMe′: 3.42
30	$CDCl_3$[a]	5.24	3.66	4.21	5.40	2.89	3.45	3.38	OMe′: 3.40
31	$CDCl_3$[a]	5.07	3.90	4.56	5.45	3.47[b]	3.74[b]	3.42	OMe′: 3.46

[a] Measurement at 500 MHz.
[b] Assignment may be inverted.

$C_6H_{10}O_5S$: C, 37.11; H, 5.14; S, 16.51. Found: C, 37.13; H, 5.15; S, 16.49.

3.12. Methyl 2-*O*-methyl-α-D-arabinofuranoside (25)

A concd methanolic solution of **20a** (3.00 g, 20.5 mmol) was added to a NaOMe solution prepared from Na (6.00 g, 261 mmol) and MeOH (50 mL). After stirring at 45 °C for 9 h, the solution was neutralised with methanolic HOAc. Subsequent filtration, evaporation of the solvent and column chromatography (EtOAc) yielded **25** (3.00 g, 16.8 mmol, 82%) as a colourless syrup: R_f 0.34 (EtOAc); IR (film): ν 3401 (OH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.40 (s, 3H, OMe), 3.42 (s, 3H, OMe′), 3.69 (dd, 1H, H-2), 3.72 (dd, 1H, H-5), 3.80 (dd, 1H, H-5′), 4.00 (ddd, 1H, H-4), 4.03 (dd, 1H, H-3), 4.88 (d, 1H, H-1) ppm; $J_{1,2}$ 1.2, $J_{2,3}$ 3.0, $J_{3,4}$ 5.9, $J_{4,5}$ 4.2, $J_{4,5'}$ 3.3, $J_{5,5'}$ 12.7 Hz; ^1H NMR (400 MHz, D_2O): δ 3.33 (s, 3H, OMe), 3.35 (s, 3H, OMe′), 3.59 (dd, 1H, H-5), 3.67 (dd, 1H, H-2), 3.73 (dd, 1H, H-5′), 3.90–3.95 (m, 2H, H-3, H-4), 4.91 (d, 1H, H-1) ppm; $J_{1,2}$ 1.4, $J_{2,3}$ 2.6, $J_{4,5}$ 5.3, $J_{4,5'}$ 2.6, $J_{5,5'}$ 12.3 Hz; ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.26 (OMe), 57.91 (OMe′), 62.19 (C-5), 75.54 (C-3), 84.54 (C-4), 91.14 (C-2), 107.03 (C-1) ppm.

Table 16. ^{1}H-^{1}H coupling constants J (Hz)[a] of methyl 2,5-anhydro-2-thio- and 3,5-anhydro-3-thiopentofuranosides

Compd	Solvent[b]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5endo}$	$J_{4,5exo}$	$J_{5,5'}$	Additional couplings
4a	$CDCl_3$	2.2	6.7	6.5	3.0	6.3	10.4	
4b	$CDCl_3$	4.9	8.0	6.9	3.4	7.2	10.5	
7	$CDCl_3$	2.3	1.9	0.0	1.5	1.8	10.7	
11a	$CDCl_3$[c]	0.0	2.4	3.0	1.3	1.7	10.7	
11b	$CDCl_3$	2.4	2.3	3.0	1.6	1.6	vd[d]	
17a	$CDCl_3$	0.0	2.3	3.0	1.3	1.9	10.7	$J_{3,OH-3}$: 9.4
17b	$CDCl_3$	2.6	2.4	2.5	1.2	2.3	11.1	
18	$CDCl_3$	0.0	2.3	2.9	1.4	1.8	10.4	
19	$CDCl_3$[c]	0.0	2.4	2.8	1.5	1.5	10.6	J_{ortho}: 9.0, J_{meta}: 2.1, J_{para}: 2.1
22a	$CDCl_3$	3.9	2.5	6.3	2.6	6.2	10.6	$J_{2,OH-2}$: 6.5
22b	$CDCl_3$	0.8	0.0	6.7	3.5	7.2	10.4	$J_{2,OH-2}$: 5.4
23	$CDCl_3$	0.7	0.0	6.7	3.6	7.2	10.3	
24	D_2O	0.0	1.1	7.2	3.0	7.4	15.2	$J_{3,5endo}$: 1.5, $J_{3,5exo}$: 2.9
24	Acetone-d_6[c]	1.4	m	6.9	3.2	7.3	14.5	$J_{3,5endo}$: 1.3, $J_{3,5exo}$: 2.8, $J_{2,OH-2}$: 5.2
28	$CDCl_3$	2.5	6.6	6.1	2.6	6.1	10.4	
30	$CDCl_3$[c]	2.2	6.7	6.4	2.8	6.0	9.5	
31	$CDCl_3$[c]	2.8	6.4	5.2	4.0	2.8	12.0	

[a] m (unresolved multiplet): J could not be determined.
[b] Measurement at 400 MHz if not stated otherwise.
[c] Measurement at 500 MHz.
[d] Virtual doublet: no coupling between H-5 and H-5′ was detectable.

Table 17. Chemical shifts δ in the ^{13}C NMR spectra (101 MHz) of methyl 2,5-anhydro-2-thio- and 3,5-anhydro-3-thiopentofuranosides

Compd	Solvent	C-1	C-2	C-3	C-4	C-5	OMe	Additional signals
4a	$CDCl_3$	107.09	82.10	43.90	79.52	31.17	55.66	OMs: 38.34
4b	$CDCl_3$	103.66	76.34	43.21	78.76	33.39	56.90	OMs: 78.72
7	$CDCl_3$	108.19	47.53	88.44	77.45	32.78	58.99	OMe′: 57.21, OCH_{2a}: 69.47,[b] OCH_{2b}: 71.85[b]
11a	$CDCl_3$[a]	109.36	49.26	78.58	76.32	34.63	55.49	OMs: 39.01
11b	$CDCl_3$	105.39	50.87	77.85	76.91	34.35	56.60	OMs: 39.02
17a	$CDCl_3$	109.10	51.43	73.10	77.13	33.87	54.99	
17b	$CDCl_3$	105.42	53.88	74.17	79.18	33.75	56.27	
18	$CDCl_3$	109.43	48.49	74.78	75.45	34.64	54.98	OAc: 20.84, C=O: 170.06
19	$CDCl_3$[a]	109.33	48.60	75.73	75.49	34.63	55.11	C-3′/5′: 123.67, C-2′/6′: 130.90, C-1′: 134.67, C-4′: 150.76, C=O: 163.70
22a	$CDCl_3$	104.28	79.62	47.55	79.73	31.45	56.30	
22b	$CDCl_3$	114.33	81.39	49.18	82.39	34.33	56.06	
23	$CDCl_3$	112.09	82.68	47.00	82.37	34.38	56.18	OAc: 20.82, C=O: 169.70
24	D_2O	113.65	75.99	88.32	65.73	73.74	55.40	
24	Acetone-d_6	114.70	76.80	88.91	64.98	73.03	55.41	
28	$CDCl_3$	108.34	85.06	44.76	80.03	31.52	58.51	OMe′: 55.76
30	$CDCl_3$	107.89	84.87	33.59	82.18	18.07	58.41	OMe′: 55.44
31	$CDCl_3$	108.08	86.10	58.02	88.36	38.97	55.86	OMe′: 59.03

[a] Measurement at 126 MHz.
[b] Assignment not possible.

3.13. Reaction of 29 with sodium hydrogen selenide

The reaction was carried out under Ar. EtOH (10 mL) was slowly added to a mixture of black selenium (0.39 g, 4.94 mmol) and $NaBH_4$ (0.20 g, 5.29 mmol). When the reaction slowed down, further $NaBH_4$ and EtOH were added until the mixture was nearly colourless. This mixture was poured into a hot (60 °C) solution of **29** (0.78 g, 2.33 mmol) in EtOH (175 mL), Na_2CO_3 (1.00 g, 9.43 mmol) was added, and the mixture was refluxed for 60 min. Subsequently the reaction mixture was stirred at the open air for 60 min in order to oxidize the excess of NaHSe to elemental selenium. Then the EtOH was evaporated, and the residue was treated with EtOAc. Filtration and column chromatography (1:1 EtOAc–petroleum ether) led to **30** as a yellow oil (0.40 g, 1.79 mmol, yield 77%). The byproduct **31** was obtained as a red oil (6%).

3.14. Methyl 3,5-anhydro-3-*O*-methyl-3-seleno-α-D-lyxofuranoside (30)

R_f 0.69 (1:1 EtOAc–petroleum ether), R_f 0.83 (EtOAc); $[\alpha]_D^{20}$ +187.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89 (dd, 1H, H-5_{endo}), 3.38 (s, 3H, OMe), 3.40

(s, 3H, OMe′), 3.45 (dd, 1H, H-5_{exo}), 3.66 (dd, 1H, H-2), 4.21 (dd, 1H, H-3), 5.24 (d, 1H, H-1), 5.40 (ddd, 1H, H-4) ppm; $J_{1,2}$ 2.2, $J_{2,3}$ 6.7, $J_{3,4}$ 6.4, $J_{4,5\text{-}endo}$ 2.8, $J_{4,5\text{-}exo}$ 6.0, $J_{5\text{-}endo,5\text{-}exo}$ 9.5 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.07 (C-5), 33.59 (C-3), 55.44 (OMe′), 58.41 (OMe), 82.18 (C-4), 84.87 (C-2), 107.89 (C-1) ppm; $J_{5,Se}$ 12.9, $J_{3,Se}$ 21.3 Hz; EIMS: m/z (%) 224 (28) [$M^{+\cdot}$], 164 (63) [$M^{+\cdot}-HCO_2Me$], 162 (31) [$M^{+\cdot}-2OMe$], 135 (19), 133 (100) [$M^{+\cdot}-HCO_2Me$, –OMe], 131 (49), 130 (22) [$M^{+\cdot}-H_2C{=}Se$], 101 (44), 84 (47), 71 (42), 69 (43), 45 (59), 41 (62), 39 (41); HRMS Calcd for $C_7H_{12}O_3Se$: m/z 223.9952. Found: m/z 223.9922.

3.15. Methyl 3,5-anhydro-2-*O*-methyl-3,5-diseleno-α-D-lyxofuranoside (31)

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.42 (s, 3H, OMe), 3.46 (s, 3H, OMe′), 3.47 (dd, 1H, H-5_{endo}), 3.74 (dd, 1H, H-5_{exo}), 3.90 (dd, 1H, H-2), 4.56 (dd, 1H, H-3), 5.07 (d, 1H, H-1), 5.45 (ddd, 1H, H-4) ppm; $J_{1,2}$ 2.8, $J_{2,3}$ 6.4, $J_{3,4}$ 5.2, $J_{4,5\text{-}endo}$ 4.0, $J_{4,5\text{-}exo}$ 2.8, $J_{5\text{-}endo,5\text{-}exo}$ 12.0 Hz; ^{13}C NMR (101 MHz, $CDCl_3$): δ 38.97 (C-5), 55.86 (OMe), 58.02 (C-3), 59.03 (OMe′), 86.10 (C-2), 88.36 (C-4), 108.08 (C-1) ppm.

4. Supplementary material

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 1223 336408, fax: +44 1223 336033; e-mail http://deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Deposition numbers: CCDC 142684 (**4a**), 142680 (**4b**), 142683 (**19**), 142681 (**22a**), 142682 (**22b**), 142689 (**24**) and 142686 (**29**). For convenience, the central atoms in the ORTEP plots (Figs. 1–3) are numbered according to the common carbohydrate nomenclature, which differs from the numbering in the CCDC files!

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their financial support. O.S. thanks the Universität Hamburg for a Graduate Scholarship.

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