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The Synthesis of Various 1,6-Disulfide-Bridged D-Hexopyranoses*

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1,6-Disulfide-bridged derivatives have been prepared for D-*gluco*-, D-*manno*-, D-*allo*-, D-*galacto*-, and D-*talo*-pyranose, in the main by the nucleophilic attack of a C6 thiolate onto an anomeric thiosulfonate. The D-*gluco* disulfide, 'angyalosan', was successfully oxidized to a single thiosulfinate.

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Introduction

Two of the great carbohydrate chemists of the twentieth century, both now retired, live in the Southern Hemisphere, in fact as residents of the Antipodes. Robin Ferrier, a Scot by birth but a Kiwi by nature, resides in Wellington, New Zealand, and is famous for at least three chemical discoveries: the glycal glycosylation method, the conversion of carbohydrates into carbocycles, and the photo-bromination of carbohydrates. Stephen Angyal, born in Hungary but now a proud Australian, lives in Sydney and spent a lifetime studying the interplay of configuration and conformation in carbohydrates, culminating in his seminal complexation studies with metal cations. While Ferrier still poses as a young man, Stephen Angyal is about to become a nonagenarian. It struck us that a fitting birthday present would be to make a new molecule for Stephen.

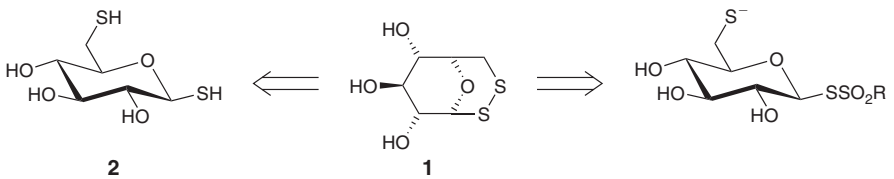
Laevoglucosan (1,6-anhydro-β-D-glucopyranose) was first prepared by Tanret in 1894.[1] The pyrolysis of starch under diminished pressure permits the preparation of laevoglucosan in kilogram quantities.[2] The related 'thiolaevoglucosan' (1,6-dideoxy-1,6-epithio-β-D-glucopyranose) has been known for several years,[3] and we have reported a synthesis of 1,6-dideoxy-1,6-episeleno-β-D-glucopyranose;[4] there are no reports to date of the elusive 1,6-dideoxy-1,6-epitelluro-β-D-glucopyranose.

A molecule that was mentioned at the Schriftfest (University of New South Wales, November, 1994) to celebrate Stephen Angyal's eightieth birthday was the disulfide **1**. As Stephen showed a great interest in such a molecule, we decided to prepare this disulfide. The disulfide **1** contains an interesting and novel ring system that encourages an exploration of its reactivity and conformation.

Results and Discussion

One of the obvious routes to the disulfide **1** is the oxidative cyclization of the 'dithiol' **2** (Scheme 1); this approach seemed prone to the formation of oligomeric by-products. A better route would involve the intramolecular reaction of a thiolate at C6 onto an anomeric thiosulfonate. Some aspects of the reaction of thiolate with thiosulfonate were explored by Field and coworkers,[5] and much used of late by Davis and coworkers.[6,7]

Towards a synthesis of **1**, we converted methyl α-D-glucopyranoside into the tosylate **3** (Scheme 2).[8] Nucleophilic displacement of tosylate from **3** gave the thioacetate **4**, and a subsequent acetolysis returned the tetraacetate **5** in moderate yield (61%)—the disulfide **6** was a significant by-product. A better yielding route was to perform the acetolysis before the introduction of the thioacetyl group (via **7**).



Scheme 1.

* In celebration of the 90th birthday of Stephen J. Angyal.

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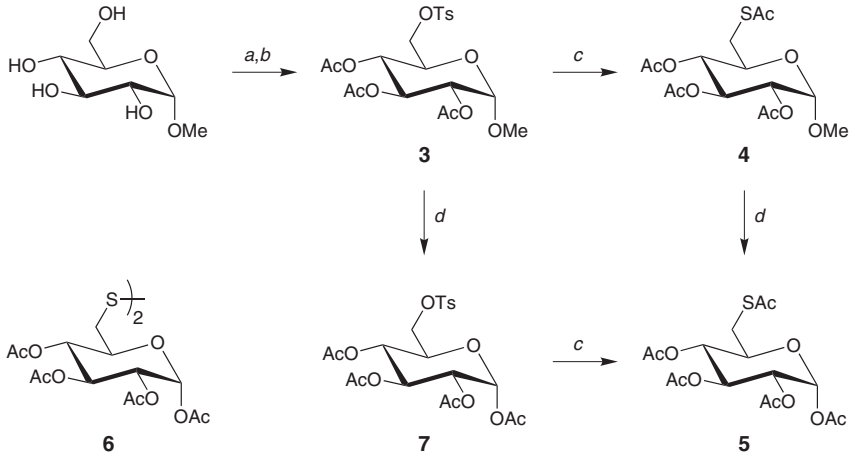
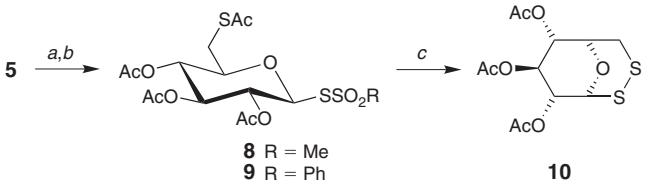


Scheme 2. (*a*) TsCl, pyridine; (*b*) Ac_2O, pyridine; (*c*) KSAc, DMF; (*d*) H_2SO_4, Ac_2O.



Scheme 3. (*a*) HBr, AcOH, CH_2Cl_2; (*b*) $NaSSO_2R$; (*c*) N_2H_5OAc, MeCN.

Treatment of the tetraacetate **5** with hydrogen bromide presumably gave the bromide,[3] which was immediately converted into the thiosulfonate **8** (Scheme 3). Initially, the latter transformation was conducted in *N*,*N*-dimethylformamide (DMF) at room temperature. Poor yields (25–40%) were obtained owing to the concomitant formation of the α-D-anomer and, more significantly, several decomposition products of both the bromide and thiosulfonate. Increasing the temperature (up to 70°C) and the number of mole equivalents of sodium methanethiosulfonate (up to ten) reduced the reaction time and improved the yield (up to 50%), still modest at best. The thiosulfonate moiety is inherently sensitive to base; as well, it has been suggested that the acidity of the methyl protons in methanethiosulfonates makes the group particularly susceptible to the alkaline conditions used in its formation.[7]

Davis and coworkers have shown that the use of acetonitrile as solvent improves the yield of these thiosulfonate displacements.[7] Indeed, it was found that refluxing a mixture of the above bromide and sodium methanethiosulfonate in acetonitrile formed the thiosulfonate **8** in an improved yield (62%). This improvement is probably a result of both reduced decomposition and increased selectivity for the β-D-anomer.

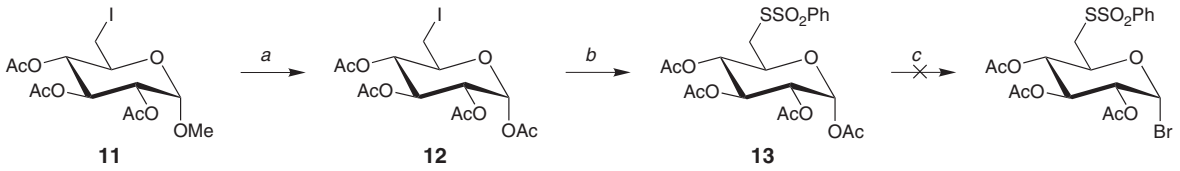
The superiority of the benzenethiosulfonate group over the methanethiosulfonate group has also been demonstrated by Davis and coworkers.[7] Benzenethiosulfonates are more stable in alkali than methanethiosulfonates, probably owing to the absence of acidic alkyl protons. The benzenethiosulfonate **9** was thus synthesized, in a fashion analogous to that for the methanethiosulfonate, but in better yield (71%; Scheme 3).

Intramolecular cyclization of both **8** and **9** to give the disulfide **10** was achieved through the selective deacetylation of S6 by the action of hydrazinium acetate (Scheme 3).[9] Naturally, the reaction was conducted at high dilution to encourage the intramolecular process; however, polymeric material was always obtained to some degree. Yields of the disulfide **10** never exceeded 65%, with the best yields and highest reaction rates being obtained for the benzenethiosulfonate **9**.

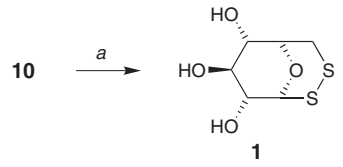
Installation of the thiosulfonate at C6 and the thioacetate at the anomeric position was attempted in order to study the alternative mode of cyclization. Acetolysis of the iodide **11**[10] gave the tetraacetate **12** (Scheme 4). The subsequent displacement of iodide from **12** using sodium benzenethiosulfonate proceeded slowly (ten hours) but in good yield to give the thiosulfonate **13**. An attempt at the bromination of **13** using hydrogen bromide proved unsuccessful, indicating that the thiosulfonate functionality should ideally be installed after the thioacetyl group. As this would necessitate a longer and inherently less efficient overall synthesis, the alternative cyclization approach was curtailed.

Deprotection of the disulfide **10** was attempted first by Zemplén transesterification. A very poor yield (3%) of the triol **1** was obtained for what is usually a quantitative procedure. The base sensitivity of the disulfides[11] was undeniably confirmed when deacetylation using triethylamine in methanol again gave a poor yield (4%) of **1**. In both cases, polymeric material maintained the balance of mass. More gratifyingly, acid-catalyzed transesterification[12] of **10** afforded 'angyalosan' **1** in quantitative yield (Scheme 5).

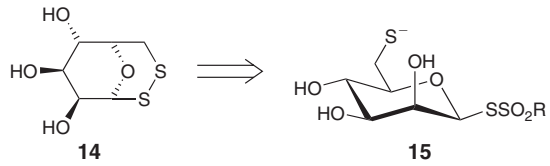
We next decided to see if we could apply our methodology to a synthesis of the D-*manno* disulfide **14**, and were well aware of the possible problems in preparing a β-D-*manno* thiosulfonate **15** (Scheme 6).[13] In a preliminary experiment, the addition of sodium benzenethiosulfonate to the bromide (prepared from the pentaacetate **16**) in refluxing acetonitrile returned the thiosulfonate **17** in high yield (86%), with complete stereoselectivity and at a high reaction rate (30 min as opposed to 3 h for the D-glucose analogue; Scheme 7). The assignment of stereochemistry at the anomeric position of D-mannose derivatives can be difficult using ^1H NMR spectroscopy, owing to similar values for $J_{1,2}$ in both the α- and β-D-anomers.[14] The product was assigned as the β-D-anomer



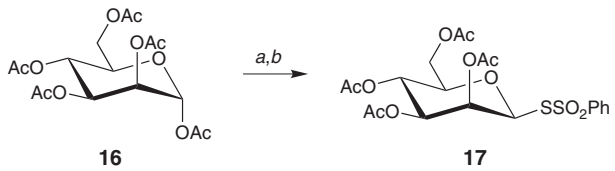
Scheme 4. (*a*) H_2SO_4, Ac_2O; (*b*) $NaSSO_2Ph$, DMF; (*c*) HBr, AcOH, CH_2Cl_2.



Scheme 5. (*a*) HCl, MeOH.



Scheme 6.



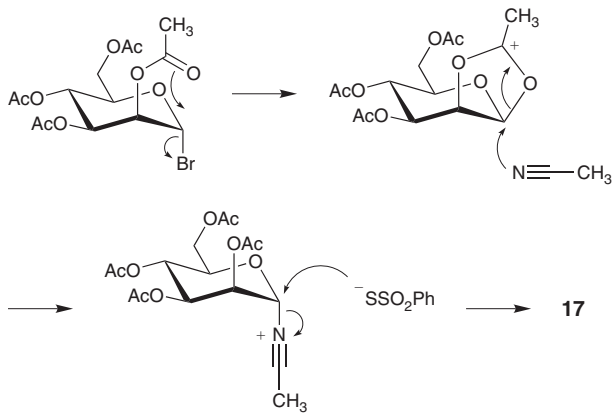
Scheme 7. (*a*) HBr, AcOH, CH_2Cl_2; (*b*) $NaSSO_2Ph$, MeCN.

based on observations of interactions between H1 and H3 and H1 and H5 in the NOESY spectrum of the product **17**.

This favourable formation of the β-D-anomer **17** may be rationalized by participation of both the acetate at C2 and the solvent (Scheme 8). The axial acetate may assist in the dissociation of the bromide, and thereby stabilize the intermediate carbenium ion (as a dioxolenium ion). Attack of this intermediate by acetonitrile would give the kinetically favoured, α-D-configured nitrilium ion.[15] Simple S_N2 displacement of acetonitrile by the benzenethiosulfonate ion would result in the β-D-anomer **17**.

Following on from the above successful result, methyl α-D-mannopyranoside was selectively sulfonylated and then acetylated, giving the tosylate **18** (Scheme 9). Under acetolysis conditions the tosylate **18** returned the tetraacetate **19** in excellent yield. Interestingly, this acetolysis proceeded much faster than that for the D-*gluco* tosylate **3**. The axial acetate at C2 probably assists in the formation and stabilization of the intermediate carbenium ion, as proposed in Scheme 8.

Displacement of tosylate from **19** gave the thioacetate **20**, once more in excellent yield. Bromination of **20**, followed by thiosulfonylation, returned the β-D-anomer **21**. The reaction was rapid, selective, and high yielding, as was expected from the results of the preliminary investigation.



Scheme 8.

Selective deacetylation of **21** formed the desired D-*manno* disulfide **22** in moderate yield. Once more, polymeric by-product was obtained. The acid-catalyzed transesterification of **22** then gave the triol **14**.

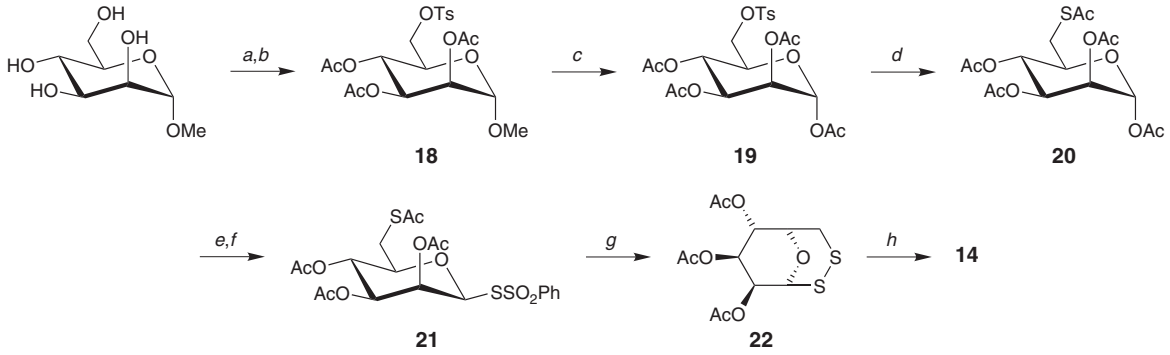
The next target was the D-*allo* disulfide **23** (Scheme 10). 'Diacetone' D-allose **24**[16,17] was converted into the triol **25**, which was selectively tosylated at O6.[18] The displacement of tosylate from **26** gave, somewhat surprisingly, the thioacetate **27**. A rationalization for the formation of **27** is given in Scheme 11 and involves, with some precedent,[19] an interesting sulfur-to-oxygen migration.

The remaining acetonide functionality in **27** was removed and the intermediate hemiacetal completely deprotected under Zemplén conditions. Subsequent acetylation returned the β-D-pyranose **28**.[17]

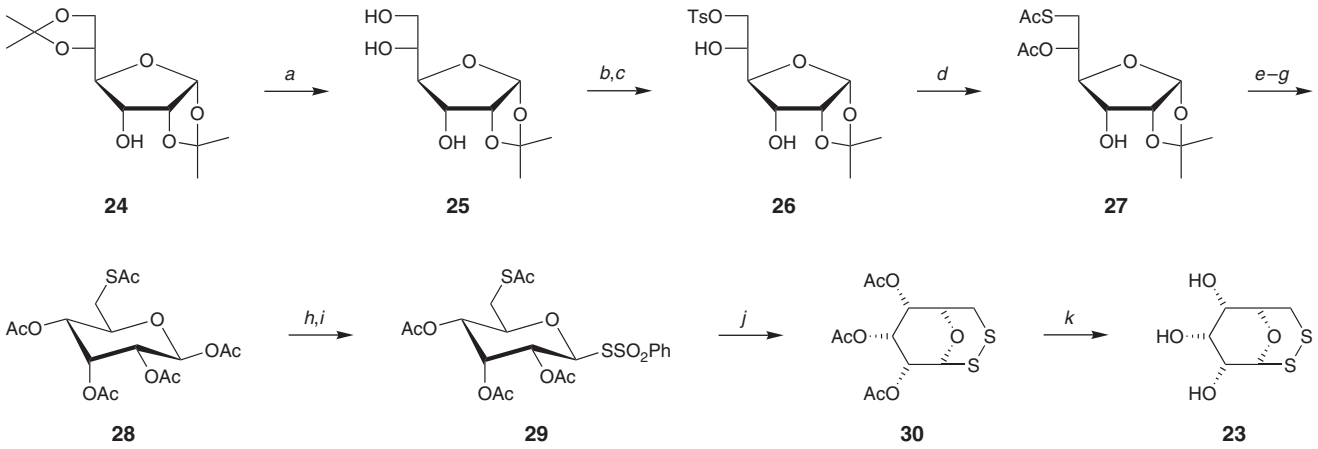
Finally, the benzenethiosulfonate moiety was installed as before to give **29** in good yield. The usual cyclization procedure returned the disulfide **30**, again with the formation of some polymeric material. The normal acid-catalyzed process then gave the target triol **23**.

Continuing on with the various epimeric D-hexoses, we approached a synthesis of the D-*galacto* disulfide **31** (Scheme 12). Similar chemistry to that previously employed in the D-glucose and D-mannose sequences was now applied to methyl α-D-galactopyranoside, to give the thiosulfonate **32**. Cyclization of **32** under the usual conditions, somewhat surprisingly, gave *two* major products, in addition to polymeric material.

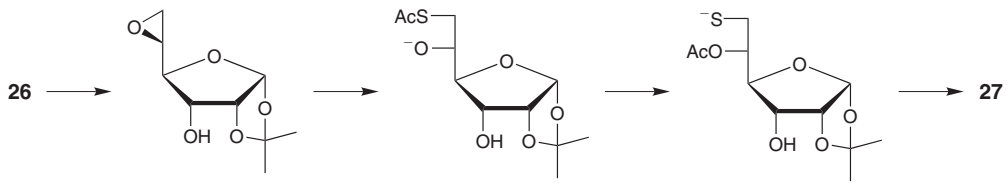
The less abundant product was significantly more polar (TLC) than the disulfides previously isolated. Characterization by ^{1}H NMR spectroscopy indicated that the pyranose ring(s) of the product existed in the $^4C_1$ conformation—this precluded any 1,6-bridged structure. No proton-containing functionalities at C1 or C6 were present. This information suggested that the product was most likely



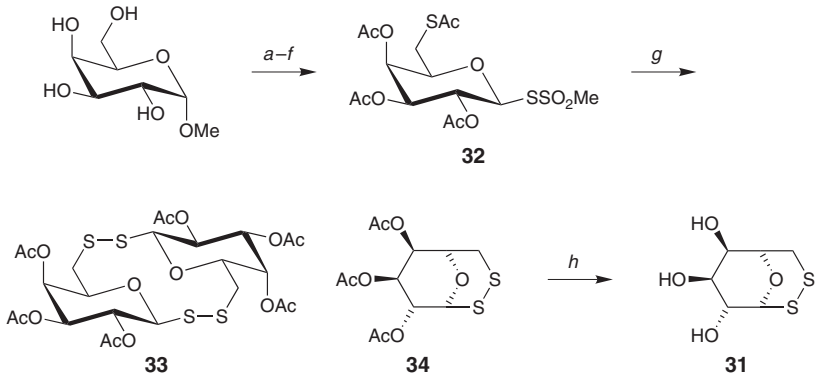
Scheme 9. (*a*) TsCl, pyridine; (*b*) Ac_2O, pyridine; (*c*) H_2SO_4, Ac_2O; (*d*) KSAc, DMF; (*e*) HBr, AcOH, CH_2Cl_2; (*f*) $NaSSO_2Ph$, MeCN; (*g*) N_2H_5OAc, MeCN; (*h*) HCl, MeOH.



Scheme 10. (*a*) AcOH, H_2O; (*b*) Bu_2SnO, PhMe; (*c*) TsCl, $CHCl_3$; (*d*) KSAc, DMF; (*e*) CF_3COOH, H_2O; (*f*) Na, MeOH; (*g*) Ac_2O, pyridine; (*h*) HBr, AcOH, CH_2Cl_2; (*i*) $NaSSO_2Ph$, MeCN; (*j*) N_2H_5OAc, MeCN; (*k*) HCl, MeOH.



Scheme 11.



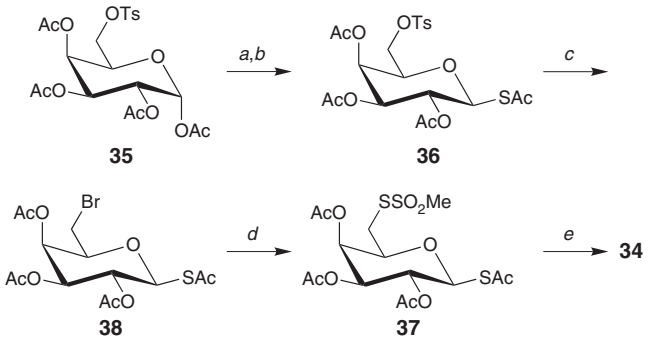
Scheme 12. (*a*) TsCl, pyridine; (*b*) Ac_2O, pyridine; (*c*) H_2SO_4, Ac_2O; (*d*) KSAc, DMF; (*e*) HBr, AcOH, CH_2Cl_2; (*f*) $NaSSO_2Me$, MeCN; (*g*) N_2H_5OAc, MeCN; (*h*) HCl, MeOH.

the bis(disulfide) **33**. High-resolution mass spectrometry (HRMS) was consistent with this assignment.

The more abundant product was of a polarity (TLC) comparable to that of the other disulfides. Indeed, HRMS confirmed that the product had a molecular formula commensurate with that of the disulfide **34**. The ^{1}H NMR spectrum, however, was severely broadened at 273 K; at 233 K, however, the spectrum sharpened significantly and indicated the presence of 14 different proton resonances—the disulfide **34** seemingly existed as a mixture of two conformers.

In an attempt to cast light on the problem, acidic deacetylation of **34** gave the triol **31** (Scheme 12). Unfortunately, the ^{1}H NMR spectrum of **31** was so broadened as to be uninterpretable.

It was decided to attempt the cyclization to the disulfide **34** with the positions of the thioacetate and thiosulfonate reversed, to see if the same products were obtained. An investigation into this functional group reversal was conducted previously for D-glucose (Scheme 4), and results indicated that the thiosulfonate at C6 had to be installed last, as it was sensitive to bromination conditions. Experimentation revealed that the addition of one mole equivalent of potassium thioacetate to the bromide (generated from the tetraacetate **35**) in DMF at 0°C resulted in selective displacement at the anomeric centre to give the β-D-thioacetate **36** in high yield (Scheme 13). Displacement of tosylate from **36** using sodium methanethiosulfonate in DMF proceeded extremely slowly (seven days); the long reaction time under these basic conditions resulted in significant decomposition of product, giving **37** in very poor yield (11%). Conversion of the tosylate **36** into the bromide **38** before displacement by methanethiosulfonate significantly reduced the reaction time and increased the yield of **37** (80%).

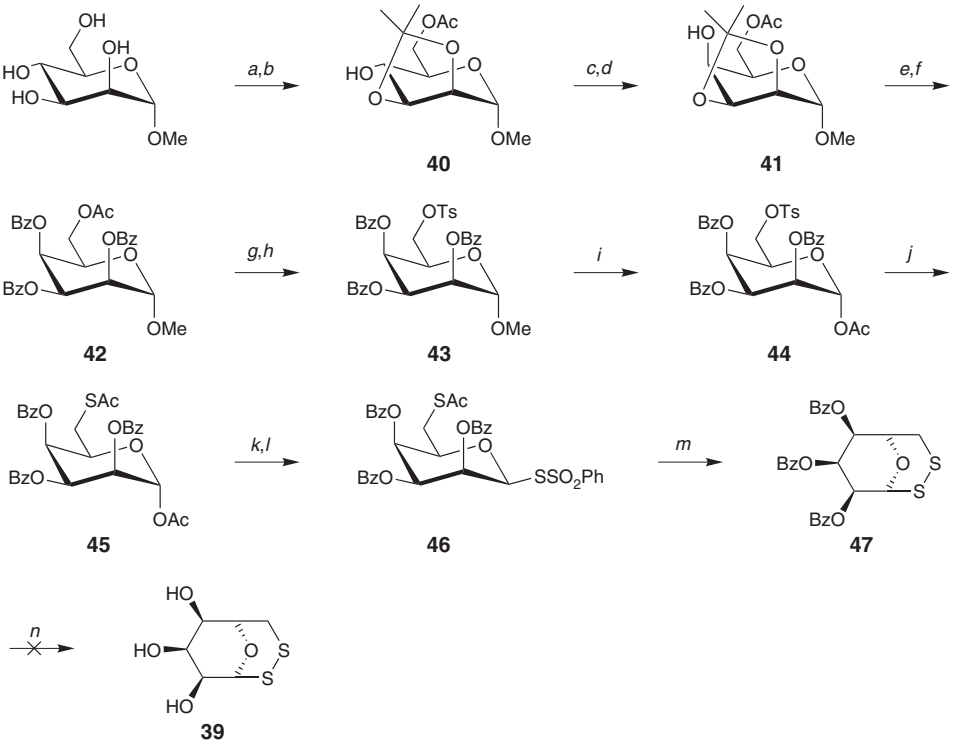


Scheme 13. (*a*) HBr, AcOH, CH_2Cl_2; (*b*) KSAc, DMF; (*c*) Bu_4NBr, MeCN; (*d*) $NaSSO_2Me$, DMF; (*e*) N_2H_5OAc, MeCN.

Cyclization of **37** under the previous conditions gave the same disulfide **34**, though in higher yield than before (63%). Far less of the bis(disulfide) **33** was obtained. Once more, polymeric material was formed in the reaction.

Our last disulfide target was the D-*talo* pyranose **39** (Scheme 14). Methyl α-D-mannopyranoside was easily converted into the alcohol **40**.[20] An oxidation/reduction sequence on **40** exploited a modified procedure of Bundle and coworkers to achieve inversion at C4, returning the D-taloside **41**.[21]

Hydrolysis of the acetonide **41** and subsequent benzoylation gave **42**. Selective deacetylation of **42** was conveniently achieved, and sulfonylation of the resulting primary alcohol



Scheme 14. (*a*) (i) DMP, camphorsulfonic acid, Me_2CO (ii) H_2O; (*b*) AcCl, pyridine; (*c*) PCC, CH_2Cl_2; (*d*) $NaBH_4$, MeOH; (*e*) AcOH, H_2O; (*f*) BzCl, pyridine; (*g*) HCl, MeOH; (*h*) TsCl, pyridine; (*i*) H_2SO_4, Ac_2O; (*j*) KSAc, DMF; (*k*) HBr, AcOH, CH_2Cl_2; (*l*) $NaSSO_2Ph$, MeCN; (*m*) N_2H_5OAc, MeCN; (*n*) HCl, MeOH.

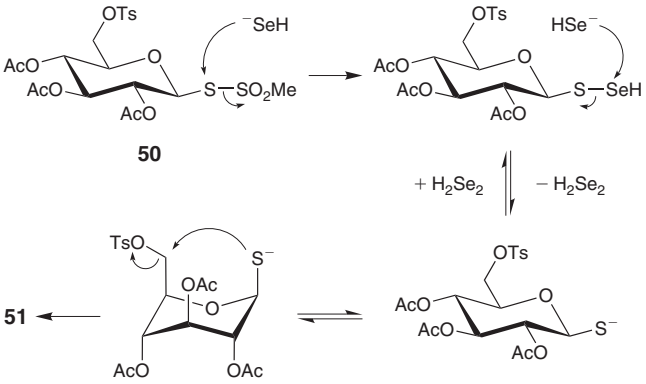
yielded the tosylate **43**, which, when subjected to acetolysis conditions, gave the acetate **44**. Potassium thioacetate was once more employed in a nucleophilic displacement, forming the thioacetate **45**. The proven methodology converted **45** into the benzenethiosulfonate **46** in good yield. As for D-mannose, both the acetolysis and thiosulfonylation of these D-talose derivatives proceeded at high rates, presumably owing to analogous participation of the ester at C2. Cyclization of **46** under the previously mentioned conditions returned the disulfide **47** in moderate yield. An attempt at debenzoylation of **47** using hydrogen chloride in methanol was unsuccessful—the formation of the triol **39** was extremely slow and, after seven days, a significant amount of polymeric by-product was evident (TLC).

At this stage we decided to investigate the synthesis of other 1,6-chalcogen-bridged D-glucopyranoses, namely the thiaselenane **48** and the diselenide **49** (Scheme 15). Towards a synthesis of **48**, the methanethiosulfonate **50** was obtained from the tetraacetate **7** (Scheme 2) via the bromide (Scheme 16). Addition of **50** to sodium hydrogen selenide resulted in clean conversion into a less polar product. Both NMR spectroscopy and HRMS revealed that the product was the known epithio compound **51**, not the desired thiaselenane. A rationalization for the formation of **51** is presented (Scheme 17).

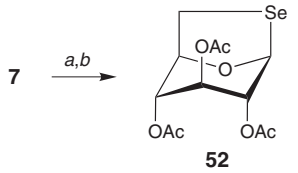
For a synthesis of the diselenide **49**, a solution of the bromide (obtained from the tetraacetate **7**) was added to sodium diselenide (Scheme 18).[22] This resulted in the formation of a single product, the known episeleno compound **52**. Red selenium was observed to be a by-product of the reaction (grey selenium was used in the preparation of the sodium diselenide), indicating that disproportionation of a diselenide was perhaps occurring before, or possibly even after, cyclization.

Based on this unfortunate result we hoped for a synthesis of the elusive 1,6-epitelluro compound **53** (Scheme 19). Thus, the above sequence was repeated but with sodium ditelluride[23] as the reagent—the only product formed was that from a simple base-induced elimination, the alkene **54**.

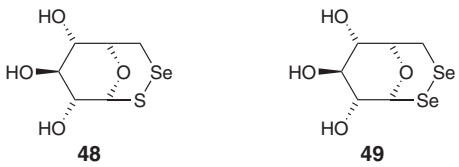
The final aspect of our work here was to investigate the oxidation of the disulfide **10**, bearing in mind that oxidation of



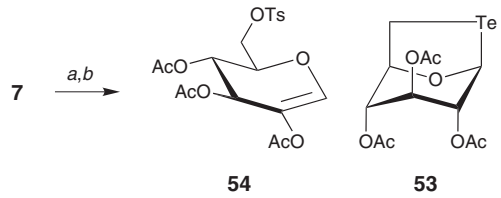
Scheme 17.



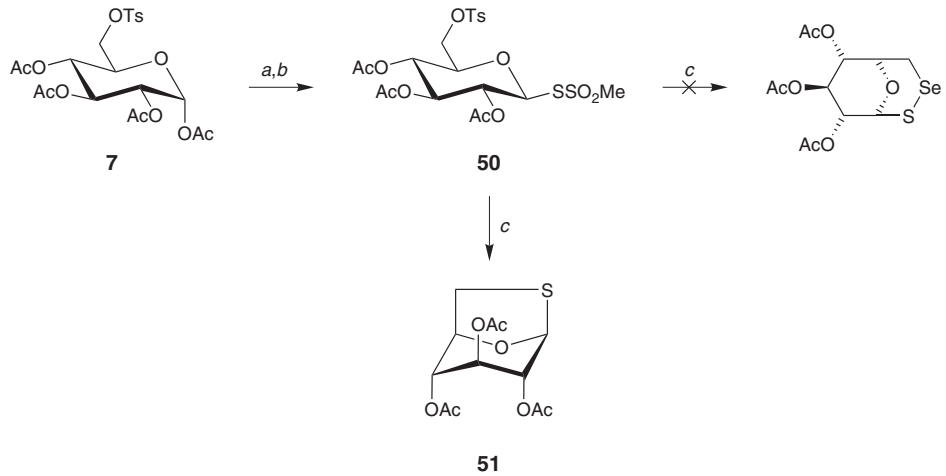
Scheme 18. (*a*) HBr, AcOH, CH_2Cl_2; (*b*) Se, NaH, DMF.



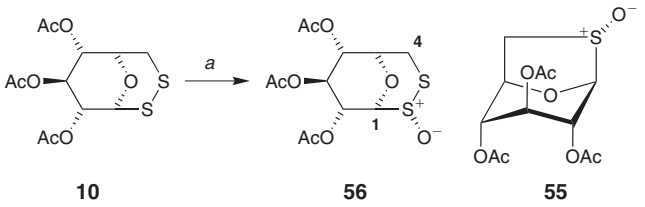
Scheme 15.



Scheme 19. (*a*) HBr, AcOH, CH_2Cl_2; (*b*) Te, NaH, DMF.



Scheme 16. (*a*) HBr, AcOH, CH_2Cl_2; (*b*) $NaSSO_2Me$, MeCN; (*c*) Se, $NaBH_4$, EtOH, DMF.



Scheme 20. (*a*) *m*-Chloroperbenzoic acid, CH_2Cl_2.

the 1,6-epithio compound **51** yields mainly the *exo*-sulfoxide **55** (Scheme 20).[24] Here, treatment of the disulfide **10** with one mole equivalent of 3-chloroperbenzoic acid led to the formation of a single product, characterized by NMR spectroscopy and HRMS as the thiosulfinate **56**. A comparison of the ^{13}C NMR spectra of the disulfide **10** and the thiosulfinate revealed changes in the chemical shift of C1 and C4 that implied oxidation had occurred at S2.[25] The ^1H NMR spectrum was also somewhat informative in that it showed a large upfield shift (about 1 ppm) for H8 relative to that in the parent disulfide **10**. The stereochemistry of the new stereogenic centre in **56** was assigned on the basis of the result for the sulfoxide **55**—in fact, confirmation of this assignment, and an investigation into the conformation of the various disulfides described here, is the subject of the following publication.[32]

Experimental

General experimental procedures have been given previously.[26]

Other General Procedures

Procedure A—Formation of the Thiosulfonates

30% Hydrogen bromide in AcOH (0.9 mL, 5 mmol) was added to the acetate (1 mmol) in CH_2Cl_2 (2 mL) and the solution kept (45 min). The solution was poured onto ice. Standard workup (CH_2Cl_2) gave the bromide, which was used without purification. Sodium benzenethiosulfonate (392 mg, 2 mmol) or $NaSSO_2Me$ (537 mg, 4 mmol) was added to the bromide in MeCN (5 mL), and the mixture refluxed for the specified time. Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography gave the thiosulfonate.

Procedure B—Formation of the Disulfides

Hydrazinium acetate (138 mg, 1.5 mmol) was added to the thiosulfonate (1.0 mmol) in MeCN (25 mL) and the mixture stirred (3 h for the benzenethiosulfonate, 5 h for the methanethiosulfonate). Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography gave the disulfide.

Procedure C—Deacetylation of the Disulfides under Acidic Conditions

Hydrogen chloride in MeOH (1 mL, 1 M) was added to the triacetate (1 mmol) in MeOH (9 mL), and the mixture stirred (36 h). Concentration of the mixture gave the triol.

Syntheses

2,3,4-Tri-O-*acetyl-6*-S-*acetyl-1*-S-*methylsulfonyl-1,6-dithio-β-D-glucose* ***8***

Treatment of the tetraacetate **5**[27] (2.03 g, 5.00 mmol) according to procedure A (refluxed for 4 h, flash chromatography with EtOAc/petrol, 1 : 4) gave the methanethiosulfonate **8** as colourless cubes (1.42 g, 62%), mp 273–274.5°C, $[\alpha]_D$ −129° (Found: C 39.2, H 5.0. $C_{15}H_{22}O_{10}S_3$ requires C 39.3, H 4.8%). ν_{max} (KBr)/cm^{-1} 1759 (C=O), 1698 (SC=O), 1330, 1141 (S–SO_2). δ_H (500 MHz) 2.01, 2.06, 2.11 (9H, 3s, $OCOCH_3$), 2.37 (s, $SCOCH_3$), 2.95 (dd, $J_{5,6}$ 7.3, $J_{6,6}$ 14.6, H6), 3.35 (dd, $J_{5,6}$ 2.7, H6), 3.49 (s, SSO_2CH_3), 3.75 (ddd, $J_{4,5}$ 9.6, H5), 5.00 (dd, $J_{3,4}$ 9.3, H4), 5.06 (dd, $J_{1,2}$ 10.4, $J_{2,3}$ 9.3, H2), 5.25 (d, H1), 5.28 (t, H3). δ_C (125.8 MHz) 20.5, 20.6 ($OCOCH_3$), 30.0 (C6), 30.5 ($SCOCH_3$), 53.0 (SSO_2CH_3), 68.6, 70.2, 73.1, 77.6 (C2,3,4,5), 86.6 (C1), 169.4, 169.7, 169.8 (3C, C=O), 193.9 (SC=O). *m/z* (FAB) 459.0456; $[M+H]^+$ requires 459.0453.

2,3,4-Tri-O-*acetyl-6*-S-*acetyl-1*-S-*phenylsulfonyl-1,6-dithio-β-D-glucose* ***9***

Treatment of the tetraacetate **5** (406 mg, 1.00 mmol) according to procedure A (refluxed for 3 h, flash chromatography with EtOAc/petrol, 3 : 7) gave the benzenethiosulfonate **9** as a colourless oil (370 mg, 71%), $[\alpha]_D$ −7.4°. ν_{max} (film)/cm^{-1} 1758 (C=O), 1697 (SC=O), 1329, 1148 (S–SO_2). δ_H (300 MHz) 1.96, 1.98, 2.05 (9H, 3s, $OCOCH_3$), 2.31 (s, $SCOCH_3$), 2.92 (dd, $J_{5,6}$ 3.5, $J_{6,6}$ 14.6, H6), 3.04 (dd, $J_{5,6}$ 5.5, H6), 3.68 (ddd, $J_{4,5}$ 9.6, H5), 4.89 (t, $J_{3,4}$ 9.6, H4), 4.97 (dd, $J_{1,2}$ 10.4, $J_{2,3}$ 9.3, H2), 5.21 (dd, H3), 5.22 (d, H1), 7.53–7.97 (m, Ph). δ_C (75.5 MHz) 20.4, 20.5, 20.6 (3C, $OCOCH_3$), 29.5 (C6), 30.3 ($SCOCH_3$), 68.6, 69.5, 73.3, 77.4 (C2,3,4,5), 86.6 (C1), 127.0, 129.3, 133.9, 145.8 (Ph), 169.3, 169.6, 169.8 (3C, C=O), 194.2 (SC=O). *m/z* (FAB) 521.0596; $[M+H]^+$ requires 521.0610.

(1S,5S,6S,7S,8R)-6,7,8-Triacetoxy-9-oxa-2,3-dithiabicyclo[3.3.1]nonane ***10***

(*a*) Treatment of the methanethiosulfonate **8** (688 mg, 1.50 mmol) according to procedure B (flash chromatography with EtOAc/petrol, 1 : 4) gave the disulfide **10** as a colourless oil (323 mg, 64%), $[\alpha]_D$ −292°. δ_H (600 MHz) 2.06, 2.07, 2.08 (9H, 3s, $OCOCH_3$), 2.80 (ddd, $J_{1,4}$ 1.2, $J_{4,4}$ 13.9, $J_{4,5}$ 2.6, H4), 3.43 (dd, $J_{4,5}$ 3.1, H4), 4.16 (ddd, $J_{5,6}$ 2.8, H5), 4.95 (dd, $J_{1,8}$ 3.7, H1), 5.22 (dd, $J_{6,7}$ 9.7, H6), 5.48 (dd, $J_{7,8}$ 10.2, H7), 6.06 (dd, H8). δ_C (150.9 MHz) 20.7, 20.8 ($OCOCH_3$), 32.3 (C4), 69.7 (C7), 74.0 (C6), 74.9 (C8), 75.1 (C5), 79.6 (C1), 169.5, 170.0, 170.8 (3C, C=O). *m/z* (EI) 336.0332; $[M]^{+\bullet}$ requires 336.0337.

(*b*) Treatment of the benzenethiosulfonate **9** (364 mg, 0.700 mmol) according to procedure B (flash chromatography with EtOAc/petrol, 1 : 4) gave the disulfide **10** as a colourless oil (167 mg, 71%), $[\alpha]_D$ −294°. The ^1H NMR spectrum of this compound was consistent with that obtained in (*a*).

1,2,3,4-Tetra-O-*acetyl-6*-S-*phenylsulfonyl-6-thio-α-D-glucose* ***13***

Sodium benzenethiosulfonate (196 mg, 1.00 mmol) was added to the iodide **12**[10] (229 mg, 0.500 mmol) in DMF (2 mL), and the mixture stirred at 60°C (10 h). Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography (EtOAc/petrol, 3 : 7) gave the benzenethiosulfonate **13** as colourless needles (197 mg, 78%), mp 141–142.5°C (EtOAc/petrol), $[\alpha]_D$ +120°. ν_{max} (KBr)/cm^{-1} 1757 (C=O), 1328, 1145 (S–SO_2). δ_H (300 MHz) 1.91, 1.93, 2.00, 2.05 (12H, 4s, $OCOCH_3$), 3.02 (dd, $J_{5,6}$ 7.3, $J_{6,6}$ 14.7, H6), 3.18 (dd, $J_{5,6}$ 3.0, H6), 4.07 (ddd, $J_{4,5}$ 10.1, H5), 4.81 (dd, $J_{1,2}$ 3.7, $J_{2,3}$ 10.3, H2), 4.84 (dd, $J_{3,4}$ 9.5, H4), 5.32 (dd, H3), 5.95 (d, H1), 7.46–7.83 (m, Ph). δ_C (75.5 MHz) 20.2, 20.4, 20.6 ($OCOCH_3$), 36.9 (C6), 68.8, 69.1, 69.9, 70.5 (C2,3,4,5), 88.1 (C1), 126.8, 129.1, 133.7, 144.2 (Ph), 168.4, 169.3, 169.4, 169.8 (4C, C=O). *m/z* (FAB) 505.0809; $[M+H]^+$ requires 505.0838.

(1S,5S,6S,7S,8R)-9-Oxa-2,3-dithiabicyclo[3.3.1]nonane-6,7,8-triol ***1****, 'angyalosan'*

Treatment of the triacetate **10** (67 mg, 0.20 mmol) according to procedure C gave the triol **1** as a colourless solid (41 mg, 98%), $[\alpha]_D$ −403° (pyridine). δ_H (600 MHz, CD_3OD) 2.36 (ddd, $J_{1,4}$ 1.2, $J_{4,4}$ 13.8, $J_{4,5}$ 2.6, H4), 3.38 (dd, $J_{4,5}$ 3.1, H4), 3.52 (dd, $J_{6,7}$ 9.1, $J_{7,8}$ 9.8, H7), 3.95 (dd, $J_{5,6}$ 3.2, H6), 4.03 (ddd, H5), 4.41 (dd, $J_{1,8}$ 3.8, H8), 4.75 (dd, H1). δ_C (150.9 MHz, CD_3OD) 33.1 (C4), 74.5 (C6), 74.8 (C7), 77.7 (C8), 78.5 (C5), 84.7 (C1). *m/z* (EI) 210.0024; $[M]^{+\bullet}$ requires 210.0021.

2,3,4,6-Tetra-O-*acetyl-1*-S-*phenylsulfonyl-1-thio-β-D-mannose* ***17***

Treatment of the pentaacetate **16** (781 mg, 2.00 mmol) according to procedure A (refluxed for 30 min, flash chromatography with EtOAc/petrol, 3 : 7) gave the benzenethiosulfonate **17** as a colourless oil (868 mg, 86%), $[\alpha]_D$ +62.8°. ν_{max} (film)/cm^{-1} 1754 (C=O), 1343, 1150 (S–SO_2). δ_H (600 MHz) 1.95, 1.98, 2.04, 2.15 (12H, 4s, $OCOCH_3$), 3.55 (dd, $J_{5,6}$ 2.4, $J_{6,6}$ 12.5, H6), 3.81 (ddd, $J_{4,5}$ 10.0, $J_{5,6}$ 3.7, H5), 4.04 (dd, H6), 4.92 (dd, $J_{2,3}$ 3.4, $J_{3,4}$ 10.0, H3), 5.29 (t, H4), 5.35 (dd, $J_{1,2}$ 1.7, H2), 5.95 (d, H1), 7.54–7.96 (m, Ph). δ_C (150.9 MHz) 20.5, 20.6, 20.7, 20.8 (4C, $OCOCH_3$), 61.2 (C6), 65.4, 69.7, 70.0, 71.3 (C2,3,4,5), 87.2 (C1), 127.4, 129.5, 134.3, 145.6 (Ph), 169.4, 169.5, 169.7, 170.5 (4C, C=O). *m/z* (FAB) 505.0863; $[M + H]^+$ requires 505.0838.

2,3,4-Tri-O-*acetyl-6*-S-*acetyl-1*-S-*phenylsulfonyl-1,6-dithio-β-D-mannose* ***21***

Treatment of the tetraacetate **20**[28] (813 mg, 2.00 mmol) according to procedure A (refluxed for 30 min, flash chromatography with EtOAc/petrol, 3 : 7) gave the benzenethiosulfonate **21** as a colourless oil (875 mg, 84%), $[\alpha]_D$ +65.8°. ν_{max} (film)/cm^{-1} 1755 (C=O), 1697 (SC=O), 1342, 1149 (S–SO_2). δ_H (300 MHz) 1.90, 1.98, 2.12 (9H, 3s, $OCOCH_3$), 2.24 (s, $SCOCH_3$), 2.61 (dd, $J_{5,6}$ 3.1, $J_{6,6}$ 14.5, H6), 2.93 (dd, $J_{5,6}$ 5.2, H6), 3.78 (ddd, $J_{4,5}$ 9.8, H5), 4.82 (dd, $J_{2,3}$ 3.3, $J_{3,4}$ 9.8, H3), 5.14 (t, H4), 5.30 (dd, $J_{1,2}$ 1.7, H2), 5.88 (d, H1), 7.51–7.94 (m, Ph). δ_C (75.5 MHz) 20.3, 20.5, 20.6 (3C, $OCOCH_3$), 29.0 (C6), 30.2 ($SCOCH_3$), 66.7, 69.3, 69.8, 72.0 (C2,3,4,5), 86.9 (C1), 127.0, 129.3, 134.0, 145.4 (Ph), 169.4, 169.5 (C=O), 194.2 (SC=O). *m/z* (FAB) 521.0623; $[M + H]^+$ requires 521.0610.

(1S,5S,6S,7S,8S)-6,7,8-Triacetoxy-9-oxa-2,3-dithiabicyclo[3.3.1]nonane ***22***

Treatment of the benzenethiosulfonate **21** (260 mg, 0.500 mmol) according to procedure B (flash chromatography with EtOAc/petrol, 3 : 7) gave the disulfide **22** as a colourless oil (87 mg, 43%), $[\alpha]_D$ −145°. δ_H (600 MHz) 2.01, 2.04, 2.15 (9H, 3s, $OCOCH_3$), 2.79 (dd, $J_{4,4}$ 13.7, $J_{4,5}$ 9.8, H4), 3.32 (d, H4), 4.93 (dd, $J_{5,6}$ 10.0, H5), 5.21 (dd, $J_{6,7}$ 10.0, $J_{7,8}$ 3.0, H7), 5.35 (t, H6), 5.43–5.44 (m, H1,H8). δ_C (150.9 MHz) 20.7, 20.9, 21.3 (3C, $OCOCH_3$), 36.9 (C4), 67.7 (C5), 69.2 (C7), 70.2 (C8), 70.5 (C6), 94.1 (C1), 169.77, 169.83, 171.0 (3C, C=O). *m/z* (FAB) 337.0396; $[M + H]^+$ requires 337.0416.

(1S,5S,6S,7S,8S)-9-Oxa-2,3-dithiabicyclo[3.3.1]-nonane-6,7,8-triol ***14***

Treatment of the triacetate **22** (67 mg, 0.20 mmol) according to procedure C gave the triol **14** as a colourless solid (41 mg, 98%), $[\alpha]_D$ −205° (pyridine). δ_H [300 MHz, $(CD_3)_2SO$] 2.23 (dd, $J_{4,4}$ 13.8, $J_{4,5}$ 9.7, H4), 2.72 (d, H4), 3.17 (dd, $J_{6,7}$ 9.2, $J_{7,8}$ 3.0, H7), 4.14 (dd, $J_{5,6}$ 9.6, H5), 4.57 (dd, H6), 4.66 (dd, $J_{1,8}$ 1.4, H8), 4.84 (d, H1). δ_C [75.5 MHz, $(CD_3)_2SO$] 36.2 (C4), 69.1, 71.0, 71.5, 73.2 (C5,6,7,8), 95.1 (C1). *m/z* (EI) 210.0016; $[M]^{+\bullet}$ requires 210.0021.

5-O-*Acetyl-6*-S-*acetyl-1,2*-O-*isopropylidene-6-thio-β-D-allofuranose* ***27***

Potassium thioacetate (685 mg, 6.00 mmol) was added to the tosylate **26**[18] (1.12 g, 3.00 mmol) in DMF (10 mL), and the mixture stirred overnight. Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography (EtOAc/petrol, 2 : 3) gave the thioacetate **27** as a colourless oil (605 mg, 63%), $[\alpha]_D$ +39.8°. δ_H (300 MHz) 1.36, 1.56 (6H, 2s, CH_3), 2.07 (s, $OCOCH_3$) 2.33 (s, $SCOCH_3$), 2.37 (br s, OH), 3.03 (dd, $J_{5,6}$ 8.5, $J_{6,6}$ 14.3, H6), 3.39 (dd, $J_{5,6}$ 4.1, H6), 3.83 (dd, $J_{3,4}$ 8.6, $J_{4,5}$ 4.8, H4), 4.04 (dd, $J_{2,3}$ 5.2, H3), 4.56 (dd, $J_{1,2}$ 3.8, H2), 5.19 (ddd, H5), 5.77 (d, H1). δ_C (75.5 MHz) 20.9 ($OCOCH_3$), 2.49, 26.53 [$C(CH_3)_2$], 29.5 (C6), 30.4 ($SCOCH_3$), 71.3, 72.7, 78.6, 79.8 (C2,3,4,5), 103.8 (C1), 112.8 [$C(CH_3)_2$], 170.2 (C=O), 194.8 (SC=O). *m/z* (FAB) 321.1014; $[M + H]^+$ requires 321.1008.

1,2,3,4-Tetra-O-*acetyl-6*-S-*acetyl-6-thio-β-D-allose* ***28***

The thioacetate **27** (32 mg, 0.1 mmol) was dissolved in CF_3COOH/H_2O (4 : 1, 1 mL) and the solution kept (30 min). The solvent was removed before co-evaporation with PhMe. Sodium (5 mg, 0.2 mmol) was added to the residue in MeOH (5 mL), and the solution kept (2 h). The solution was quenched with resin (Amberlite IR-120, H^+), and the mixture was filtered and concentrated. Acetic anhydride (0.14 mL, 1.5 mmol) was added to the residue in pyridine (1 mL), and the solution kept (4 h). MeOH (1 mL) was added and the mixture concentrated. Standard workup (EtOAc) and flash chromatography (EtOAc/toluene, 2 : 25) gave the thioacetate **28** as a colourless oil (29 mg, 72%), $[\alpha]_D$ −43.6°. δ_H (300 MHz) 2.00, 2.05, 2.11, 2.15 (12H, 4s, $OCOCH_3$), 2.33 (s, $SCOCH_3$), 3.17–3.20 (2H, m, H6), 4.19 (ddd, $J_{4,5}$ 10.1, $J_{5,6}$ 3.8, $J_{5,6}$ 5.1, H5), 4.86 (dd, $J_{3,4}$ 2.9, H4), 4.94 (dd, $J_{1,2}$ 8.7, $J_{2,3}$ 3.0, H2), 5.66 (dd, H3), 5.95 (d, H1). δ_C (75.5 MHz) 20.5, 20.6, 20.7, 20.9 (4C, $OCOCH_3$), 29.8 (C6), 30.4 ($SCOCH_3$), 67.5, 68.1, 68.2, 71.7 (C2,3,4,5), 89.9 (C1), 169.0, 169.3, 169.8 (C=O), 194.8 (SC=O). *m/z* (EI) 406.0971; $[M]^{+\bullet}$ requires 406.0934.

2,3,4-Tri-O-*acetyl-6*-S-*acetyl-1*-S-*phenylsulfonyl-1,6-dithio-β-D-allose* ***29***

Treatment of the tetraacetate **28** (284 mg, 0.700 mmol) according to procedure A (refluxed for 3 h, flash chromatography with EtOAc/petrol, 1 : 2) gave the benzenethiosulfonate **29** as a colourless oil (288 mg, 79%), $[\alpha]_D$ −20.0°. ν_{max} (film)/cm^{-1} 1755 (C=O), 1697 (SC=O), 1330, 1147 (S–SO_2). δ_H (300 MHz) 1.94, 1.99, 2.16 (9H, 3s, $OCOCH_3$), 2.26 (s, $SCOCH_3$), 2.84 (dd, $J_{5,6}$ 3.5, $J_{6,6}$ 14.4, H6), 3.05 (dd, $J_{5,6}$ 5.1, H6), 3.99 (ddd, $J_{4,5}$ 10.1, H5), 4.70 (dd, $J_{3,4}$ 2.8, H4), 4.91 (dd, $J_{1,2}$ 10.5, $J_{2,3}$ 2.9, H2), 5.52 (d, H1), 5.59 (dd, H3), 7.50–7.96 (m, Ph). δ_C (75.5 MHz) 20.3, 20.4, 20.6 (3C, $OCOCH_3$), 29.4 (C6), 30.2 ($SCOCH_3$), 66.4, 67.2, 67.8, 73.8 (C2,3,4,5), 84.2 (C1), 126.8, 129.1, 133.7, 146.0 (Ph), 168.8, 169.1, 169.6 (3C, C=O), 194.2 (SC=O). *m/z* (FAB) 521.0609; $[M + H]^+$ requires 521.0610.

(1S,5S,6S,7R,8R)-6,7,8-Triacetoxy-9-oxa-2,3-dithiabicyclo[3.3.1]nonane ***30***

Treatment of the benzenethiosulfonate **29** (156 mg, 0.300 mmol) according to procedure B (flash chromatography with EtOAc/petrol, 3 : 7) gave the disulfide **30** as a colourless oil (63 mg, 62%), $[\alpha]_D$ −92.9°. δ_H (300 MHz) 2.04, 2.11, 2.12 (9H, 3s, $OCOCH_3$), 2.58 (ddd, $J_{1,4}$ 0.8, $J_{4,4}$ 14.2, $J_{4,5}$ 2.7, H4), 3.54 (dd, $J_{4,5}$ 3.9, H4), 4.29 (ddd, $J_{5,6}$ 1.8, H5), 5.00 (dd, $J_{1,8}$ 2.4, H1), 5.31 (dd, $J_{6,7}$ 4.5, H6), 5.63 (dd, $J_{7,8}$ 4.0, H8), 6.62 (t, H7). δ_C (75.5 MHz) 20.6, 20.8 ($OCOCH_3$), 29.4 (C4), 65.3 (C7), 69.3 (C6), 71.8 (C5), 72.0 (C8), 75.7 (C1), 169.7, 169.8, 170.1 (3C, C=O). *m/z* (FAB) 336.0360; $[M]^{+\bullet}$ requires 336.0337.

(1S,5S,6S,7R,8R)-9-Oxa-2,3-dithiabicyclo[3.3.1]-nonane-6,7,8-triol ***23***

Treatment of the triacetate **30** (67 mg, 0.20 mmol) according to procedure C gave the triol **23** as a colourless solid (41 mg, 98%), $[\alpha]_D$ −212° (pyridine). δ_H [600 MHz, $(CD_3)_2SO$] 2.67 (dd, $J_{1,4}$ 0.6, $J_{4,4}$ 14.0, $J_{4,5}$ 3.1, H4), 3.30 (dd, $J_{4,5}$ 4.7, H4), 3.82 (dd, $J_{1,8}$ 2.1, $J_{7,8}$ 2.3, H8), 3.98 (dd, $J_{6,7}$ 3.5, H7), 4.17 (ddd, $J_{5,6}$ 3.7, H5), 4.94 (dd, H6), 5.02 (d, H1). δ_C [150.9 MHz, $(CD_3)_2SO$] 28.1 (C4), 65.3, 71.3, 73.1, 74.9 (C5,6,7,8), 78.1 (C1). *m/z* (ES) 232.9909; $[M + Na]^+$ requires 232.9918.

2,3,4-Tri-O-*acetyl-6*-S-*acetyl-1*-S-*methylsulfonyl-1,6-dithio-β-D-galactose* ***32***

Treatment of 1,2,3,4-tetra-*O*-acetyl-6-*S*-acetyl-6-thio-α-D-galactose[29] (2.24 g, 5.50 mmol) according to procedure A (refluxed for 4 h, flash chromatography with EtOAc/petrol, 3 : 7) gave the methanethiosulfonate **32** as colourless plates (2.04 g, 81%), mp 146–147.5°C, $[\alpha]_D$ +41.5° (Found: C 39.0, H 4.9. $C_{15}H_{22}O_{10}S_3$ requires C 39.3, H 4.8%). ν_{max} (KBr)/cm^{-1} 1754 (C=O), 1696 (SC=O), 1329, 1141 (S–SO_2). δ_H (300 MHz) 1.89, 1.99, 2.10 (9H, 3s, $OCOCH_3$), 2.27 (s, $SCOCH_3$), 2.87 (dd, $J_{5,6}$ 8.2, $J_{6,6}$ 14.1, H6), 3.10 (dd, $J_{5,6}$ 5.3, H6), 3.42 (s, SSO_2CH_3), 3.83 (ddd, $J_{4,5}$ 1.0, H5), 5.04–5.21 (m, H1,H2,H3), 5.40 (dd, $J_{3,4}$ 3.1,

H4). δ_C (75.5 MHz) 20.4, 20.5, 20.6 (3C, OCO*C*H$_3$), 28.9 (C6), 30.4 (SCO*C*H$_3$), 52.9 (SSO$_2$CH$_3$), 65.6, 68.0, 71.3, 76.5 (C2,3,4,5), 87.0 (C1), 169.57, 159.64, 170.0 (3C, C=O), 194.0 (SC=O). *m/z* (FAB) 459.0473; $[M + H]^+$ requires 459.0453.

2,3,4-Tri-O-*acetyl-1*-S-*acetyl-1-thio-6*-O-*(4-methylphenylsulfonyl)-β-D-galactose* ***36***

30% Hydrogen bromide in AcOH (0.9 mL, 5 mmol) was added to the tetraacetate **35**[29] (502 mg, 1.00 mmol) in CH_2Cl_2 (2 mL), and the solution kept (45 min). The solution was poured onto ice. Standard workup (CH_2Cl_2) presumably gave the bromide, which was used immediately. Potassium thioacetate (141 mg, 1.1 mmol) was added to the bromide in DMF (5 mL) at 0°C, and the mixture stirred (90 min). Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography (EtOAc/petrol, 1 : 2) gave the thioacetate **36** as a pale yellow oil (446 mg, 86%), $[\alpha]_D$ +2.7°. δ_H (600 MHz) 1.95, 2.00, 2.03 (9H, 3s, OCOCH$_3$), 2.36 (s, SCOCH$_3$), 2.44 (s, ArC*H*$_3$), 3.94–4.07 (3H, m, H5,H6), 5.05 (dd, $J_{2,3}$ 9.7, $J_{3,4}$ 3.4, H3), 5.20 (d, $J_{1,2}$ 10.4, H1), 5.25 (dd, H2), 5.42 (d, H4), 7.33, 7.73 (AA′BB′, Ar). δ_C (150.9 MHz) 20.58, 20.60, 20.8 (3C, OCO*C*H$_3$), 21.8 (Ar*C*H$_3$), 30.9 (SCO*C*H$_3$), 65.6 (C6), 66.3, 66.9, 71.8, 74.5 (C2,3,4,5), 80.7 (C1), 128.2, 130.1, 132.3, 145.3 (Ar), 169.6, 169.8, 169.9 (3C, C=O), 191.9 (SC=O). *m/z* (FAB) 519.1035; $[M + H]^+$ requires 519.0995.

2,3,4-Tri-O-*acetyl-1*-S-*acetyl-6-bromo-6-deoxy-1-thio-β-D-galactose* ***38***

Tetrabutylammonium bromide (484 mg, 1.5 mmol) was added to the tosylate **36** (156 mg, 0.3 mmol) in MeCN (3 mL), and the mixture refluxed (48 h). Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography (EtOAc/petrol, 2 : 3) gave the bromide **38** as a colourless oil (118 mg, 92%), $[\alpha]_D$ +18.6°. δ_H (300 MHz) 1.96, 2.01, 2.14 (9H, 3s, OCOCH$_3$), 2.37 (s, SCOCH$_3$), 3.24 (dd, $J_{5,6}$ 7.9, $J_{6,6}$ 10.4, H6), 3.35 (dd, $J_{5,6}$ 6.1, H6), 4.01 (ddd, $J_{4,5}$ 1.0, H5), 5.08–5.31 (m, H1,2,3), 5.62 (dd, $J_{3,4}$ 3.3, H4). δ_C (75.5 MHz) 20.5, 20.56, 20.64 (3C, OCO*C*H$_3$), 27.1 (C6), 30.8 (SCO*C*H$_3$), 66.0, 67.4, 71.9, 77.1 (C2,3,4,5), 80.5 (C1), 169.5, 169.8, 169.9 (3C, C=O), 192.0 (SC=O). *m/z* (FAB) 427.0040; $[M + H]^+$ requires 427.0062.

2,3,4-Tri-O-*acetyl-1*-S-*acetyl-6*-S-*methylsulfonyl-1,6-dithio-β-D-galactose* ***37***

Sodium methanethiosulfonate (80 mg, 0.60 mmol) was added to the bromide **38** (26 mg, 0.06 mmol) in DMF (1 mL), and the mixture stirred at 70°C (72 h). Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography (EtOAc/petrol, 7 : 13) gave the methanethiosulfonate **37** as a colourless oil (22 mg, 80%), $[\alpha]_D$ +34.2°. ν_{max} (film)/cm^{-1} 1755 (C=O), 1713 (SC=O), 1326, 1136 (S–SO$_2$). δ_H (300 MHz) 1.98, 2.03, 2.18 (9H, 3s, OCOCH$_3$), 2.38 (s, SCOCH$_3$), 3.21 (dd, $J_{5,6}$ 4.6, $J_{6,6}$ 14.9, H6), 3.30 (dd, $J_{5,6}$ 8.5, H6), 3.34 (s, SSO$_2$CH$_3$), 4.07 (ddd, $J_{4,5}$ 1.1, H5), 5.08–5.35 (m, H1,2,3), 5.46 (dd, $J_{3,4}$ 3.4, H4). δ_C (75.5 MHz) 20.7, 20.9 (OCO*C*H$_3$), 31.0 (SCO*C*H$_3$), 36.6 (C6), 51.0 (SSO$_2$CH$_3$), 66.2, 68.7, 72.0, 76.7 (C2,3,4,5), 80.9 (C1), 169.7, 170.0, 170.5 (3C, C=O), 192.2 (SC=O). *m/z* (FAB) 459.0464; $[M + H]^+$ requires 459.0453.

(1S,5S,6R,7S,8R)-6,7,8-Triacetoxy-9-oxa-2,3-dithiabicyclo[3.3.1]nonane ***34*** *and (1S,5S,6R,7S,8R,9S,13S,14R,15S,16R)-6,7,8,14,15,16-hexaacetoxy-17,18-dioxa-2,3,10,11-tetrathiatricyclo[11.3.1.1^{5,9}]octadecane* ***33***

(*a*) The methanethiosulfonate **32** (688 mg, 1.50 mmol) was treated according to procedure B (flash chromatography with EtOAc/petrol, 1 : 4). The disulfide **34** was the first to elute as a colourless oil (222 mg, 44%), $[\alpha]_D$ −14.2°. δ_H (500 MHz)* 1.98, 1.99, 2.06, 2.08, 2.19, 2.20 (6s, OCOCH$_3$), 2.57 (dd, $J_{4,4}$ 13.5, $J_{4,5}$ 6.5, H4^a), 2.91 (dd, $J_{4,4}$ 14.0, $J_{4,5}$ 12.0, H4^b), 3.17 (d, H4^a), 3.34 (d, H4^b), 3.64 (d, H5^b), 4.50 (d, H5^a), 4.51 (d, $J_{1,8}$ 9.5, H1^b), 4.79 (d, $J_{1,8}$ 5.5, H1^a), 5.05 (dd, $J_{6,7}$ 3.0, $J_{7,8}$ 10.0, H7^b), 5.11–5.14 (m, H7^a,8^a), 5.23 (d, H6^b), 5.52 (d, $J_{6,7}$ 0.7, H6^a), 5.80 (dd, H8^b). δ_C (125.8 MHz) 20.80, 20.82, 20.9, 21.0, 21.08, 21.10 (OCO*C*H$_3$), 34.2 (C4^a), 44.3 (C4^b), 64.0 (C8^b), 66.7 (C8^a), 68.2 (C6^a), 69.0 (C6^b), 71.7 (C7), 73.4 (C5^a), 75.7 (C5^b), 84.8 (C1^b), 94.5 (C1^a), 169.2, 170.31, 170.34, 170.4, 170.5, 170.9 (C=O). *m/z* (FAB) 337.0397; $[M + H]^+$ requires 337.0416.

Next to elute was the bis(disulfide) **33** as a colourless oil (96 mg, 19%), $[\alpha]_D$ −132°. δ_H (300 MHz) 1.98, 2.05, 2.16 (3s, OCOCH$_3$), 2.81 (dd, $J_{5,6}$ 7.9, $J_{6,6}$ 13.5, H6), 3.21 (dd, $J_{5,6}$ 5.2, H6), 4.03 (ddd, $J_{4,5}$ 1.1, H5), 4.59 (d, $J_{1,2}$ 9.8, H1), 5.10 (dd, $J_{2,3}$ 10.0, $J_{3,4}$ 3.3, H3), 5.42 (dd, H2), 5.53 (dd, H4). δ_C (75.5 MHz) 20.5, 20.7 (OCO*C*H$_3$), 38.7 (C6), 66.2, 67.6, 71.8, 75.8 (C2,3,4,5), 88.3 (C1), 169.2, 170.0 (C=O). *m/z* (FAB) 672.0671; $[M]^{+\bullet}$ requires 672.0675.

(*b*) Treatment of the methanethiosulfonate **37** (22 mg) according to procedure B (flash chromatography with EtOAc/petrol, 1 : 4) gave the disulfide **34** as a colourless oil (10 mg, 63%), $[\alpha]_D$ −15.8°.

(1S,5S,6R,7S,8R)-9-Oxa-2,3-dithiabicyclo[3.3.1]-nonane-6,7,8-triol ***31***

Treatment of the triacetate **34** (67 mg, 0.20 mmol) according to procedure C gave the triol **31** as a colourless solid (41 mg, 98%), $[\alpha]_D$ −33.2° (pyridine).† *m/z* (EI) 210.0031; $[M]^{+\bullet}$ requires 210.0021.

Methyl 6-O-*Acetyl-2,3*-O-*isopropylidene-α-D-talopyranoside* ***41***

Pyridinium chlorochromate (862 mg, 4.00 mmol) was added to the alcohol **40**[30] (553 mg, 2.00 mmol) in CH_2Cl_2 (10 mL), and the mixture refluxed (4 h). Filtration through a short silica pad (CH_2Cl_2) and concentration of the eluent gave a colourless oil. Sodium borohydride (76 mg, 2.0 mmol) was added to the residue in EtOH (5 mL) at 0°C and the mixture stirred (15 min). The solution was poured into saturated $NaHCO_3$ solution (30 mL). Standard workup (CH_2Cl_2) and flash chromatography (EtOAc/petrol, 3 : 7) gave the alcohol **41** as a colourless oil (409 mg, 74%), $[\alpha]_D$ +40.7°. δ_H (300 MHz) 1.31, 1.50 (6H, 2s, CH$_3$), 2.01 (s, OCOCH$_3$), 2.41 (br s, OH), 3.35 (s, OCH$_3$), 3.70 (dd, $J_{1,2}$ 0.9, $J_{2,3}$ 4.9, H2), 3.84 (ddd, $J_{4,5}$ 1.1, $J_{5,6}$ 4.7, $J_{5,6}$ 7.7, H5), 3.98 (dd, $J_{3,4}$ 6.3, H4), 4.15 (dd, H3), 4.24 (dd, $J_{6,6}$ 11.7, H6), 4.30 (dd, H6), 4.91 (d, H1). δ_C (75.5 MHz) 20.7 (OCO*C*H$_3$), 25.0, 25.7 [C(*C*H$_3$)$_2$], 54.9 (OCH$_3$), 63.8 (C6), 64.0, 66.8, 72.1, 73.3 (C2,3,4,5), 98.2 (C1), 109.4 [*C*(CH$_3$)$_2$], 170.6 (C=O). *m/z* (FAB) 277.1265; $[M + H]^+$ requires 277.1287.

Methyl 6-O-*Acetyl-2,3,4-tri*-O-*benzoyl-α-D-taloside* ***42***

The acetate **41** (277 mg, 1.00 mmol) was dissolved in 80% AcOH/H$_2$O (5 mL), and the solution heated at 80°C (30 min). The solvent was removed and the residue co-evaporated with PhMe. Benzoyl chloride (0.52 mL, 4.5 mmol) was added to the residue in pyridine (5 mL), and the mixture stirred (1 h). Methanol (2 mL) was added and the mixture concentrated. Standard workup (CH_2Cl_2) and flash chromatography (EtOAc/petrol, 2 : 8) gave the tribenzoate **42** as a colourless oil (428 mg, 78%), $[\alpha]_D$ +28.6°. δ_H (300 MHz) 2.05 (s, OCOCH$_3$), 3.52 (s, OCH$_3$), 4.30 (dd, $J_{5,6}$ 6.0, $J_{6,6}$ 11.3, H6), 4.38 (dd, $J_{5,6}$ 6.8, H6), 4.48 (ddd, $J_{4,5}$ 1.2, H5), 5.09 (d, $J_{1,2}$ 0.9, H1), 5.49 (ddd, $J_{2,4}$ 1.4, $J_{3,4}$ 4.0, H4), 5.76 (t, $J_{2,3}$ 4.0, H3), 5.83 (ddd, H2), 7.17–8.06 (15H, m, Ph). δ_C (75.5 MHz) 20.7 (OCO*C*H$_3$), 55.4 (OCH$_3$), 62.5 (C6), 66.2, 66.7, 66.8, 68.3 (C2,3,4,5), 99.4 (C1), 128.2–133.2 (Ph), 165.1, 165.9, 166.1, 170.5 (C=O). *m/z* (FAB) 549.1778; $[M + H]^+$ requires 549.1761.

Methyl 2,3,4-Tri-O-*benzoyl-6*-O-*(4-methylphenylsulfonyl)-α-D-taloside* ***43***

The tribenzoate **42** (329 mg, 0.600 mmol) was dissolved in HCl/MeOH (10 mL, 1 M), and the solution kept (14 h). The solvent was removed and the residue co-evaporated with PhMe. Tosyl chloride (172 mg, 0.900 mmol) was added to the residue in pyridine (5 mL), and the mixture heated at 50°C (1 h). Methanol (1 mL) was added and

* The spectrum was obtained at 233 K and two sets of resonances were observed, assigned to two conformers, a and b. The ^{1}H and ^{13}C resonances for each conformer were assigned using COSY, HSQC, and HMBC two-dimensional spectra.

† The ^{1}H and ^{13}C NMR spectra [300 MHz, (CD$_3$)$_2$SO] were uninterpretable at 293 K.

the mixture concentrated. Standard workup (CH_2Cl_2) and flash chromatography (EtOAc/petrol, 2 : 8) gave the tosylate **43** as a colourless oil (293 mg, 74%), $[\alpha]_D$ +9.1°. δ_H (300 MHz) 2.28 (s, ArCH_3), 3.48 (s, OCH_3), 4.19 (dd, $J_{5,6}$ 5.8, $J_{6,6}$ 10.1, H6), 4.36 (dd, $J_{5,6}$ 6.9, H6), 4.51 (ddd, $J_{4,5}$ 1.0, H5), 5.04 (d, $J_{1,2}$ 0.8, H1), 5.46 (dd, $J_{3,4}$ 3.8, H4), 5.72 (t, $J_{2,3}$ 3.8, H3), 5.76 (dd, H2), 7.14–8.09 (19H, m, Ar). δ_C (75.5 MHz) 21.5 (ArCH_3), 55.5 (OCH_3), 66.0, 66.2, 66.6, 68.7 (C2,3,4,5), 67.3 (C6), 99.3 (C1), 127.8–144.9 (Ar), 164.8, 165.5, 165.9 (3C, C=O). *m/z* (FAB) 661.1762; $[M + H]^+$ requires 661.1744.

1-O-*Acetyl-2,3,4-tri*-O-*benzoyl-6*-O-*(4-methylphenylsulfonyl)-α-*D*-talose* ***44***

Concentrated H_2SO_4 (0.1 mL) in Ac_2O (2 mL) was added dropwise to the tosylate **43** (264 mg) in Ac_2O (2 mL) at 0°C, and the solution stirred (30 min). The solution was poured onto ice. Standard workup (CH_2Cl_2) gave the acetate **44** as a colourless oil (243 mg, 88%), $[\alpha]_D$ +18.0°. δ_H (300 MHz) 2.24 (s, $OCOCH_3$), 2.26 (s, ArCH_3), 4.17 (dd, $J_{5,6}$ 6.9, $J_{6,6}$ 10.6, H6), 4.31 (dd, $J_{5,6}$ 6.3, H6), 4.64 (ddd, $J_{4,5}$ 1.6, H5), 5.48 (ddd, $J_{2,4}$ 0.9, $J_{3,4}$ 4.1, H4), 5.77 (t, $J_{2,3}$ 4.1, H3), 5.84 (ddd, $J_{1,2}$ 1.2, H2), 6.40 (d, H1), 7.12–7.92 (19H, m, Ar). δ_C (75.5 MHz) 20.9 ($OCOCH_3$), 21.6 (ArCH_3), 65.5, 65.7, 67.0, 68.8 (C2,3,4,5), 66.3 (C6), 91.3 (C1), 127.9–145.0 (Ar), 165.0, 165.3, 165.6, 168.0 (4C, C=O). *m/z* (FAB) 629.1452; $[M - OAc]^+$ requires 629.1476.

1-O-*Acetyl-6*-S-*acetyl-2,3,4-tri*-O-*benzoyl-6-thio-α-*D*-talose* ***45***

Potassium thioacetate (51 mg, 0.45 mmol) was added to the tosylate **44** (207 mg, 0.300 mmol) in DMF (2 mL), and the mixture stirred overnight. Concentration of the mixture and standard workup (EtOAc) followed by flash chromatography (EtOAc/petrol, 1 : 3) gave the thioacetate **45** as a pale yellow oil (165 mg, 93%), $[\alpha]_D$ +13.8°. δ_H (300 MHz) 2.22 (s, $OCOCH_3$), 2.32 (s, $SCOCH_3$), 3.22 (2H, m, H6), 4.37 (dt, $J_{4,5}$ 1.3, $J_{5,6}$ 7.3, H5), 5.50 (ddd, $J_{2,4}$ 0.8, $J_{3,4}$ 4.1, H4), 5.77 (t, $J_{2,3}$ 4.1, H3), 5.88 (ddd, $J_{1,2}$ 1.4, H2), 6.43 (d, H1), 7.16–8.08 (15H, m, Ph). δ_C (75.5 MHz) 20.8 ($OCOCH_3$), 29.0 (C6), 30.4 ($SCOCH_3$), 66.2, 66.9, 70.3 (C2,3,4,5), 91.6 (C1), 128.2–133.3 (Ph), 165.1, 165.8, 168.1 (C=O), 194.7 (SC=O). *m/z* (FAB) 533.1272; $[M - OAc]^+$ requires 533.1265.

6-S-*Acetyl-2,3,4-tri*-O-*benzoyl-1*-S-*phenylsulfonyl-1,6-dithio-β-*D*-talose* ***46***

Treatment of the acetate **45** (148 mg, 0.250 mmol) according to procedure A (refluxed for 30 min, flash chromatography with EtOAc/petrol, 1 : 3) gave the benzenethiosulfonate **46** as a colourless oil (143 mg, 81%), $[\alpha]_D$ +52.0°. ν_{max} (film)/cm^{-1} 1731 (C=O), 1702 (SC=O), 1329, 1149 (S–SO_2). δ_H (300 MHz) 2.23 (s, $SCOCH_3$), 2.64 (dd, $J_{5,6}$ 6.2, $J_{6,6}$ 13.8, H6), 3.13 (dd, $J_{5,6}$ 7.9, H6), 4.20 (dd, H5), 5.36 (t, $J_{2,3}$ 3.8, $J_{3,4}$ 3.8, H3), 5.61 (d, H4), 5.76 (d, H2), 6.35 (s, H1), 7.13–8.06 (20H, m, Ph). δ_C (75.5 MHz) 28.0 (C6), 30.3 ($SCOCH_3$), 66.3, 66.9, 68.7, 71.2 (C2,3,4,5), 88.2 (C1), 127.2–145.4 (Ph), 164.8, 165.5, 165.6 (3C, C=O), 193.8 (SC=O). *m/z* (FAB) 707.1081; $[M + H]^+$ requires 707.1079.

*(1*S*,5*S*,6*R*,7*S*,8*S*)-6,7,8-Tribenzoyloxy-9-oxa-2,3-dithiabicyclo[3.3.1]nonane* ***47***

Treatment of the benzenethiosulfonate **46** (71 mg, 0.10 mmol) according to procedure B (flash chromatography with EtOAc/petrol, 1 : 4) gave the disulfide **47** as a colourless glass (27 mg, 51%), $[\alpha]_D$ −195°. δ_H (600 MHz) 2.82 (dd, $J_{4,4}$ 13.6, $J_{4,5}$ 11.1, H4), 3.54 (d, H4), 5.51 (d, H5), 5.70–5.72 (m, H7,H8), 5.98 (s, H1), 6.13 (s, H6), 7.18–8.10 (15H, m, Ph). δ_C (150.9 MHz) 33.4 (C4), 65.5 (C6), 67.7 (C7), 68.7 (C5), 69.0 (C8), 94.7 (C1), 128.5–133.6 (Ph), 165.0, 165.9 (C=O). *m/z* (FAB) 523.0857; $[M + H]^+$ requires 523.0885.

2,3,4-Tri-O-*acetyl-1*-S-*methylsulfonyl-6*-O-*(4-methylphenylsulfonyl)-1-thio-β-*D*-glucose* ***50***

Treatment of the tetraacetate **7**[31] (502 mg, 1.00 mmol) according to procedure A (refluxed for 5 h, flash chromatography with EtOAc/petrol, 2 : 3) gave the methanethiosulfonate **50** as fine, colourless needles (427 mg, 77%), mp 172–173.5°C (EtOAc/petrol), $[\alpha]_D$ −2.5° (Found: C 43.3, H 4.7. $C_{20}H_{26}O_{12}S_3$ requires C 43.0, H 4.8%). ν_{max} (film)/cm^{-1} 1760 (C=O), 1331, 1141 (S–SO_2). δ_H (300 MHz) 1.99, 2.04 (9H, 2s, $OCOCH_3$), 2.46 (s, ArCH_3), 3.36 (s, SSO_2CH_3), 3.84 (ddd, $J_{4,5}$ 10.2, $J_{5,6}$ 2.8, $J_{5,6}$ 6.5, H5), 4.07 (dd, $J_{6,6}$ 11.3, H6), 4.14 (dd, H6), 4.91 (dd, $J_{3,4}$ 9.3, H4), 4.99 (dd, $J_{1,2}$ 10.4, $J_{2,3}$ 9.2, H2), 5.22 (d, H1), 5.26 (dd, H3), 7.37, 7.76 (AA′BB′, Ar). δ_C (75.5 MHz) 20.4, 21.7 ($OCOCH_3$), 21.7 (ArCH_3), 52.9 (SSO_2CH_3), 67.2 (C6), 67.9, 68.3, 72.9, 75.9 (C2,3,4,5), 86.4 (C1), 127.9, 130.0, 132.3, 145.5 (Ar), 169.31, 169.34, 169.7 (3C, C=O). *m/z* (FAB) 555.0654; $[M + H]^+$ requires 555.0665.

2,3,4-Tri-O-*acetyl-1,6-dideoxy-1,6-epithio-β-*D*-glucose*[§] ***51***

Sodium borohydride (18 mg, 0.50 mmol) was added to grey Se (36 mg, 0.45 mmol) in EtOH (2 mL) at 0°C, and the mixture stirred (15 min). The tosylate **50** (166 mg, 0.300 mmol) in DMF (5 mL) was added dropwise, and the mixture stirred (45 min). The mixture was concentrated and standard workup (EtOAc) followed by flash chromatography (EtOAc/petrol, 3 : 7) gave the epithio compound **51** as colourless plates (72 mg, 79%), mp 79.5–81.0°C (EtOH; lit.[4] 79–81°C), $[\alpha]_D$ −54.2° (lit.[4] −51.6°). The ^{1}H NMR spectrum and HRMS data for this compound agreed with those reported.[4]

2,3,4-Tri-O-*acetyl-1,6-dideoxy-1,6-episeleno-β-*D*-glucose*[¶] ***52***

30% Hydrogen bromide in AcOH (1.8 mL, 10 mmol) was added to the tetraacetate **7** (1.00 g, 2.00 mmol) in CH_2Cl_2 (5 mL), and the solution kept (45 min). The solution was poured onto ice. Standard workup (CH_2Cl_2) presumably gave the bromide, which was used without purification. Sodium hydride (398 mg, 10.0 mmol) was added to grey Se (790 mg, 10.0 mmol) in DMF (10 mL), and the mixture heated at 70°C (2 h). The bromide in DMF (15 mL) was added dropwise to the deep red solution and the mixture stirred (room temp., 2 h). The solvent was removed and the residue filtered through Celite (CH_2Cl_2). Concentration of the eluent and flash chromatography (EtOAc/petrol, 1 : 3) gave the episeleno compound **52** as a pale yellow solid (471 mg, 67%), mp 73.5–74.5°C (MeOH; lit.[4] 74–75°C), $[\alpha]_D$ −76.9° (lit.[4] −74.5°). The ^{1}H NMR spectrum and HRMS data for this compound agreed with those reported.[4]

2,3,4-Tri-O-*acetyl-1,5-anhydro-6*-O-*(4-methylphenylsulfonyl)-*D*-arabino-hex-1-enitol* ***54***

30% Hydrogen bromide in AcOH (0.9 mL, 5 mmol) was added to the tetraacetate **7** (502 mg, 1.00 mmol) in CH_2Cl_2 (5 mL), and the solution kept (45 min). The solution was poured onto ice. Standard workup (CH_2Cl_2) presumably gave the bromide, which was used without purification. Sodium hydride (88 mg, 2.2 mmol) was added to Te (255 mg, 2.00 mmol) in DMF (5 mL), and the mixture heated at 70°C (4 h). The bromide in DMF (15 mL) was added dropwise to the deep purple solution and the mixture stirred (room temp., 1 h). The mixture was concentrated and standard workup (CH_2Cl_2) followed by flash chromatography (EtOAc/petrol, 3 : 7) gave the alkene **54** as a colourless oil (320 mg, 72%), $[\alpha]_D$ +10.6°. δ_H (300 MHz) 2.01, 2.04, 2.06 (9H, 3s, $OCOCH_3$), 2.43 (s, ArCH_3), 4.17–4.37 (3H, m, H5,6), 5.14 (dd, $J_{3,4}$ 3.9, $J_{4,5}$ 4.1, H4), 5.47 (d, H3), 6.48 (s, H1), 7.34, 7.77 (AA′BB′, Ar). δ_C (75.5 MHz) 20.4, 20.57, 20.60 (3C, $OCOCH_3$), 21.6 (ArCH_3), 65.6, 67.0, 73.2 (C3,4,5), 65.6 (C6), 127.2 (C2), 127.9, 129.8, 132.3, 145.2 (Ar), 138.8 (C1), 169.2, 169.4, 169.9 (3C, C=O). *m/z* (FAB) 443.1017; $[M + H]^+$ requires 443.1012.

*(1*S*,2*S*,5*S*,6*S*,7*S*,8*R*)-6,7,8-Triacetoxy-9-oxa-2,3-dithiabicyclo[3.3.1]nonane 2-oxide* ***56***

3-Chloroperbenzoic acid (39 mg, 0.16 mmol) was added to the disulfide **10** (50 mg, 0.15 mmol) in dry CH_2Cl_2 (1 mL) at 0°C and the mixture stirred (room temp., 45 min). Standard workup (CH_2Cl_2) and flash chromatography (EtOAc/petrol, 2 : 3) gave the thiosulfinate **56** as

§ [1*S*,4*S*,5*S*,6*S*,7*R*]-5,6,7-Triacetoxy-8-oxa-2-thiabicyclo[3.2.1]octane.

¶ [1*S*,4*S*,5*S*,6*S*,7*R*]-5,6,7-Triacetoxy-8-oxa-2-selenabicyclo[3.2.1]octane.

a colourless oil (44 mg, 83%), $[\alpha]_D$ +14.6°. ν_{max} (film)/cm^{-1} 1755 (C=O), 1107 (S=O). δ_H (500 MHz) 2.09, 2.10 (9H, 3s, $OCOCH_3$), 2.87 (ddd, $J_{1,4}$ 1.0, $J_{4,4}$ 14.3, $J_{4,5}$ 2.6, H4), 3.94 (dd, $J_{4,5}$ 3.0, H4), 4.34 (dt, $J_{5,6}$ 3.0, H5), 4.84 (dd, $J_{1,8}$ 3.6, H1), 5.11 (dd, $J_{7,8}$ 10.1, H8), 5.25 (dd, $J_{6,7}$ 9.8, H6), 5.75 (dd, H7). δ_C (125.8 MHz) 20.5, 20.6, 20.7 (3C, $OCOCH_3$), 21.6 (C4), 69.0, 69.3, 73.0, 74.5 (C5,6,7,8), 91.4 (C1), 169.6, 170.0, 170.8 (3C, C=O). *m/z* (FAB) 353.0375; $[M+H]^+$ requires 353.0365.

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