Applications of Cyclic Sulfates of *vic*-Diols: Synthesis of Episulfides, Olefins, and Thio Sugars

Francisco G. Calvo-Flores, Pilar García-Mendoza, Fernando Hernández-Mateo, Joaquín Isac-García, and Francisco Santoyo-González*

Instituto de Biotecnología, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

Received November 4, 1996[⊗]

A new efficient and expeditious one-pot synthesis of thiiranes and olefins from cyclic sulfates of *vic*-diols is described. Opening of cyclic sulfates with potassium thioacetate or potassium thiocyanate followed by treatment with sodium methoxide led to episulfides. Olefins were obtained when potassium selenocyanate was used as nucleophile, and the obtained monoesters were treated with sodium borohydride. This method was applied to acyclic polyols derived from chiral glycerine, 1,2-isopropylidenehexofuranoses with different subtituents at C-3, and dimethyl acetals derived from pentoses and hexoses. The methodology is highly versatile, and its applicability has been demonstrated by the synthesis of different 4- and 5-thiosugars by opening of the thiirane ring with sodium acetate or lithium aluminum hydride. Reduction with lithium aluminum hydride of the thiocyanate sulfate potassium salt obtained by the opening of cyclic sulfate with KSCN allowed the direct synthesis of 5-deoxy-4-thio- and 6-deoxy-5-thiosugars. Cyclic thiosugars with the sulfur atom in the ring are obtained by acidic hydrolysis of the 5-thiol derivatives of 1,2-*O*-isopropylidene-hexofuranoses and 4-thiopentose dimethyl acetals. Using this method, an efficient synthesis of 5-thio-L-fucose as well as the synthesis of 2,5-dideoxy-4-thiofuranose is described.

Introduction

vic-Diols have been widely used as precursors for the synthesis of episulfides and olefins, which are very versatile functions in organic synthesis. The synthesis of episulfides[1] generally involves the previous transformation of the diol into the corresponding epoxide and opening with thiocyanate ions or with thiourea,[2−12] which are the most common reagents used for this transformation. A recently described method for the synthesis of thiiranes involves a previous transformation of allylic alcohols into cyclic xanthates.[13−15] Olefins can be obtained from *vic*-diols by a variety of different methods.[16,17] For example, direct conversion of *vic*-diols into alkenes is possible by treatment with tungsten reagents,[18] titanium metals,[19,20] $Me_3SiCl-NaI$,[21] Ph_3P−imidazole−I_2,[22] and PBr_3−CuBr−ether followed by zinc powder.[23] *vic*-Diols can also be deoxygenated indirectly by their previous conversion into sulfonate ester derivatives,[24−28] bisdithiocarbonates,[29] cyclic thionocarbonates,[30−43] oxiranes,[44−49] episulfides,[14,50−54] cyclic orthoformiates,[32,55]

* To whom correspondence should be addressed. Tel.: +34-58-243187. Fax: +34-58-243320. E-mail: fsantoyo@goliat.ugr.es.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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S0022-3263(96)02066-X CCC: $14.00

and cyclic phosphates, phosphoroamidates,[56−58] and sulfates.[59,60]

In spite of the variety of available methods for the synthesis of episulfides and olefins from *vic*-diols, mentioned above, the use of the cyclic sulfates for the preparation of these functions has not been explored in depth. Cyclic sulfites and cyclic sulfates have been known for a long time, and the use of these compounds has been recently reviewed.[61−63] Nucleophilic reactions using cyclic sulfates as substrates are perhaps the most commonly studied reactions, and the high reactivity of these compounds as nucleophile acceptors is well known. Analogous to epoxides, cyclic sulfates can be opened by attack of a variety of nucleophiles at either carbon center. However, unlike oxiranes, the cyclic sulfate opening involves the generation of a sulfate monoester, allowing further transformations. The generated sulfate is itself a leaving group and can be subsequently displaced by a nucleophile, giving rise to an overall substitution of both OH groups. Since a SO_4^{2-} dianion is a much worse leaving group than a $ROSO_3^-$ anion, the second displacement would be effected by the nucleophile incorporated to the molecule in an intramolecular fashion. These double displacement scenarios suggest a variety of useful transformations than can make the chemistry of cyclic sulfates more versatile than that of epoxides. To the best of our knowledge, this methodology has only been applied to the synthesis of cyclopropanes by reaction of cyclic sulfates with malonate anion[64] and methyl benzylideneglicinate.[65−67] Taking into account all of these facts and considerations, we have explored the use of cyclic sulfates as precursors of episulfides and olefins. Preliminary studies have shown[68] that the treatment of cyclic sulfates with potassium thioacetate followed by reaction with sodium methoxide allowed the one-pot transformation into episulfides. Similarly, reaction with potassium selenocyanate followed by treatment with sodium borohydride led to olefins also in one pot (see Figure 1). Simultaneously to our studies, cyclic sulfates of *vic*-diols have also been transformed into olefins by treatment with phosphine[69] or by telluride ion generated *in situ* by reduction of elemental Te.[70]

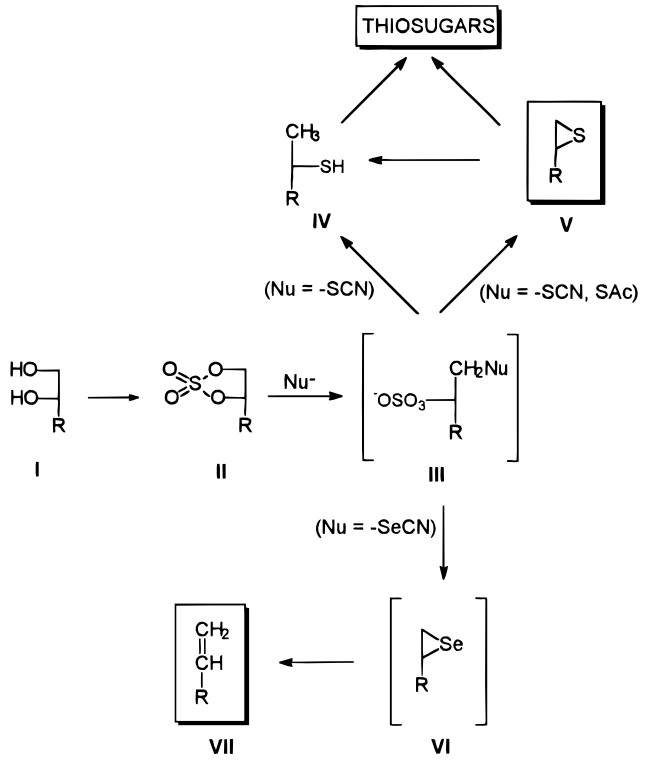

Figure 1.

On the other hand, in both chemical and biochemical conversion of carbohydrates, cleavage and formation of carbon−oxygen bonds at the anomeric center are the most important reactions wherein the ring oxygen in the furanose or pyranose structure plays a decisive role. It is for this reason that thio sugars (sulfur in the ring of the sugar) as sugar analogs have attracted attention.[71] Most syntheses of thio sugars such as 4-thiofuranoses and 5-thiopyranoses are based on the introduction of a thiol group at the 4- or 5-position, respectively. A classical approach for this functionalization, involving episulfide opening by nucleophiles, has been used to synthesize 5-thio-D-glucopyranose,[72−75] 5-thio-D-mannopyranose,[76] 5-thio-D-galactopyranose,[77] 2-acetamido-2-deoxy-5-thio-D-glucopyranose (5-thio-*N*-acetyl-D-glucosamine),[78−80] 2-acetamido-2-deoxy-5-thio-α-D-man-

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nopyranose,[81] 5-thio-L-idopyranose,[82,83] 5-thio-L-fucose,[84] D- and L-2-deoxy-4-thioriboses,[15] and 4-thiofuranoses.[85] Nucleophilic replacement of a sulfonyloxy group by an RS^- group has been the common way for the introduction of sulfur into sugar molecules such as 5-thio-D-xylopyranose,[83,86,87] 5-thio-D-ribopyranose,[74] 5-thio-L-rhamnose,[88] 5-thio-L-fucose,[89] 4-thio-D-ribofuranose,[90,91] and 5-thio-D-arabinopyranose.[89] In addition to such classical approaches, new routes to sulfur ring thio sugars based on intramolecular cyclization of dithioacetals,[92−96] conversion of pyranosides into 5-thiopyranoside *via* monothioacetals,[97,98] modification of optically pure Diels−Alder aducts,[99] and enzymatic synthesis[100,101] have also been reported.

In this paper, we expand upon our preliminary results[68] and report on the versatility of cyclic sulfates as precursors of olefins, episulfides and thiols as well their uses in the synthesis of thio sugars (thiofuranoses and thiopyranoses) (see Figure 1).

Results and Discussion

The following *vic*-diols were selected for this study: Acyclic polyols derived from chiral glycerine (**1**) and D-mannitol (**35**) were chosen for their structural simplicity; 1,2-*O*-isopropylidenehexofuranoses with different subtituents at C-3 (**7a**,**c**−**f**) were chosen in order to carry out the synthesis of 5-thio sugars; and dimethyl acetals derived from pentoses (**13b**) and hexoses (**13a**) were chosen in order to carry out the synthesis of 5-thiopyranoses and 4-thiofuranoses. The cyclic sulfates (**3**, **9a**,**c**−**f**, **15a**,**b**, **36**) of these diols were easily obtained in high yields *via* the corresponding cyclic sulfites following the general procedure described by Gao and Sharpless.[64] In general, the diasteromeric mixtures of cyclic sulfites were not separated and were directly used in the oxidation reaction with $NaIO_4$−$RuCl_3{\cdot}3H_2O$. All of these sulfates are stable compounds at low temperature (−5 °C) for periods of 2 months. In addition to these cyclic sulfates, the commercial cyclic sulfate **19** derived from 1,2:5,6-di-*O*-isopropylidene-D-mannitol was also used (Schemes 1 and 2).

The synthesis of episulfides was carried out by nucleophilic ring opening of the cyclic sulfates with potassium thioacetate and potassium thiocyanate. As expected, in terminal cyclic sulfates of type II the nucleophilic attack happened in a regiospecific fashion to the less hindered primary position leading to β-acetylthio or β-thiocyanate sulfates type III (Figure 1). We performed the reactions of cyclic sulfates **3**, **9a**,**c**−**f**, **15a**,**b** with potassium thioacetate or potassium thiocyanate in dry acetone at room temperature, and the corresponding salts (**4**, **5**, **10a**,**c**−**f**, **11a**,**c**−**f**, **16a**,**b**, **17a**) were easily isolated in high yields (72−100%) as stable solids that can be stored under vacuum for several months (Scheme 1). These salts were purified in order to carry out the complete characterization of these compounds, but for preparative purposes they were directly used without purification. Treatment of these potassium salts with NaOMe−MeOH generated the corresponding sodium thiolates that produced the intramolecular displacement of the β-sulfate groups, affording the corresponding episulfides (**6**, **12b**−**f**, **18a**,**b**) in good to high yields (63−95%). The nucleophilic displacement occurred *via* an inversion of the configuration at the β-chiral atom (Scheme 1).

The opening of the nonterminal cyclic sulfate **19** could not be accomplished with potassium thioacetate even when the experimental conditions (temperature and solvent) were changed. However, when sodium sulfide was used as nucleophile in boiling methanol, the desired episulfide **20** was directly obtained in 42% yield (Scheme 2). Considering this result, we attempted the direct synthesis of episulfides from terminal cyclic sulfates using sodium sulfide, but reaction of compounds **9a**,**d** with this reagent led to the sulfides **21** and **22**, respectively, in good yields (Scheme 2). The different behavior of compounds **19** and **9a**,**d** showed that when the cyclic sulfate was sterically hindered, as in the nonterminal cyclic sulfate **19**, the intramolecular attack was favored. Nonetheless, in the less hindered terminal cyclic sulfate, such as **9a**,**d**, the intermolecular displacement was favored and the corresponding dimeric sulfides are exclusively obtained. As a result, in our laboratory we are investigating the exploitation of this method for the synthesis of sulfides.

The method described above constitutes a short, easy, and efficient method for the synthesis of episulfides from *vic*-diols. Access to episulfides can be had by using either the potassium thioacetate or thiocyanate salts, but yields are slightly higher when the former salt is employed. It should also be mentioned that similar compounds to **6**, namely, (2*R*)- and (2*S*)-1-*O*-(*tert*-butyldiphenylsilyl)-2,3-epithiopropanol, have recently been synthesized starting from (*R*)- and (*S*)-glycidol by reaction with thiourea and employed in a high-yielding synthesis of 2′,3′-dideoxy- and 2′,3′-didehydro-2′,3′-dideoxy-4′-thionucleosides, which showed a marked anti-HBV and anti-HIV activity.[102]

When we observed the good results obtained on the synthesis of episulfides, we considered the use of this

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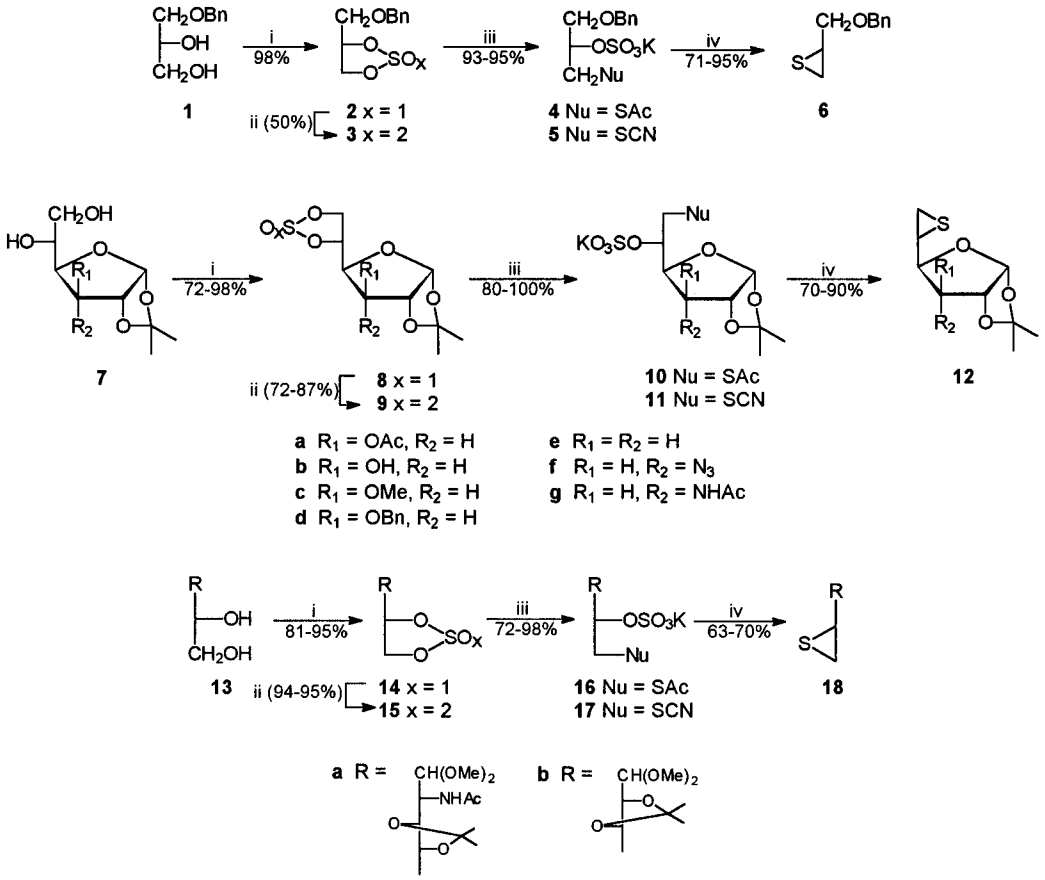
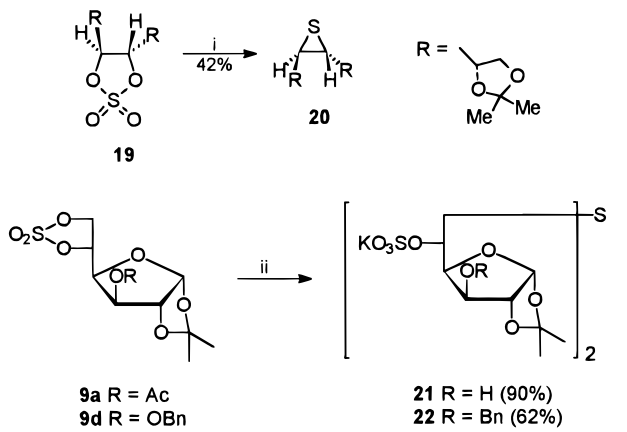
Scheme 1[a]



[a] Key: (i) $SOCl_2$, Et_3N, CH_2Cl_2; (ii) $RuCl_3 \cdot 3H_2O$, $NaIO_4$, MeCN, CCl_4, H_2O; (iii) KSAc or KSCN, acetone; (iv) NaOMe, MeOH.

Scheme 2[a]



[a] Key: (i) $Na_2S \cdot 9H_2O$, methanol, reflux; (ii) $Na_2S \cdot 9H_2O$, acetone–H_2O, rt.

methodology for the preparation of thietanes from 1,3-diols. With this objective in mind, we performed the synthesis of the cyclic sulfates **24** and **28** (Scheme 3). Both compounds were stable crystalline solids that were obtained from diols **23** and **27**, as described above, in 48% and 58% overall yields, respectively. Nucleophilic ring opening of the cyclic sulfate with potassium thioacetate gave the γ-acetylthio sulfates **25** (86% yield) and **29** (94% yield). However, neither of these two compounds could be transformed into the desired thietanes **26** and **30** when treated with NaOMe–MeOH (Scheme 3). In this case, the formation of highly polar compounds was observed, but the compounds were not further investigated.

Given the synthesis of episulfides, one would expect that seliranes could be obtained by treatment of cyclic sulfates with potassium selenocyanate. However, it is known that seliranes are unstable and easily expel the selenium atom giving alkenes;[103] thus, cyclic sulfates could be converted to olefins in one pot. This hypothesis was confirmed when we performed the reaction of **9a**,**c**–**f** and **15a** with potassium selenocyanate (Scheme 4). The corresponding seleno derivatives **31a**,**c**–**f** and **33** were isolated as solids in high yields. These compounds, unlike the thioacetate and thiocyanate salts, are unstable and slowly decomposed at rt. We isolated these salts for their characterization, but for preparative purposes they were used without purification in the next step. Reaction of the furanose selenocyanate salts **31a**,**c**–**f** with sodium borohydride in methanol at room temperature gave the olefins **32b**–**f** in 50–94% yields. Similar treatment of the acyclic dimethyl acetal **33** led to the olefin **34** in 59% yield. These compounds could be used as precursors of 5-hexenals, which have been employed in radical cyclization reactions for the synthesis of cyclopentanols.[104,105] As in **34**, the diolefin **37** was synthesized in moderate yield (45%) from the cyclic disulfate **36** by reaction of **36** with potassium selenocyanate followed by treatment with sodium borohydride.

Given that by following the methodology described above L-sugar episulfides are obtained from D-sugars, we could apply such methodology as an expeditious and

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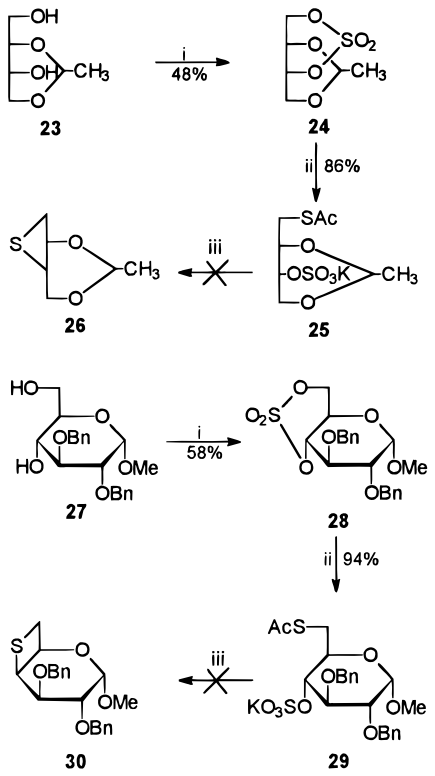
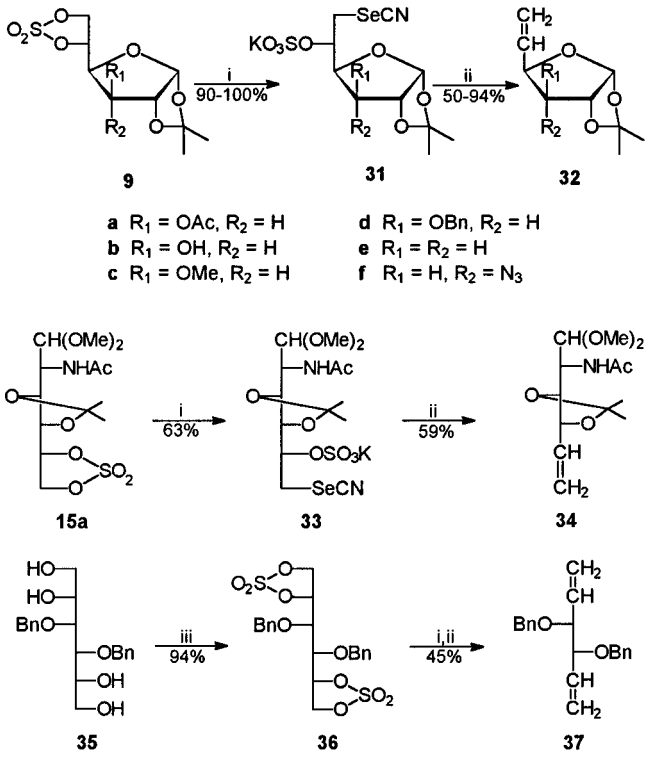
Scheme 3[a]



[a] Key: (i) (a) $SOCl_2$, Et_3N, CH_2Cl_2; (b) $RuCl_3 \cdot 3H_2O$, $NaIO_4$, MeCN, CCl_4, H_2O; (ii) KSAc, acetone; (iii) NaOMe, MeOH.

Scheme 4[a]



[a] Key: (i) KSeCN, acetone, rt; (ii) $NaBH_4$, MeOH; (iii) (a) $SOCl_2$, Et_3N, CH_2Cl_2; (b) $RuCl_3 \cdot 3H_2O$, $NaIO_4$, MeCN, CCl_4, H_2O.

inexpensive strategy for the synthesis of L-thio sugars. The nucleophilic ring opening of the episulfide **6** with sodium acetate in acetic acid−acetic anhydride at 120 °C under an argon atmosphere allowed the isolation of the acetylated thiol derivatives **38** in moderate yield (37%) together with the elimination product allyl benzyl ether. Similar reaction with the episulfide furanose derivatives **12a**,**c**,**d** gave exclusively the 5-thio-L-idofuranoses derivatives **39a**,**c**,**d** in good yields (61−95%). When the starting material was the thiirane derived from L-idosamine **18a**, the corresponding 5-thio sugar **42a** was isolated as the major product (60% yield) together with the olefin **34** as the minor compound (15%) (Scheme 5). It should be noted that formation of olefins from episulfides is not an unusual process, as thiirane thermal desulfurization has previously been described.[106−112] 6-Deoxy-5-thio-L-sugars **40b**,**d** and **43a** and 5-deoxy-4-thio-L-sugars **43b** were obtained by reduction of the corresponding episulfides **12b**,**d**, **18a**, and **18b**, respectively (Scheme 5). Lithium aluminum hydride was employed as the reducing reagent, and the reactions were performed at room temperature using a 4-fold molar excess of this reagent relative to the thiirane, thus allowing the isolation of the thiol derivatives in good to high yields (66−98%). These results are in sharp contrast with those that were recently described by Kuszmann *et al.*[113] on the synthesis of 6-deoxy-5-thio-D-glucose using 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-D-glucofuranose and its 3-*O*-allyl derivative as starting materials. Under similar reaction conditions, these authors reported the isolation of 6-deoxy-1,2-*O*-isopropylidene-5-thio-α-D-glucofuranose in low yields along with the formation of di- and trimers.

In spite of the satisfactory results obtained in the synthesis of L-thio sugars by means of the sequence of reactions described above (formation of cyclic sulfate−ring opening with potassium thiocyanate or thioacetate−formation of the episulfide−reduction), we thought that the number of steps could be reduced if the potassium thiocyanate salts of type III (Nu = SCN) (Figure 1) reacted directly with lithium aluminum hydride. We anticipated that the reduction of the thiocyanate function would afford the Li-thiolate salt and that this compound would undergo the intramolecular nucleophilic displacement of the β-sulfate group, yielding the corresponding episulfide. In addition, under the reducing conditions, the episulfide formed would be reduced and the thiol derivative of type IV would be obtained. As expected, treatment of **11a**,**c**,**d** and **17a** with $LiAlH_4$ (6 equiv) at rt afforded the thiol derivatives **40b**,**c**,**d** and **43a**, respectively, with yields in the range of 31−84%. Conventional acetylation of **40b**,**c**,**d** gave the corresponding acetylated derivatives **41a**,**c**,**d**, respectively (Scheme 5). When the reduction was performed on the thiocyanate potassium salt **11f**, simultaneous reduction of the azido group happened and the 3-amino-3,6-dideoxy-5-thio sugar **41g** was isolated as its N,S-diacetyl derivative after standard acetylation of the crude product (Scheme 5). This route may allow a short synthesis of 3-amino-3,6-dideoxy-5-thio- and 3-amino-2,3,6-trideoxy-5-thio-L-sugars, which are analogs to the important antibiotic components

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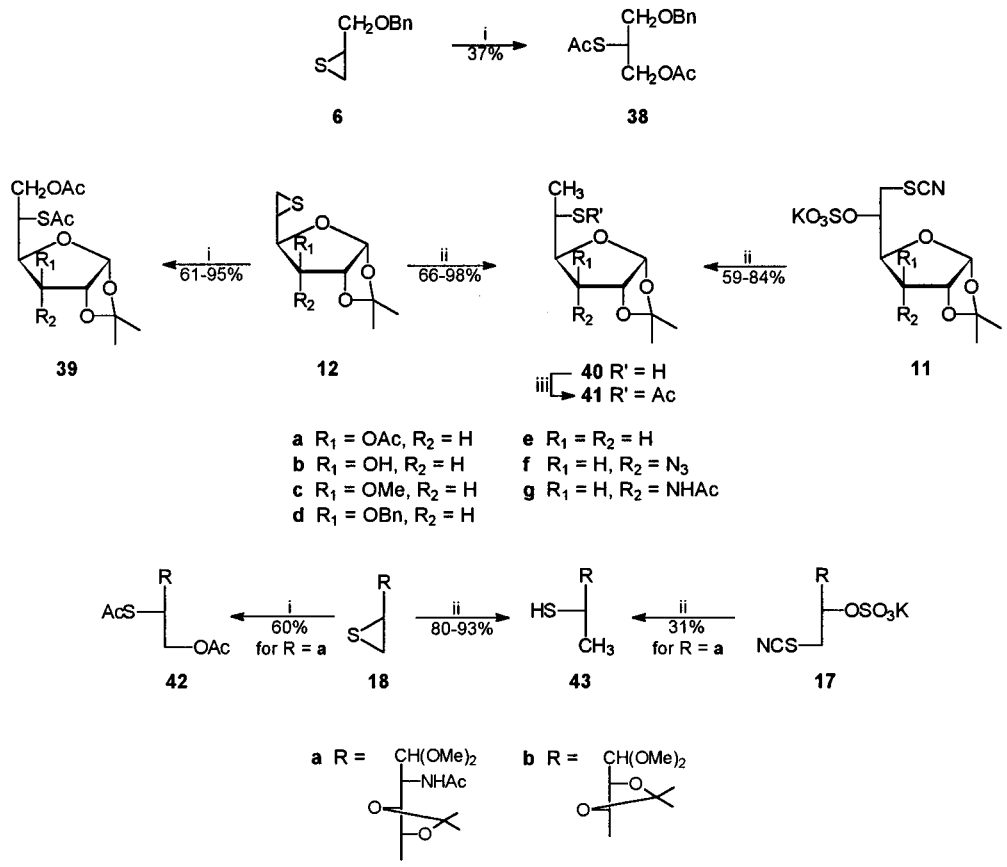
Scheme 5[a]



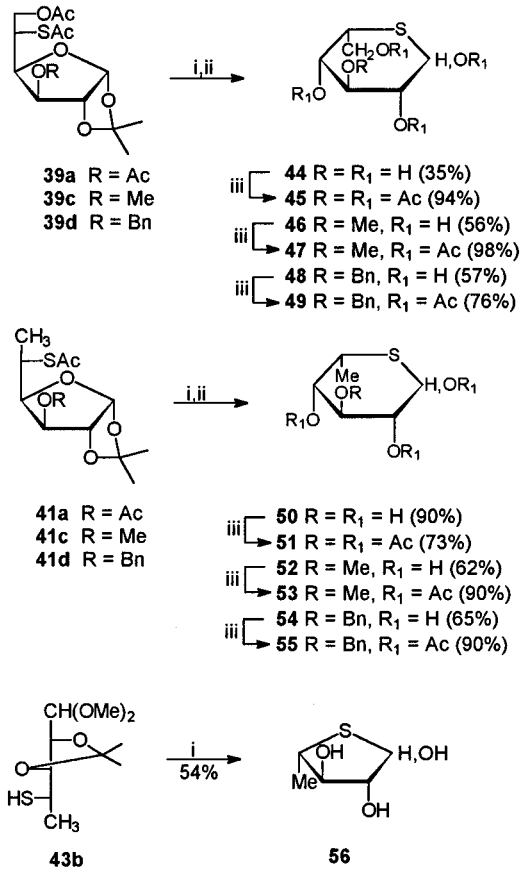
[a] Key: (i) Ac_2O, AcOH, NaOAc; (ii) $LiAlH_4$, THF; (iii) Ac_2O−Py.

3-amino-2,3,6-trideoxy-L-hexoses.[114] Implementation of this strategy with this purpose is currently under research in our laboratory.

The next step, the incorporation of the sulfur atom into the carbohydrate ring in order to obtain the thio sugars as thiohexopyranoses and thiopentofuranoses, was carried out by acid treatment of the thiol derivatives obtained in the thiirane opening by the nucleophilic acetate or hydride. We performed this transformation using only compounds **39a**,**c**,**d**, **41a**,**c**,**d**, and **43b**. Hydrolysis of the 1,2-*O*-isopropylidene group in **39a**,**c**,**d** and **41a**,**c**,**d** using aqueous acetic acid was followed by treatment with catalytic amounts of NaOMe−MeOH (Zemplén deacetylation). The 5-thio-L-idopyranoses **44**, **46**, **48**, **50**, **52**, and **54** were obtained as an α,β mixture of anomers in 35−90% yields. We transformed these compounds into the corresponding peracetylated derivatives **45**, **47 49**, **51**, **53**, and **55**, respectively, by standard acetylation. Compound **43b** was also submitted to hydrolysis with aqueous acetic acid, and the 5-deoxy-4-thio-α,β-L-arabinofuranose **56** was obtained in 54% yield (Scheme 6).

It should be noted that the spectroscopic ^1H NMR data for the 5-thio-L-idopyranose hydroxyl derivatives **44**, **46**, **48**, **50**, **52**, and **54** indicate that the preferred conformation for both α and β anomers is the $^4C_1$, as deduced from the $^3J_{1,2}$ coupling constant values that are in the range 7.1−8.3 Hz for the α-anomer and 2.5−3.4 Hz for the β-anomer. The same is observed for the β-anomer in the per-*O*-acetyl derivatives **45**, **47 49**, **51**, **53**, and **55**, which

Scheme 6[a]



[a] Key: (i) AcOH−H_2O; (ii) NaOMe, MeOH; (iii) Ac_2O−Py.

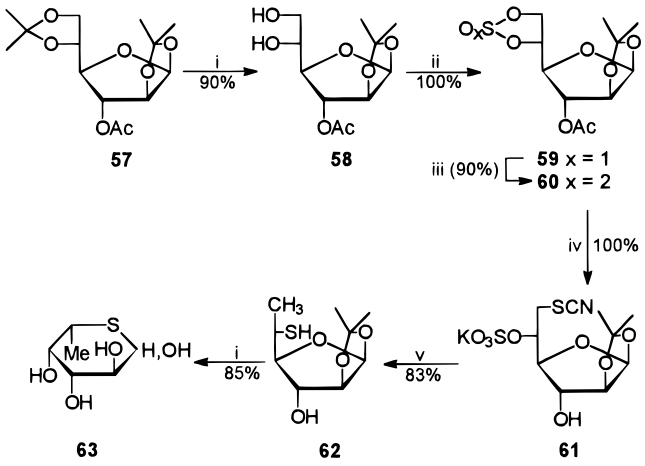
(114) Sztaricskai, F.; Pelyvás, I. F. In *Glycopeptide Antibiotics*; Nagarajan, R., Ed.; Marcel Dekker, Inc.: New York, 1994; pp 105−193.

showed $^3J_{1,2}$ values of 3.4−3.6 Hz. However, the α-anomer of these compounds suffers a puckering of the ring as deduced from the decrease of the $^3J_{1,2}$ coupling constant (5.5−7.2 Hz). These data are in agreement with the prediction reported by Lambert *et al.*[115] for 5-thio-D-glucose. Unambiguous assignment of the ^{13}C NMR signals was possible by 2D correlation experiments in compounds **44**, **47**−**51**, and **53**−**55**. In all cases, the resonances of C-1 are in the range 71.4−75.5 ppm, in accordance with the data reported by Lambert *et al.*[115] for 5-thio-D-glucose. However, a slight shielding of the α-anomer carbon-1 with respect to the *β*-anomer carbon-1 is observed in each pair of anomers. This is in contrast to the generally observed fact[116] that the chemical shift of the signals of an anomeric carbon bearing an equatorial substituent is at lower field (∼5 ppm) than that with an axial one. This behavior is also observed in the thiofuranoses **56** where the differences of the resonances are even smaller (78.5 ppm for C-1b and 78.0 ppm for C-1a).

Once the efficiency of the method described above for the synthesis of L-thio sugars was demonstrated, the strategy was applied in the synthesis of 5-thio-L-fucose and 2-deoxy-4-thiofuranoses, both important because of their biological significance. Hashimoto *et al.*[84] were the first authors to report the synthesis 5-thio-α-L-fucose and its specific and potent inhibitory activity against bovine α-L-fucosidases with K_i values in the millimolar range. These authors have later described other methods for the synthesis of 5-thio-α-L-fucose[89] and some fucopyranoside derivatives[117] as well as several 5-thio-α-L-fucopyranosyl disaccharides[118] and analogues of the blood group antigen H-type 2 and of Lewis X (Le^x).[119] We envisaged the synthesis of 5-thio-L-fucose using 1,2:5,6-di-*O*-isopropylidene-*β*-D-altrofuranose[120,121] **57** as starting material and following the sequence of reactions indicated in Scheme 7. All the reactions were high yielding (>83%), and an α,*β* anomeric mixture of 5-thio-L-fucose (**63**) was obtained in 57.0% overall yield from **57**. As expected, the α-anomer was the major component and the *β*-anomer was only detected in the mother liquors of crystallization. When compared with the method described by Hashimoto *et al.*,[84] which also employed **57** as the starting material, the use of the cyclic sulfate strategy allowed a considerable increase in the overall yield of the synthesis (57.0% *vs* 18.0%).

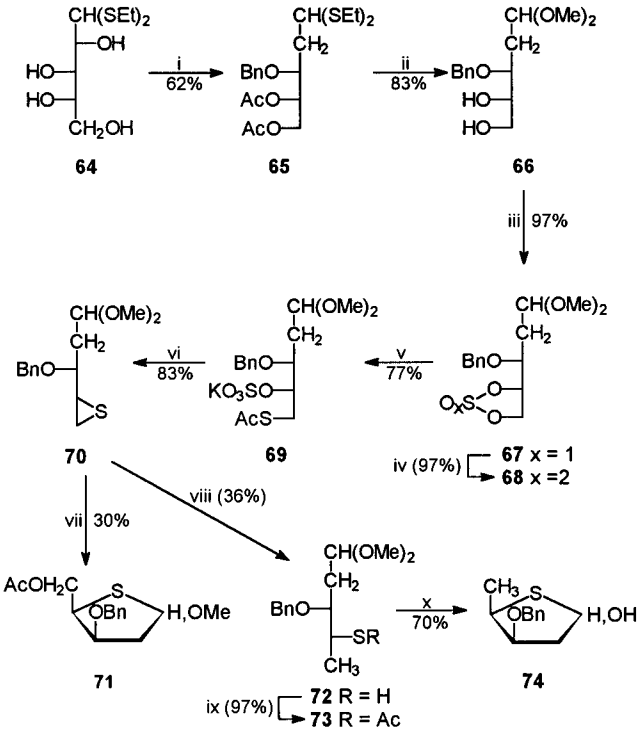
On the other hand, the synthesis of nucleosides in which the sugar moiety is modified by the replacement of furanose ring oxygen atom with a sulfur atom has attracted attention because an increase in the metabolic stability of these compounds toward phosphorylase enzymes is known to occur.[122] Consequently, 2′-deoxy-4′-thionucleosides could be especially advantageous to an antiviral strategy when incorporated into a DNA matrix.[123] Several routes for the synthesis of these thio sugars, with a special emphasis in the preparation of 2-deoxy-4-thioribose, have been published[96] using carbohydrate and nonsaccharide compounds as starting materials. Use of cyclic sulfates allows a new route for the synthesis of 2-deoxy-4-thiofuranosides as depicted in Scheme 8. 3-*O*-Benzyl-2-deoxyaldehydo-L-*erythro*-pentose dimethyl acetal (**66**) was chosen as the starting hydroxylated derivative as this compound is easily prepared from L-arabinose diethyl dithioacetal[124] accord-

Scheme 7[a]



[a] Key: (i) AcOH, H_2O; (ii) $SOCl_2$, Et_3N, CH_2Cl_2; (iii) $RuCl_3 \cdot 3H_2O$, $NaIO_4$, MeCN, CCl_4, H_2O; (iv) KSCN, acetone; (v) $LiAlH_4$, THF.

Scheme 8[a]



[a] Key: (i) (a) $Me_2C(OMe)_2$, acetone, P_2O_5; (b) K^{t}BuO, DMSO, THF; (c) $LiAlH_4$, THF; (d) BnBr, NaH, THF; (e) AcOH, H_2O; Ac_2O−Py; (ii) (a) NBS, MeOH; (b) NaOMe, MeOH; (iii) $SOCl_2$, Et_3N, CH_2Cl_2; (iv) $RuCl_3 \cdot 3H_2O$, $NaIO_4$, MeCN, CCl_4, H_2O; (v) KSAc, acetone, 77%; (vi) NaOMe, MeOH; (vii) Ac_2O, AcOH, NaOAc; (viii) $LiAlH_4$, THF, 36%; (ix) Ac_2O−Py; (x) AcOH, H_2O; NaOMe, MeOH; 70%.

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ing to the procedure developed by Wong and Gray.[125] Cyclic sulfate **68** was obtained in high yield (95.0%) following the general procedure described in this paper, but, unlike other cyclic sulfates, it decomposed not only during its column chromatographic purification but also when the crude product was left at rt for several hours. Therefore, compound **68** was used immediately after workup and transformed into the episulfide **70** *via* the potassium thioacetate salt **69** in 64.0% overall yield. When episulfide **70** was heated in acetic acid and acetic anhydride in the presence of sodium acetate methyl 2-deoxy-4-thiofuranoside **71** was isolated in low yield (30%). This direct transformation of episulfides into thiofuranoses occurred in accordance with previous observations described by Uenishi *et al.*[15] for similar 2-deoxy acetals of pentoses but was not being observed in acetal **18a**, which has an acetamido group at the C-2 position. 2,5-Dideoxy-4-thiofuranose **74** was obtained from episulfide **70** following the sequence of reactions described for the synthesis of thiopyranoses in 24% yield. Both 2-deoxythiosugars **71** and **74** were isolated as inseparable mixtures of α,β-anomers.

Conclusion

The results described in this paper demonstrate that *vic*-diols are easily transformed into thiiranes and olefins *via* cyclic sulfates in an expeditious form: *vic*-diol → cyclic sulfite → cyclic sulfate → acyclic sulfate potassium salt → thiirane or olefin. Both routes require four reactions but need only two steps as the purification of the cyclic sulfite and the acyclic potassium salts is not necessary. In addition, all the reactions occurred with good to high yields. The methodology is highly versatile, and its applicability has been demonstrated for the synthesis of thio sugars not only by conventional opening of the episulfide ring with sodium acetate but also by direct hydride reduction of the thiocyanate sulfate potassium salt. For example, among other thio sugars synthesized using this methodology we efficiently synthesized 5-thio-L-fucose.

Experimental Section[126]

Starting Materials. Compounds **1** and **19** were purchased from Sigma and Fluka Co, respectively. Compounds **7a**,**c**,**d** were prepared from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose in two steps by conventional acetylation or alkylation (methylation or benzylation) followed by selective hydrolysis of the 5,6-*O*-isopropylidene group. Compounds **7e**,**f** were obtained according to the procedures described by Just *et al.*[127] and by Baer *et al.*,[128] respectively. Compounds **13a**,**b** were obtained following the procedure described by Hasegawa *et al.*[129] Compound **57** was obtained from methyl α-D-altropyranose[120,130] following the method described by Fuller *et al.*[121]

3-*O*-Benzyl-L-*erythro*-*aldehydo*-pentose Dimethyl Acetal (66). L-Arabinose was converted to L-arabinose diethyl dithioacetal (**64**) (90%) using the method described by Zinner *et al.*[124] The reaction of this compound with acetone according with to the procedure described by van Es[131] gave 2,3:4,5-di-*O*-isopropylidene-L-arabinose diethyl dithioacetal (92%). Following the method of Wong and Gray,[125] this protected arabinose derivative was converted to 2-deoxy-4,5-*O*-isopropylidene-L-*erythro*-pen-1-enose diethyl dithioacetal that was isolated as a syrup (96% yield): $[\alpha]_D$ −6° (*c* 6.5, chloroform); IR (neat) 3411, 1683, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91 (d, 1 H, J = 7.9 Hz), 4.89 (m, 1 H), 4.16 (dt, 1 H, J = 6.7, 4.3 Hz), 3.97 (dd, 1 H, J = 8.2, 6.6 Hz), 3.87 (dd, 1 H, J = 8.3, 6.9 Hz), 2.92−2.65 (m, 4 H), 2.25 (d, 1 H, J = 2.9 Hz), 1.43, 1.35 (2 s, 6 H), 1.25, 1.23 (2 t, 6 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 135.7, 133.0, 109.5, 78.0, 69.7, 65.1, 27.6, 27.2, 26.5, 25.3, 15.1, 14.0; MS *m*/*z* 261 ($M^+ + 1 - H_2O$). This compound was treated with $LiAlH_4$ to give 2-deoxy-4,5-*O*-isopropylidene-L-*erythro*-pentose diethyl dithioacetal as a syrup (90% yield): $[\alpha]_D$ +8° (*c* 2, chloroform); IR (neat) 3450, 1258, 1215, 1156, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.09−3.91 (m, 5 H), 2.76−2.54 (m, 4 H), 2.00 (ddd, 1 H, J = 14.6, 9.2, 2.5 Hz), 1.86 (ddd, 1 H, J = 14.6, 9.4, 5.3 Hz), 1.42, 1.35 (2 s, 6 H), 1.27, 1.26 (2 t, 6 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 109.3, 78.4, 70.3, 65.6, 48.3, 38.9, 26.6, 26.2, 24.4, 23.9, 14.5, 14.4. Conventional benzylation of this compound followed by hydrolysis with aqueous acetic acid (70%) at 70 °C and standard acetylation with acetic anhydride−pyridine gave after workup 4,5-di-*O*-acetyl-3-*O*-benzyl-2-deoxy-L-*erythro*-pentose diethyl dithioacetal (**65**) as a syrup (78.2% yield): $[\alpha]_D$ −2° (*c* 4, chloroform); IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (m, 5 H), 5.29 (ddd, 1 H, J = 7.2, 3.4, 3.4 Hz), 4.62 (AB system, 2 H, J = 11.1 Hz, $\delta\nu$ = 29.6 Hz), 4.35 (dd, 1 H, J = 12.1, 3.4 Hz), 4.14 (dd, 1 H, J = 12.1, 7.3 Hz), 4.00 (ddd, 1 H, J = 9.6, 3.3, 3.2 Hz), 3.94 (dd, 1 H, J = 10.5, 4.3 Hz), 2.69−2.49 (m, 4 H), 2.14 (ddd, 1 H, J = 14.5, 9.6, 4.3 Hz), 2.08, 2.94 (2 s, 6 H), 1.84 (ddd, 1 H, J = 14.5, 10.5, 3.2 Hz), 1.22 (t, 6 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.3, 138.0, 128.5, 128.1, 127.9, 76.2, 73.0, 72.4, 62.7, 47.7, 37.9, 24.5, 23.5, 21.1, 20.8, 14.5; MS *m*/*z* 354 ($M^+ + 1 - C_2H_4O_2$), 265, 247.

Compound **65** was treated with NBS in anhydrous methanol[132] followed by Zemplén de-*O*-acetylation affording 3-*O*-benzyl-2-deoxy-L-*erythro*-*aldehydo*-pentose dimethyl acetal (**66**) as a syrup in 83.0% yield: $[\alpha]_D$ +22° (*c* 1, ethyl acetate); IR (neat) 3407, 1073 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.20 (m, 5 H), 4.60 (AB system, 2 H, J = 11.5 Hz, $\delta\nu$ = 16.8 Hz), 4.57 (dd, 1 H, J = 7.6, 4.0 Hz), 3.80−3.50 (m, 6 H), 3.26, 3.24 (2 s, 6 H), 1.94 (ddd, 1 H, J = 14.4, 7.6, 3.4 Hz), 1.79 (ddd, 1 H, J = 14.4, 8.8, 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ 141.9, 130.8, 130.3, 129.9, 104.8, 79.8, 76.1, 74.6, 65.7, 54.6, 54.5, 36.8.

General Procedure for the Synthesis of Cyclic Sulfites 2, 8a,c−f, 14a,b, 59, and 67. An ice-cooled and magnetically stirred solution of the diol **1**, **7a**,**c**−**f**, **13a**,**b**, **58**, and **66** (5 mmol) and Et_3N (20 mmol) in dry CH_2Cl_2 (20 mL) was added to a CH_2Cl_2 solution (15 mL) of $SOCl_2$ (7.5 mmol) dropwise over a period of 10 min. Stirring was continued at 0 °C, until TLC (ether) showed complete disappearance of starting material. The mixture was diluted with CH_2Cl_2 (50 mL) and washed with water (2 × 50 mL) and brine (100 mL). The organic solution was dried (Na_2SO_4) and filtered. The filtrate was concentrated on a rotary evaporator under reduced pressure to give a mixture of the corresponding cyclic sulfites, which were purified by a short column chromatography.

(2*R*)-1-*O*-Benzylglycerol 2,3-Cyclic Sulfite (2). Column chromatography (ether−hexane 1:1) of the crude product gave **2** (mixture of stereoisomers) (98.5%) as a syrup: IR (neat) 1208, 1106 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30−7.25 (m, 5 H), 5.07 (m, ∼0.5 H), 4.69 (dd, ∼0.5 H, J = 8.4, 6.6 Hz), 4.66 (m, ∼0.5 H), 4.60−4.52 (m, 3 H), 4.31 (dd, ∼0.5 H, J = 8.4, 5.2 Hz), 3.87 (dd, ∼0.5 H, J = 10.2, 5.3 Hz), 3.78 (dd, ∼0.5 H, J = 10.2, 6.0 Hz), 3.62 (dd, ∼0.5 H, J = 10.4, 4.8 Hz), 3.55 (dd, ∼0.5 H, J = 10.4, 5.5 Hz); ^{13}C NMR ($CDCl_3$) δ 137.3, 128.6, 128.1,-127.9, 127.8, 81.1, 78.5, 73.8, 73.7, 70.2, 69.4, 68.8, 68.4; MS *m*/*z* 229 ($M^+ + 1$), 181, 91.

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3-*O*-Acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-Cyclic Sulfite (8a). Column chromatography (ether) of the crude product gave **8a** (82%). The mixture of the two stereoisomers could be resolved by column chromatography (ether−hexane, 1:1) using an analytical sample. The first stereoisomer was a solid that showed the following physical data: mp 120−121 °C; $[\alpha]_D$ +62° (*c* 1, chloroform); IR (KBr) 1731, 1384, 1265, 1242, 1185 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.01 (d, 1 H, J = 3.8 Hz), 5.00 (d, 1 H, J = 2.3 Hz), 4.71 (d, 1 H, J = 3.8 Hz), 4.56 (dd, 1 H, J = 13.3, 7.7 Hz), 4.44−4.36 (m, 3 H), 2.10 (s, 3 H), 1.51, 1.35 (2s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.7, 113.1, 105.2, 83.4, 74.1, 73.2, 69.2, 63.7, 26.8, 26.4, 20.8; MS *m*/*z* 309 (M^+ + 1), 293, 251, 245, 187. Anal. Calcd for $C_{11}H_{16}O_8S$: C, 42.85; H, 5.23; S, 10.40. Found: C, 42.81; H, 5.26; S, 10.08. The second stereoisomer eluted was a solid that showed the following physical data: mp 110−111 °C; $[\alpha]_D$ −67° (*c* 1, chloroform); IR (KBr) 1749, 1376, 1265, 1209, 1166 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.89 (d, 1 H, J = 3.6 Hz), 5.29 (d, 1 H, J = 3.2 Hz), 5.03 (ddd, 1 H, J = 8.0, 6.4, 4.1 Hz), 4.77 (dd, 1 H, J = 8.9, 6.4 Hz), 4.61 (dd, 1 H. J = 8.9, 4.1 Hz), 4.52 (d, 1 H, J = 3.6 Hz), 4.22 (dd, 1 H, J = 8.0, 3.2 Hz), 2.12 (s, 3 H), 1.50, 1.30 (2s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.2, 112.9, 105.3, 83.4, 77.8, 76.2, 75.5, 69.1, 26.8, 26.2, 20.9; MS *m*/*z* 309 (M^+ + 1), 293, 251, 245,187. Anal. Calcd for $C_{11}H_{16}O_8S$: C, 42.85; H, 5.23; S, 10.40. Found: C, 42.61; H, 5.36; S, 10.00.

1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-glucofuranose 5,6-Cyclic Sulfite (8c). Column chromatography (ether−hexane 1:1) of the crude product gave **8c** (mixture of stereoisomers) (85%) as a syrup: IR (neat) 1295, 1213, 1165, 1124 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.87 (d, 1 H, J = 3.5 Hz), 5.12 (dt, 0.5 H, J = 6.6, 4.8 Hz), 4.73−4.56 (m, 3 H), 4.52 (dd, 0.5 H, J = 8.8, 4.8 Hz), 4.43 (dd, 0.5 H, J = 8.0, 3.2 Hz), 4.21 (dd, 0.5 H, J = 6.6, 3.3 Hz), 3.86 (d, 0.5 H, J = 3.2 Hz), 3.79 (d, 0.5 H, J = 3.3 Hz), 3.45, 3.43 (2s, 3 H), 1.48, 1.31 (2s, 6 H); ^{13}C NMR ($CDCl_3$) δ 112.4, 105.6, 105.5, 83.6, 83.4, 81.8, 81.6, 81.2, 79.0, 78.0, 76.7, 70.4, 68.8, 58.3, 26.9, 26.3; MS *m*/*z* 281 (M^+ + 1), 265, 217.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-Cyclic Sulfite (8d). Column chromatography (1:1 ether−hexane) of the crude product gave **8d** (mixture of stereoisomers) (89%) as a syrup: IR (neat) 1455, 1378, 1212, 1164, 1076 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (m, 5 H), 5.91 (d, 1 H, J = 3.6 Hz), 5.90 (d, 1 H, J = 3.4 Hz), 5.16 (dt, 0.5 H, J = 6.6, 4.9 Hz), 4.80−4.45 (m, 6 H), 4.25 (dd, 0.5 H, J = 6.6, 3.3 Hz), 4.13 (d, 0.5 H, J = 3.2 Hz), 4.04 (d, 0.5 H, J = 3.4 Hz), 1.49, 1.48, 1.31 (3 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 137.2, 136.9, 128.8, 128.7, 128.4, 128.2, 128.0, 127.9, 112.5, 112.4, 105.7, 105.6, 82.6, 82.3, 81.7, 81.4, 81.3, 79.2, 78.1, 76.9, 72.8, 72.7, 70.5, 69.0, 27.0, 26.9, 26.3, 26.3; MS *m*/*z* 357 (M^+ + 1), 341, 281, 181, 91.

3-Deoxy-1,2-*O*-isopropylidene-α-D-ribohexofuranose 5,6-Cyclic Sulfite (8e). Column chromatography (ether) of the crude product gave **8e** (85%). The mixture of the two stereoisomers could be resolved by column chromatography (ether: hexane 1:3) using an analytical sample. The first stereoisomer was a solid that showed the following physical data: mp 66−67 °C; $[\alpha]_D$ −53° (*c* 1, chloroform); IR (KBr) 1205, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.82 (d, 1 H, J = 3.6 Hz), 4.79 (pseudo-t, 1 H, J = 4.2 Hz), 4.66−4.40 (m, 4 H), 2.36 (d, 1 H, J = 13.6, 4.1 Hz), 1.86 (ddd, 1 H, J = 13.6, 10.0, 4.8 Hz), 1.51, 1.32 (2s, 6 H); ^{13}C NMR ($CDCl_3$) δ 112.0, 105.8, 83.5, 80.5, 78.2, 69.8, 36.3, 26.9, 26.2; MS *m*/*z* 251 (M^+ + 1), 235. Anal. Calcd for $C_9H_{14}O_6S$: C, 43.25; H, 5.60; S, 12.80. Found: C, 43.21; H, 5.46; S, 12.42. The second stereoisomer eluted was a solid that showed the following physical data: mp 45−46 °C; $[\alpha]_D$ −64° (*c* 1, chloroform); IR (KBr) 1380, 1323, 1258, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79 (d, 1 H, J = 3.5 Hz), 4.85−4.71 (m, 3 H), 4.40 (dd, 1 H, J = 8.6, 4.4 Hz), 4.15 (ddd, 1 H, J = 10.5, 6.8, 4.5 Hz), 2.26 (dd, 1 H, J = 13.6, 4.5 Hz), 1.66 (ddd, 1 H, J = 13.6, 10.5, 4.7 Hz), 1.49, 1.30 (2s, 6 H); ^{13}C NMR ($CDCl_3$) δ 111.9, 105.8, 80.9, 80.3, 76.9, 69.3, 36.2, 26.8, 26.1; MS *m*/*z* 251 (M^+ + 1), 235. Anal. Calcd for $C_9H_{14}O_6S$: C, 43.25; H, 5.60; S, 12.80. Found: C, 43.21; H, 5.46; S, 12.52.

3-Azido-3-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose 5,6-Cyclic Sulfite (8f). Column chromatography (ether−hexane 1:1) of the crude product gave **8f** (98%) as a syrup: IR (neat) 2114, 1377, 1254, 1218, 1163, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (d, 0.5 H, J = 3.6 Hz), 5.79 (d, 0.5 H, J = 3.4 Hz), 4.96 (ddd, 0.5 H, J = 6.4, 4.5 Hz), 4.81−4.60 (m, 3 H), 4.49 (dd, 0.5 H, J = 4.6, 8.9 Hz), 4.26 (dd, 0.5 H, J = 9.1, 4.6 Hz), 4.03 (dd, 0.5 H, J = 9.2, 6.2 Hz), 3.70 (dd, 0.5 H, J = 9.1, 4.8 Hz), 3.45 (dd, 0.5 H, J = 9.2, 4.7 Hz), 1.57, 1.56, 1.36, 1.35 (4s, 6 H); ^{13}C NMR ($CDCl_3$) δ 113.8, 113.7, 104.2, 81.7, 80.5, 80.4, 79.3, 77.3, 76.6, 68.9, 68.5, 62.9, 62.5, 26.6, 26.5, 26.4, 26.4; MS *m*/*z* 292 (M^+ + 1).

2-Acetamido-2-deoxy-3,4-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal 5,6-Cyclic Sulfite (14a). Column chromatography (ethyl acetate) of the crude product gave **14a** (95%) as a syrup: IR (neat) 3298, 1662, 1541, 1455, 1373, 1213, 1124, 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (d, 0.5 H, J = 8.7 Hz), 5.80 (d, 0.5 H, J = 8.5 Hz), 4.87 (ddd, 0.5 H, J = 7.3, 6.4, 4.1 Hz), 4.72 (dd, 0.5 H, J = 8.8, 6.4 Hz), 4.69 (t, 0.5 H, J = 9.2 Hz), 4.63 (dd, 0.5 H, J = 9.1, 6.6 Hz), 4.52 (dd, 0.5 H, J = 8.9, 4.2 Hz), 4.51 (dt, 0.5 H, J = 9.1, 6.6 Hz), 4.45−4.25 (m, 2.5 H), 4.18 (dd, 0.5 H, J = 8.0, 1.1 Hz), 4.02 (t, 0.5 H, J = 7.1 Hz), 3.62 (t, 0.5 H, J = 7.7 Hz), 3.37, 3.37, 3.33, 3.29 (4s, 6 H), 1.99, 1.99 (2s, 3H), 1.37, 1.34 (2s, 6 H); ^{13}C NMR ($CDCl_3$) δ 170.1, 169.9, 110.3, 110.2, 103.2, 102.9, 82.3, 80.4, 77.5, 77.5, 77.3, 75.9, 69.2, 55.5, 55.1, 53.8, 52.9, 49.5, 49.2, 27.0, 27.0, 26.9, 23.3; MS *m*/*z* 354 (M^+ + 1), 322; MS (calcd mass for $C_{13}H_{23}NO_8S$ + H 354.1222) obsd *m*/*z* 354.1225.

2,3-*O*-Isopropylidene-*aldehydo*-D-xylose Dimethyl Acetal 4,5-Cyclic Sulfite (14b). Column chromatography (ethyl acetate) of the crude product gave **14b** (81%) as a syrup: IR (neat) 1027, 999 cm^{-1}; ^1H NMR ($CDCl_3$) (selected signals) δ 5.06 (ddd, ~0.5 H, J = 6.9, 5.0, 2.5 Hz), 4.72 (dd, ~0.5 H, J = 8.3, 6.9 Hz), 4.42 (d, 0.5 H, J = 5.5 Hz), 3.47, 3.46, 3.45, 3.44 (4 s, 6 H), 1.46, 1.44, 1.43, 1.40 (4 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 111.8, 111.4, 104.8, 104.6, 83.2, 79.2, 77.2, 76.8, 76.2, 75.5, 69.1, 67.4, 56.5, 56.3, 54.4, 54.3, 27.1, 26.8, 26.6.

3-*O*-Acetyl-1,2-*O*-isopropylidene-β-D-altrofuranose 5,6-Cyclic Sulfite (59). Column chromatography (ether−hexane 5:1) of the crude product gave **59** (100%) as a syrup: IR (neat) 1749, 1217, 1029 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93 (d, 1 H, J = 3.8 Hz), 5.42, 5.33 (2 s, 1 H), 5.15 (ddd, 0.5 H, J = 10.0, 6.2, 3.7 Hz), 4.81−4.55 (m, 3 H), 4.41 (d, ~0.5 H, J = 9.6 Hz), 4.13−4.00 (m, 0.5 H), 3.94 (d, 0.5 H, J = 10.0 Hz), 2.11, 2.10 (2 s, 3 H), 1.55, 1.52, 1.31 (3 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.5, 112.9, 112.7, 106.3, 86.8, 84.4, 84.3, 80.3, 78.4, 77.3, 77.1, 70.6, 69.2, 26.7, 25.5, 20.8; MS (calcd mass for $C_{11}H_{16}O_8S$ + H 309.0644) obsd *m*/*z* 309.0657.

3-*O*-Benzyl-2-deoxy-L-*erythro*-*aldehydo*-pentose Dimethyl Acetal 4,5-Cyclic Sulfite (67). Column chromatography (ether−hexane 5:1) of the crude product gave **67** (98%) as a syrup: IR (neat) 1210, 1125, 1028 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (m, 5 H), 4.98 (ddd, 0.5 H, J = 10.5, 6.9, 4.4 Hz), 4.72−4.47 (m, 5 H), 4.43 (dd, 0.5 H, J = 8.3, 5.9 Hz), 3.99 (dt, 0.5 H, J = 7.3, 4.7 Hz), 3.81 (m, 0.5 H), 3.32, 3.31, 3.28 (3 s, 6 H), 1.98−1.80 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 128.6, 128.3, 128.1, 128.0, 101.5, 101.4, 84.5, 81.6, 75.2, 74.3, 73.6, 73.5, 68.5, 68.2, 53.3, 53.2, 52.8, 35.4, 35.2; MS *m*/*z* 285 (M^+ + 1 − CH_3OH).

General Procedure for Formation of Cyclic Sulfates 3, 9a,c−f, 15a,b, 24, 28, 36, 60, and 68. To a solution of the cyclic sulfites **2**, **8a**,**c**−**f**, **14a**,**b**, **59**, and **67** (5 mmol) in a mixture of MeCN (20 mL)/CCl_4 (20 mL) was added $NaIO_4$ (1.5 equiv) followed by a catalytic amount of $RuCl_3 \cdot 3H_2O$ and water (20 mL). The resulting mixture was stirred for 15−60 min at rt until TLC showed complete disappearance of the starting material. The mixture was diluted with ether (50 mL/mmol). The organic layer was washed with water (2 × 100 mL) and brine (100 mL). The organic solution was dried (Na_2SO_4) and filtered. The filtrate was evaporated under reduced pressure to give the corresponding cyclic sulfate, which was purified by column chromatography. Compounds **24**, **28**, and **36** were obtained from the corresponding diols **23**, **27**, and **35**, respectively, following the general procedures described above for the synthesis of cyclic sulfites and cyclic sulfates without the purification of the intermediate cyclic sulfite.

(2*R*)-1-*O*-Benzylglycerol 2,3-Cyclic Sulfate (3). Column chromatography (ether−hexane 1:1) of the crude product gave **3** (50%) as a syrup: $[\alpha]_D$ +2.4° (*c* 4, chloroform); IR (neat) 1386, 1211, 1108, 1058, 984 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.30 (m, 5 H), 5.04 (tt, 1 H, J = 6.6, 4.9 Hz), 4.69 (dd, 1 H, J = 8.8, 6.6 Hz), 4.62−4.56 (m, 3 H), 3.76 (d, 2 H, J = 4.9 Hz); ^{13}C NMR

($CDCl_3$) δ 136.8, 128.7, 128.3, 127.9, 80.0, 73.9, 69.8, 67.5; MS *m/z* 244 (M^+), 105, 91; MS (calcd mass for $C_{10}H_{12}O_5S$ 244.0405) obsd *m/z* 244.0401.

3-*O*-Acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-Cyclic Sulfate (9a). Column chromatography (ether−hexane 2:1) of the crude product gave **9a** (87%) as a solid: mp 142−144 °C (from ether−hexane); $[\alpha]_D$ −45° (*c* 1, chloroform); IR (KBr) 1756, 1395, 1214, 1162, 1077, 1060, 1034 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.90 (d, 1 H, *J* = 3.5 Hz), 5.30 (d, 1 H, *J* = 3.3 Hz), 5.03 (dt, 1 H, *J* = 7.7, 6.4 Hz), 4.80−4.75 (m, 2 H), 4.56 (dd, 1 H, *J* = 7.7, 3.3 Hz), 4.55 (d, 1 H, *J* = 3.6 Hz), 2.12 (s, 3 H), 1.53, 1.31 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.0, 113.3, 105.3, 83.3, 77.3, 76.6, 75.6, 70.3, 26.8, 26.2, 20.8; MS *m/z* 325 (M^+ + 1), 309, 295, 267. Anal. Calcd for $C_{11}H_{16}O_9S$: C, 40.74; H, 4.97; S, 9.88. Found: C, 41.30; H, 4.97; S, 9.41.

1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-glucofuranose 5,6-Cyclic Sulfate (9c). Column chromatography (ether−hexane 5:1) of the crude product gave **9c** (85%) as a solid: mp 83−84 °C; $[\alpha]_D$ −43° (*c* 1, chloroform); IR (Nujol) 1284, 1203, 1164, 1134, 1085, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91 (d, 1 H, *J* = 3.6 Hz), 5.15 (dt, 1 H, *J* = 6.6, 6.0 Hz), 4.79 (dd, 1 H, *J* = 9.0, 6.7 Hz), 4.71 (dd, 1 H, *J* = 9.0, 6.6 Hz), 4.61 (d, 1 H, *J* = 3.6 Hz), 4.54 (dd, 1 H, *J* = 5.9, 3.4 Hz), 3.88 (d, 1 H, *J* = 3.4 Hz), 3.43 (s, 3 H), 1.50, 1.33 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 112.7, 105.6, 83.5, 81.2, 78.4, 78.1, 70.3, 58.1, 26.9, 26.2; MS *m/z* 297 (M^+ + 1), 281, 239. Anal. Calcd for $C_{10}H_{16}O_8S$: C, 40.54; H, 5.44; S, 10.82. Found: C, 40.18; H, 5.44; S, 10.80.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-Cyclic Sulfate (9d). Column chromatography (ether−hexane 1:1) of the crude product gave **9d** (83.0%) as a solid: mp 87−88 °C; $[\alpha]_D$ −48° (*c* 1, chloroform); IR (KBr) 1383, 1270, 1210, 1075, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.23 (m, 5 H), 5.93 (d, 1 H, *J* = 3.6 Hz), 5.12 (q, 1 H, *J* = 6.5 Hz), 4.78 (dd, 1 H, *J* = 9.1, 6.5 Hz), 4.72−4.50 (m, 4 H), 4.62 (d, 1 H, *J* = 3.6 Hz), 4.10 (d, 1 H, *J* = 3.4 Hz), 1.49, 1.32 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 136.5, 128.9, 128.6, 128.1, 112.8, 105.7, 82.1, 81.3, 78.6, 77.8, 72.7, 70.4, 27.0, 26.3. Anal. Calcd for $C_{16}H_{20}O_8S$: C, 51.56; H, 5.41; S, 8.61. Found: C, 51.12; H, 5.44; S, 8.63.

3-Deoxy-1,2-*O*-isopropylidene-α-D-ribohexofuranose 5,6-Cyclic Sulfate (9e). Column chromatography (ether) of the crude product gave **9e** (72%) as a solid: mp 100−102 °C; $[\alpha]_D$ −48° (*c* 1, chloroform); IR (KBr) 1388, 1209, 1049, 1016, 983 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.83 (d,1 H, *J* = 3.5 Hz), 4.87−4.75 (m, 3 H), 4.61 (dd, 1 H, *J* = 8.7, 6.2 Hz), 4.42 (ddd, 1 H, *J* = 10.4, 6.2, 4.4 Hz), 2.37 (dd, 1 H, *J* = 13.5, 4.6 Hz), 1.80 (ddd, 1 H, *J* = 13.5, 10.4, 4.7 Hz), 1.52, 1.33 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 112.3, 105.9, 81.5, 80.7, 76.4, 70.4, 35.7, 26.9, 26.1; MS *m/z* 251 ($M^+ - CH_3$). Anal. Calcd for $C_9H_{14}O_7S$: C, 40.60; H, 5.30; S, 12.04. Found: C, 40.75; H, 4.92; S, 12.35.

3-Azido-3-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose 5,6-Cyclic Sulfate (9f). Column chromatography (ether−hexane 5:1) of the crude product gave **9f** (83%) as a solid: mp 130 °C; $[\alpha]_D$ +119° (*c* 1, chloroform); IR (KBr) 2116, 1387, 1256, 1207 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.82 (d, 1 H, *J* = 3.6 Hz), 5.06 (dt, 1 H, *J* = 6.8, 4.8 Hz), 4.82 (dd, 1 H, *J* = 6.5, 3.7 Hz), 4.80−4.73 (m, 2 H), 4.21 (dd, 1 H, *J* = 9.3, 4.8 Hz), 3.68 (dd, 1 H, *J* = 9.3, 4.7 Hz), 1.58, 1.38 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 114.2, 104.3, 80.2, 79.9, 76.4, 68.9, 61.7, 26.6, 26.4; MS *m/z* 292 ($M^+ - CH_3$), 249. Anal. Calcd for $C_9H_{13}N_3O_7S$: C, 35.18; H, 4.26; N, 13.67; S, 10.43. Found: C, 35.33; H, 4.17; N, 13.29; S, 10.09.

2-Acetamido-2-deoxy-3,4-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal 5,6-Cyclic Sulfate (15a). Column chromatography (ethyl acetate) of the crude product gave **15a** (95%) as a solid: mp 124−125 °C; $[\alpha]_D$ −8°, $[\alpha]_{436}$ −16° (*c* 2, chloroform); IR (Nujol) 3420, 1666, 1533 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.84 (d, 1 H, *J* = 8.9 Hz), 4.98 (dt, 1 H, *J* = 6.4, 5.5 Hz), 4.80 (dd, 1 H, *J* = 9.1, 6.3 Hz), 4.73 (dd, 1 H, *J* = 9.1, 6.7 Hz), 4.41 (d, 1 H, *J* = 5.2 Hz), 4.30−4.25 (m, 2 H), 4.05 (dd, 1 H, *J* = 7.5, 5.3 Hz), 3.41, 3.36 (2 s, 6 H), 2.03 (s, 3 H, MeCO), 1.39, 1.38 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 170.4, 110.7, 103.2, 80.4, 76.2, 76.1, 69.5, 55.8, 53.9, 50.1, 27.0, 26.9, 23.3; MS *m/z* 370 (M^+ + 1), 338; MS (calcd mass for $C_{13}H_{23}NO_9S$ + H 370.1172) obsd *m/z* 370.1186.

2,3-*O*-Isopropylidene-*aldehydo*-D-xylose Dimethyl Acetal 4,5-Cyclic Sulfate (15b). Column chromatography (ethyl acetate) of the crude product gave **15b** (94%) as a solid: mp 62 °C; $[\alpha]_D$ −11° (*c* 1, chloroform); IR (neat) 1389, 1380, 1213, 1111, 1071 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.04 (bdt, 1 H, *J* = 7.0, 2.2 Hz), 4.75 (dd, 1 H, *J* = 8.7, 7.9 Hz), 4.68 (dd, 1 H, *J* = 8.7, 6.8 Hz), 4.45 (bd, 1 H, *J* = 4.8 Hz), 4.14−4.11 (m, 2 H), 3.49, 3.46 (2 s, 6 H), 1.46 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 111.5, 104.2, 80.6, 76.2, 75.3, 69.7, 56.9, 54.6, 27.1, 26.4; MS (calcd mass for $C_{10}H_{18}O_8S$ + H 299.0801) obsd *m/z* 299.0798.

3-*O*-Acetyl-1,2-*O*-isopropylidene-β-D-altrofuranose 5,6-Cyclic Sulfate (60). Column chromatography (ether) of the crude product gave **60** (90%) as a solid: mp 121−122 °C; $[\alpha]_D$ +8°, $[\alpha]_{438}$ +13.5° (*c* 1, chloroform); IR (KBr) 1742, 1389, 1212, 1021 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.94 (d, 1 H, *J* = 3.7 Hz), 5.30 (s, 1 H), 5.13 (dt, 1 H, *J* = 9.9, 6.1 Hz), 4.78 (dd, 1 H, *J* = 9.4, 6.4 Hz), 4.70 (dd, 1 H, *J* = 8.4, 6.1 Hz), 4.62 (d, 1 H, *J* = 3.7 Hz), 4.34 (d, 1 H, *J* = 9.9 Hz), 2.12 (s, 3 H), 1.53, 1.46 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.4, 113.0, 106.3, 84.2, 83.7, 78.3, 76.7, 70.2, 26.7, 25.3, 20.7. Anal. Calcd for $C_{11}H_{16}O_9S$: C, 40.74; H, 4.97; S, 9.88. Found: C, 40.92; H, 4.92; S, 9.49.

3-*O*-Benzyl-2-deoxy-L-*erythro*-*aldehydo*-pentose Dimethyl Acetal 4,5-Cyclic Sulfate (68). Compound **68** is obtained as a nonstable product in 97% yield as a syrup being used directly in the next step without purification by column chromatography: IR (neat) 1386, 1211, 1123, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 4.98 (dt, 1 H, *J* = 7.0, 4.2 Hz), 4.73−4.58 (m, 4 H), 4.48 (dd, 1 H, *J* = 5.8, 5.0 Hz), 4.01 (dt, 1 H, *J* = 5.8, 4.0 Hz), 3.31, 3.29 (2 s, 6 H), 1.93−1.86 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 137.2, 128.8, 128.4, 101.2, 83.0, 73.8, 73.3, 69.2, 53.6, 53.5, 34.2.

2,4-*O*-Ethylidene-D-erythritol 1,3-Cyclic Sulfate (24). Compound **23**[133] was transformed *via* the cyclic sulfite into the cyclic sulfate **24** following the general procedure described above without purification of the cyclic sulfite. Column chromatography (ether−hexane 1:1) of the crude product gave **24** (48% overall yield from **23**) as a solid: mp 81−82 °C; $[\alpha]_D$ +6° (*c* 1, chloroform); IR (KBr) 1322, 1207, 1164, 1119, 1041 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.82 (q, 1 H, *J* = 5.0 Hz), 4.67 (dt, 1 H, *J* = 10.2, 5.0 Hz), 4.66 (t, 1 H, *J* = 10.6 Hz), 4.52 (dd, 1 H, *J* = 10.5, 5.0 Hz), 4.24 (dd, 1 H, *J* = 10.5, 5.0 Hz), 3.98 (ddd, 1 H, *J* = 10.8, 9.6, 5.0 Hz), 3.72 (t, 1 H, *J* = 10.4 Hz), 1.37 (d, 3 H, *J* = 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 100.8, 75.3, 72.6, 71.0, 66.8, 20.03; MS *m/z* 211 (M^+ + 1), 195 ($M^+ - CH_3$), 167 ($M^+ - C_2H_3O$); MS (calcd mass for $C_6H_{10}O_6$ + H 211.0276) obsd *m/z* 211.0270.

Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside 4,6-Cyclic Sulfate (28). Compound **27** was transformed *via* the cyclic sulfite into the cyclic sulfate following the general procedure described above without purification of the cyclic sulfite. Column chromatography (ether) of the crude product gave **28** (58% overall yield from **27**) as a solid: mp 93−96 °C; $[\alpha]_D$ +18° (*c* 1, chloroform); IR (KBr) 1402, 1174, 1112, 1058, 991 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.30 (m, 10 H), 4.82 (bs, 2 H), 4.74 (AB system, 2 H, *J* = 12.1 Hz, $\delta\nu$ = 36.0 Hz), 4.60 (t, 1 H, *J* = 10.7 Hz), 4.57 (t, 1 H, *J* = 9.5 Hz), 4.56 (d, 1 H, *J* = 3.6 Hz), 4.47 (dd, 1 H, *J* = 10.4, 5.1 Hz), 4.15 (dt, 1 H, *J* = 10.7, 5.1 Hz), 4.04 (t, 1 H, *J* = 9.3 Hz), 3.52 (dd, 1 H, *J* = 9.3, 3.8 Hz), 3.42 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 137.8, 137.6, 128.7, 128.5, 128.3, 128.1, 128.0, 99.3, 84.6, 78.7, 77.0, 60.5, 75.6, 74.1, 72.2, 56.1; MS *m/z* 435 (M^+ − 1), 345, 181. Anal. Calcd for $C_{21}H_{24}O_8S$: C, 57.79; H, 5.54; S, 7.34. Found: C, 57.97; H, 5.42; S, 7.05.

3,4-Di-*O*-benzyl-D-mannitol 1,2:5,6-Cyclic Disulfate (36). Compound **35**[134] was transformed via the cyclic sulfite into the cyclic sulfate following the general procedure described above without purification of the cyclic sulfite. Column chromatography (ether−hexane 1:1) of the crude product gave **36** (94% overall yield from **35**) as a solid: mp 112 °C; $[\alpha]_D$ +7°, $[\alpha]_{436}$ +13° (*c* 1, chloroform); IR (KBr) 1382, 1208, 1101, 1049 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41−7.26 (m, 10 H), 4.70 (AB system, 4 H, *J* = 11.0 Hz, $\delta\nu$ = 53.3 Hz), 4.87−4.78 (m, 4 H), 4.50 (dd, 2 H, *J* = 7.0, 4.5 Hz), 4.20 (bs, 2 H); ^{13}C NMR ($CDCl_3$) δ 135.7, 129.4, 129.2, 129.0, 82.2, 76.9, 75.7, 69.1; MS *m/z* 391 (M^+ +

(133) Baker, R.; McDonald, D. L. *J. Am. Chem. Soc.* **1960**, *32*, 2301.
(134) Jurzak, J.; Bauer, T.; Chmielewski, M. *Carbohydr. Res.* **1987**, *164*, 493.

1 − SO_4), 315, 269, 189, 147. Anal. Calcd for $C_{20}H_{22}O_{10}S_2$: C, 49.37; H, 5.56; S, 13.18. Found: C, 49.47; H, 5.58; S, 13.22.

General Procedure for the Opening of Cyclic Sulfates with the Potassium Salt of Thioacetate, Thiocyanate, and Selenocyanate Anions. To a solution of the cyclic sulfate **3**, **9a**,**c**−**f**, **15a**,**b**, **24**, **28**, **36**, **60**, or **68** (1 equiv) in dry acetone (20 mL) was added the nucleophile (KSAc, KSCN, or KSeCN) (1.1 equiv). The resulting solution or suspension was then stirred at rt until no cyclic sulfate remained (TLC). The solution was then concentrated, and the crude product was purified by chromatography on silica gel.

(2*S*)-3-*S*-Acetyl-1-(benzyloxy)-2-hydroxy-3-thiopropane-2-*O*-sulfonic Acid Potassium Salt (4). Column chromatography (methanol−chloroform 1:3) of the crude product gave **4** (93%) as a hygroscopic syrup: $[\alpha]_D$ +13° (*c* 1.6, methanol); IR (neat) 1736, 1236, 1099, 1029 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (bs, 5 H), 4.70 (m, 1 H), 4.48 (AB system, 2 H, J = 12.3 Hz, $\delta\nu$ = 18.0 Hz), 3.61 (m, 2 H), 3.41 (bd, 1 H, J = 13.5 Hz), 3.20 (dd, 1 H, J = 13.5, 7.7 Hz), 2.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.9, 137.9, 128.4, 128.0, 127.7, 76.6, 73.2, 69.4, 30.5, 29.5; MS (FAB) *m*/*z* 379 (M^+ − 2 H + Na).

(2*S*)-1-(Benzyloxy)-3-*S*-cyano-2-hydroxy-3-thiopropane-2-*O*-sulfonic Acid Potassium Salt (5). Column chromatography (methanol−chloroform 1:3) of the crude product gave **5** (95.5%) as a hygroscopic syrup: $[\alpha]_D$ +2.5° (*c* 3.4, methanol); IR (neat) 2159, 1218, 1093, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (bs, 5 H), 4.90 (bs, 1 H), 4.40 (bs, 2 H), 3.69 (bs, 2 H), 3.43 (bs, 1 H), 3.19 (bs, 1 H); (DMSO-d_6) δ 7.36 (m, 5 H), 4.52 (bs, 2 H), 4.45 (m, 1 H), 3.69 (dd, 1 H, J = 10.1, 4.3 Hz), 3.60 (dd, 1 H, J = 10.1, 6.2 Hz), 3.46 (dd, 1 H, J = 13.2, 5.2 Hz), 3.36 (dd, 1 H, J = 13.3, 5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 137.4, 128.6, 128.1, 114.1, 75.9, 73.4, 68.5, 34.5; MS (FAB) *m*/*z* 380 (M^+ + K), 364 (M^+ + Na), 348 (M^+ − K + 2 Na).

3-*O*-Acetyl-6-*S*-acetyl-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-glucofuranose Potassium Salt (10a). Column chromatography (methanol−chloroform 1:3) of the crude product gave **10a** (97%) as a solid: mp 163−164 °C dec; $[\alpha]_D$ −29° (*c* 1, water); IR (KBr) 1737, 1693, 1252, 1232 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.84 (d, 1 H, J = 3.7 Hz), 4.96 (d, 1 H, J = 2.6 Hz), 4.57 (ddd, 1 H, J = 8.0, 4.8, 4.0 Hz), 4.48 (d, 1 H, J = 3.8 Hz), 4.18 (dd, 1 H, J = 8.0, 2.8 Hz), 3.47 (dd, 1 H, J = 13.5, 4.0 Hz), 3.15 (dd, 1 H, J = 13.5, 4.8 Hz), 2.31 (s, 3 H), 1.99 (s, 3 H), 1.40, 1.24 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 194.8, 169.6, 113.3, 104.3, 82.4, 78.2, 74.9, 70.8, 31.4, 30.5, 26.5, 26.2, 20.8; HRMS (FAB) calcd for $C_{13}H_{19}O_{10}S_2K$ + K 476.9694 (M + K)$^+$, found 476.9714.

6-*S*-Acetyl-1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-sulfo-6-thio-α-D-glucofuranose Potassium Salt (10c). Column chromatography (methanol−chloroform 1:4) of the crude product gave **10c** (87%) as a solid: mp 164 °C; $[\alpha]_D$ −25° (*c* 1, methanol)); IR (KBr) 1685, 1218, 1115, 1087, 1022 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.78 (d, 1 H, J = 3.7 Hz), 4.57 (d,1 H, J = 3.8 Hz), 4.53 (dt, 1 H, J = 6.0, 3.7 Hz), 4.15 (dd, 1 H, J = 6.4, 2.9 Hz), 3.64 (d,1 H, J = 3.0 Hz), 3.41 (dd, 1 H, J = 13.4, 3.7 Hz), 3.32 (s, 3 H), 3.04 (dd,1 H, J = 13.4, 6.1 Hz), 2.28 (s, 3 H), 1.37, 1.25 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) 195.1, 110.8, 104.3, 82.9, 80.8, 80.0, 70.5, 57.3, 31.3, 30.4, 26.6, 26.2. Anal. Calcd for $C_{12}H_{19}O_9S_2K{\cdot}H_2O$: C, 33.64; H, 4.94. Found: C, 33.35; H, 4.76.

***6*-*S*-Acetyl-3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-glucofuranose Potassium Salt (10d).** Column chromatography (methanol−chloroform 1:5) of the crude product gave **10d** (100%) as a solid: mp 105−106 °C; $[\alpha]_D$ −15° (*c* 1, methanol); IR (KBr) 1691, 1260, 1219, 1075 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.45−7.25 (m, 5 H), 5.80 (d, 1 H, J = 3.4 Hz), 4.70−4.50 (m, 4 H), 4.18 (dd, 1 H, J = 6.0, 2.5 Hz), 3.90 (bs, 1 H), 3.47 (dd, 1 H, J = 13.4, 3.6 Hz), 3.11 (dd,1 H, J = 13.4, 5.5 Hz), 2.28 (s, 3 H), 1.37, 1.24 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 195.0, 138.1, 128.2, 128.0, 127.5, 110.9, 104.3, 81.5, 80.9, 79.9, 71.3, 70.6, 31.4, 30.4, 26.6, 26.2; MS (FAB) *m*/*z* 525 (M^+ + K), 509 (M^+ + Na), 493 (M^+ − K + 2 Na). Anal. Calcd for $C_{18}H_{23}O_9S_2K$: C, 44.44; H, 4.76. Found: C, 44.47; H, 4.99.

6-*S*-Acetyl-3-deoxy-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-ribohexofuranose Potassium Salt (10e). Crystallization from the reaction mixture gave **10e** (80%) as a solid: mp 217−218 °C; $[\alpha]_D$ +1° (*c* 1, methanol); IR (KBr) 1694, 1238, 1224 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.73 (d, 1 H, J = 3.7 Hz), 4.69 (t, 1 H, J = 4.1 Hz), 4.19−10 (m, 2 H), 3.22 (dd, 1 H, J = 13.4, 4.7 Hz), 3.14 (dd, 1 H, J = 13.4, 4.4 Hz), 2.31 (s, 3 H), 1.96 (dd, 1 H, J = 14.0, 4.4 Hz), 1.74 (ddd, 1 H, J = 14.0, 9.8, 4.1 Hz), 1.36, 1.23 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 195.0, 110.3, 105.1, 79.8, 77.8, 75.0, 35.1, 30.5, 30.4, 26.7, 26.3; MS (FAB) *m*/*z* 419 (M^+ + K), 403 (M^+ + Na). Anal. Calcd for $C_{11}H_{17}O_8S_2K{\cdot}H_2O$: C, 33.16; H, 4.81; S, 16.09. Found: C, 33.29; H, 4.51; S, 15.71.

6-*S*-Acetyl-3-azido-3-deoxy-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-allofuranose Potassium Salt (10f). Column chromatography (methanol−chloroform 1:3) of the crude product gave **10f** (99%) as a solid: mp 195−198 °C dec; $[\alpha]_D$ +82° (*c* 1, methanol); IR (KBr) 3466, 2104, 1681, 1268, 1232, 1020 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.77 (d, 1 H, J = 3.6 Hz), 4.76 (t, 1 H, J = 4.3 Hz), 4.35−4.22 (m, 2 H), 3.61 (dd, 1 H, J = 9.1, 4.9 Hz), 3.20 (d, 1 H, J = 13.8, 4.6 Hz), 3.07 (d, 1 H, J = 13.8, 5.8 Hz), 2.31 (s, 3 H), 1.42, 1.28 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 195.0, 112.1, 104.0, 80.1, 77.8, 73.8, 60.5, 30.4, 29.7, 26.6, 26.3. Anal. Calcd for $C_{11}H_{16}N_3O_8S_2K{\cdot}H_2O$: C, 30.06; H, 4.13; N, 9.56; S, 14.83. Found: C, 30.45; H, 3.75; N, 9.45; S, 14.83.

3-*O*-Acetyl-6-*S*-cyano-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-glucofuranose Potassiun Salt (11a). Crystallization from the reaction mixture gave **11a** (94%) as a solid: mp 238 °C dec; $[\alpha]_D$ −68° (*c* 1, methanol); IR (KBr) 2163, 1734, 1252, 1222, 1026 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.87 (d, 1 H, J = 3.7 Hz), 5.01 (d, 1 H, J = 3.0 Hz), 4.59 (dt, 1 H, J = 8.0, 4.0 Hz), 4.52 (d, 1 H, J = 3.7 Hz), 4.29 (dd, 1 H, J = 8.2, 2.9 Hz), 3.71 (dd, 1 H, J = 13.5, 3.9 Hz), 3.33 (dd, 1 H, J = 13.5, 3.9 Hz), 2.00 (s, 3 H), 1.43, 1.24 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 169.3, 113.2, 111.5, 104.4, 82.3, 77.4, 74.5, 69.5, 36.6, 26.4, 26.0, 20.6; MS (FAB) *m*/*z* 460 (M^+ + K), 444 (M^+ + Na). Anal. Calcd for $C_{12}H_{16}NO_9S_2K$: C, 34.20; H, 3.83; N, 3.32; S, 15.21. Found: C, 34.17; H, 3.92; N, 3.34; S, 15.69.

6-*S*-Cyano-1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-sulfo-6-thio-α-D-glucofuranose Potassium Salt (11c). Column chromatography (methanol−chloroform 1:3) of the crude product gave **11c** (82%) as a solid: mp 170 °C dec; $[\alpha]_D$ −33° (*c* 1, methanol); IR (KBr) 2165, 1385, 1375, 1252, 1233, 1116, 1080, 1023 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.79 (d, 1 H, J = 3.6 Hz, H-1), 4.61 (d, 1 H, J = 3.7 Hz), 4.58 (m, 1 H), 4.24 (dd, 1 H, J = 6.3, 3.1 Hz), 3.68 (d, 1 H, J = 3.0 Hz), 3.60 (dd, 1 H, J = 13.2, 3.4 Hz), 3.34 (s, 3 H), 3.25 (dd, 1 H, J = 13.2, 5.1 Hz), 1.38, 1.24 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 113.7, 111.1, 104.4, 82.8, 80.8, 79.4, 70.6, 57.6, 36.7, 26.6, 26.2. Anal. Calcd for $C_{11}H_{16}NO_8S_2K{\cdot}H_2O$: C, 32.11; H, 4.41; N, 3.41; S, 15.58. Found: C, 32.42; H, 4.57; N, 3.24; S, 15.24.

3-*O*-Benzyl-6-*S*-cyano-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-glucofuranose Potassium Salt (11d). Column chromatography (methanol−chloroform 1:3) of the crude product gave **11d** (100%) as a hygroscopic solid: mp 105−106 °C; $[\alpha]_D$ −31° (*c* 1, water); IR (KBr) 1259, 1222, 1163, 1081, 1015 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.45−7.22 (m, 5 H), 5.82 (d, 1 H, J = 3.6 Hz), 4.71 (m, 1 H), 4.68 (d, 1 H, J = 3.6 Hz), 4.61 (bs, 2 H), 4.28 (dd,1 H, J = 6.6, 2.9 Hz), 3.94 (d, 1 H, J = 3.0 Hz), 3.60 (dd, 1 H, J = 13.4, 3.6 Hz), 3.31 (dd, 1 H, J = 13.3, 4.7 Hz), 1.40, 1.25 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) 137.7, 128.1, 128.0, 127.5, 113.5, 111.1, 104.3, 81.4, 80.5, 79.1, 71.4, 70.3, 36.6, 26.5, 26.1; MS (FAB) *m*/*z* 508 (M + K)$^+$, 492 (M + Na)$^+$, 476 (M − K + 2 Na)$^+$. Anal. Calcd for $C_{17}H_{20}NO_8S_2K{\cdot}H_2O$: C, 41.89; H, 4.52; N, 2.87; S, 13.14. Found: C, 41.42; H, 4.30; N, 3.11; S, 13.06.

6-*S*-Cyano-3-deoxy-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-ribohexofuranose Potassium Salt (11e). Column chromatography (methanol−chloroform 1:4) of the crude product gave **11e** (80%) as a solid: mp 225 °C dec; $[\alpha]_D$ −9° (*c* 1, methanol); IR (KBr) 1242, 1222, 1018 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.75 (d, 1 H, J = 4.6 Hz), 4.72 (t, 1 H, J = 3.8 Hz), 4.31−4.21 (m, 2 H), 3.52 (dd, 1 H, J = 13.3, 4.1 Hz), 3.37 (dd, 1 H, J = 13.3, 4.6 Hz), 2.04 (dd, 1 H, J = 14.4, 4.6 Hz), 1.75 (ddd, 1 H, J = 14.4, 9.6, 4.5 Hz), 1.40, 1.24 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 113.8, 110.6, 105.2), 79.8, 77.2, 74.8, 35.8, 35.4, 26.7, 26.2; MS (FAB) *m*/*z* 370 (M − K + 2 Na)$^+$. Anal. Calcd for $C_{10}H_{14}O_7NS_2K$: C, 33.05; H, 3.88; N, 3.85. Found: C, 33.25; H, 4.23; N, 3.69.

3-Azido-6-*S*-cyano-3-deoxy-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-α-D-allofuranose Potassium Salt (11f). Column chromatography (methanol−chloroform 1:3) of the crude product gave **11f** (99%) as a solid: mp 118−121 °C; $[\alpha]_D$ +75° (*c* 1, methanol); IR (KBr) 3486, 2161, 2113, 1376, 1235, 1011, 886 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.77 (d, 1 H, J = 3.5 Hz), 4.77 (t, 1 H, J = 4.4 Hz), 4.38 (m, 1 H), 4.31 (dd, 1 H, J = 9.5, 4.4 Hz), 3.68 (dd, 1 H, J = 9.5, 4.8 Hz), 3.54 (dd, 1 H, J = 13.4, 4.1 Hz), 3.30 (d, 1 H, J = 13.4, 5.9 Hz), 1.44, 1.29 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 113.6, 112.3, 104.1, 80.1, 77.6, 73.5, 60.6, 34.8, 26.5, 26.4. Anal. Calcd for $C_{10}H_{13}N_4O_7S_2K\cdot H_2O$: C, 28.43; H, 3.58; N, 13.26; S, 15.18. Found: C, 28.89; H, 3.45; N, 13.47; S, 14.98.

2-Acetamido-6-*S*-acetyl-2-deoxy-3,4-*O*-isopropylidene-5-*O*-sulfo-6-thio-*aldehydo*-D-glucose Dimethyl Acetal Potassium Salt (16a). Column chromatography (methanol−chloroform 1:3) of the crude product gave **16a** (95%) as a hygroscopic solid: mp 120 °C; $[\alpha]_D$ −2.4° (*c* 0.5, water); IR (KBr) 3580, 1665, 1541, 1244, 1067 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.48 (d, 1 H, J = 9.7 Hz), 4.28 (d, 1 H, J = 7.0 Hz), 4.28−4.08 (m, 3 H), 3.70 (t, 1 H, J = 7.0 Hz), 3.30−3.10 (m, 2 H), 3.22, 3.21 (2 s, 6 H), 2.29, 1.84 (2 s, 6 H), 1.30, 1.28 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 195.1, 169.3, 109.2, 102.6, 77.5, 77.2, 74.9, 53.5, 52.6, 50.3, 30.9, 30.5, 27.2, 27.1, 22.7; MS (FAB) calcd for $C_{15}H_{26}NO_{10}S_2K$ + H 484.0713, found 484.0685.

5-*S*-Acetyl-2,3-*O*-isopropylidene-4-*O*-sulfo-5-thio-*aldehydo*-D-xylose Dimethyl Acetal Potassium Salt (16b). Column chromatography (methanol−chloroform 1:3) of the crude product gave **16b** (72%) as a solid: mp 140−142 °C; $[\alpha]_D$ −18° (*c* 1, methanol); IR (KBr) 1685, 1252, 1086, 1003 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.30 (d, 1 H, J = 5.8 Hz), 4.23 (t, 1 H, J = 5.8 Hz), 4.07 (ddd, 1 H, J = 9.6, 4.8, 1.6 Hz), 3.98 (dd, 1 H, J = 5.7, 1.6 Hz), 3.35 (dd, 1 H, J = 12.7, 4.8 Hz), 3.30, 3.28 (2 s, 6 H), 3.01 (dd, 1 H, J = 12.7, 9.6 Hz), 2.31 (s, 3 H), 1.30, 1.28 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 109.5, 104.7, 77.4, 75.4, 72.3, 55.0, 53.7, 30.5, 29.8, 27.3, 26.7; MS (FAB) *m*/*z* 451 (M + K)$^+$, 435 (M + Na)$^+$, 419 (M − K + 2 Na)$^+$.

2-Acetamido-6-*S*-cyano-2-deoxy-3,4-*O*-isopropylidene-5-*O*-sulfo-6-thio-*aldehydo*-D-glucose Dimethyl Acetal Potassium Salt (17a). Column chromatography (methanol−chloroform 1:5) of the crude product gave **17a** (98%) as a solid: mp 176−177 °C; $[\alpha]_D$ −16° (*c* 1, methanol); IR (Nujol) 3347, 2070, 1653, 1541, 1274, 1073 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.60 (d, 1 H, J = 9.0 Hz), 4.14 (m, 1 H), 4.12 (d, 1 H, J = 7.1 Hz), 4.08 (dd, 1 H, J = 6.6, 2.7 Hz), 3.95 (ddd, 1 H, J = 9.0, 7.0, 2.5 Hz), 3.62 (t, 1 H, J = 7.3 Hz), 3.37 (dd, 1 H, J = 13.2, 5.0 Hz), 3.17 (dd, 1 H, J = 13.2, 3.6 Hz), 3.04, 3.02 (2 s, 6 H), 1.66 (s, 3 H), 1.14, 1.10 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 169.4, 113.5, 109.4, 102.4, 77.6, 76.2, 74.6, 53.3, 52.6, 50.1, 36.2, 27.1, 27.0, 22.6. Anal. Calcd for $C_{14}H_{23}N_2O_9S_2K$: C, 36.05; H, 4.97; N, 6.01. Found: C, 35.90; H, 5.05; N, 5.90.

(2*R*,4*R*,5*R*)-4-[(Acetylthio)methyl]-2-methyl-5-*O*-sulfo-1,3-dioxane Potassium Salt (25). Column chromatography (methanol−chloroform 1:4) of the crude product gave **25** (86%) as a solid: mp 81−82 °C; $[\alpha]_D$ +6° (*c* 1, methanol); IR (KBr) 1322, 1207, 1164, 1119, 1041 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.66 (q, 1 H, J = 5.0 Hz), 4.15 (dd, 1 H, J = 10.6, 5.2 Hz), 3.80 (dt, 1 H, J = 10.1, 5.4 Hz), 3.53 (dd, 1 H, 1 H, J = 13.7, 2.6 Hz), 3.45 (dt, 1 H, J = 9.3, 2.6 Hz), 3.34 (t, 1 H, J = 10.6 Hz), 2.64 (dd, 1 H, J = 13.7, 8.6 Hz), 2.32 (s, 3 H), 1.16 (d, 3 H, J = 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 98.1, 77.6, 68.4, 30.6, 30.4, 20.0; MSFAB *m*/*z* 363 (M + K)$^+$, 347 (M + Na)$^+$, 339 (M − K + 2 Na)$^+$.

Methyl 6-*S*-Acetyl-2,3-di-*O*-benzyl-4-*O*-sulfo-6-thio-α-D-glucopyranoside Potassium Salt (29). Column chromatography (methanol−chloroform 1:3) of the crude product gave **29** (94%) as a solid: mp 168−169 °C; $[\alpha]_D$ +93° (*c* 1, methanol); ^1H NMR (DMSO-d_6) δ 7.40−7.20 (m, 10 H), 4.77 (AB system, 2 H, J = 10.9 Hz, $\delta\nu$ = 80.8 Hz), 4.71 (d, 1 H, J = 3.5 Hz), 4.59 (AB system, 2 H, J = 12.0 Hz, $\delta\nu$ = 13.0 Hz), 3.95 (t, 1 H, J = 9.3 Hz), 3.80 (dd, 1 H, J = 13.9, 2.2 Hz), 3.58 (t, 1 H, J = 9.6 Hz), 3.48 (dt, 1 H, J = 9.8, 2.5 Hz), 3.38 (dd, 1 H, J = 9.6, 3.5 Hz), 3.26 (s, 3 H), 2.80 (dd, 1 H, J = 14.1, 10.0 Hz), 2.30 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 194.7, 139.3, 138.6, 128.2, 127.7, 127.5, 127.3, 127.0, 96.8, 79.5, 78.5, 73.8, 71.7, 68.7, 54.3, 30.8, 30.4. Anal. Calcd for $C_{23}H_{27}O_9S_2K$: C, 50.18; H, 4.95. Found: C, 49.82; H, 5.14.

3-*O*-Acetyl-6-*Se*-cyano-1,2-*O*-isopropylidene-6-seleno-5-*O*-sulfo-α-D-glucofuranose Potassium Salt (31a). Column chromatography (methanol−chloroform 1:3) of the crude product gave **31a** (97%) as a solid: mp 160 °C dec; $[\alpha]_D$ −65° (*c* 1, methanol); IR (KBr) 2160, 1743 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.89 (d, 1 H, J = 3.6 Hz), 5.01 (d, 1 H, J = 2.8 Hz), 4.57 (m, 1 H), 4.53 (d, 1 H, J = 3.6 Hz), 4.26 (dd, 1 H, J = 8.2, 3.0 Hz), 3.63 (dd, 1 H, J = 12.1, 4.3 Hz), 3.43 (dd, 1 H, J = 12.1, 5.0 Hz), 2.01 (s, 3 H), 1.44, 1.25 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 169.4, 111.6, 104.5, 82.5, 78.7, 74.6, 70.5, 32.2, 26.5, 26.1, 20.7. Anal. Calcd for $C_{12}H_{16}NO_9SeSK$: C, 30.77; H, 3.44; N, 2.99. Found: C, 30.76; H, 4.01; N, 2.72.

6-*Se*-Cyano-1,2-*O*-isopropylidene-3-*O*-methyl-6-seleno-5-*O*-sulfo-α-D-glucofuranose Potassium Salt (31c). Column chromatography (methanol−chloroform 1:3) of the crude product gave **31c** (90%) as a hygroscopic solid: mp 102−104 °C dec; $[\alpha]_D$ −3°, $[\alpha]_{436}$ −7° (*c* 1, methanol); IR (KBr) 1221, 1078, 1015, 946 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.75 (d, 1 H, J = 3.6 Hz), 4.57 (d, 1 H, J = 3.7 Hz), 4.56 (m, 1 H), 4.20 (dd, 1 H, J = 7.7, 2.6 Hz), 3.61 (d, 1 H, J = 2.6 Hz), 3.32 (s, 3 H), 3.22 (dd, 1 H, J = 13.0, 3.7 Hz), 2.68 (dd, 1 H, J = 13.0, 4.0 Hz), 1.38, 1.24 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 110.9, 104.3, 82.5, 81.1, 79.9, 71.1, 57.5, 32.6, 26.6, 26.2.

3-*O*-Benzyl-6-*Se*-cyano-1,2-*O*-isopropylidene-6-seleno-5-*O*-sulfo-α-D-glucofuranose Potassium Salt (31d). Column chromatography (chloroform-methanol 5:1) of the crude product gave **31d** as a solid (100%): mp 105−107 °C dec; $[\alpha]_D$ −30° (*c* 1, methanol); IR (KBr) 2165, 1375, 1259, 1221, 1161, 1107, 1087, 1005 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.41−7.25 (m, 5 H), 5.83 (d, 1 H, J = 3.6 Hz), 4.68 (d, 1 H, J = 3.7 Hz), 4.67 (m, 1 H), 4.62 (bs, 2 H), 4.22 (dd, 1 H, J = 6.9, 2.9 Hz), 3.93 (d, 1 H, J = 3.0 Hz), 3.66 (dd, 1 H, J = 12.2, 4.2 Hz), 3.42 (dd, 1 H, J = 12.2, 4.6 Hz), 1.40, 1.25 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 137.8, 128.2, 128.1, 127.6, 111.2, 104.8, 104.1, 81.5, 80.4, 80.0, 71.5, 70.8, 32.4, 26.7, 26.2; MS (FAB) *m*/*z* 516 (M$^+$). Anal. Calcd for $C_{17}H_{20}NO_8SeSK\cdot 2H_2O$: C, 36.96; H, 4.38; N, 2.54; S, 5.80. Found: C, 37.26; H, 4.70; N, 1.91; S, 5.56.

6-*Se*-Cyano-3-deoxy-1,2-*O*-isopropylidene-6-seleno-5-*O*-sulfo-α-D-ribohexofuranose Potassium Salt (31e). Column chromatography (methanol−chloroform 1:3) of the crude product gave **31e** (100%) as a non stable solid: mp 105−110 °C dec; $[\alpha]_D$ −13° (*c* 0.5, methanol); IR (KBr) 2071, 1248, 1209, 1160, 1006, 1065, 1023 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.74 (dd, 1 H, J = 3.3 Hz), 4.71 (t, 1 H, J = 3.7 Hz), 4.25 (m, 2 H), 3.04 (m, 2 H), 2.04 (m, 1 H), 1.75 (m, 1 H), 1.39, 1.23 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 110.6, 105.2, 105.2, 79.8, 78.4, 75.1, 35.2, 31.0, 26.7, 26.2, 20.7.

3-Azido-6-*Se*-cyano-3-deoxy-1,2-*O*-isopropylidene-6-seleno-5-*O*-sulfo-α-D-allofuranose Potassium Salt (31f). Column chromatography (methanol−chloroform 1:5) of the crude product gave **31f** (100%) as a hygroscopic foam: $[\alpha]_D$ +42° (*c* 1.5, methanol); IR (neat) 2114, 1259, 1112, 1071, 1022 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.77 (d, 1 H, J = 3.5 Hz), 4.77 (pseudo-t, 1 H, J = 4.1 Hz), 4.40 (m, 1 H), 4.24 (dd, 1 H, J = 9.7, 4.3 Hz), 3.68 (dd, 1 H, J = 9.7, 4.9 Hz), 3.60−3.30 (m, 2 H), 1.44, 1.28 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 112.5, 104.1, 80.2, 78.6, 73.8, 60.7, 30.1, 26.6, 26.5. Anal. Calcd for $C_{10}H_{13}N_4O_7SSeK$: C, 26.61; H, 2.90; N, 12.41; S, 7.10. Found: C, 26.27; H, 3.30; N, 11.93; S, 7.03.

2-Acetamido-6-*Se*-cyano-2-deoxy-3,4-*O*-isopropylidene-6-seleno-5-*O*-sulfo-*aldehydo*-D-glucose Dimethyl Acetal Potassium Salt (33). Column chromatography (methanol−chloroform 1:5) of the crude product gave **33** (63%) as a solid: mp 183 °C dec; $[\alpha]_D$ +15° (*c* 1, methanol); IR (Nujol) 3402, 2077, 1652, 1558, 1219, 1152, 1087 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.61 (d, 1 H, J = 9.6 Hz), 4.35 (m, 1 H), 4.31 (d, 1 H, J = 7.2 Hz), 4.27 (dd, 1 H, J = 6.7, 2.5 Hz), 4.14 (ddd, 1 H, J = 9.6, 7.2, 2.4 Hz), 3.74 (t, 1 H, J = 7.0 Hz), 3.49 (dd, 1 H, J = 11.9, 5.3 Hz), 3.42 (dd, 1 H, J = 11.9, 4.7 Hz), 3.24, 3.22 (2 s, 6 H), 1.86 (s, 3 H), 1.34, 1.31 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 179.5, 109.4, 105.0, 102.4, 77.5, 77.4, 75.2, 53.3, 52.0, 50.1, 31.3, 27.1, 27.0, 22.6.

3-*O*-Acetyl-6-*S*-cyano-1,2-*O*-isopropylidene-5-*O*-sulfo-6-thio-β-D-altrofuranose Potassium Salt (61). Column

chromatography (methanol−chloroform 1:3) of the crude product gave **61** (100%) as a hygroscopic solid: mp 62 °C; $[\alpha]_D$ −6.5° (*c* 1, methanol); IR (KBr) 2161, 1742, 1252, 1163, 1069, 1019 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.92 (d, 1 H, J = 4.0 Hz), 5.29 (s, 1 H), 4.67 (dt, 1 H, J = 10.0, 3.5 Hz), 4.59 (d, 1 H, J = 3.8 Hz), 4.05 (d, 1 H, J = 10.1 Hz), 3.71 (dd, 1 H, J = 13.2, 3.9 Hz), 3.35 (dd, 1 H, J = 13.2, 3.1 Hz), 2.05 (s, 3 H), 1.42, 1.22 (2 s, 6 H); ^{13}C NMR (DMSO-d_6) δ 169.4, 113.4, 111.4, 105.8, 83.8, 83.3, 77.2, 71.7, 36.0, 26.0, 25.4, 20.7. Anal. Calcd for $C_{10}H_{14}NO_8S_2K$: C, 31.65; H, 3.72; N, 3.69. Found: C, 31.38; H, 3.94; N, 3.41.

***5-S*-Acetyl-3-*O*-benzyl-2-deoxy-4-*O*-sulfo-5-thio-L-*erythro*-*aldehydo*-pentose Dimethyl Acetal Potassium Salt (69).** Column chromatography (methanol−chloroform 1:6) of the crude product gave **69** (77%) as a syrup: $[\alpha]_D$ +1° (*c* 5, methanol); IR (neat) 1686, 1261, 1211, 1120, 1058, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (m, 5 H), 4.56 (AB system, 2 H, J = 11.5 Hz, $\delta\nu$ = 33.7 Hz), 4.41 (dd, 1 H, J = 7.7, 3.7 Hz), 4.20 (m, 1 H), 3.89 (dt, 1 H, J = 9.6, 3.2 Hz), 3.40−3.15 (m, 2 H), 3.19, 3.15 (2 s, 6 H), 2.30 (s, 3 H), 1.77 (ddd, 1 H, J = 13.0, 8.0, 3.6 Hz), 1.62 (ddd, 1 H, J = 13.0, 9.3, 3.5 Hz); ^{13}C NMR (DMSO-d_6) δ 195.3, 138.8, 128.1, 127.7, 127.3, 101.8, 76.9, 75.8, 72.1, 52.5, 45.8, 35.0, 30.5, 29.3.

General Procedure for the Synthesis of Episulfides 6, 12b−g, 18a,b, and 70. (a) To a solution of the potassium salt (1 mmol) in anhydrous methanol (15 mL) was added a solution of NaMeO (3 mmol when the *S*-acetyl derivatives **4**, **10a**,**c**−**f**, **16a**,**b**, and **69** were used and 5 mmol when the *S*-cyano derivatives **5**, **11a**, and **17a** were used) in methanol. The reaction mixture was left at rt until TLC (methanol−chloroform 1:5) showed complete disappearance of the starting material. A saturated solution of ammonium chloride (15 mL) was added, and the methanol was removed *in vacuo*. Water (15 mL) was added, and the resulting solution was extracted with ethyl acetate (3 × 25 mL). The organic layers were collected, dried, and evaporated.

(2*R*)-1-(Benzyloxy)-2,3-epithiopropane (6). Column chromatography (ether) of the crude product gave **6** (95% from **4** and 71% from **5**) as a syrup: $[\alpha]_D$ +11° (*c* 10, chloroform); IR (neat) 1451, 1368, 1096, 1047; ^1H NMR ($CDCl_3$) δ 7.38 (m, 5 H), 4.60 (bs, 2 H), 3.70 (ddd, 1 H, J = 10.6, 5.7, 0.7 Hz), 3.51 (dd, 2 H, J = 10.6, 6.7 Hz), 3.12 (m, 1 H), 2.52 (bd, 1 H, J = 6.2 Hz), 2.22 (dd, 1 H, J = 5.4, 1.2 Hz); ^{13}C NMR ($CDCl_3$) 137.9, 128.4, 127.7, 74.6, 73.0, 32.1, 23.7; MS *m*/*z* 181 (M^+ + 1), 147, 91; MS (CI^+) (calcd mass for $C_{10}H_{12}OS$ + H 181.0687) obsd *m*/*z* 181.0588.

5,6-Dideoxy-5,6-epithio-1,2-*O*-isopropylidene-*β*-L-idofuranose (12b). Column chromatography (ether) of the crude product gave **12b** (90% from **10a** and 70% from **11a**) as a solid: mp 168−170 °C (lit.[135] mp 164−165 °C); $[\alpha]_D$ −5° (*c* 1, chloroform) (lit.[134] $[\alpha]_D$ −16°); IR (KBr) 3418, 1221, 1162, 1092, 1066, 1002 cm^{-1}; ^1H NMR ($CDCl_3$) 5.94 (d, 1 H, J = 3.7 Hz), 4.53 (d, 1 H, J = 3.7 Hz), 4.20 (dd, 1 H, J = 6.1, 2.7 Hz), 3.87 (dd, 1 H, J = 7.3, 2.7 Hz), 3.15 (ddd, 1 H, J = 7.1, 6.8, 5.5 Hz), 2.50 (dd, 1 H, J = 6.6, 1.4 Hz), 2.33 (dd, 1 H, J = 5.5, 1.4 Hz), 2.05 (d, 1 H, J = 6.1 Hz), 1.46, 1.30 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 112.1, 104.6, 85.6, 83.6, 31.1, 26.8, 26.3, 20.4; MS *m*/*z* 218 (M^+), 203 ($M^+ - CH_3$); MS (calcd mass for $C_9H_{14}O_4S$ 218.0613) obsd *m*/*z* 218.0621. Anal. Calcd for $C_9H_{14}O_4S$: C, 59.52; H, 6.46, S, 14.69. Found: C, 49.06; H, 6.30; S, 15.00.

5,6-Dideoxy-5,6-epithio-3-*O*-methyl-1,2-*O*-isopropylidene-*β*-L-idofuranose (12c). Column chromatography (ether−hexane 2:1) of the crude product gave **12c** (79% from **10c**) as a solid: mp 89−90 °C; $[\alpha]_D$ −47° (*c* 1, chloroform); IR (KBr) 1185, 1163, 1120, 1081, 1017 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93 (d, 1 H, J = 3.9 Hz), 4.61 (d, 1 H, J = 3.8 Hz), 3.68 (d, 1 H, J = 3.3 Hz), 3.62 (dd, 1 H, J = 8.4, 3.3 Hz), 3.46 (s, 3 H), 3.15 (ddd, 1 H, J = 8.4, 6.5, 4.4 Hz), 2.49 (dd, 1 H, J = 6.5, 1.4 Hz), 2.22 (dd, 1 H, J = 5.4, 1.4 Hz), 1.44, 1.31 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 111.8 (*C*Me_2), 104.9, 86.1, 85.4, 82.0, 58.2, 31.3, 26.9, 26.3, 20.9; MS *m*/*z* 233 (M^+ + 1). Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.71; H, 6.94, S, 13.80. Found: C, 51.77; H, 6.95; S, 12.97.

(135) Creighton, A. M.; Owen, L. N. *J. Chem. Soc.* **1960**, 1024.

3-*O*-Benzyl-5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-*β*-L-idofuranose (12d). Column chromatography (ether−hexane 2:1) of the crude product gave **12d** (86% from **10d**) as a solid: mp 71−71 °C; $[\alpha]_D$ −68° (*c* 1, chloroform); IR (Nujol) 1163, 1128, 1076, 1027 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (m, 5 H), 5.97 (d, 1 H, J = 3.8 Hz), 4.64 (AB system, 2 H, J = 12.1 Hz, $\delta\nu$ = 40.8 Hz), 4.65 (d, 1 H, J = 3.8 Hz), 3.89 (d, 1 H, J = 3.3 Hz), 3.61 (dd, 1 H, J = 8.4, 3.3 Hz), 3.21 (ddd, 1 H, J = 8.4, 6.5, 5.5 Hz), 2.36 (dd, 1 H, J = 6.5, 1.5 Hz), 2.08 (dd, 1 H, J = 5.5, 1.5 Hz), 1.43, 1.31 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 137.4, 128.6, 128.2, 127.8, 111.9, 105.1, 86.2, 82.8, 82.8, 72.1, 31.5, 26.9, 26.4, 20.7; MS *m*/*z* 309 (M^+ + 1), 251. Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.31; H, 6.54; S, 10.40. Found: C, 62.29; H, 6.49; S, 10.21.

3,5,6-Trideoxy-5,6-epithio-1,2-*O*-isopropylidene-*β*-L-idofuranose (12e). Column chromatography (ether−hexane 5:1) of the crude product gave **12e** (91% from **10e**) as a solid: mp 124−125 °C; $[\alpha]_D$ +8° (*c* 1, chloroform); IR (Nujol) 1260, 1214, 1163, 1079, 1054, 1021 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.76 (d, 1 H, J = 3.7 Hz), 4.70 (dd, 1 H, J = 4.5, 3.8 Hz), 4.06 (ddd, 1 H, J = 10.5, 6.1, 4.5 Hz), 2.96 (pseudo-q, 1 H, J = 6.5 Hz), 2.42 (dd, 1 H, J = 6.5, 1.3 Hz), 2.30 (dd, 1 H, J = 5.5, 1.3 Hz), 2.19 (dd, 1 H, J = 13.4, 4.5 Hz), 1.69 (ddd, 1 H, J = 13.4, 10.5, 4.8 Hz), 1.43, 1.26 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 111.3, 105.5, 80.5, 80.1, 38.7, 36.0, 26.8, 26.2, 21.3; MS *m*/*z* 202 (M^+), 187; MS (calcd mass for $C_9H_{14}O_3S$ 202.0664) obsd *m*/*z* 202.0671. Anal. Calcd for $C_9H_{14}O_3S$: C, 53.44; H, 6.98; S, 15.85. Found: C, 53.89; H, 7.04; S, 15.50.

3-Azido-3,5,6-trideoxy-5,6-epithio-1,2-*O*-isopropylidene-*β*-L-talofuranose (12f). Column chromatography (ether) of the crude product gave **12f** (83% from **10f**) as a solid: mp 54 °C; $[\alpha]_D$ +284° (*c* 1, chloroform); IR (BrK) 2110, 1260, 1218, 1167, 1112, 1078, 1046, 1018 cm^{-1}; ^1H NMR ($CDCl_3$) 5.77 (d, 1 H, J = 3.7 Hz), 4.73 (pseudo-t, 1 H, J = 4.2 Hz), 3.38 (dd, 1 H, J = 9.3, 6.4 Hz), 3.35 (dd, 1 H, J = 9.3, 4.6 Hz), 3.02 (t, 1 H, J = 6.5 Hz), 2.53 (dd, 1 H, J = 6.5, 1.4 Hz), 2.45 (dd, 1 H, J = 5.4, 1.4 Hz), 1.52, 1.33 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 113.4, 104.0, 80.2, 65.3, 34.2, 26.4, 26.2, 21.3; MS *m*/*z* 228 ($M^+ - CH_3$), 186. Anal. Calcd for $C_9H_{13}N_3O_3S$: C, 44.43; H, 5.39; N, 17.27; S, 13.18. Found: C, 44.45; H, 5.40; N, 17.00; S, 13.041.

2-Acetamido-2,5,6-trideoxy-5,6-epithio-3,4-*O*-isopropylidene-*aldehydo*-L-idose Dimethyl Acetal (18a). Column chromatography (ethyl acetate) of the crude product gave **18a** (70% from **16a** and 63% from **17a**) as a solid: mp 135−36 °C; $[\alpha]_D$ +55° (*c* 1, chloroform); IR (Nujol) 3283, 1645, 1541, 1084 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (d, 1 H, J = 9.7 Hz), 4.43 (d, 1 H, J = 6.9 Hz), 4.28 (ddd, 1 H, J = 9.8, 6.9, 1.3 Hz), 4.18 (dd, 1 H, J = 8.5, 1.3 Hz), 3.44, 3.34 (2 s, 6 H), 3.27 (pseudo-t, 1 H, J = 8.0 Hz), 2.97 (ddd, 1 H, J = 7.6, 6.4, 5.3 Hz), 2.53 (dd, 1 H, J = 5.3, 1.4 Hz), 2.49 (dd, 1 H, J = 6.4, 1.4 Hz), 2.03 (s, 3 H), 1.45, 1.39 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.9, 109.4, 102.9, 81.8, 78.6, 55.5, 52.5, 48.6, 34.0, 27.1, 27.0, 23.3, 21.3; MS (calcd mass for $C_{13}H_{24}NO_5S$ 306.1365) obsd *m*/*z* 306.1375.

4,5-Dideoxy-4,5-epithio-2,3-*O*-isopropylidene-*aldehydo*-L-xylose Dimethyl Acetal (18b). Column chromatography (ether−hexane 2:1) of the crude product gave **18b** (67% from **16b)** as a syrup: $[\alpha]_D$ +32° (*c* 1, chloroform); IR (neat) 1213, 1152, 1081 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.38 (d, 1 H, J = 5.4 Hz), 4.04 (dd, 1 H, J = 7.0, 5.4 Hz), 3.78 (t, 1 H, J = 6.7 Hz), 3.48, 3.46 (2 s, 6 H), 3.05 (dt, 1 H, J = 6.4, 5.3 Hz), 2.52 (dd, 1 H, J = 6.3, 1.3 Hz), 2.39 (dd, 1 H, J = 5.3, 1.3 Hz), 1.46, 1.43 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 110.3, 104.3, 81.1, 80.1, 56.1, 54.4, 34.4, 27.3, 27.1, 22.3; MS (calcd mass for $C_{10}H_{18}O_4S$ + H 235.1004) obsd *m*/*z* 235.1007.

3-*O*-Benzyl-2,4,5-trideoxy-4,5-epithio-*aldehydo*-D-*threo*-pentose Dimethyl Acetal (70). Column chromatography (ether−hexane 3:1) of the crude product gave **70** (83% from **69**) as a syrup: $[\alpha]_D$ +42° (*c* 1, chloroform); IR (neat) 1232, 1182, 1124, 1098, 1073 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36−7.30 (m, 5 H), 4.72 (AB system, 2 H, J = 11.6 Hz, $\delta\nu$ = 35.5 Hz), 4.56 (dd, 1 H, J = 7.3, 4.2 Hz), 3.30, 3.26 (2 s, 6 H), 3.28−3.22 (m, 1 H), 2.97 (ddd, 1 H, J = 7.7, 6.5, 5.6 Hz), 2.43(dd, 1 H, J = 6.5, 1.4 Hz), 2.13 (dd, 1 H, J = 5.6, 1.4 Hz), 2.01 (ddd, 1 H, J = 14.1, 8.6, 4.2 Hz), 1.91 (ddd, 1 H, J = 14.1, 7.4, 4.1 Hz); ^{13}C NMR ($CDCl_3$) δ 138.4, 128.3, 127.9, 127.6, 101.8, 80.1, 71.7, 53.4, 52.7, 38.6, 36.5, 20.0; MS *m*/*z* 237 (M^+ + 1 − CH_4O), 205, 179, 147.

Synthesis of 3,4-Dideoxy-3,4-epithio-1,2:5,6-di-*O*-isopropylidene-D-iditol (20). To a solution of **19** (1mmol) in methanol (60 mL) was added $NaS_2 \cdot 9H_2O$ (0.27 g). The reaction mixture was heated under reflux for 30 min. After cooling and evaporation under vacuum, the crude was dissolved in EtOAc (75 mL) and washed with water (25 mL). The organic layer was dried, filtered, and evaporated. The residue was purified by column chromatography (ether−hexane 4:1) to give **20** (110 mg, 42%) as a solid: mp 45−47 °C; $[\alpha]_D$ −15° (*c* 2, chloroform); IR (KBr) 1370, 1253, 1209, 1152, 1050, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.17 (dd, 1 H, J = 8.6, 4.6 Hz), 4.15 (dd, 1 H, J = 8.6, 4.1 Hz), 4.04−3.95 (m, 2 H), 3.88−3.80 (m, 2 H), 3.06 (dd, 1 H, J = 7.6, 4.3 Hz), 2.98 (dd, 1 H, J = 8.2, 4.3 Hz), 1.45, 1.40, 1.36, 1.31 (4s, 12 H); ^{13}C NMR ($CDCl_3$) δ 110.3, 109.9, 75.2, 74., 68.6, 66.6, 57.5, 56.0, 26.9, 26.7, 25.6, 25.3; MS *m*/*z* 245 ($M^+ - CH_3$), 229. Anal. Calcd for $C_{12}H_{20}O_4S$: C, 55.36; H, 7.35. Found: C, 55.56; H, 8.00.

Treatment of the Cyclic Sulfates 9a,d with Sodium Sulfide. To a solution of the cyclic sulfate **9a**,**d** (1 mmol) in acetone (15 mL) was added a solution of $Na_2S \cdot 9H_2O$ (0.24 g, 1 mmol) in acetone−water (15:2 mL). The reaction mixture was left at rt for 2 h until TLC (methanol−chloroform 1:3) showed complete disappearance of the starting material. The reaction mixture was evaporated under vacuum and coevaporated with toluene (3 × 10 mL), giving a crude product that was purified by column chromatography (methanol−chloroform 1:2).

Bis[1,2-*O*-isopropylidene-5-*O*-sulfo-α-D-glucofuranosid-6-yl] Sulfide Disodium Salt (21). Column chromatography of the crude product gave **21** (0.290 g, 90%) isolated as a solid: mp 170−172 °C; $[\alpha]_D$ −29° (*c* 1, methanol); IR (KBr) 3444, 1221, 1074, 956, 912 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.82 (d, 2 H, J = 3.6 Hz), 5.12 (d, 2 H, J = 2.6 Hz), 4.42 (d, 2 H, J = 3.6 Hz), 4.32 (dt, 2 H, J = 9.7, 2.9 Hz), 4.22 (dd, 2 H, J = 9.6, 2.1 Hz), 4.05 (t, 2 H, J = 2.4 Hz), 3.04 (dd, 2 H, J = 14.4, 3.2 Hz), 2.89 (dd, 2 H, J = 14.4, 2.6 Hz), 1.38, 1.23 (2 s, 12 H); ^{13}C NMR (DMSO-d_6) δ 110.8, 104.6, 84.1, 79.3, 73.7, 71.9, 36.7, 26.7, 26.3; MS (FAB) *m*/*z* 665 (M^+ + Na). Anal. Calcd for $C_{18}H_{28}O_{16}S_3Na_2 \cdot 3H_2O$: C, 31.03; H, 4.92. Found: C, 31.29; H, 4.62.

Bis[1,2-*O*-isopropylidene-3-*O*-benzyl-5-*O*-sulfo-α-D-glucofuranosid-6-yl] Sulfide Disodium Salt (22). Column chromatography of the crude product gave **22** (0.514 g, 62.5%) isolated as a solid: mp 144 °C dec; $[\alpha]_D$ −14° (*c* 1, methanol); IR (KBr) 1219, 1164, 1078, 1035, 995, 958 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.45−7.30 (m, 10 H), 5.76 (d, 2 H, J = 3.8 Hz), 4.67−4.51 (m, 6 H), 4.60 (d, 2 H, J = 3.9 Hz), 4.30 (dd, 2 H, J = 7.9, 2.7 Hz), 3.89 (d, 2 H, J = 2.5 Hz), 3.20 (dd, 2 H, J = 4.1, 3.3 Hz), 2.83 (dd, 2 H, J = 14.1, 3.5 Hz), 1.40, 1.24 (2 s, 12 H); ^{13}C NMR (DMSO-d_6) δ 138.3, 128.3, 128.0, 127.4, 110.9, 104.3, 81.8, 80.9, 79.2, 72.4, 71.5, 35.9, 26.9, 26.5. Anal. Calcd for $C_{32}H_{40}O_{16}S_3Na_2$: C, 46.71; H, 4.90. Found: C, 46.79; H, 5.26.

General Procedure for the Synthesis of Olefins 32b−f, 34, and 37. Cyclic sulfate **9a**,**c**−**f**, **15a**, or **36** (1 mmol) was treated with potassium selenium cyanate following the general procedure described above (except for **36** where 2.2 mmol of KSeCN was used). After evaporation of the acetone, the crude product was disolved in methanol (15 mL), and $NaBH_4$ (5 mmol) was then added portionwise under stirring. The reaction mixture was left at rt until TLC (methanol−chloroform 1:5) showed complete disappearance of the selenium cyanate salt (4−12 h). Methanol was removed *in vacuo*, and then water (25 mL) was added. The aqueous solution was extracted with AcOEt (3 × 25 mL), and the organic layers were collected, dried, and evaporated.

5,6-Dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (32b). Column chromatography (ether−hexane 2:1) of the crude product gave **32b** (50%) as a solid: mp 62−64 °C (lit.[32] mp 61−65 °C); $[\alpha]_D$ −36° (*c* 1, chloroform) [lit.[32] $[\alpha]_D$ −60° (*c* 2, chloroform)]; IR (Nujol) 3422, 1292, 1246, 1125, 1162, 1114, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) 5.90 (d, 1 H, J = 4.0 Hz), 5.85 (ddd, 1 H, J = 17.0, 11.0, 5.0 Hz), 5.47 (dt, 1 H, J = 17.0, 2.0 Hz), 5.35 (dt, 1 H, J = 11.0, 2.0 Hz), 4.66 (m, 1 H), 4.51 (d, 1 H, J = 4.0 Hz), 4.04 (d, 1 H, J = 2.0 Hz), 2.20 (s, 1 H), 1.46, 1.27 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 131.4, 119.6, 111.7, 104.6, 85.0, 85.1, 75.8, 26.7, 26.2; MS *m*/*z* 187 (M^+ + 1), 171, 169; MS (calcd mass for $C_9H_{15}O_4$ + H 187.0970) obsd *m*/*z* 187.0976. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.04; H, 7.70.

5,6-Dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-hex-5-enofuranose (32c). Column chromatography (ether−hexane 3:1) of the crude product gave **32c** (50%) as a syrup: $[\alpha]_D$ −70° (*c* 1, chloroform); IR (Nujol) 1645, 1256, 1217, 1195, 1165, 1116, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.96−5.87 (m, 2 H), 5.41 (bd, 1 H, J = 17.3 Hz), 5.28 (bd, 1 H, J = 10.5 Hz), 4.58 (m, 2 H), 3.64 (bs, 1 H), 3.35 (s, 3 H), 1.49, 1.31 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 132.0, 118.6, 111.4, 104.7, 85.6, 82.0, 81.2, 58.1, 26.7, 26.1; MS *m*/*z* 201 (M^+ + 1), 185 (M^+), 143; MS (calcd mass for $C_{10}H_{16}O_4$ + H 201.1127) obsd *m*/*z* 201.1111.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (32d). Column chromatography (ether−hexane 1:2) of the crude product gave **32d** (94.0%) as a syrup: $[\alpha]_D$ −79° (*c* 1, chloroform) [lit.[136] $[\alpha]_D$ −56.4° (*c* 3.22, chloroform)]; IR (neat) 1645, 1494, 1253, 1225, 1165, 1066, 1008 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (m, 5 H), 6.02 (ddd, 1 H, J = 17.5, 10.4, 7.1 Hz), 5.96 (d, 1 H, J = 3.8 Hz), 5.43 (bd, 1 H, J = 17.3 Hz), 5.31 (bd, 1 H, J = 10.5 Hz), 4.63 (m, 1 H), 4.62 (d, 1 H, J = 3.3 Hz), 4.59 (AB system, 2 H, J = 12.2 Hz, $\delta\nu$ = 21.0 Hz), 3.88 (d, 1 H, J = 3.1 Hz), 1.50, 1.32 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 137.6, 128.5, 127.9, 127.6, 132.3, 119.0, 111.5, 104.9, 83.5, 83.0, 81.6, 72.1, 26.9, 26.3; MS *m*/*z* 277 (M^+ + 1), 219.

3,5,6-Trideoxy-1,2-*O*-isopropylidene-α-D-*erythro*-hex-5-enofuranose (32e). Column chromatography (ether−hexane 2:1) of the crude product gave **32e** (67%) as a syrup: $[\alpha]_D$ −2.5° (*c* 1, chloroform); IR (neat) 1457, 1215, 1162, 1117, 1076, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (ddd, 1 H, J = 17.2, 10.4, 6.6 Hz), 5.80 (d, 1 H, J = 3.1 Hz), 5.31 (dt, 1 H, J = 17.2, 1.2 Hz), 5.16 (dt, 1 H, J = 10.4, 1.2 Hz), 4.70 (t, 1 H, J = 4.3 Hz), 4.60 (m, 1 H), 2.14 (dd, 1 H, J = 13.4, 4.4 Hz), 1.57 (ddd, 1 H, J = 13.4, 10.5, 4.7 Hz), 1.49, 1.29 (2 s, 6 H); MS *m*/*z* 171 (M^+ + 1), 113.

3-Azido-3,5,6-trideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hex-5-enofuranose (32f). Column chromatography (ether−hexane 1:3) of the crude product gave **32f** (60%) as a solid: mp 55−57 °C; $[\alpha]_D$ +99° (*c* 1, chloroform); IR (KBr) 2108, 2160, 1069 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (ddd, 1 H, J = 17.2, 10.3, 6.8 Hz), 5.82 (d, 1 H, J = 3.8 Hz), 5.51 (d, 1 H, J = 17.2 Hz), 5.36 (d, 1 H, J = 10.4 Hz), 4.71 (t, 1 H, J = 4.2 Hz), 4.49 (dd, 1 H, J = 9.6, 6.9 Hz), 3.18 (dd, 1 H, J = 9.6, 4.6 Hz), 1.59, 1.35 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) 133.7, 120.2, 113.1, 104.0, 79.9, 78.6, 64.9, 26.4, 26.3; MS *m*/*z* 292 ($M^+ - CH_3$), 249. Anal. Calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.20; N, 19.89. Found: C, 51.36; H, 6.46; N, 19.54.

2,5,6-Trideoxy-2-acetamido-3,4-*O*-isopropylidene-*aldehydo*-D-*xylo*-hex-5-ene Dimethyl Acetal (34). Column chromatography (ethyl acetate) of the crude product gave **34** (59%) as a solid: mp 109−110 °C; $[\alpha]_D$ +14°, $[\alpha]_{436}$ +24.5° (*c* 1, chloroform); IR (Nujol) 3277, 1647, 1558, 1312, 1292, 1244, 1151, 1076 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.00 (d, 1 H, J = 9.6 Hz), 5.82 (ddd, 1 H, J = 17.2, 10.3, 7.0 Hz), 5.45 (ddd, 1 H, J = 17.2, 1.4, 0.8 Hz), 5.28 (ddd, 1 H, J = 10.3, 1.4, 0.8 Hz), 4.39 (d, 1 H, J = 6.5 Hz), 4.24 (ddd, 1 H, J = 9.8, 6.6, 1.2 Hz), 4.05 (bt, 1 H, J = 8.0 Hz), 3.95 (dd, 1 H, J = 8.7, 1.2 Hz), 3.40, 3.32 (2 s, 6 H), 2.06 (s, 3 H), 1.43, 1.41 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.7, 134.2, 119.6, 109.2, 103.0, 79.2, 78.5, 55.1, 52.6, 47.6, 27.0, 26.8, 23.2; MS (calcd mass for $C_{13}H_{23}NO_5$ + H 274.1654) obsd *m*/*z* 274.1665. Anal. Calcd for $C_{13}H_{23}NO_5$: C, 57.13; H, 8.48; N, 5.12. Found: C, 57.28; H, 8.22; N, 5.40.

(3*R*,4*R*)-3,4-Bis(benzyloxy)-1,5-hexadiene (37). Column chromatography (ether−hexane 1:1) of the crude product gave **37** (45%) as a liquid: $[\alpha]_D$ −10°, $[\alpha]_{436}$ −15.6° (*c* 1.5, chloroform); IR (neat) 3064, 3029, 1494, 1092, 1070, 1028 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43−7.30 (m, 10 H), 5.94−5.83 (m, 2 H), 5.34 (d, 2 H, J = 16.2 Hz), 5.32 (dd, 2 H, J = 6.0, 1.0 Hz), 4.62 (AB system, 4 H, J = 12.2 Hz, $\delta\nu$ = 35.7 Hz), 3.94 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ, 138.7, 128.4, 127.8, 127.5, 135.3, 118.6, 82.5, 70.8; MS (calcd mass for $C_{20}H_{22}O_2$ + H 295.1698) obsd *m*/*z* 295.1687.

General Procedure for the Opening of Episulfides with Sodium Acetate. A mixture of episulfide **6**, **12a**,**c**,**d**,

(136) English, J.; Levy, M. F. *J. Am. Chem. Soc.* **1956**, *78*, 2846.

18a,**b**, or **70** (1 mmol) and anhydrous sodium acetate (1.5 g) in acetic anhydride (7 mL) and acetic acid (1.5 mL) was heated at 140 °C under an argon atmosphere until TLC showed complete disappearance of the starting material. The reaction was cooled and then was poured into ice−water, and the aqueous solution was extracted with chloroform (100 mL). The chloroform solution was successively washed with a saturated aqueous solution of sodium bicarbonate (3 × 100 mL) and water (50 mL), dried, and evaporated.

(2*R*)-1-Acetoxy-2-(acetylthio)-3-(benzyloxy)propane (38). Column chromatography (ether−hexane 1:3) of the crude product gave **38** (37%) as a syrup: $[\alpha]_D$ +1.5° (*c* 4.5, chloroform); IR (neat) 1742, 1692, 1235, 1108, 1030, 954 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38−7.30 (m, 5 H), 4.54 (bs, 2 H), 4.30 (dd, 1 H, J = 11.2, 6.3 Hz), 4.25 (dd, 1 H, J = 11.2, 5.5 Hz), 3.12 (ddt, 1 H, J = 6.3, 5.5, 4.6 Hz), 3.66 (dd, 1 H, J = 9.9, 4.6 Hz), 3.57 (dd, 1 H, J = 9.9, 6.3 Hz), 2.34, 2.01 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 137.8, 128.5, 127.8, 127.7, 73.2, 68.8, 63.3, 42.5, 30.7, 20.8; MS (calcd mass for $C_{14}H_{18}O_4S$ + H 283.1004) obsd *m*/*z* 283.0995.

3,6-Di-*O*-acetyl-5-*S*-acetyl-1,2-*O*-isopropylidene-5-thio-*β*-L-idofuranose (39a). Column chromatography (ether−hexane 1:2) of the crude product gave **39a** (61%) as a solid: mp 60−61 °C (lit.[83] mp 69−70 °C); $[\alpha]_D$ +9.5° (*c* 1, chloroform) [lit.[83] $[\alpha]_D$ +10° (*c* 0.6, chloroform)]; IR (KBr) 1736, 1688, 1431, 1375, 1214, 1164, 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79 (d, 1 H, J = 3.8 Hz), 5.13 (d, 1 H, J = 3.0 Hz), 4.44 (d, 1 H, J = 3.8 Hz), 4.29 (dd, 1 H, J = 8.4, 2.9 Hz), 4.16 (dd, 1 H, J = 13.2, 8.2 Hz), 4.10−3.99 (m, 2 H), 2.28, 2.05, 1.94 (3 s, 9 H), 1.42, 1.22 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 193.7, 170.2, 169.6, 112.1, 104.0, 83.5, 77.2, 76.2, 63.8, 41.4, 30.5, 26.5, 26.1, 20.8, 20.5 MS *m*/*z* 363 (M^+ + 1), 306, 305, 245. Anal. Calcd for $C_{15}H_{22}O_8S$: C, 49.72; H, 6.12, S, 8.85. Found: C, 49.90; H, 6.34; S, 8.75.

6-*O*-Acetyl-5-*S*-acetyl-3-*O*-methyl-1,2-*O*-isopropylidene-5-thio-*β*-L-idofuranose (39c). Column chromatography (ether−hexane 3:1) of the crude product gave **39c** (92%) as a syrup: $[\alpha]_D$ −31° (*c* 4.3, chloroform); IR (neat) 1743, 1692, 1232, 1165, 1114, 1077, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (d, 1 H, J = 3.9 Hz), 4.57 (d, 1 H, J = 3.9 Hz), 4.31−4.13 (m, 4 H), 3.68 (d, 1 H, J = 2.8 Hz), 3.39 (s, 3 H), 2.32, 2.04 (2 s, 6 H), 1.46, 1.29 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 194.1, 170.6, 111.7, 104.7, 84.0, 81.3, 78.6, 64.2, 57.5, 42.0, 30.6, 26.7, 26.2, 20.8; MS *m*/*z* 335 (M^+ + 1), 319, 275, 217; MS (calcd mass for $C_{14}H_{22}O_7S$ 335.1164) obsd *m*/*z* 335.1151.

6-*O*-Acetyl-5-*S*-acetyl-3-*O*-benzyl-1,2-*O*-isopropylidene-5-thio-*β*-L-idofuranose (39d). Column chromatography (ether−hexane 1:1) of the crude product gave **39d** (95%) as a syrup: $[\alpha]_D$ −36° (*c* 1, chloroform); IR (neat) 1742, 1696, 1227, 1164, 1075, 1029 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35−7.30 (m, 5 H), 5.92 (d, 1 H, J = 3.8 Hz), 4.63 (d, 1 H, J = 3.8 Hz), 4.60 (AB system, 2 H, J = 11.7 Hz, $\delta\nu$ = 32.5 Hz), 4.34−4.14 (m, 4 H), 3.95 (d, 1 H, J = 3.1 Hz), 2.31, 2.02, (2 s, 6 H), 1.48, 1.31 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 194.2, 170.5, 136.8, 128.6, 127.9, 127.5, 111.8, 104.8, 81.9, 78.5, 71.9, 64.0, 42.1, 30.5, 26.8, 26.3, 20.7; MS *m*/*z* 411 (M^+ + 1), 353, 351, 293; MS (calcd mass for $C_{20}H_{26}O_7S$ + H 411.1477) obsd *m*/*z* 411.1471.

2-Acetamido-6-*O*-acetyl-5-*S*-acetyl-2-deoxy-3,4-*O*-isopropylidene-5-thio-*aldehydo*-L-idose Dimethyl Acetal (42a). Column chromatography (ethyl acetate-hexane 2:1) of the crude product gave **34** (15%) first. Eluted second was **42a** (60%) as a syrup: $[\alpha]_D$ +21° (*c* 0.9, chloroform); IR (neat) 3258, 1746, 1689, 1637, 1559, 1231, 1099 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.87 (d, 1 H, J = 9.4 Hz), 4.31 (d, 1 H, J = 5.6 Hz), 4.27−3.95 (m, 6 H), 3.34, 3.31 (2 s, 6 H), 2.34, 2.03, 1.99 (3 s, 9 H), 1.36, 1.31 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 194.0, 170.5, 169.8, 109.6, 103.4, 76.4, 76.0, 64.3, 55.2, 53.6, 48.9, 43.5, 30.6, 27.0, 23.2, 20.7; MS (calcd mass for $C_{17}H_{29}NO_8S$ + H 408.1692) obsd *m*/*z* 408.1660.

Methyl 5-*O*-acetyl-3-*O*-benzyl-2-deoxy-1,4-dithio-α,*β*-D-*threo*-pentofuranoside (71). Column chromatography (ether−hexane 1:3) of the crude product gave **71** (mixture of stereoisomers) (30%) as a syrup: IR (neat) 1740, 1239, 1082 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38−7.30 (m, 5 H), 5.08 (dd, ∼0.4 H, J = 5.2, 4.9 Hz), 5.03 (dd, ∼0.6 H, J = 5.0, 4.3 Hz), 4.65−4.40, 4.27−4.11 (2 m, 5 H), 3.75 (dt, ∼0.6 H, J = 7.7, 6.0 Hz), 3.63 (ddd, 0.4 H, J = 6.4, 5.5 Hz), 3.29, 3.27 (2 s, 3 H), 2.40−2.27 (m, 2 H), 2.01, 2.00 (2s, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.7, 137.8, 128.3, 127.8, 127.7, 88.2, 86.6, 80.6, 80.0, 72.1, 71.2, 64.5, 57.0, 56.6, 48.2, 45.9, 40.8, 40.0, 20.9, 20.8; MS *m*/*z* 297 (M^+ + 1), 295, 237.

General Procedure for the Synthesis of the Thiol Derivatives 40b−d, 43a,b, and 72. A mixture of the potassium salts **11a**,**c**,**d** and **17a** (1 mmol) or the episulfide **12b**,**d**, **18a**,**b**, or **70** (1 mmol) and lithium aluminum hydride (6 mmol for **11a**,**c**,**d** and **17a** and 4 mmol for **12b**,**d**, **18a**,**b**, and **70**) in dry THF (20 mL) was stirred at rt until TLC showed complete disappearance of the starting material. After cooling, ethyl acetate (25 mL) was added. The solid was filtered through Celite, and the solution was evaporated. The residue was dissolved in ethyl acetate (100 mL) and washed with water (30 mL). The organic layer was dried, concentrated, and evaporated.

6-Deoxy-1,2-*O*-isopropylidene-5-thio-*β*-L-idofuranose (40b). Column chromatography (ether) of the crude product gave **40b** (84% from **11a** and 98% from **12b**) as a solid: mp 91−92 °C (from ether−hexane) (lit.[134] mp 93−94 °C); $[\alpha]_D$ −20° (*c* 1, chloroform) (lit.[134] $[\alpha]_D$ −24°); IR (KBr) 3467, 1217, 1165, 1071, 1013 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91 (d, 1 H, J = 3.8 Hz), 4.50 (d, 1 H, J = 3.8 Hz), 4.15 (dd, 1 H, J = 6.4, 2.7 Hz), 3.94 (dd, 1 H, J = 8.4, 2.7 Hz), 3.28 (ddq, 1 H, J = 8.4, 6.9, 5.4 Hz), 2.27 (dd, 1 H, J = 6.5 Hz), 2.12 (d, 1 H, J = 5.4 Hz), 1.49, 1.30 (2 s, 6 H), 1.34 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 111.9, 104.3, 85.8, 85.4, 75.0, 33.7, 26.8, 26.3, 20.7; MS *m*/*z* 220 (M^+), 205, 159. Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32, S, 14.55. Found: C, 49.18; H, 7.12; S, 14.16.

6-Deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-5-thio-*β*-L-idofuranose (40c). Column chromatography (ether−hexane 1:1) of the crude product gave **40c** (65% from **11c**) as a syrup: $[\alpha]_D$ −68° (*c* 1, chloroform); IR (neat) 2580, 1256, 1216, 1190, 1167, 1118, 1079, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.88 (d, 1 H, J = 3.9 Hz), 4.61 (d, 1 H, J = 3.9 Hz), 3.94 (dd, 1 H, J = 9.7, 3.1 Hz), 3.64 (d, 1 H, J = 3.1 Hz), 3.40 (s, 3 H), 3.31 (ddq, 1 H, J = 9.7, 6.9, 5.0 Hz), 2.11 (dd, 1 H, J = 5.0 Hz), 1.51, 1.33 (2 s, 6 H), 1.25 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 111.6, 104.6, 86.3, 83.4, 81.6, 57.6, 33.4, 26.8, 26.2, 19.3; MS *m*/*z* 234 (M^+), 173; MS (calcd mass for $C_{10}H_{18}O_4S$ + H 235.1004) obsd *m*/*z* 235.0993.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-thio-*β*-L-idofuranose (40d). Column chromatography (ether−hexane 1:2) of the crude product gave **40d** (59% from **11d** and 66% from **12d**) as a solid: mp 54−56 °C; $[\alpha]_D$ −66° (*c* 1, chloroform); IR (neat) 2588, 1256, 1219, 1168, 1080, 1027 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.25 (m, 5 H), 5.91 (d, 1 H, J = 3.8 Hz), 4.56 (AB system, 2 H, J = 11.6 Hz, $\delta\nu$ = 45.1 Hz), 4.66 (d, 1 H, J = 3.8 Hz), 3.94 (dd, 1 H, J = 9.7, 3.2 Hz), 3.87 (d, 1 H, J = 3.2 Hz), 3.39 (ddq, 1 H, J = 9.6, 6.9, 4.2 Hz), 2.11 (d, 1 H, J = 4.2 Hz), 1.50, 1.32 (2 s, 6 H), 1.13 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 137.0, 128.5, 128.1, 127.9, 111.7, 104.6, 86.3, 82.1, 81.0, 71.8, 33.3, 26.8, 26.3, 19.1. Anal. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14. Found: C, 62.12; H, 7.14.

2-Acetamido-2,6-dideoxy-3,4-*O*-isopropylidene-5-thio-*aldehydo*-L-idose Dimethyl Acetal (43a). Column chromatography (ether) of the crude product gave **43a** (31% from **17a** and 80% from **18a**) as a solid: mp 95−96 °C; $[\alpha]_D$ +37° (*c* 1, chloroform); IR (KBr) 3275, 3082, 2582, 1647, 1559, 1312, 1256, 1212, 1109, 1068 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91 (d, 1 H, J = 9.6 Hz), 4.40 (d, 1 H, J = 6.4 Hz), 4.30−4.20 (m, 2 H), 3.62 (dd, 1 H, J = 8.1, 4.9 Hz), 3.42, 3.33 (2 s, 6 H), 3.04 (ddq, 1 H, J = 7.3, 7.1, 4.9 Hz), 2.05 (s, 3 H), 1.83 (d, 1 H, J = 7.3 Hz), 1.43, 1.41 (2 s, 6 H), 1.39 (d, 1 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 169.8, 109.2, 103.2, 81.9, 77.2, 55.4, 52.8, 49.4, 36.7, 27.3, 27.2, 23.3, 22.1; MS (calcd mass for $C_{13}H_{25}NO_5S$ + H 308.1531) obsd *m*/*z* 308.1552.

5-Deoxy-2,3-*O*-isopropylidene-4-thio-*aldehydo*-L-*arabino*-pentose Dimethyl Acetal (43b). Column chromatography (ether) of the crude product gave **43b** (93% from **18b**) as a syrup: $[\alpha]_D$ +2.5° (*c* 2, chloroform); IR (neat) 2580, 1240, 1213, 1137, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.37 (d, 1 H, J = 5.8 Hz), 4.03 (dd, 1 H, J = 6.3, 4.7 Hz), 3.95 (dd, 1 H, J = 6.2, 5.9 Hz), 3.44 (s, 6 H), 3.04 (ddq, 1 H, J = 7.3, 7.1, 4.9 Hz), 1.78 (d, 1 H, J = 7.3 Hz), 1.40 (s, 6 H), 1.35 (d, 1 H, J = 6.9

Hz); ^{13}C NMR ($CDCl_3$) δ 110.4, 105.1, 83.1, 78.3), 56.1, 54.2, 36.7, 27.5, 27.4, 19.7; MS *m*/*z* 237 ($M^+ + 1$), 147.

3-*O*-Benzyl-2,5-dideoxy-4-thio-*aldehydo*-D-*threo*-pentose Dimethyl Acetal (72). Column chromatography (ether−hexane 1:1) of the crude product gave **72** (36% from **70**) as a syrup: $[\alpha]_{365}$ +66° (*c* 1, chloroform); IR (neat) 2568, 1494, 1451, 1126, 1065, 1028 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38−7.25 (m, 5 H), 4.58 (AB system, 2 H, J = 11.4 Hz, $\delta\nu$ = 19.9 Hz), 4.57 (dd, 1 H, J = 7.7, 3.1 Hz), 3.57 (dt, 1 H, J = 7.8, 3.8 Hz), 3.34, 3.31 (2 s, 6 H), 3.18 (m, 1 H), 2.07 (ddd, 1 H, J = 11.3, 7.7, 3.5 Hz), 1.83 (ddd, 1 H, J = 11.3, 7.7, 3.5 Hz), 1.62 (d, 1 H, J = 7.5 Hz), 1.35 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 138.4, 128.4, 127.7, 127.4, 102.1, 80.2, 72.3, 52.9, 52.3, 37.4, 33.6, 20.1.

6-Deoxy-1,2-*O*-isopropylidene-5-thio-α-L-galactofuranose (62). Cyclic sulfate **60** was reacted with potassium thiocyanate following the general procedure described above for the opening of cyclic sulfates. The corresponding potassium salt **61** was then treated directly with $LiAlH_4$. Column chromatography (ether) of the crude product gave **62** (83% overall yield from **60**) as a syrup: $[\alpha]_D$ +40° (*c* 1, methanol), [lit.[84] $[\alpha]_D$ +41.7° (*c* 1, dichloromethane)]; IR (KBr) 3446, 2582, 1164, 1069, 1017 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.84 (d, 1 H, J = 4.0 Hz), 4.52 (d, 1 H, J = 3.9 Hz), 4.19 (bs, 1 H), 3.68 (dd, 1 H, J = 8.5, 3.2 Hz), 3.40 (bs, 1 H), 3.25 (ddq, 1 H, J = 7.0, 5.2, 3.2 Hz), 2.06 (d, 1 H, J = 5.2 Hz), 1.49, 1.28 (2 s, 6 H), 1.31 (d, 1 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 113.0, 104.8, 91.5, 87.3, 76.1, 36.4, 27.2, 26.2, 20.1.

5-*S*-Acetyl-3-acetamido-3,6-dideoxy-1,2-*O*-isopropylidene-5-thio-β-L-talofuranose (41g). A mixture of **11f** (1 mmol) and lithium aluminum hydride (7 mmol) in dry THF (25 mL) was stirred at rt under an argon atmosphere for 20 h. After cooling, the reaction was mixed with ethyl acetate (10 mL) and methanol (10 mL), filtered through Celite, and evaporated The crude product was conventionally acetylated using Ac_2O−Py (5:5 mL). After standard workup, the crude was purified by column chromatography (ethyl acetate), yielding **41g** (55%) as a solid: mp 172−173 °C; $[\alpha]_D$ +28° (*c* 1, chloroform); IR (KBr) 1680, 1646, 1548, 1375, 1105, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.82 (d, 1 H, J = 3.6 Hz), 5.73 (d, 1 H, J = 9.9 Hz), 4.59 (dd, 1 H, J = 4.8, 3.8 Hz), 4.50 (dt, 1 H, J = 9.3, 4.8 Hz), 3.95−3.86 (m, 2 H), 2.38, 2.06 (2 s, 6 H), 1.59, 1.37 (2 s, 6 H), 1.46 (d, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 194.5, 169.9, 112.5, 103.9, 81.8, 78.9, 52.7, 39.4, 30.7, 26.7, 26.3, 23.2, 19.3; MS (calcd mass for $C_{13}H_{21}O_5NS$ + H 304.1218) obsd *m*/*z* 304.1218. Anal. Calcd for $C_{13}H_{21}NO_5S$: C, 51.47; H, 6.98; N, 4.62. Found: C, 51.25; H, 7.10; N, 4.68.

General Procedure for the Acetylation of the Thiol Derivatives 40b,c,d and 72. The thiol (1 mmol) was acetylated overnight at rt with acetic anhydride (4 mL) and pyridine (2.0 mL). Processing of the mixture by treatment with excess of methanol and evaporation with several portions of added methanol followed by toluene gave a crude product.

3-*O*-Acetyl-5-*S*-acetyl-6-deoxy-1,2-*O*-isopropylidene-5-thio-β-L-idofuranose (41a). Column chromatography (ether−hexane 2:1) of the crude product gave **41a** (94%) as a solid: mp 75 °C; $[\alpha]_D$ −13° (*c* 2, chloroform); IR (KBr) 1747, 1689, 1230, 1097, 1066, 1051, 1023 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.90 (d, 1 H, J = 3.8 Hz), 5.20 (d, 1 H, J = 2.9 Hz), 4.51 (d, 1 H, J = 3.8 Hz), 4.20 (dd, 1 H, J = 9.9, 2.9 Hz), 3.84 (dq, 1 H, J = 9.9, 6.9 Hz), 2.34, 2.14 (2 s, 6 H), 1.51, 1.30 (2 s, 6 H), 1.29 (d, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 194.7, 169.8, 112.1, 104.5, 83.5, 80.3, 75.9, 37.9, 30.7, 26.6, 26.1, 20.8, 18.2; MS *m*/*z* 305 ($M^+ + 1$), 247, 187; MS (calcd mass for $C_{30}H_{20}O_6S$ + H 305.1059) obsd *m*/*z* 305.1048.

5-*S*-Acetyl-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-5-thio-β-L-idofuranose (41c). Column chromatography (ether−hexane 1:3) of the crude product gave **41c** (86%) as a syrup: $[\alpha]_D$ −44° (*c* 3, chloroform); IR (neat) 1686, 1215, 1167, 1116, 1080, 1021 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.89 (d, 1 H, J = 3.9 Hz), 4.60 (d, 1 H, J = 3.9 Hz), 4.08 (dd, 1 H, J = 10.2, 3.1 Hz), 3.90 (dq, 1 H, J = 10.2, 6.8 Hz), 3.66 (d, 1 H, J = 3.1 Hz), 3.42 (s, 3 H), 2.32 (s, 3 H), 1.49, 1.32 (2 s, 6 H), 1.32 (d, 3 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 195.0, 111.6, 104.9, 83.8, 81.5, 81.2, 57.6, 38.5, 30.8, 26.8, 26.3, 18.2; MS *m*/*z* 277 ($M^+ + 1$), 261, 219, 159; MS (calcd mass for $C_{12}H_{20}O_5S$ + H 277.1109) obsd *m*/*z* 277.1087.

5-*S*-Acetyl-3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-5-thio-β-L-idofuranose (41d). Column chromatography (ether−hexane 1:4) of the crude product gave **41d** (87%) as a syrup: $[\alpha]_D$ −33° (*c* 1, chloroform); IR (neat) 1686, 1216, 1166, 1112, 1075, 1022 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40−7.30 (m, 5 H), 5.92 (d, 1 H, J = 3.8 Hz), 4.64 (d, 1 H, J = 3.8 Hz), 4.60 (AB system, 2 H, J = 11.8 Hz, $\delta\nu$ = 39.8 Hz), 4.11 (dd, 1 H, J = 10.1, 3.1 Hz), 3.97 (dq, 1 H, J = 10.1, 6.8 Hz), 3.89 (d, 1 H, J = 3.1 Hz), 2.30 (s, 3 H), 1.49, 1.31 (2 s, 6 H), 1.22 (d, 3 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 195.0, 137.0, 128.5, 128.0, 127.9, 111.6, 104.9, 81.7, 81.5, 81.4, 71.8, 38.5, 30.8, 26.8, 26.3, 18.6; MS *m*/*z* 353 ($M^+ + 1$), 295, 235; MS (calcd mass for $C_{18}H_{24}O_5S$ + H 353.1423) obsd *m*/*z* 353.1406.

4-*S*-Acetyl-3-*O*-benzyl-2,5-dideoxy-4-thio-*aldehydo*-D-*threo*-pentose Dimethyl Acetal (73). Column chromatography (ether−hexane 1:1) of the crude product gave **73** (97%) as a syrup: $[\alpha]_D$ +73° (*c* 2, chloroform); IR (neat) 1689, 1125, 1090, 1056 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40−7.30 (m, 5 H), 4.64 (AB system, 2 H, J = 11.7 Hz, $\delta\nu$ = 20.7 Hz), 4.50 (dd, 1 H, J = 6.6, 5.1 Hz), 3.95 (dq, 1 H, J = 7.2, 3.2 Hz), 3.64 (ddd, 1 H, J = 8.2, 5.1, 3.2 Hz), 3.31, 3.23 (2 s, 6 H), 2.34 (s, 3 H), 1.81−1.76 (m, 2 H), 1.30 (d, 3 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 195.4, 138.5, 128.4, 127.9, 127.7, 102.3, 78.0, 72.0, 53.1, 52.8, 40.6, 34.2, 30.8, 15.4.

General Procedure for the Synthesis of Thiosugars 44, 46, 48, 50, 52, 54, and 74. A solution of the S-acetyl derivative **39a**,**c**,**d**, **41a**,**c**,**d**, or **73** (2 mmol) in 70% aqueous acetic acid (20 mL) was heated at ∼80 °C until TLC showed complete disappearance of the starting material. After cooling, the reaction mixture was concentrated and coevaporated with toluene. The crude product was dissolved in anhydrous methanol (25 mL), and a 0.5 N solution of sodium methoxide in methanol (0.5 mL) was added. The reaction mixture was left at rt for 3 h. After deoinization by Amberlite IR-120(H^+) resin the solution was evaporated and the product was purified.

5-Thio-α,β-L-idopyranose (44). Column chromatography (methanol−chloroform 1:3) of the crude product gave **44** (35%) (∼1:2 mixture of α/β steroisomers) as a syrup: $[\alpha]_D$ +17° (*c* 1, methanol) (3 h); IR (neat) 3355, 1269, 1052, 969 cm^{-1}; ^{1}H NMR (D_2O) δ 4.96 (d, J = 7.1 Hz, H-1α), 4.95 (d, J = 3.4 Hz, H-1β), 4.10 (dd, J = 11.5, 6.7 Hz, H-6β), 4.04 (t, J = 9.7 Hz, H-3α), 4.02 (t, J = 9.1 Hz, H-3β), 3.92 (dd, J = 11.5, 4.7 Hz, H-6′β), 3.90 (m, H-6α), 3.88 (t, J = 9.2 Hz, H-4β), 3.80 (m, H-6′α), 3.78 (dd, J = 9.3, 3.3 Hz, H-2β), 3.61 (t, J ∼ 8.6 Hz, H-2α), 3.56 (t, J ∼ 8.7 Hz, H-4α), 3.20 (m, H-5β), 3.12 (m, H-5α); ^{13}C NMR (D_2O) δ 77.6 (C-2α), 75.6 (C-2β), 73.9 (C-3β), 73.5 (C-1β), 73.3 (C-3α), 73.0 (C-4α), 72.3 (C-1α), 70.2 (C-4β), 61.2 (C-6β), 59.5 (C-6α), 46.1 (C-5β), 45.8 (C-5α); MS *m*/*z* 196 (M^+), 178 ($M^+ - H_2O$), 160 ($M^+ - 2\ H_2O$); MS (calcd mass for $C_6H_{12}O_5S$ 196.0405) obsd *m*/*z* 196.0401.

3-*O*-Methyl-5-thio-α,β-L-idopyranose (46). Column chromatography (methanol−chloroform 1:5) of the crude product gave **46** (56%) (∼1:2 mixture of α/β stereoisomers) as a syrup: $[\alpha]_D$ +10° (*c* 3.4, methanol) (5 min); IR (neat) 3294, 1192, 1105, 974, 904 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.18 (d, J = 7.2 Hz, exchangeable with D_2O), 5.85 (d, J = 6.8 Hz, exchangeable with D_2O), 5.13−4.96 (several m, exchangeables with D_2O), 4.80−4.71 (m, after isotopic exchange was transformed in two doublets at δ 4.75, J = 7.9 Hz and δ 4.70, J = 2.8 Hz), 3.78−3.10 (several m), 3.40, 3.39 (2 s, 3 H), 2.99 (m), 2.83 (m); ^{13}C NMR (DMSO-d_6) δ 83.3, 81.3, 76.0, 74.1, 73.7, 71.2, 60.9, 60.6, 59.7, 59.4, 46.0, 44.8; MS *m*/*z* 210 (M^+), 192, 178, 149.

3-*O*-Benzyl-5-thio-α,β-L-idopyranose (48). Column chromatography (methanol−chloroform 1:7) of the crude gave **48** (57%) as a solid: mp 102−103 °C (from ether); $[\alpha]_D$ +9°, $[\alpha]_{436}$ +18° (5 min), $[\alpha]_D$ +5°, $[\alpha]_{436}$ +12° (24 h) (*c* 2, methanol); IR (KBr) 3314, 1118, 1101, 1066, 1026 cm^{-1}; ^{1}H NMR (D_2O, 500 MHz) δ 7.45−7.18 (m, Ph), 5.00 (d, J = 2.5 Hz, H-1β), 4.98 (d, J = 7.7 Hz, H-1α), 4.76−4.70 (m, PhCH_2), 4.14 (dd, J = 7.0, 5.0 Hz, H-4α), 4.13 (dd, J = 7.5, 5.1 Hz, H-4β), 4.07 (dd, J = 11.3, 6.7 Hz, H-6β), 3.95 (dd, J = 11.5, 4.8 Hz, H-6α), 3.93−3.86 (m, H-2β,3β,6′β), 3.81 (dd, J = 11.6, 8.0 Hz, H-6′α), 3.79 (t, J = 7.7 Hz, H-2α), 3.62 (t, J = 8.0 Hz, H-3α), 3.24 (m, H-5α,β); ^{13}C NMR (D_2O, 100 MHz) δ 139.5, 139.2, 129.3, 128.6, 128.1, 127.8, 127.1, 125.7 (C_6H_5), 81.0 (C-3α), 79.5 (C-3β), 76.0

(C-2α), 75.1 (Ph*C*H$_2$*β*), 74.9 (C-2*β*), 74.7 (Ph*C*H$_2$α), 73.7 (C-1*β*), 73.0 (C-1α), 72.3 (C-4α,*β*), 61.3 (C-6*β*), 60.1 (C-6α), 46.1 (C-5*β*), 44.5 (C-5α); MS *m*/*z* 269 ($M^+ + 1 - H_2O$), 25, 161, 145, 143; MS (FAB) *m*/*z* 287 ($M^+ + 1$). Anal. Calcd for $C_{13}H_{18}O_5S$: C, 54.53; H, 6.34; S, 11.20. Found: C, 54.36; H, 6.45; S, 11.19.

6-Deoxy-5-thio-α,*β*-L-idopyranose (50). Column chromatography (methanol−chloroform 1:3) of the crude product gave **50** (90%) (∼1:1.3 mixture of α/*β* steroisomers) as a syrup: [α]$_D$ −11° (5 min), −9.5° (24 h) (*c* 1, water); IR (neat) 3378, 1076, 1053, 1010 cm^{-1}; ^{1}H NMR (D$_2$O, 400 MHz) *δ* 5.01 (d, *J* = 3.2 Hz, H-1*β*), 4.89 (d, *J* = 8.2 Hz, H-1α), 3.95−3.87 (m, H-4α, H-4*β*, H-3*β*), 3.78 (dd, *J* = 8.5, 3.2 Hz, H-2*β*), 3.60−3.53 (m, H-2α, H-3α), 3.11−3.06 (m, H-5α,*β*), 1.47 (d, *J* = 7.4 Hz, Me *β*-anomer), 1.36 (d, *J* = 7.4 Hz, Me α-anomer); ^{13}C NMR (D$_2$O) *δ* 78.1 (C-2α), 75.7 (C-2*β*), 74.9 (C-4*β*), 74.6 (C-1*β*), 74.5 (C-4α), 72.5 (C-3α), 71.8 (C-1α), 69.3 (C-3*β*), 39.0 (C-5α), 37.9 (C-5*β*), 17.4 (C-6α), 14.7 (C-6*β*); MS *m*/*z* 186 (M^+), 169; MS (calcd mass for $C_6H_{12}O_4S$ 186.0405) obsd *m*/*z* 186.0401.

6-Deoxy-3-*O*-methyl-5-thio-α,*β*-L-idopyranose (52). Column chromatography (ether) of the crude product gave **52** (62%) (∼1:1.25 mixture of α/*β* steroisomers) as a syrup: [α]$_D$ −7.5° (*c* 2.1, methanol) (5 min); IR (neat) 3398, 1232, 1051, 1030, 970 cm^{-1}; ^{1}H NMR (D$_2$O, 500 MHz) *δ* 5.02 (d, *J* = 3.1 Hz), 4.89 (d, *J* = 8.3 Hz), 4.01 (dd, *J* = 8.2, 4.6 Hz), 3.99 (dd, *J* = 8.6, 4.7 Hz), 3.87 (dd, *J* = 9.2, 3.3 Hz), 3.69 (dd, *J* = 8.4, 8.0 Hz), 3.60 (s), 3.59 (dd, *J* = 9.2, 8.8 Hz), 3.58 (s), 3.32 (dd, *J* = 8.6, 8.4 Hz), 3.12 (m), 1.48 (d, *J* = 7.4 Hz), 1.37 (d, *J* = 7.4 Hz); ^{13}C NMR (DMSO-*d*$_6$) *δ* 82.8, 80.4, 80.4, 76.7, 74.5, 73.1, 73.0, 59.1, 59.8, 38.6, 37.0, 17.4, 15.4; MS *m*/*z* 194 (M^+), 176, 162.

3-*O*-Benzyl-6-deoxy-5-thio-α,*β*-L-idopyranose (54). Column chromatography (ether) of the crude product gave **54** (65%) (∼1:2 mixture of α/*β* steroisomers) as a syrup: [α]$_D$ −11.0° (*c* 1.6, methanol) (5 min); IR (neat) 3393, 1209, 1096, 1075, 1028 cm^{-1}; ^{1}H NMR (D$_2$O, 500 MHz) *δ* 7.45−7.18 (m, 5 H, Ph), 5.07 (d, *J* = 2.5 Hz, H-1*β*), 4.90 (d, *J* = 7.8 Hz, H-1α), 4.86−4.78 (m, PhC*H*$_2$), 4.08 (dd, *J* = 8.0, 4.1 Hz, H-4α), 3.97 (dd, *J* = 7.5, 4.2 Hz, H-4*β*), 3.93 (dd, *J* = 7.9, 2.8 Hz, H-2*β*), 3.88 (t, *J* = 7.7 Hz, H-3*β*), 3.76 (t, *J* = 7.9 Hz, H-2α), 3.59 (t, *J* = 8.0 Hz, H-3*β*), 3.20 (m, H-5α,*β*), 1.46 (d, *J* = 7.2 Hz, Me of *β*-anomer), 1.26 (d, *J* = 7.3 Hz, Me of α-anomer); ^{13}C NMR (D$_2$O) *δ* 139.3, 139.2, 130.3, 130.2, 130.1 130.1, 129.8, 129.3, 128.9 (C$_6$H$_5$), 82.1(C-3α), 80.0 (C-3*β*), 80.0 (C-2*β*), 77.3 (C-2α), 75.5 (C-1*β*), 74.7 (C-4α,*β*), 74.2 (C-1α), 76.0, 75.9 (Ph*C*H$_2$), 40.2 (C-5α), 38.1 (C-5*β*), 18.6 (Me of *β*-anomer), 16.4 (Me of α-anomer); MS *m*/*z* 270 (M^+), 252 ($M^+ - H_2O$), 239 ($M^+ - CH_3O$), 185 ($M^+ - C_3H_5OS$); HRMS (EI$^+$) calcd for $C_{13}H_{18}O_4S$ 270.0926 (M^+), found 270.0922.

3-*O*-Benzyl-2,5-dideoxy-4-thio-α,*β*-D-*threo*-pentofuranose (74). Column chromatography (ether−hexane 1:1) of the crude product gave **74** (70%) (∼1.4:1 mixture of α/*β* steroisomers) as a syrup: [α]$_D$ +30° (5 min); ^{1}H NMR (CDCl$_3$) *δ* 7.40−7.25 (m), 5.48−5.42 (m), 4.68−4.52 (m), 4.35 (dt, *J* = 9.3, 5.4 Hz), 4.08 (m), 3.69 (dq, *J* = 6.9, 6.0 Hz), 3.60 (bs), 3.54 (dq, *J* = 6.8, 3.9 Hz), 2.61 (dd, *J* = 13.9, 1.1 Hz), 2.42 (bs), 2.32 (ddd, *J* = 13.2, 9.2, 5.3 Hz), 2.19 (ddd, *J* = 13.2, 5.0, 2.6 Hz), 1.97 (ddd, *J* = 13.9, 4.9, 3.0 Hz), 1.48 (d, *J* = 6.8 Hz), 1.23 (d, *J* = 7.0 Hz); ^{13}C NMR (CDCl$_3$) *δ* 137.5, 128.6, 128.5, 128.1, 127.9, 127.8, 127.6, 127.0, 83.9, 83.3, 81.5, 65.3, 72.0, 48.7, 44.4, 43.1, 41.9, 17.0, 16.0.

Synthesis of 5-Deoxy-4-thio-α,*β*-L-arabinofuranose (56). A solution of **43b** (1.5 mmol) in 70% aqueous acetic acid (6 mL) was heated at ∼55 °C for 40 h. After cooling, the reaction mixture was concentrated and coevaporated with toluene. The crude product was purified by column chromatography (methanol−chloroform 1:10). Eluted first was a complex mixture (70 mg, R_f = 0.7 in methanol:chloroform 1:7) that was not further investigated. Eluted second was **27b** (120 mg, 54%) (∼1.4:1 mixture of α/*β* steroisomers) as a syrup: IR (neat) 3352, 1098, 1067, 1026, 298 cm^{-1}; ^{1}H NMR (D$_2$O) *δ* 5.24 (d, *J* = 6.0 Hz, H-1*β*), 5.12 (d, *J* = 4.7 Hz, H-1α), 3.95 (dd, *J* = 10.1, 4.7 Hz, H-2α), 3.93 (dd, *J* = 8.9, 6.0 Hz, H-2*β*), 3.80 (dd, *J* = 10.0, 8.7 Hz, H-3α), 3.58 (t, *J* = 9.0 Hz, H-3*β*), 3.43 (dq, *J* = 9.3, 6.4 Hz, H-4*β*), 3.09 (dq, *J* = 8.7, 6.5 Hz, H-4α), 1.39 (d, *J* = 6.6 Hz, Me of α-anomer), 1.31 (d, *J* = 6.4 Hz, Me of *β*-anomer); ^{13}C NMR (D$_2$O) *δ* 83.4 (C-2*β*), 80.4 (C-3*β*), 79.8 (C-3α), 78.5 (C-1*β*), 78.0 (C-2α), 74.7 (C-1α), 41.9 (C-4*β*), 40.0 (C-4α), 19.6 (C-5α), 17.7 (C-5*β*); MS *m*/*z* (CI$^+$) 150 (M^+), 132 ($M^+ - H_2O$), 114 ($M^+ - 2\ H_2O$); HRMS (EI$^+$) calcd for $C_5H_{10}O_3S$ 150.0351 (M^+), found 150.0346.

Synthesis of 6-Deoxy-5-thio-α,*β*-L-galactopyranose (5-Thio-α,*β*-L-fucose) (63). A solution of **62** (2.31 mmol) in 50% aqueous acetic acid (10 mL) was heated at 75 °C for 3 h. After cooling, the reaction mixture was concentrated and coevaporated with toluene, yielding a crystalline residue that was recrystallized from methanol to give **63** (α-anomer) (250 mg): mp 159−160 °C (lit.[84] mp 159−160 °C); [α]$_D$ −200° (5 min) and [α]$_D$ −210° (2 d) (*c* 1, water) [lit.[84] [α]$_D$ −259.1° (5 min) and [α]$_D$ −233.0 (2 days) (*c* 1.2, water)]; ^{1}H NMR (D$_2$O, 400 MHz) *δ* 4.90 (d, 1 H, *J* = 3.2 Hz, H-1), 4.04 (bs, 1 H, H-4), 3.93 (dd, 1 H, *J* = 10.2, 3.2 Hz, H-2), 3.80 (dd, 1 H, *J* = 10.2, 2.9 Hz, H-3), 3.49 (q, 1 H, *J* = 7.0 Hz, H-5), 1.09 (d, 1 H, *J* = 7.0 Hz, Me); ^{13}C NMR (D$_2$O, 100 MHz) *δ* 75.6 (C-4), 75.1 (C-1), 72.1 (C-2), 71.5 (C-3), 37.4 (C-5), 17.0 (C-6); ^{13}C NMR (DMSO-*d*$_6$, 75 MHz) *δ* 74.3 (C-4), 73.9 (C-1), 71.0 (C-2), 70.1 (C-3), 36.3 (C-5), 16.7 (C-6). The mother liquors were purified by column chromatography (methanol−chloroform 1:3), giving **63** (∼3.7:1 mixture of α/*β* anomers) (105 mg) (85% overall yield) as a solid: ^{1}H NMR (DMSO-*d*$_6$ + D$_2$O, 300 MHz) *δ* 4.62 (d, *J* = 3.1 Hz, H-1α), 4.45 (d, *J* = 8.8 Hz, H-1*β*), 3.75 (dd, 1 H, *J* = 2.7, 1.6 Hz, H-4α), 3.67 (dd, *J* = 10.0, 3.1 Hz, H-2α), 3.64 (m, H-4*β*), 3.53 (dd, *J* = 10.0, 3.9 Hz, H-3α), 3.47 (dd, *J* = 10.0, 8.8 Hz, H-2*β*), 3.29 (dq, *J* = 7.0, 1.6 Hz, H-5α), 3.10 (dd, *J* = 9.6, 2.9 Hz, H-3*β*), 3.01 (dq, *J* = 7.0, 1.6 Hz, H-5*β*), 1.06 (d, *J* = 7.1 Hz, Me of the α-anomer), 1.05 (d, *J* = 7.1 Hz, Me of the *β*-anomer).

General Procedure for the Acetylation of Thiosugars 44, 46, 48, 50, 52, and 54. The thiosugar (1 mmol) (α/*β* mixture of steroisomer for **44**, **46**, **50**, **52**, **54** and *β* steroisomer for **48**) was acetylated overnight at rt with acetic anhydride (4 mL) and pyridine (2.0 mL). Processing of the mixture by treatment with excess of methanol and evaporation with several portions of added methanol followed by toluene gave a crude product.

1,2,3,4,6-Penta-*O*-acetyl-5-thio-α,*β*-L-idopyranose (45). Column chromatography (ether−hexane 1:1) of the crude product gave **45** (94%) as a solid. Physical properties ([α]$_D$, IR, ^{1}H and ^{13}C NMR) are identical to those described in literature[82] for this compound.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-methyl-5-thio-α,*β*-L-idopyranose (47). Column chromatography (ether−hexane 1:1) of the crude product gave **47** (98%) (2.2:1 mixture of *β*/α steroisomers) as a solid: mp 78−87 °C; [α]$_D$ +43° (*c* 1, chloroform); IR 1736, 1216, 1114, 1032, 945 cm^{-1}; ^{1}H NMR (CDCl$_3$) *δ* 6.07 (d, *J* = 3.5 Hz, H-1*β*), 5.97 (d, *J* = 6.0 Hz, H-1α), 5.25 (dd, *J* = 10.0, 5.4 Hz, H-4*β*), 5.23−5.18 (m, H-2,4α), 5.13 (dd, *J* = 9.8, 3.5 Hz, H-2*β*), 4.54 (dd, *J* = 11.5, 8.0 Hz, H-6*β*), 4.48 (dd, *J* = 11.5, 6.3 Hz, H-6′*β*), 4.29 (dd, *J* = 11.4, 6.7 Hz, H-6α), 4.21 (dd, *J* = 11.3, 6.2 Hz, H-6′α), 3.69 (t, *J* = 10.0 Hz, H-3*β*), 3.67−3.42 (m, H-5*β*, H-3,5α), 3.52 (s, MeO*β*), 3.48 (s, MeOα), 2.16−2.06 (6 s, 4 MeCO); ^{13}C NMR (CDCl$_3$) *δ* 170.5, 170.0, 169.6, 169.0 (4 CO), 75.8 (C-3*β*), 74.7 (C-2*β*), 74.6 (C-4*β*), 72.3 (C-1*β*), 77.2 (C-3α), 71.4 (C-1α), 69.7 (C-2α), 69.6 (C-4α), 64.1 (C-6*β*), 62.6 (C-6α), 61.3 (MeO*β*), 59.6 (MeOα), 41.0 (C-5*β*), 37.0 (C-5α), 21.1, 20.9, 20.8, 20.7 (MeCO). Anal. Calcd for $C_{15}H_{22}O_9S$: C, 47.61; H, 5.86; S, 8.47. Found: C, 47.91; H, 6.03; S, 8.51.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-5-thio-*β*-L-idopyranose (49). Column chromatography (ether−hexane1:3) of the crude product gave **49** (76%) as a solid: mp 112−120 °C; [α]$_D$ +66° (*c* 1, chloroform); IR (neat) 1734, 1222, 1116, 1054, 1025, 940 cm^{-1}; ^{1}H NMR (CDCl$_3$) *δ* 7.40−7.26 (m, 5 H, Ph), 6.09 (dd, *J* = 3.4, 0.7 Hz, H-1), 5.34 (dd, *J* = 9.9, 5.4 Hz, H-4), 5.22 (dd, *J* = 9.9, 3.4 Hz, H-2), 4.72 (bs, 2 H, PhC*H*$_2$), 4.55 (dd, *J* =11.5, 7.8 Hz, H-6), 4.50 (dd, *J* = 11.5, 6.4 Hz, H-6′), 4.00 (t, *J* = 9.9 Hz, H-3), 3.48 (dq, *J* = 7.0, 0.7 Hz, H-5), 2.16, 2.07, 2.01, 1.95 (4 s, 12 H, 4 MeCO); ^{13}C NMR (CDCl$_3$) *δ* 170.5, 169.5, 169.5, 169.0 (4 CO), 138.0, 128.4, 127.5, 127.3 (C$_6$H$_5$), 75.9 (Ph*C*H$_2$), 74.8 (C-2), 74.7 (C-3), 74.6 (C-4), 72.3 (C-1), 64.1 (C-6), 41.0 (C-5), 21.1, 20.8, 20.6 (4 MeCO). Anal. Calcd for $C_{21}H_{26}O_9S$: C, 55.49; H, 5.77; S, 7.05. Found: C, 55.75; H, 5.92; S, 6.80.

1,2,3,4-Tetra-*O*-acetyl-6-deoxy-5-thio-α,*β*-L-idopyranose (51). Column chromatography (ether−hexane 1:1) of the

crude product gave **51** (73%) (~1:1.5 mixture of α/β steroisomers) as a solid: mp 75−77 °C; $[\alpha]_D$ +28° (*c* 1, chloroform); IR (neat) 1750, 1219, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.10 (d, *J* = 3.5 Hz, H-1β), 5.93 (d, *J* = 7.2 Hz, H-1α), 5.60 (t, *J* = 10.3 Hz, H-3β), 5.23 (dd, *J* = 10.3, 5.6 Hz, H-4β), 5.20 (dd, *J* = 10.4, 3.6 Hz, H-2β), 5.22−5.19 (m, H-2,3α), 5.15 (dd, *J* = 7.8, 3.9 Hz, H-4α), 3.40 (dq, *J* = 7.3, 3.8 Hz, H-5α), 3.24 (dq, *J* = 7.3, 5.6 Hz, H-5β), 2.15−1.99 (8 s, 4 MeCO), 1.53 (d, *J* = 7.4 Hz, Me of β-anomer), 1.37 (d, *J* = 7.3 Hz, Me of α-anomer); ^{13}C NMR ($CDCl_3$) δ 169.9−168.8 (eigth peaks, CO), 74.1 (C-4β), 73.2 (C-2α), 72.3 (C-4α), 72.2 (C-1β), 70.9 (C-2β), 70.8 (C-1α), 69.3 (C-3α), 66.3 (C-3β), 37.0 (C-5β), 34.1 (C-5α), 21.1−20.5 (five peaks, MeCO), 18.0 (C-6β), 15.4 (C-6α); MS *m*/*z* 348 (M^+), 289, 228, 186. Anal. Calcd for $C_{14}H_{20}O_8S$: C, 48.27; H, 5.79; S, 9.20. Found: C, 48.20; H, 5.79; S, 8.80.

1,2,4-Tri-*O*-acetyl-6-deoxy-3-*O*-methyl-5-thio-α,β-L-idopyranose (53). Column chromatography (ether−hexane 1:1) of the crude product gave **53** (90%) (~1:2 mixture of α/β steroisomers) as a solid: mp 40−46 °C; $[\alpha]_D$ +49.6° (*c* 1, chloroform); IR (neat) 1750, 1219, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.09 (bd, *J* = 3.6 Hz, H-1β), 5.85 (d, *J* = 5.7 Hz, H-1α), 5.18 (dd, *J* = 9.9, 5.0 Hz, H-2α), 5.17 (dd, *J* = 10.0, 4.9 Hz, H-4β), 5.14 (dd, *J* = 9.9, 3.6 Hz, H-2β), 5.09 (dd, *J* = 5.8, 3.3 Hz, H-4α), 3.74 (t, *J* = 9.8 Hz, H-3β), 3.54−3.45 (m, H-3,5α), 3.51 (s, OMeβ), 3.48 (s, OMeα), 2.14, 2.13, 2.10, 2.06 (4 s, 3 MeCO), 1.50 (d, *J* = 7.4 Hz, Me of β anomer), 1.28 (d, *J* = 7.2 Hz, Me of α anomer); ^{13}C NMR ($CDCl_3$) δ 170.2−169.1 (six peaks, 3 CO), 77.3 (C-3α), 75.8 (C-4β), 75.4 (C-3β), 74.8 (C-2β), 72.8 (C-1β), 72.2 (C-4α), 71.9 (C-1α), 69.2 (C-2α), 61.0 (OMeβ), 59.4 (OMeα), 36.9 (C-5β), 32.6 (C-5α), 21.2, 20.0, 20.9, 20.8 (*Me*CO), 18.1 (C-6β), 15.5 (C-6α). Anal. Calcd for $C_{13}H_{20}O_7S$: C, 48.74; H, 6.29; S, 10.01. Found: C, 49.19; H, 6.43; S, 10.28.

1,2,4-Tri-*O*-acetyl-6-deoxy-3-*O*-benzyl-5-thio-α,β-L-idopyranose (55). Column chromatography (ether−hexane 1:2) of the crude product gave **55** (90%) (~1:2 mixture of α/β steroisomers) as a solid: mp 59−65 °C; $[\alpha]_D$ +50° (*c* 1, chloroform); IR (neat) 1748, 1247, 1116, 998, 943, 911 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.30 (m, Ph), 6.12 (d, *J* = 3.5 Hz, H-1β), 5.86 (d, *J* = 5.5 Hz, H-1α), 5.30−5.20 (m, H-2,4β, H-2α), 5.14 (dd, *J* = 5.6, 3.1 Hz, H-4α), 4.73 (s, PhCH_2β),. 4.68 (s, PhCH_2α), 4.02 (t, *J* = 9.7 Hz, H-3β), 3.79 (t, *J* = 5.6 Hz, H-3α), 3.59 (dq, *J* = 7.2, 3.2 Hz, H-5α), 3.28 (dq, *J* = 7.4, 5.1 Hz, H-5β), 2.14, 2.02, 1.96 (3 s, MeCOβ), 2.08, 2.05, 2.03 (3 s, MeCOα), 1.51 (d, *J* = 7.3 Hz, Me of β anomer), 1.27 (d, *J* = 7.2 Hz, Me of α anomer); ^{13}C NMR ($CDCl_3$) δ 170.2−169.1 (six peaks, 3 CO), 138.2−127.3 (eight peaks, C_6H_5), 75.9 (C-4β), 74.9 (C-2β), 74.3 (C-3β), 72.9 (C-1β), 75.4 (C-3α), 72.2 (C-2α), 72.1 (C-1α), 69.0 (C-4α), 75.6 (Ph*C*H_2 of the β anomer), 73.6 (Ph*C*H_2 of the α anomer), 37.0 (C-5β), 32.4 (C-5α), 21.1, 20.9, 20.7 (*Me*CO), 18.1 (C-6β), 15.8 (C-6α). Anal. Calcd for $C_{19}H_{24}O_7S$: C, 57.56; H, 6.10; S, 8.09. Found: C, 57.58; H, 6.39; S, 8.36.

Acknowledgment. We thank the Comision Asesora de Investigación Científica y Técnica for financial support (Proyect No. PB92/0936). Dr. A. Vargas-Berenguel (Universidad de Almeria, Spain) is also acknowledged for his suggestions during the preparation of this paper.

Supporting Information Available: NMR (^1H and ^{13}C) spectra for new substances that were not characterized by combustion analysis or high-resolution MS (40 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO962066B