DOI: 10.1002/ejoc.200900573

Synthetic Approaches to Novel Thiosugar Scaffolds Containing α,β-Unsaturated Carbonyl Groups

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Keywords: Carbohydrates / Sulfur heterocycles / Lactones / Enones / Ring expansion / Thiosugars

The synthesis of new classes of highly functionalized thiosugar derivatives containing α,β-unsaturated carbonyl functions has been accomplished through simple and efficient strategies. 5-Thiosugar-fused butenolides and a 5-thiohex-1-enopyran-3-ulose were constructed from easily available starting 3-uloses by practical and reliable approaches. The reaction sequence used for the bicyclic fused derivatives involved Wittig olefination of protected pento- or hexofuran-3-uloses, introduction of a sulfhydryl group at C-5 of the intermediate unsaturated ester and acid-promoted deprotection, which allowed intramolecular lactonization and conversion into the 5-thiopyranose form. For the synthesis of a 5-thiohex-1-enopyran-3-ulose, a sulfhydryl functionality was introduced at C-5 on a masked 3-ulose derived from 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose. Acid hydrolysis displaced the equilibrium towards the 5-thiopentopyran-3-ulose, which on pyridine-mediated acetylation underwent 1,2-elimination of acetic acid to give the desired α,β-unsaturated 5-thiopyranulose. This straightforward pathway provided the target compound in 37% overall yield.

Introduction

Thiosugars containing sulfur as a heteroatom in the ring possess interesting chemical and biological properties and have attained considerable importance in glycobiology and in drug design as glycosidase inhibitors or as potential anticancer and anti-HIV agents.[1,2] The different electronic properties of the sulfur and oxygen atoms (i.e., electronegativity and polarizability), and the changes in flexibility and conformation of the ring when an oxygen atom is replaced by sulfur, together with the distinct chemical reactivity of the sulfide function relative to the corresponding ether moiety, are assumed to contribute to the differences in the biological properties of thiosugars and their carbohydrate analogues.[3,4]

A few examples of naturally occurring thiosugars have appeared in the literature;[2] the first isolated compound was 5-thio-D-mannose, from the marine sponge *Clathria pyramida* in 1987.[5] Since the first synthesis of 5-thio-α-D-xylopyranose in 1961,[6] a variety of approaches for the preparation of thiosugars by transformation of carbohydrate or non-carbohydrate precursors have been developed, and some reviews covering the methodologies have been published.[3,7]

Owing to their potential value as bioactive compounds, the search for new classes of thiosugars remains highly relevant. In this context we turned our attention to the synthesis of thiosugar derivatives containing α,β-unsaturated carbonyl functions, such as ketones and lactones. This functionality possesses inherent bioactivity due to its ability to undergo Michael additions by enzymes' nucleophilic components, especially cysteine sulfhydryl groups.[8,9] Moreover, sugars containing such systems are building blocks of high synthetic versatility and have been used as intermediates for a variety of important sugar derivatives, including disaccharides, branched-chain sugars and bioactive natural products.[10] In particular, previous contributions in this field from our research group have shown the efficacy of furanose C–C-linked α,β-unsaturated γ-lactones as antifungal[11] and insecticidal agents.[12] In addition, we were also able to use sugar-fused unsaturated lactones as starting materials for the synthesis of the sugar moiety, and its epimer, contained in miharamycins,[13] antibiotics known as potent inhibitors of *Pyricularia oryzae*, which produces the rice blast disease and is considered a bioterrorism agent.

Combining thiosugar units and α,β-unsaturated carbonyl systems may therefore be a valuable tool for the design of new potentially biologically active substances, also providing highly functionalized templates for the synthesis of new thiosugar derivatives. The key structural feature of thiolactomycin and its analogues, based on an unsaturated thiolactone moiety, and their pharmacological properties, namely activity against bacteria (e.g., *Mycobacterium tuberculosis*)[14] and parasitic organisms (e.g., *Trypanosoma* sp. and *Plasmodium falciparum*),[15] additionally support these considerations.

With these motivations in mind we envisioned the synthesis of new thiosugar scaffolds containing such unsatu-

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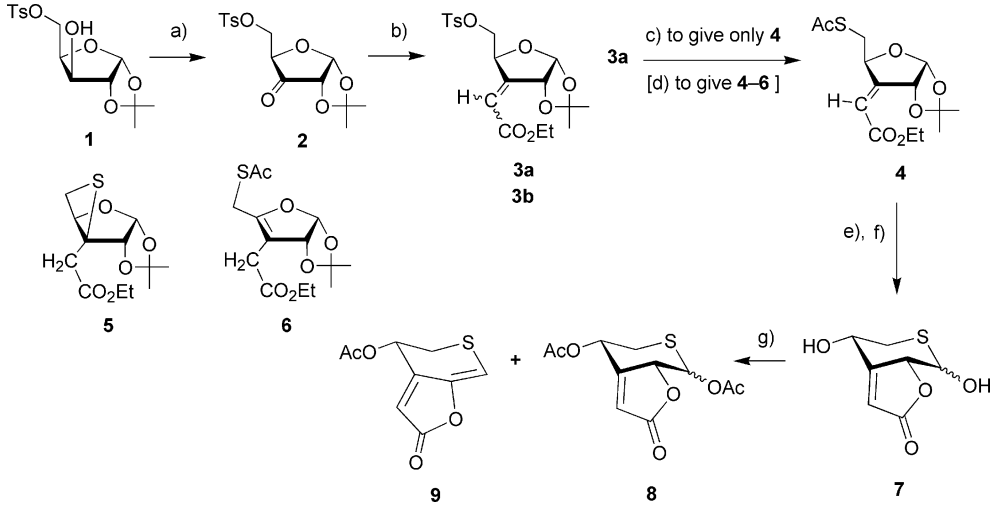
rated systems: namely, 5-thiopyranose-fused butenolides and a 1-eno-5-thiopentopyran-3-ulose. For this purpose, easily available furanos-3-uloses were used as starting materials and the methodologies used were based on intramolecular cyclization approaches, taking advantage of the ability of the free sugars to undergo furanose–pyranose isomerization. For the synthesis of thiosugar-fused butenolides we explored our recently reported Wittig olefination/intramolecular lactonization method,[16] with the introduction of additional sulfhydryl functionality at C-5 of the intermediate α,β-unsaturated ester. The strategy for the preparation of a 5-thiohex-1-enopyran-3-ulose was based on the conversion of a hemiacetal, derived from 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose by partial hydrolysis and intramolecular cyclisation of the resulting primary alcohol with the carbonyl group, into the corresponding 5-SH analogue, followed by acid removal of 1,2-*O*-isopropylidene group. Under these reaction conditions, the equilibrium between the hemiacetal and its ulose isomer and the furanose–pyranose equilibrium favoured the formation of the 5-thiopyran-3-ulose, which by acetylation/1,2-elimination, gave the target α,β-unsaturated 5-thiopyranulose.

Results and Discussion

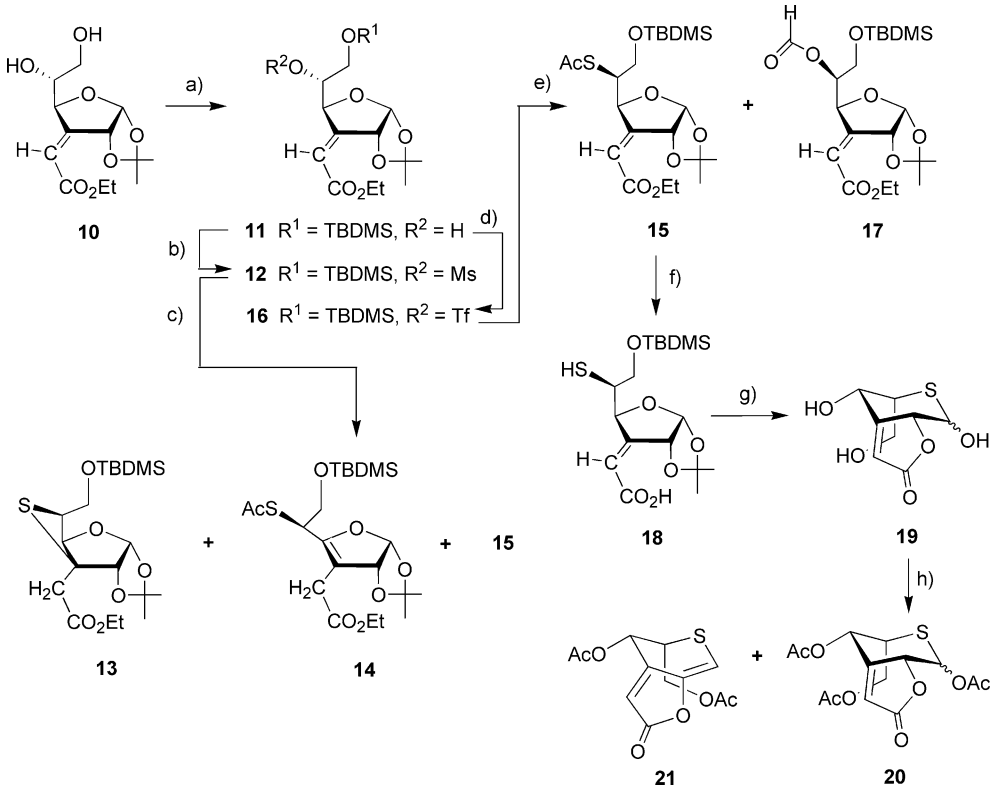
1. 5-Thiopyranose-Fused Butenolides

The synthesis of a butenolide 2,3-fused to a 5-thiopentopyranose unit started with the commercially available 1,2-*O*-isopropylidene-α-D-xylofuranose, which was converted into the 5-*O*-tosyl derivative **1**[17] (Scheme 1) as a key intermediate for the introduction of a 5-thio group. Oxidation of **1** with pyridinium dichromate/acetic anhydride afforded the 3-ulose **2** along with its hydrate in 77% yield.[18] Wittig-type treatment of **2** with the stabilized ylide [(ethoxycarbonyl)methylene]triphenylphosphorane gave the (*Z*)-α,β-unsaturated ester **3a** as the main product (77%), together with the *E* adduct **3b** (17%). Substitution of the tosylate of **3a** by treatment with potassium thioacetate was efficiently achieved in DMF at 40 °C, giving the desired product **4** in 84% yield. Use of a higher reaction temperature (90 °C) also led to the formation of the thietane derivative **5**, resulting from Michael addition, and of the allylic rearrangement product **6**, both of which were inseparable from **4** by chromatography and were identified by NMR analysis of the mixture. Deacetylation and ester hydrolysis of **4** with sodium hydroxide in aq. methanol was followed by treatment with aq. acetic acid (70%) under reflux to cleave the 1,2-*O*-isopropylidene group. Concomitant isomerization and intramolecular lactonization furnished the target 5-thiosugar-fused butenolide 7 in 35% overall yield. In the ^{13}C NMR spectrum of **7**, the signal at δ = 174.8 ppm for the carbonyl group is consistent with an α,β-unsaturated lactone skeleton. Subsequent acetylation of **7** with acetic anhydride in pyridine provided the corresponding diacetate derivative **8** as a mixture of both anomers (α/β ratio 1:0.3) in 80% yield, together with traces of the 5-thioglycal-fused butenolide **9**. The structure of the elimination product **9** was supported by ^1H NMR and HRMS data. A long-range coupling between H-1 and H-3′ with a constant of 1.5 Hz and the high chemical shift of H-1 (δ = 6.47 ppm) is indicative of the conjugated system of **9**.

The feasibility and scope of this approach were then studied for the preparation of 5-thiohexopyranose-fused butenolides. The 5,6-diol **10** was prepared by Wittig olefination of 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose, followed by selective hydrolysis of the primary acetonide as described previously.[16a] Silylation of the primary hydroxy group (Scheme 2) was carried out with *tert*-butyldimethylsilyl chloride (TBDMSCl) and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) in pyridine (15 h), providing compound **11** (87%). Other standard



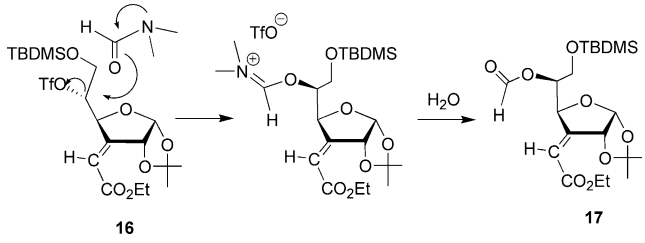
Scheme 1. Reactions and conditions: a) PDC/Ac_2O, CH_2Cl_2, reflux, 2 h 30 min, 77%; b) $Ph_3P{=}CHCO_2Et$, $CHCl_3$, reflux, 1 h, 77% (**3a**) and 17% (**3b**); c) KSAc, DMF, 40 °C, 1 h 45 min, 84%; d) KSAc, DMF, 90 °C, 2 h; e) NaOH, MeOH/H_2O, room temp., 15 min; f) AcOH 70% aq., reflux, 2 h, 35%, 2 steps; g) Ac_2O, py, room temp., 5 min, 80% (**8**) and traces of **9**.



Scheme 2. Reactions and conditions: a) TBDMSCl, py, catalytic DMAP, room temp., 15 h, 87%; b) MsCl, py, 0 °C to room temp., 40 min, 95%; c) KSAc, DMF, 90 °C, 24 h, 15% (**13**), 19% (**14**) and 24% (**15**); d) Tf_2O, py, CH_2Cl_2, –5 °C, 15 min; e) KSAc, DMF, room temp., 1 h, 25% (**15**) and 6% (**17**), two steps; f) NaOH, MeOH/H_2O, room temp., 1 h, 66%; g) TFA 60% aq., 40 °C, 20 min, quantitative; h) Ac_2O, py, room temp., 5 min, 82% (**21**) and traces of **20**.

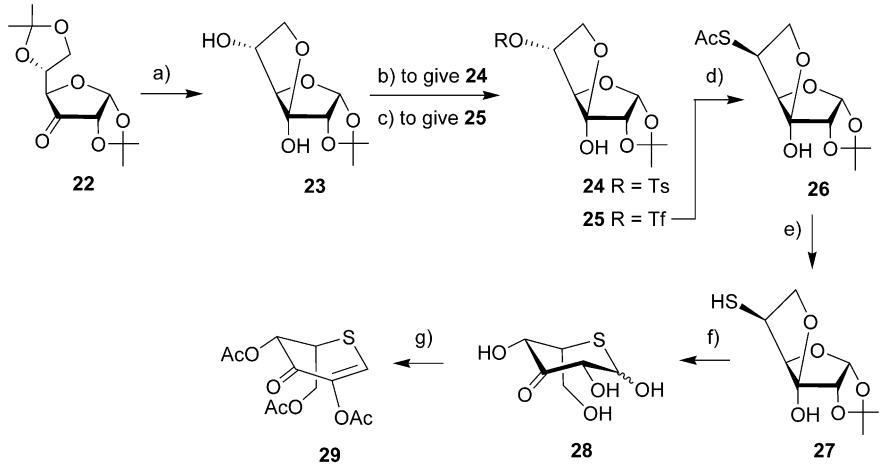
methods such as imidazole in DMF (16%) or Et_3N/cat. DMAP in CH_2Cl_2 (42%) were less efficient. Mesylation, chosen to avoid possible steric hindrance caused by the *O*-TBDMS group, was achieved by treatment of **11** with methanesulfonyl chloride in pyridine, giving **12** in 95% yield. A high temperature (90 °C) was required to substitute the mesylate by a thioacetate in DMF. The desired compound **15** was obtained in 24% yield together with the furanose-fused thietane **13** (15%) and **14** (19%) formed by migration of the exocyclic double bond.

Separation of **14** from **15** could not be achieved by column chromatography. To overcome this drawback, a one-pot, two-step procedure consisting of triflation/nucleophilic substitution was employed. Treatment of **11** with trifluoromethanesulfonic anhydride (Tf_2O)/pyridine and then of the crude triflate **16** with potassium thioacetate in DMF gave **15** in modest yield (25%), together with a small amount of the 5-*O*-formyl derivative **17** (6%). The structure of **17** was established by NMR spectroscopy and HRMS. In the ^1H NMR spectrum a broad triplet for H-5 appeared at rather low field (δ = 5.21 ppm) and COSY experiments showed a weak coupling with the formyl proton (δ = 8.04 ppm). The ^{13}C NMR spectrum showed a quaternary carbon atom at δ = 164.8 ppm, corresponding to the *O*-formyl carbonyl group. The unexpected formation of **17** can be explained by a reaction between the triflate **16** and the solvent DMF. The formed iminium intermediate is readily converted into the formate **17** by hydrolysis during the workup (Scheme 3). A formylation method under similar conditions has been described previously.[19]



Scheme 3. Possible mechanism for the formation of the by-product **17**.

Although the yield of **15** was not improved by the second approach, separation was easily achieved by column chromatography. Compound **15** was treated with NaOH in aq. methanol (Scheme 2) to provide the corresponding α,β-unsaturated acid derivative **18**, containing a free sulfhydryl group at C-5, in 66% yield. Further hydrolysis of **18** with aq. TFA (60%) at 40 °C afforded the desired 5-thiosugar-fused butenolide **19** (quantitative). The ^{13}C NMR spectrum showed the resonance of the carbonyl carbon of the lactone moiety at δ = 172.3 ppm.



Scheme 4. Reactions and conditions: a) AcOH, 60% aq., room temp., 15 h, 92%; b) TsCl, py, room temp., 40 h, 34%; c) Tf_2O, py, CH_2Cl_2, –5 °C, 10 min; d) KSAc, DMF, room temp., 1 h 15 min, 47%, two steps; e) NaOH, MeOH/H_2O, room temp., 5 min, 90%; f) TFA 60% aq., 40 °C, 15 min, quantitative; g) Ac_2O, py, room temp., 5 min, 94%.

In contrast with the reaction described above, acetylation of **19** under conditions similar to those used for the analogous compound **7** (Scheme 1) proceeded with elimination to give the thioglycal-fused butenolide **21**, isolated in 82% yield. The triacetate derivative **20** was obtained only in trace amounts and was inseparably contaminated with compound **21**, as determined by mass spectrometry. The difference in the reaction modes found for compounds **7** and **19** may be explained either by electronic or by conformational factors. In both bicyclic compounds **8** and **20**, elimination at C1–C2 results in a highly stable α,β,γ,δ-unsaturated carbonyl system. The main driving force for the conversion of **20** into **21**, however, is the presence of a pseudoaxial acetyloxymethyl group at C-5 in **20**, which further destabilizes the distorted chair conformation of the thiopyranose ring. Elimination from **20** to give the corresponding thioglycal **21**, which may adopt a sofa conformation, therefore occurs to overcome the steric destabilizing effect of the C-5 substituent.

2. Synthesis of a Pyranoid Thiosugar Containing an α,β-Unsaturated Ketone Functionality

Synthesis of a 5-thiohex-1-enopyran-3-ulose was accomplished by starting from the key intermediate hemiacetal **23**,[20] obtained by selective hydrolysis of 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose **22** and subsequent cyclization of the 5,6-diol formed (Scheme 4). In order to introduce a sulfur functionality at C-5, the synthesis of the tosylated derivative **24** was attempted. However, the conversion was slow and compound **24** was obtained only in 34% yield after 40 h. Moreover, substitution of **24** with KSAc failed and no conversion was observable by TLC after 48 h at 40 °C. Increasing the temperature to 70 °C did not significantly improve the conversion, and at 90 °C decomposition was observed by TLC.

Instead, **23** was triflated and the crude triflate **25** was directly treated with KSAc to give the desired 5-*S*-acetyl derivative **26** in 47% yield. Deacetylation with NaOH in aq. methanol afforded **27** in 90% yield. Treatment of this with aq. TFA (60%) produced the thiohexopyran-3-ulose **28** in quantitative yield as an α/β anomeric mixture. Subsequent acetylation and in situ β-elimination with Ac_2O in pyridine gave the target thiosugar-derived enone **29** in a nearly quantitative yield. This is consistent with the observation reported by Lichtenthaler and co-workers that β-acylated hexopyranuloses are prone to undergo β-elimination.[21] In accordance with the NMR spectroscopic data reported for sugar enones, the resonance of the C-3 carbonyl C-atom in the ^{13}C NMR spectrum of **29** appeared at δ = 182.5 ppm, whereas in the ^1H NMR spectrum a long-range coupling between H-1 and H-5 (J = 1.5 Hz) was observed.[21b]

Conclusions

This contribution has demonstrated synthetic approaches for new classes of highly functionalized thiosugar derivatives containing α,β-unsaturated carbonyl moieties, such as lactones and ketones, through the use of easily available furan-3-uloses as starting materials. The methodologies include the introduction of sulfhydryl groups at C-5 on appropriate furanose intermediates, such as an unsaturated ester and a hemiacetal sugar, and take advantage of the furanose–pyranose equilibrium. The synthesised molecules are valuable intermediates for further chemical transformations, in particular for syntheses of miharamycin analogues. In addition these compounds are potential bioactive candidates, in view of the biological profiles of the structural units involved.

Experimental Section

General Methods: Melting points were determined with a Stuart Scientific SMP 3 apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 343 polarimeter at 20 °C. ^1H and ^{13}C NMR spectra were recorded with a BRUKER Avance 400

spectrometer operating at 400.13 MHz for ^1H or 100.62 MHz for ^{13}C. Chemical shifts are expressed in parts per million and are reported relative to internal TMS, in the case of $CDCl_3$, or relative to the respective solvent peak as reference. HRMS spectra were acquired with an Apex Ultra FTICR Mass Spectrometer fitted with an Apollo II Dual ESI/MALDI ion source, from Bruker Daltonics, and a 7T actively shielded magnet from Magnex Scientific.

All reactions were monitored by TLC on Merck 60 F_{254} silica gel aluminium plates with detection under UV light (254 nm) and/or by spraying with a solution of H_2SO_4 in EtOH (10%) or with a solution of 0.2% (w/v) cerium(IV) sulfate/5% ammonium molybdate in aq. H_2SO_4 (6%). Column chromatography was carried out on silica gel 60 G (0.040–0.063 mm, E. Merck).

1,2-*O*-Isopropylidene-5-*O*-tosyl-α-D-*erythro*-pentofuranos-3-ulose (2): Acetic anhydride (1.4 mL) and PDC (1.44 g, 3.83 mmol) were added under argon to a solution of 1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (1.68 g, 4.88 mmol)[17] in dry CH_2Cl_2 (24 mL). The resulting mixture was stirred under reflux for 2 h 30 min and was then allowed to cool to room temp. The solvent was removed in vacuo. EtOAc (15 mL) was added to the residue and the mixture was filtered through a short pad of Florisil. After evaporation of the solvent, the crude product was purified by column chromatography (EtOAc/petroleum ether, 1:1) to afford **2** as a colourless oil, along with its hydrate in a 1:0.3 ratio (1.29 g, 77%); R_f = 0.25 (EtOAc/petroleum ether, 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, ^3J = 8.1 Hz, 2 H, a-H, Ts), 7.37 (d, 2 H, b-H, Ts), 6.04 (d, $^3J_{1,2}$ = 4.3 Hz, 1 H, 1-H), 4.51 (t, 1 H, 4-H), 4.35 (d, 1 H, 2-H), 4.31 (dd, part A of ABX system, $^3J_{4,5a}$ = 2.5, $^2J_{5a,5b}$ = 11.1 Hz, 1 H, 5a-H), 4.19 (dd, part B of ABX system, $^3J_{4,5b}$ = 3.0 Hz, 1 H, 5b-H), 2.46 (s, 3 H, Me, Ts), 1.44 (s, 3 H, Me, *i*Pr), 1.40 (s, 3 H, Me, *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.7 (CO), 145.4 (Cq-a, Ts), 132.4 (Cq-b), 130.1 (CH-b, Ts), 127.9 (CH-a, Ts), 114.5 (Cq, *i*Pr), 103.2 (C-1), 76.8 (C-4), 76.0 (C-2), 68.1 (C-5), 27.4 (Me, *i*Pr), 27.0 (Me, *i*Pr), 21.6 (Me, Ts) ppm. HRMS: calcd. for $C_{15}H_{18}O_7S$ [M + Na]$^+$ 365.0665; found 365.0673. Hydrate, HRMS: calcd. for $C_{15}H_{20}O_8S$ [M + Na]$^+$ 383.0771; found 383.0779.

Ethyl (3*Z*)-(3-Deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-*erythro*-pentofuranos-3-ylidene)acetate (3a) and Ethyl (3*E*)-(3-Deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-*erythro*-pentofuranos-3-ylidene)acetate (3b): [(Ethoxycarbonyl)methylene]triphenylphosphorane (0.47 g, 1.35 mmol) was added to a solution of the 3-ulose **2** (0.35 g, 1.03 mmol) in dry $CHCl_3$ (8.3 mL). The mixture was stirred under reflux for 1 h. After evaporation of the solvent, the residue was purified by column chromatography (EtOAc/petroleum ether, 1:8 then 1:6) to afford the *Z* adduct **3a** (0.329 g, 77%) and its *E* isomer **3b** (0.074 g, 17%) as colourless oils.

Data for 3a: R_f = 0.21 (EtOAc/petroleum ether, 1:8). $[\alpha]_D^{20}$ = +147 (c = 1.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, ^3J = 8.1 Hz, 2 H, a-H, Ts), 7.36 (d, 2 H, b-H, Ts), 5.83 (t, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.8 Hz, 1 H, 3′-H), 5.79 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 5.67 (dt, $^4J_{2,3'}$ = $^4J_{2,4}$ = 1.8 Hz, 1 H, 2-H), 4.98–4.93 (m, 1 H, 4-H), 4.28–4.21 (m, ^3J = 7.1 Hz, 3 H, CH_2CH$_3$, 5a-H), 4.12 (dd, $^3J_{4,5b}$ = 3.5, $^2J_{5a,5b}$ = 11.1 Hz, 1 H, 5b-H), 2.46 (s, 3 H, Me, Ts), 1.45 (s, 3 H, Me, *i*Pr), 1.40 (s, 3 H, Me, *i*Pr), 1.32 (t, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5 (CO), 153.4 (C-3), 145.4 (Cq-a, Ts), 132.4 (Cq-b), 130.1 (CH-b, Ts), 128.1 (CH-a, Ts), 117.8 (C-3′), 113.3 (Cq, *i*Pr), 105.2 (C-1), 78.2 (C-2, C-4), 69.4 (C-5), 61.1 (*C*H$_2$CH$_3$), 27.5 (Me, *i*Pr), 27.2 (Me, *i*Pr), 21.8 (Me, Ts), 14.3 (CH$_2$*C*H$_3$) ppm. HRMS: calcd. for $C_{19}H_{24}O_8S$ [M + Na]$^+$ 435.1084; found 435.1082.

Data for 3b: R_f = 0.16 (EtOAc/petroleum ether, 1:6). $[\alpha]_D^{20}$ = +153 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, ^3J = 8.1 Hz, 2 H, a-H, Ts), 7.34 (d, 2 H, b-H, Ts), 6.09 (t, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.8 Hz, 1 H, 3′-H), 5.85 (d, $^3J_{1,2}$ = 4.6 Hz, 1 H, 1-H), 5.63–5.60 (m, 1 H, 4-H), 5.06 (dt, $^4J_{2,3'}$ = $^4J_{2,4}$ = 1.8 Hz, 1 H, 2-H), 4.46 (dd, $^3J_{4,5a}$ = 1.8, $^2J_{5a,5b}$ = 10.4 Hz, 1 H, 5a-H), 4.20–4.09 (m, ^3J = 7.1, $^3J_{4,5b}$ = 2.0 Hz, 3 H, CH_2CH$_3$, 5b-H) 2.45 (s, 3 H, Me, Ts), 1.41 (s, 3 H, Me, *i*Pr), 1.36 (s, 3 H, Me, *i*Pr), 1.28 (t, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3 (CO), 157.4 (C-3), 145.2 (Cq-a, Ts), 132.6 (Cq-b), 130.0 (CH-b, Ts), 128.0 (CH-a, Ts), 118.5 (C-3′), 113.6 (Cq, *i*Pr), 104.5 (C-1), 81.7 (C-2), 79.3 (C-4), 71.8 (C-5), 60.9 (*C*H$_2$CH$_3$), 27.9 (Me, *i*Pr), 27.8 (Me, *i*Pr), 21.8 (Me, Ts), 14.2 (CH$_2$*C*H$_3$) ppm. HRMS: calcd. for $C_{19}H_{24}O_8S$ [M + Na]$^+$ 435.1084; found 435.1094.

Ethyl (3*E*)-(5-*S*-Acetyl-3-deoxy-1,2-*O*-isopropylidene-5-thio-α-D-*erythro*-pentofuranos-3-ylidene)acetate (4): Potassium thioacetate (34 mg, 0.30 mmol) was added under argon to a solution of ethyl (3*Z*)-(3-deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-*erythro*-pentofuranos-3-ylidene)acetate (0.10 g, 0.25 mmol) in anhydrous DMF (2.5 mL). The whole solution was stirred at 40 °C for 1 h 45 min. Water was added (12 mL) and the organic phase was extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with water and dried with $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by column chromatography (EtOAc/petroleum ether, 1:11) to afford **4** (66 mg, 84%) as a colourless oil; R_f = 0.35 (EtOAc/petroleum ether, 1:4). $[\alpha]_D^{20}$ = +105 (c = 1.1, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.94 (t, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.5 Hz, 1 H, 3′-H), 5.88 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 5.72 (dt, $^4J_{2,3'}$ = $^4J_{2,4}$ = 1.5 Hz, 1 H, 2-H), 5.01–4.96 (m, 1 H, 4-H), 4.28–4.21 (m, ^3J = 7.1 Hz, 2 H, CH_2CH$_3$), 3.41 (dd, part A of ABX system, $^3J_{4,5a}$ = 3.8, $^2J_{5a,5b}$ = 14.1 Hz, 1 H, 5a-H), 3.09 (dd, part B of ABX system, $^3J_{4,5b}$ = 6.3 Hz, 1 H, 5b-H), 2.36 (s, 3 H, Me, SAc), 1.48 (s, 3 H, Me, *i*Pr), 1.41 (s, 3 H, Me, *i*Pr), 1.31 (t, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9 (CO, SAc), 164.9 (CO), 156.0 (C-3), 117.1 (C-3′), 112.9 (Cq, *i*Pr), 104.8 (C-1), 78.6 (C-4), 78.2 (C-2), 61.0 (*C*H$_2$CH$_3$), 32.1 (C-5), 30.6 (Me, SAc), 27.4 (Me, *i*Pr), 27.2 (Me, *i*Pr), 14.3 (CH$_2$*C*H$_3$) ppm. HRMS: calcd. for $C_{14}H_{20}O_6S$ [M + Na]$^+$ 339.0872; found 339.0867.

Ethyl (3,5-Anhydro-1,2-*O*-isopropylidene-5-thio-α-D-*erythro*-pentofuranos-3-*C*-yl)acetate (5) and Ethyl (5-*S*-Acetyl-3-deoxy-1,2-*O*-isopropylidene-5-thio-α-D-*glycero*-pent-3-enofuranos-3-*C*-yl)acetate (6): These compounds were obtained in an inseparable mixture also containing **4** (ratio 1:2:0.8, **4/5/6**, 38 mg starting from 49 mg of **3a**) after a procedure similar to that described previously for compound **4**, but with the reaction being carried out at 90 °C.

Data for 5: R_f = 0.52 (EtOAc/petroleum ether, 1:9). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.02 (d, $^3J_{1,2}$ = 3.0 Hz, 1-H), 5.06 (d, 2-H), 4.93 (br. t, 4-H), 4.28–4.18 (m, CH_2, Et), 3.40 (br. d, part A of AB system, $^2J_{5a,5b}$ = 12.6 Hz, 5a-H), 3.26 (d, part A of AB system, $^2J_{3a,3b}$ = 16.7 Hz, 3′a-H), 3.18 (br. d, part B of AB system, 5b-H), 2.80, 2.75 (d, part B of AB system, 3′b-H), 1.53 (Me, *i*Pr), 1.36 (Me, *i*Pr), 1.29 (t, CH_3, Et) ppm.

Data for 6: R_f = 0.45 (EtOAc/petroleum ether, 1:9). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.98 (d, $^3J_{1,2}$ = 5.3 Hz, 1-H), 5.33 (d, 2-H), 4.16 (qd, CH_2, Et), 3.71 (d, part A of AB system, $^2J_{5a,5b}$ = 14.4 Hz, 5a-H), 3.59 (d, part B of AB system, 5b-H), 3.37 (d, part A of AB system, $^2J_{3a,3b}$ = 16.7 Hz, 3′a-H), 3.18 (d, part B of AB system, 3′b-H), 2.34 (s, SAc), 1.44 (s, Me, *i*Pr), 1.36 (s, Me, *i*Pr), 1.31 (t, CH_3, Et) ppm.

3-Deoxy-2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)-5-thio-D-*erythro*-pentopyranose (7): Ethyl (3*E*)-(5-*S*-acetyl-3-deoxy-1,2-*O*-isopropylidene-5-thio-α-D-*erythro*-pentofuranos-3-ylidene)acetate (0.45 g,

1.43 mmol) was dissolved in MeOH/H_2O (20 mL, 1.5:1 v/v) and NaOH solution (10 M, 0.27 mL) was added. After the system had been stirred at rt for 15 min, Amberlite IR-120 H^+ was added until neutralization. The resin was then filtered off and the solvents were evaporated. The resulting residue was dissolved in aq. AcOH (70%, 18 mL) and the solution was stirred under reflux for 2 h. The solvent was coevaporated with toluene and the crude product was purified by column chromatography (EtOAc/petroleum ether, 2:3 then 3:2) to afford **7** (93 mg, 35%, two steps) as a colourless oil; R_f = 0.26 (EtOAc/petroleum ether, 3:2). $[\alpha]_D^{20}$ = +130 (*c* = 1.1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, α anomer): δ = 6.02 (t, $^4J_{3',4}$ = $^4J_{2,3'}$ = 1.5 Hz, 1 H, 3′-H), 5.26–5.22 (m, 2 H, 1-H, 2-H), 4.68 (ddd, $^3J_{4,5a}$ = 6.1, $^3J_{4,5b}$ = 10.9 Hz, 1 H, 4-H), 2.92 (dd, 5a-H, $^2J_{5a,5b}$ = 12.6 Hz, 1 H, part A of ABX system), 2.78 (dd, part B of ABX system, 1 H, 5b-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 174.8 (CO, lac), 171.9 (C-3), 115.5 (C-3′), 84.6 (C-2), 73.3 (C-1), 70.4 (C-4), 31.3 (C-5) ppm. HRMS: calcd. for $C_7H_8O_4S$ [M + Na]$^+$ 211.0036; found 211.0031.

1,4-Di-*O*-acetyl-3-deoxy-2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)-5-thio-D-*erythro*-pentopyranose (8) and 4-*O*-Acetyl-l,5-anhydro-3-deoxy-2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)-5-thio-D-*glycero*-pent-l-enitol (9): Acetic anhydride (0.35 mL) was added to a solution of 3-deoxy-2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)-5-thio-D-*erythro*-pentopyranose (7 mg, 37 μmol) in pyridine (0.7 mL), and the mixture was stirred at room temp. for 5 min. After coevaporation with toluene, the crude product was purified by column chromatography (EtOAc/petroleum ether, 2:3) to afford **8** (8 mg, 80%) as a colourless oil and traces of the corresponding glycal **9**.

Data for 8: R_f = 0.21 (EtOAc/petroleum ether, 2:3). $[\alpha]_D^{20}$ = +50 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.27 (d, $^3J_{1,2(\alpha)}$ = 3.8 Hz, 1α-H), 6.08 (t, 3′α-H), 6.07 (t, $^4J_{2,3'} \approx {}^4J_{3',4} \approx$ 1.8 Hz, 3′β-H), 5.78 (dddd, 4α-H), 5.69 (dddd, 4β-H), 5.60 (d, $^3J_{1,2(\alpha)}$ = 9.1 Hz, 1β-H), 5.23 (ddd, 2α-H), 5.13 (ddd, 2β-H), 3.13 (dd, $^3J_{4,5a(\beta)}$ = 5.3, $^2J_{5a,5b(\beta)}$ = 13.1 Hz, 5aβ-H), 3.01 (dd, part A of ABX system, $^3J_{4,5a(\alpha)}$ = 5.3, $^2J_{5a,5b(\alpha)}$ = 12.9 Hz, 5aα-H), 2.91 (dd, part B of ABX system, $^3J_{4,5b(\alpha)}$ = 10.9 Hz, 5bα-H), 2.73 (dd, $^3J_{4,5b(\beta)}$ = 10.9 Hz, 5bβ-H), 2.21 (s, Meα, Ac), 2.08 (s, Meα, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major anomer): δ = 170.4 (CO), 169.4, 168.6 (CO, Ac), 162.3 (C-3), 116.4 (C-3′), 80.0 (C-2), 70.7 (C-1), 69.3 (C-4), 28.9 (C-5), 20.9 (Me, Ac), 20.8 (Me, Ac) ppm. HRMS: calcd. for $C_{11}H_{12}O_6S$ [M + Na]$^+$ 295.0247; found 295.0254.

Data for 9: R_f = 0.53 (EtOAc/petroleum ether, 3:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (d, $^5J_{1,3'}$ = 1.5 Hz, 1 H, 1-H), 6.03 (t, $^5J_{1,3'}$ = $^4J_{3',4}$ = 1.5 Hz, 1 H, 3′-H), 5.97 (td, $J_{4,5a}$ = $J_{4,5b}$ = 7.3 Hz, 1 H, 4-H), 3.16 (br. d, 2 H, 5-CH_2), 2.19 (s, 3 H, Me, Ac) ppm. HRMS: calcd. for $C_9H_8O_4$ [M + H]$^+$ 213.0216; found 213.0223; calcd. for [M + Na]$^+$ 235.0036; found 235.0044.

Ethyl (3*Z*)-[(6-*O*-(*tert*-Butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ylidene]acetate (11): DMAP (16 mg, 0.13 mmol) and TBDMSCl (0.58 g, 3.85 mmol) were added at room temp. under argon to a solution of ethyl (3*Z*)-(3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ylidene)acetate[16a] (0.52 g, 1.8 mmol) in dry pyridine (2 mL). After stirring for 15 h, the reaction mixture was poured into water (12 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with water and brine and dried with anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by column chromatography (EtOAc/petroleum ether, 1:6) to afford **11** (0.632 g, 87%) as a colourless oil; R_f = 0.33 (EtOAc/cyclohexane, 1:5). $[\alpha]_D^{20}$ = +111 (*c* = 1.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.44 (br. s, 1 H, 3′-H), 5.82 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 5.72 (br. d, 1 H, 2-H), 4.66 (br. d, $^3J_{4,5}$ = 7.6 Hz, 1 H, 4-H), 4.21 (q, ^3J = 7.1 Hz, 2 H, CH_2CH$_3$), 3.79–3.69 (m, 6a-H, 6b-H), 3.65–3.57 (m, 1 H, 5-H), 2.74 (d, ^3J = 6.1 Hz, 1 H, 5-OH), 1.47 (s, 3 H, Me, *i*Pr), 1.39 (s, 3 H, Me, *i*Pr), 1.28 (t, 3 H, CH$_2$CH_3), 0.88 (s, 9 H, *t*Bu, TBDMS), 0.07 (2 × s, 6 H, Me, TBDMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5 (CO), 156.3 (C-3), 117.6 (C-3′), 112.8 (Cq, *i*Pr), 104.9 (C-1), 78.9 (C-4), 78.4 (C-2), 73.2 (C-5), 63.8 (C-6), 60.7 (*C*H$_2$CH$_3$), 27.4 (Me, *i*Pr), 27.3 (Me, *i*Pr), 25.9 (3 × Me, *t*Bu), 18.4 (Cq, *t*Bu), 14.3 (CH$_2$*C*H$_3$), –5.3 (Me, TBDMS), –5.3 (Me, TBDMS) ppm. HRMS: calcd. for $C_{19}H_{34}O_7Si$ [M + Na]$^+$ 425.1966; found 425.1981.

Ethyl (3*Z*)-[6-*O*-(*tert*-Butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-5-*O*-mesyl-α-D-*ribo*-hexofuranos-3-ylidene]acetate (12): Methanesulfonyl chloride (0.03 mL, 0.43 mmol) was added under argon at 0 °C to a solution of ethyl (3*Z*)-[6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ylidene]-acetate (0.116 g, 0.29 mmol) in dry pyridine (2.9 mL). The ice bath was removed and the solution was kept stirring at room temp. for 40 min. Water (12 mL) was added to the solution, and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with water and dried with anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by column chromatography (EtOAc/petroleum ether, 1:3) to afford **12** (0.131 g, 95%) as a colourless oil; R_f = 0.47 (EtOAc/petroleum ether, 1.5:3.5). $[\alpha]_D^{20}$ = +91 (*c* = 1.1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.07 (t, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.8 Hz, 1 H, 3′-H), 5.89 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 5.69 (dt, $^4J_{2,3'}$ = $^4J_{2,4}$ = 1.8 Hz, 1 H, 2-H), 5.15 (ddd, 1 H, 4-H), 4.71 (ddd, 1 H, 5-H), 4.23 (qd, ^3J = 7.1 Hz, 2 H, CH_2CH$_3$), 3.89 (dd, part A of ABX system, $^3J_{5,6a}$ = 6.6, $^2J_{6a,6b}$ = 11.4 Hz, 1 H, 6a-H), 3.80 (dd, part B of ABX system, $^3J_{5,6b}$ = 5.8 Hz, 1 H, 6b-H), 3.08 (s, 3 H, Me, Ms), 2.26 (br. s, 1 H, OH-6), 1.45 (s, 3 H, Me, *i*Pr), 1.41 (s, 3 H, Me, *i*Pr), 1.30 (t, 3 H, CH$_2$CH_3), 0.87 (s, 9 H, *t*Bu, TBDMS), 0.07 (s, 3 H, Me, TBDMS), 0.06 (s, 3 H, Me, TBDMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6 (CO), 153.7 (C-3), 118.6 (C-3′), 113.4 (Cq, *i*Pr), 105.6 (C-1), 82.7 (C-5), 79.8 (C-4), 78.8 (C-2), 61.4 (C-6), 60.9 (*C*H$_2$CH$_3$), 38.8 (Me, Ms), 27.6 (Me, *i*Pr), 27.4 (Me, *i*Pr), 25.9 (3 × Me, *t*Bu), 18.4 (Cq, *t*Bu), 14.2 (CH$_2$*C*H$_3$), 5.3 (Me, TBDMS), –5.4 (Me, TBDMS) ppm. HRMS: calcd. for $C_{20}H_{36}O_9SSi$ [M + Na]$^+$ 503.1742; found 503.1760.

Ethyl [3,5-Anhydro-6-*O*-(*tert*-butyldimethylsilyl)-1,2-*O*-isopropylidene-5-thio-β-L-*ido*-hexofuranos-3-*C*-yl]acetate (13) and Ethyl [5-*S*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-5-thio-β-L-*threo*-hex-3-enofuranos-3-*C*-yl]acetate (14): Potassium thioacetate (36 mg, 0.31 mmol) was added under argon to a solution of ethyl (3*Z*)-[6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-5-*O*-mesyl-α-D-*ribo*-hexofuranos-3-ylidene]acetate (0.125 g, 0.26 mmol) in anhydrous DMF (2.7 mL). The whole solution was stirred at 90 °C for 24 h. Water was added (12 mL) and the organic phase was extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with water and dried with $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by column chromatography (EtOAc/cyclohexane, 1:16) to afford **13** (12 mg, 15%) as a colourless oil, **14** (23 mg, 19%) and **15** (29 mg, 24%). Separation of **14** from **15** by chromatography was not possible.

Data for 13: R_f = 0.47 (EtOAc/cyclohexane, 1:6). $[\alpha]_D^{20}$ = +14 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.03 (d, $^3J_{1,2}$ = 3.0 Hz, 1 H, 1-H), 5.04 (d, 1 H, 2-H), 4.73 (dd, $^3J_{4,5}$ = 1.3 Hz, 1 H, 4-H), 4.56 (dd, $^3J_{5,6a}$ = 9.9, $^2J_{6a,6b}$ = 13.6 Hz, 1 H, 6a-H), 4.25–4.15 (m, ^3J = 7.1 Hz, 2 H, CH_2CH$_3$), 3.86–3.78 (m, 2 H, 5-H, 6b-H), 3.25 (d, part A of AB system, $^2J_{3'a,3'b}$ = 16.9 Hz, 1 H, 3′a-H), 2.78 (d, part B of AB system, 1 H, 3′b-H), 1.51 (s, 3 H, Me, *i*Pr),

1.35 (s, 3 H, Me, *i*Pr), 1.29 (t, 3 H, CH_2CH_3), 0.89 (s, 9 H, *t*Bu, TBDMS), 0.07 (br. s, 6 H, Me, TBDMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.3 (Cq, *i*Pr), 106.7 (C-1), 89.9 (C-4), 86.5 (C-2), 64.0 (C-5), 61.4, 61.3 (C-6, CH_2CH_3), 27.7 (Me, *i*Pr), 27.2 (Me, *i*Pr), 26.0 (3 × Me, *t*Bu), 18.4 (Cq, *t*Bu), 14.3 (CH_2CH_3), –5.4 (2 × Me, TBDMS) ppm. HRMS: calcd. for $C_{19}H_{34}O_6SSi$ [M + Na]$^+$ 441.1738; found 441.1756.

Data for 14: R_f = 0.37 (EtOAc/cyclohexane, 1:6). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.96 (d, $^3J_{1,2}$ = 5.3 Hz, 1 H, 1-H), 5.40 (d, 1 H, 2-H), 4.48 (dd, $^3J_{5,6a}$ = 7.8, $^3J_{5,6b}$ = 6.8 Hz, 1 H, 5-H), 4.17–4.10 (m, ^3J = 7.1 Hz, 2 H, CH_2CH_3), 3.83 (t, $^2J_{6a,6b}$ = 10.1 Hz, 1 H, 6a-H), 3.68 (dd, 1 H, 6b-H), 3.41 (d, part A of AB system, $^2J_{3'a,3'b}$ = 16.9 Hz, 1 H, 3′a-H), 3.14 (d, part B of AB system, 1 H, 3′b-H), 2.32 (s, 3 H, Me, SAc), 1.44 (s, 3 H, Me, *i*Pr), 1.35 (s, 3 H, Me, *i*Pr), 1.27 (t, 3 H, CH_2CH_3), 0.85 (s, 9 H, *t*Bu, TBDMS), 0.04 (s, 3 H, Me, TBDMS), 0.03 (s, 3 H, Me, TBDMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.3 (CO, SAc), 170.8 (CO), 152.2 (C-4), 112.3 (Cq, *i*Pr), 106.6 (C-3), 104.5 (C-1), 85.3 (C-2), 62.7 (C-6), 60.9 (CH_2CH_3), 41.0 (C-5), 30.6 (Me, SAc), 29.9 (C-3′), 28.1 (2 × Me, *i*Pr), 25.9 (3 × Me, *t*Bu), 18.4 (Cq, *t*Bu), 14.3 (CH_2CH_3), –5.3 (Me, TBDMS), –5.4 (Me, TBDMS) ppm. HRMS: calcd. for $C_{21}H_{36}O_7SSi$ [M + Na]+ 483.1843; found 483.1875.

Ethyl (3*E*)-[5-*S*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-5-thio-β-L-*lyxo*-hexofuranos-3-ylidene]acetate (15) and Ethyl (3*E*)-[6-*O*-(*tert*-Butyldimethylsilyl)-3-deoxy-5-*O*-formyl-1,2-*O*-isopropylidene-β-L-*lyxo*-hexofuranos-3-ylidene]acetate (17): A solution of ethyl (3*Z*)-[6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ylidene]acetate (0.241 g, 0.6 mmol) and dry pyridine (0.1 mL, 1.2 mmol) in dry dichloromethane (3 mL) was cooled to –11 °C (MeOH/ice bath) under argon. Trifluoromethanesulfonic anhydride (0.11 mL, 0.66 mmol) was added dropwise and the reaction mixture was stirred for 15 min, whilst the temperature was kept below –5 °C. The solution was diluted with EtOAc (10 mL) and sequentially washed with a satd. $NaHCO_3$ solution (5 mL) and aq. HCl solution (2 M, 5 mL). The aqueous layer was extracted twice with EtOAc and the combined organic phases were dried with anhydrous $MgSO_4$. After filtration and concentration to dryness, the crude triflate **16** was used immediately for the next step without further purification; R_f = 0.53 (EtOAc/cyclohexane, 1:5).

Potassium thioacetate (75 mg, 0.66 mmol) was added to the crude triflate **16** in DMF (6 mL). The solution was stirred at room temp. for 40 min. Water (12 mL) was then added to the solution and it was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with water and brine and dried with anhydrous $MgSO_4$. After filtration and evaporation under vacuum, the residue was purified by column chromatography (EtOAc/petroleum ether, 1:14) to afford **15** (70 mg, 25%) and **17** (15 mg, 6%) as colourless oils.

Data for 15: R_f = 0.41 (EtOAc/petroleum ether, 1:5). $[\alpha]_D^{20}$ = +67 (*c* = 1.2, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.86 (d, $^3J_{1,2}$ = 4.3 Hz, 1 H, 1-H), 5.83 (t, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.8 Hz, 1 H, 3′-H), 5.70 (dt, 1 H, 2-H), 5.42–5.39 (m, 1 H, 4-H), 4.28–4.15 (m, ^3J = 7.1 Hz, 2 H, CH_2CH_3), 3.87 (ddd, 1 H, 5-H), 3.78 (t, $^3J_{5,6a}$ = $^2J_{6a,6b}$ = 9.6 Hz, 1 H, 6a-H), 3.67 (dd, $^3J_{5,6b}$ = 5.6 Hz, 1 H, 6b-H), 2.31 (s, 3 H, Me, SAc), 1.47 (s, 3 H, Me, *i*Pr), 1.42 (s, 3 H, Me, *i*Pr), 1.30 (t, 3 H, CH_2CH_3), 0.89 (s, 9 H, *t*Bu, TBDMS), 0.09 (s, 3 H, Me, TBDMS), 0.08 (s, 3 H, Me, TBDMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9 (CO, SAc), 165.1 (CO), 156.3 (C-3), 116.3 (C-3′), 113.0 (Cq, *i*Pr), 105.4 (C-1), 78.5, 78.2 (C-4, C-2), 63.0 (C-6), 60.9 (CH_2CH_3), 48.9 (C-5), 30.8 (Me, SAc), 27.5 (2 × Me, *i*Pr), 25.9 (3 × Me, *t*Bu), 18.4 (Cq, *t*Bu), 14.3 (CH_2CH_3), –5.2 (Me, TBDMS), –5.3 (Me, TBDMS) ppm. HRMS: calcd. for $C_{21}H_{36}O_7SSi$ [M + Na]$^+$ 483.1843; found 483.1856.

Data for 17: R_f = 0.28 (EtOAc/petroleum ether, 1:5). $[\alpha]_D^{20}$ = +88 (*c* = 1.1, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1 H, OC*H*O), 5.95–5.91 (m, $^3J_{1,2}$ = 4.3, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.5 Hz, 2 H, 1-H, 3′-H), 5.69 (dt, $^4J_{2,3'}$ = $^4J_{2,4}$ = 1.5 Hz, 1 H, 2-H), 5.21 (td, $^3J_{5,6a}$ = $^3J_{5,6b}$ = 6.8 Hz, 1 H, 5-H), 5.14–5.12 (m, 1 H, 4-H), 4.28–4.18 (m, ^3J = 7.1 Hz, 2 H, CH_2CH_3), 3.87–3.77 (m, $^2J_{6a,6b}$ = 10.1 Hz, 1 H, 6a-H, 6b-H), 1.48 (s, 3 H, Me, *i*Pr), 1.44 (s, 3 H, Me, *i*Pr), 1.30 (t, 3 H, CH_2CH_3), 0.88 (s, 9 H, *t*Bu, TBDMS), 0.08 (s, 3 H, Me, TBDMS), 0.08 (s, 3 H, Me, TBDMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8 (CO, O*C*HO), 160.1 (CO), 154.7 (C-3), 117.4 (C-3′), 113.4 (Cq, *i*Pr), 105.6 (C-1), 78.6, 78.5 (C-4, C-2), 73.6 (C-5), 61.1, 61.0 (CH_2CH_3, C-6), 30.8 (Me, SAc), 27.7 (Me, *i*Pr), 27.4 (Me, *i*Pr), 25.9 (3 × Me, *t*Bu), 18.3 (Cq, *t*Bu), 14.2 (CH_2CH_3), –5.3 (Me, TBDMS), –5.3 (Me, TBDMS) ppm. HRMS: calcd. for $C_{17}H_{30}O_6SSi$ [M + Na]$^+$ 413.1915; found 453.1915; calcd. for [M + K]$^+$ 469.1655; found 469.1656.

(3*E*)-[6-*O*-(*tert*-Butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-5-sulfanyl-β-L-*lyxo*-hexofuranos-3-ylidene]acetic Acid (18): Ethyl (3*E*)-[5-*S*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-5-thio-β-L-*lyxo*-hexofuranos-3-ylidene]acetate (41 mg, 0.09 mmol) was dissolved in MeOH/H_2O (2:1, 1.3 mL), and NaOH solution (10 M, 0.04 mL) was added. The solution was stirred at room temp. for 1 h, and then neutralized with Amberlite IR-120 H^+. After filtration of the resin and evaporation of the solvent, the residue was purified by column chromatography (EtOAc/petroleum ether, 1:1) to afford **18** (23 mg, 66%) as a colourless oil; R_f = 0.4 (EtOAc/petroleum ether, 1:1). ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ = 6.00 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 5.97 (t, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.5 Hz, 1 H, 3′-H), 5.72 (dt, $^4J_{2,3'}$ = $^4J_{2,4}$ = 1.5 Hz, 1 H, 2-H), 5.39–5.35 (m, 1 H, 4-H), 3.81 (dd, $^3J_{5,6a}$ = 5.6, $^2J_{6a,6b}$ = 9.9 Hz, 1 H, 6a-H), 3.71 (t, $^3J_{5,6b}$ = $^2J_{6a,6b}$ = 9.9 Hz, 1 H, 6b-H), 3.21 (tdd, 1 H, 5-H), 1.71 (d, $^3J_{SH,H-5}$ = 10.1 Hz, 1 H, SH), 1.40 (s, 3 H, Me, *i*Pr), 1.34 (s, 3 H, Me, *i*Pr), 0.92 (s, 9 H, *t*Bu, TBDMS), 0.12 (s, 3 H, Me, TBDMS), 0.12 (s, 3 H, Me, TBDMS) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = 166.1 (*C*OOH), 158.4 (C-3), 117.4 (C-3′), 112.9 (Cq, *i*Pr), 106.7 (C-1), 79.6, 79.5 (C-2, C-4), 66.5 (C-6), 46.0 (C-5), 27.7 (Me, *i*Pr), 27.6 (Me, *i*Pr), 26.2 (3 × Me, *t*Bu), 18.8 (Cq, *t*Bu), 14.3 (CH_2CH_3), –5.2 (Me, TBDMS), –5.3 (Me, TBDMS) ppm. HRMS: calcd. for $C_{17}H_{30}O_6SSi$ [M + Na]$^+$ 413.1425; found 413.1435; calcd. for [M + K]$^+$ 429.1164; found 429.1171.

3-Deoxy-[2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)]-5-thio-L-*lyxo*-hexopyranose (19): A solution of (3*E*)-[6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-1,2-*O*-isopropylidene-5-sulfanyl-β-L-*lyxo*-hexofuranos-3-ylidene]acetic acid (18 mg, 46 μmol) in aq. TFA (60%, 1 mL) was stirred at 40 °C for 20 min. The solvent was coevaporated with toluene and the crude product was purified by column chromatography (EtOAc) to afford **19** (10 mg, quantitative) as a colourless oil; R_f = 0.41 (EtOAc). ^1H NMR (400 MHz, $(CD_3)_2CO$): δ = 6.02 (br. d, *J* = 1.5 Hz, 3′β-H), 6.00 (t, $^4J_{2,3'}$ = $^4J_{3',4}$ = 1.8 Hz, 3′α-H), 5.22–5.16 (m, 2α-H, 1α-H, 1β-H), 5.10–5.05 (m, 4α-H, 4β-H), 4.98 (dd, $^3J_{1,2(\beta)}$ = 8.6 Hz, 2β-H), 4.31 (dd, $^3J_{5,6a}$ = 3.5, $^2J_{6a,6b}$ = 11.6 Hz, 6a-H), 3.90 (d, $^3J_{5,CH_2\text{-}6}$ = 5.8 Hz, 6-CH_2), 3.72 (dd, $^3J_{5,6b}$ = 4.3 Hz, 6b-H), 3.40 (ddd, 1 H, 5-H), 3.20 (q, $^3J_{5,6\text{-}CH_2}$ = $^3J_{4,5}$ = 5.8 Hz, 5-H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = 172.3 (CO, lac), 170.7 (C-3), 116.1 (C-3′), 115.8 (C-3′), 86.3 (C-2β), 83.0, 76.6, 73.0 (C-2α, C-1α, C-1β), 71.6, 70.2 (C-4α, C-4β), 62.7, 62.1 (C-6α, C-6β), 50.3, 49.2 (C-5α, C-5β) ppm. HRMS: calcd. for $C_8H_{10}O_5S$ [M + Na]$^+$ 241.0141; found 241.0147; calcd. for [M + K]$^+$ 256.9881; found 256.9888.

1,4,6-Tri-*O*-acetyl-3-deoxy-[2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)]-5-thio-L-*lyxo*-hexopyranose (20) and 4,6-Di-*O*-acetyl-l,5-anhydro-3-de-

oxy-[2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)]-5-thio-L-*threo*-hex-l-enitol (21): Acetic anhydride (0.35 mL) was added to a solution of 3-deoxy-[2-*O*,3-*C*-(1-oxoethan-1-yl-2-ylidene)]-5-thio-L-*lyxo*-hexopyranose (8 mg, 37 μmol) in pyridine (0.7 mL), and the mixture was stirred at room temp. for 5 min. After coevaporation with toluene, the crude product was purified by column chromatography (EtOAc/petroleum ether, 1:4) to afford the thioglycal-fused butenolide **21** (8.5 mg, 82%) as a colourless oil, together with traces of the triacetate derivative **20** (α/β ratio 1:1).

Data for 21: R_f = 0.15 (EtOAc/petroleum ether, 1:4). $[\alpha]_D^{20}$ = +8 (*c* = 0.7, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.35 (d, $^5J_{1,3'}$ = 1.5 Hz, 1 H, 1-H), 6.16 (dd, $^4J_{3',4}$ = 1.3, $^3J_{4,5}$ = 4.0 Hz, 1 H, 4-H), 6.10 (t, 1 H, 3′-H), 4.40 (dd, $^3J_{5,6a}$ = 5.3, $^2J_{6a,6b}$ = 11.6 Hz, 1 H, 6a-H), 4.25 (dd, $^3J_{5,6a}$ = 7.8 Hz, 1 H, 6b-H), 3.67 (ddd, 1 H, 5-H), 2.20 (s, 3 H, Me, Ac), 2.09 (s, 3 H, Me, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5 (CO), 123.4 (C-2), 114.3 (C-3′), 106.2 (C-1), 66.6 (C-4), 60.7 (C-6), 43.6 (C-5), 20.8 (CH_3, Me, Ac) ppm. HRMS: calcd. for $C_{12}H_{12}O_6S$ [M + H]$^+$ 285.0427; found 285.0434; calcd. for [M + Na]$^+$ 307.0247; found 307.0254.

Data for 20: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.27 (d, $^3J_{1,2(\alpha)}$ = 4.5 Hz, 1α-H), 6.22 (br. s, 3′α-H), 6.11–6.07 (m, 1β-H, 3′β-H), 6.04 (br. dd, $^3J_{4,5(\alpha)}$ = 6.1 Hz, 4α-H), 5.97 (br. dd, $^3J_{4,5(\beta)}$ = 6.6 Hz, 4β-H), 5.60 (d, $3J_{1,2(\alpha)}$ = 9.1 Hz, 1β-H), 5.24 (br. d, 2α-H), 5.17 (ddd, $^3J_{1,2(\beta)}$ = 8.6 Hz, 2β-H), 4.48–4.19 (m, 6aα-H, 6bα-H, 6aβ-H, 6bβ-H), 3.72 (ddd, 5α-H), 3.58 (ddd, 5β-H), 2.22, 2.21, 2.17, 2.12, 2.07, 2.06 (3 × Me, Ac, α, 3 × Me, Ac, β) ppm. HRMS: calcd. for $C_{14}H_{16}O_8S$ [M + Na]$^+$ 367.0458; found 367.0467.

(3*R*)-1,2-*O*-Isopropylidene-α-D-*ribo*-hexos-3-ulo-1,4:3,6-difuranose (23): A protocol similar to that described in ref.[20] was used with slight modifications. A solution of 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranosid-3-ulose (1.61 g, 6.23 mmol) in aq. AcOH (60%, 18 mL) was stirred at room temp. overnight. The solvent was coevaporated with toluene (3×) and the residue was purified by column chromatography (EtOAc) to afford **23** (1.25 g, 92%). Physical data were in agreement with those reported. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.97 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.56–4.47 (m, 1 H, 5-H), 4.46–4-42 (m, 2 H, 2-H, 3-OH), 4.31–4.22 (m, $^3J_{5,6a}$ = 6.3, $^2J_{6a,6b}$ = 9.3 Hz, 2 H, 4-H, 6a-H), 3.78 (dd, $^3J_{5,6b}$ = 5.6 Hz, 1 H, 6b-H), 2.87 (d, $^3J_{5,OH}$ = 6.1 Hz, 1 H, 5-OH), 1.59 (s, 3 H, Me, *i*Pr), 1.41 (s, 3 H, Me, *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.1 (Cq, *i*Pr), 111.0 (C-3), 107.1 (C-1), 84.2 (C-2), 82.9 (C-4), 73.9 (C-6), 71.2 (C-5), 27.3 (Me, *i*Pr), 27.3 (Me, *i*Pr) ppm.

(3*R*)-1,2-*O*-Isopropylidene-5-*O*-tosyl-α-D-*ribo*-hexos-3-ulo-1,4:3,6-difuranose (24): *p*-Toluenesulfonyl chloride (0.107 g, 0.56 mmol) was added under argon to a solution of (3*R*)-1,2-*O*-isopropylidene-α-D-*ribo*-hexos-3-ulo-1,4:3,6-difuranose (0.111 g, 0.51 mmol) in dry pyridine (2 mL). The solution was kept stirring at room temp. for 40 h. Water (12 mL) was added to the solution, and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with water and dried with anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by column chromatography (EtOAc/petroleum ether, 3:7) to afford **24** (65 mg, 34%) as a colourless oil; R_f = 0.35 (EtOAc/petroleum ether, 3:7). $[\alpha]_D^{20}$ = +39 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, ^3J = 8.3 Hz, 2 H, a-H, Ts), 7.36 (d, 2 H, b-H, Ts), 5.93 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 5.03 (ddd, 1 H, 5-H), 4.36 (d, 1 H, 2-H), 4.33 (d, $^3J_{4,5}$ = 4.3 Hz, 1 H, 4-H), 4.25 (dd, $^3J_{5,6a}$ = 7.1, $^2J_{6a,6b}$ = 9.3 Hz, 1 H, 6a-H), 3.94 (dd, $^3J_{5,6b}$ = 7.1 Hz, 1 H, 6b-H), 2.46 (s, 3 H, Me, Ts), 1.51 (s, 3 H, Me, *i*Pr), 1.37 (s, 3 H, Me, *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5 (Cq-a, Tos), 132.8 (Cq-b), 130.1 (CH-b, Tos), 128.2 (CH-a, Ts), 114.1 (Cq, *i*Pr), 110.8 (C-3), 107.1 (C-1), 82.6, 82.4 (C-2, C-4), 77.0 (C-5), 70.0 (C-6), 27.3 (Me, *i*Pr), 27.2 (Me, *i*Pr), 21.8 (Me, Ts) ppm. HRMS: calcd. for $C_{16}H_{20}O_8S$ [M + Na]$^+$ 395.0771; found 395.0785.

(3*R*)-5-*S*-Acetyl-1,2-*O*-isopropylidene-5-thio-β-L-*lyxo*-hexos-3-ulo-1,4:3,6-difuranose (26): A solution of (3*R*)-1,2-*O*-isopropylidene-α-D-*ribo*-hexos-3-ulo-1,4:3,6-difuranose (0.347 g, 1.59 mmol) and dry pyridine (0.29 mL, 3.6 mmol) in dry dichloromethane (8 mL) was cooled to –11 °C (MeOH/ice bath) under argon. Trifluoromethanesulfonic anhydride (0.29 mL, 1.75 mmol) was added dropwise and the reaction mixture was stirred whilst the temperature was kept below –5 °C. After 10 min, TLC showed total consumption of **23**, and EtOAc (25 mL) was added. The solution was then washed with a sat. $NaHCO_3$ solution (12 mL) and aq. HCl solution (2 M, 12 mL). The aqueous layer was extracted twice with EtOAc and the combined organic phases were dried with anhydrous $MgSO_4$. After filtration and concentration to dryness, the crude triflate **25** was used immediately for the next step without further purification; R_f = 0.76 (EtOAc/petroleum ether, 2:3) [R_f (**23**) = 0.15 (EtOAc/petroleum ether, 2:3)].

Potassium thioacetate (0.2 g, 1.75 mmol) was added to the crude triflate **25** in DMF (15 mL). The solution was stirred at room temp. for 1 h 15 min. Water (30 mL) was then added to the solution, and it was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with water and brine and dried with anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by column chromatography (EtOAc/cyclohexane, 1:5) to afford **26** (0.205 g, 47%) as a white solid; R_f = 0.35 (EtOAc/petroleum ether, 1.5:3.5). m.p. 68.8–69.9 °C. $[\alpha]_D^{20}$ = +36 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91 (d, $^3J_{1,2}$ = 4.3 Hz, 1 H, 1-H), 4.57–4.49 (m, 1 H, 6a-H), 4.42 (d, 1 H, 2-H), 4.41 (s, 1 H, 4-H), 4.12–4.05 (m, 2 H, 5-H, 6b-H), 3.75 (s, 1 H, OH), 2.37 (s, 3 H, Me, SAc), 1.57 (s, 3 H, Me, *i*Pr), 1.38 (s, 3 H, Me, *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6 (CO, SAc), 117.1 (C-3′), 113.5 (Cq, *i*Pr), 111.8 (C-3), 106.2 (C-1), 88.8 (C-4), 81.3 (C-2), 75.2 (C-6), 44.8 (C-5), 30.6 (Me, SAc), 27.3 (Me, *i*Pr), 27.3 (Me, *i*Pr) ppm. HRMS: calcd. for $C_{11}H_{16}O_6S$ [M + Na]$^+$ 299.0560; found 299.0567; calcd. for [M + K]$^+$ 315.0299; found 315.0310.

(3*R*)-1,2-*O*-Isopropylidene-5-sulfanyl-β-L-*lyxo*-hexos-3-ulo-1,4:3,6-difuranose (27): (3*R*)-5-*S*-Acetyl-1,2-*O*-isopropylidene-5-thio-β-L-*lyxo*-hexos-3-ulo-1,4:3,6-difuranose (50 mg, 0.18 mmol) was dissolved in MeOH/H_2O (2:1, 2.6 mL), and NaOH solution (10 M, 0.02 mL) was added. After the system had been stirred at room temp. for 5 min, TLC showed total conversion of **27**. The solution was then neutralized with Amberlite IR-120 H^+, the resin was filtered off, and the solvent was evaporated. The residue was purified by column chromatography (EtOAc/cyclohexane, 1:5) to afford **27** (37.5 mg, 90%) as a white solid; R_f = 0.5 (EtOAc/petroleum ether, 1.5:3.5). m.p. 64.4–66.3 °C. $[\alpha]_D^{20}$ = +22 (*c* = 1.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 4.49 (s, 1 H, 4-H), 4.48–4-40 (m, $^3J_{5,6a}$ = 6.3, $^2J_{6a,6b}$ = 9.3 Hz, 2 H, 2-H, 6a-H), 4.15 (dd, $^3J_{5,6b}$ = 3.0 Hz, 1 H, 6b-H), 3.83 (s, 1 H, 3-OH), 3.39 (ddd, 1 H, 5-H), 2.24 (d, $^3J_{SH,5}$ = 9.6 Hz, 1 H, SH), 1.59 (s, 3 H, Me, *i*Pr), 1.39 (s, 3 H, Me, *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.5 (Cq, *i*Pr), 112.1 (C-3), 105.8 (C-1), 91.0 (C-2), 81.8 (C-4), 77.8 (C-6), 40.4 (C-5), 27.3 (Me, *i*Pr), 27.3 (Me, *i*Pr) ppm. HRMS: calcd. for $C_9H_{14}O_5S$ [M + Na]$^+$ 257.0454; found 257.0456.

5-Thio-L-*lyxo*-hexopyranos-3-ulose (28): A solution of (3*R*)-1,2-*O*-isopropylidene-5-sulfanyl-β-L-*lyxo*-hexos-3-ulo-1,4:3,6-difuranose (22 mg, 94 μmol) in aq. TFA (60%, 1 mL) was stirred at 40 °C for 20 min. The solvent was coevaporated with toluene and the crude product was purified by column chromatography (EtOAc) to afford **28** (18 mg, quantitative) as a colourless oil; R_f = 0.22 (EtOAc).

$[\alpha]_D^{20}$ = +23 (*c* = 1.2, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ = 5.31 (d, $^3J_{1,2(\beta)}$ = 8.6 Hz, 1β-H), 5.14 (d, $^3J_{1,2(\alpha)}$ = 4.0 Hz, 1α-H), 4.79 (dd, $^4J_{2,4(\alpha)}$ = 1.0, $^3J_{4,5(\alpha)}$ = 6.8 Hz, 4α-H), 4.68–4.63 (m, 2α-H, 4β-H), 4.31 (dd, $^4J_{2,4(\beta)}$ = 1.0 Hz, 2β-H), 4.16 (dd, $^3J_{5,6a(\alpha)}$ = 4.0, $^2J_{6a,6b(\alpha)}$ = 11.1 Hz, 6aα-H), 4.01 (dd, $^3J_{5,6a(\beta)}$ = 4.0, $^2J_{6a,6b(\beta)}$ = 11.1 Hz, 6aβ-H), 3.72 (dd, $^3J_{5,6b(\beta)}$ = 2.8 Hz, 6bβ-H), 3.62 (dd, $^3J_{5,6b(\alpha)}$ = 2.8 Hz, 6bα-H), 3.52 (ddd, 5α-H), 3.11 (ddd, 5β-H) ppm. ^{13}C NMR (100 MHz, CD_3OD, major anomer): δ = 207.7 (CO), 79.5 (C-2α), 79.3 (C-1α), 76.5 (C-4α), 62.2 (C-6α), 52.4 (C-5α) ppm. HRMS: calcd. for $C_8H_{10}O_5S$ [M + Na]$^+$ 217.0141; found 217.0143; calcd. for [M + K]$^+$ 232.9881; found 232.9883.

2,4,6-Tri-*O*-acetyl-l,5-anhydro-5-thio-L-*threo*-hex-l-enopyran-3-ulose (29): Acetic anhydride (0.35 mL) was added to a solution of 5-thio-L-*lyxo*-hexopyranos-3-ulose (11 mg, 57 μmol) in pyridine (0.7 mL), and the mixture was stirred at room temp. for 5 min. After coevaporation with toluene, the crude product was purified by column chromatography (EtOAc/petroleum ether, 2:3) to afford **29** (16 mg, 94%) as a colourless oil; R_f = 0.52 (EtOAc/petroleum ether, 2:3). $[\alpha]_D^{20}$ = –6 (*c* = 0.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, $^6J_{1,5}$ = 1.5 Hz, 1 H, 1-H), 5.97 (d, $^3J_{4,5}$ = 5.1 Hz, 1 H, 4-H), 4.50–4.45 (m, 2 H, 6a-H, 6b-H), 3.66 (dddd, 1 H, 5-H), 2.22 (s, 3 H, Me, 2-Ac), 2.21 (s, 3 H, Me, 4-Ac), 2.08 (s, 3 H, Me, 6-Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.5 (CO), 170.6, 169.3, 168.6 (3 × CO, Ac), 138.6 (C-2), 130.6 (C-1), 73.0 (C-4), 60.8 (C-6), 43.6 (C-5), 20.8, 20.6, 20.3 (3 × Me, Ac) ppm. HRMS: calcd. for $C_{12}H_{14}O_7S$ [M + Na]$^+$ 325.0352; found 325.0346.

Acknowledgments

The authors thank Fundação para a Ciência e a Tecnologia (FCT) for financial support of the project POCI-PPCDT/QUI/59672/2004, PhD grants SFRH/BD/39251/2007 and SFRH/BD/27614/2006 and network REDE/1501/REM/2005. Dr. K.-H. Hellwich and Dr. G. Moss are gratefully acknowledged for their suggestions for the IUPAC names of some compounds.

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Received: May 25, 2009
Published Online: September 1, 2009

