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Straightforward Synthesis of Thiodisaccharides by Ring-Opening of Sugar Epoxides

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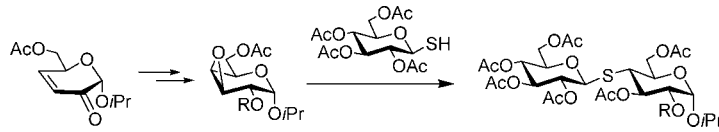

3,4-Anhydro hexopyranosides have been prepared by diastereoselective epoxidation of derivatives of 2-propyl 3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (**5**), selectively protected at HO-2 and HO-6. The allylic group at C-2, in **5** and derivatives, plays a critical role in the facial selectivity of the epoxidation reaction. Thus, the free HO-2 in **3** (the 6-*O*-acetyl derivative of **5**) directs the attack of *m*-chloroperbenzoic acid from the more hindered α face of the molecule to give 2-propyl 6-*O*-acetyl-3,4-anhydro-α-D-allopyranoside (**7**) accompanied by the β epoxide **6** as a very minor product. Reverse diastereoselectivity has been obtained when the HO-2 in **3** was substituted by a bulky *tert*-butyldimethylsilyl (TBS) group. In this case, the major isomer was the 2-*O*-TBS derivative of **6** (α-D-*galacto* configuration). The ring-opening of sugar epoxides by nucleophilic per-*O*-acetyl-1-thio-β-D-glucopyranose (**11**) was employed as a convenient approach to the synthesis of (1→3)- and (1→4)-thiodisaccharides. For example, ring-opening of the oxirane **7** by **11** led to the expected regioisomeric per-*O*-acetyl thiodisaccharides β-D-Glc-*S*-(1→3)-4-thio-α-D-Glc-*O*-iPr (**12**) and β-D-Glc-*S*-(1→4)-4-thio-α-D-Gul-*O*-iPr (**13**). Regioselectivity in the construction of the (1→4)-thioglycosidic linkage could be achieved by hindering C-3 of the 3,4-anhydro sugar with a bulky silyloxy group at the vicinal C-2. For instance, coupling of the 2-*O*-TBS derivative of **7** with **11** led regioselectively to the protected thiodisaccharide β-D-Glc-*S*-(1→4)-4-thio-α-D-Glc-*O*-iPr (**27**). The utility of the approach was demonstrated through the synthesis of sulfur-linked analogues of naturally occurring (laminarabiose and cellobiose) and non-natural disaccharides (i.e., β-D-Glc-(1→4)-α-D-Gul).

Introduction

Glycosidases are crucial in many biological processes as they are involved in a variety of metabolic disorders and diseases.[1] Therefore, inhibition of glycosylation pathways is useful in structural biology and represents an innovative modality for drug development. Glycosidase inhibitors are being applied as agrochemicals and therapeutic agents,[2] and also in cancer therapies.[3] Well-known inhibitors of glycosidases are analogues of carbohydrates in which one or more oxygen atoms have been replaced by sulfur[4] or other heteroatoms.[5] In particular, thiooligosaccharides are sugar mimetics with at least one interglycosidic linkage mediated by sulfur. They are usually resistant to metabolic processes and frequently employed as useful tools for glycobiology.[6] The understanding of enzyme−inhibitor interactions is essential to provide structural insight into binding and recognition events, and also for the rational design of potent

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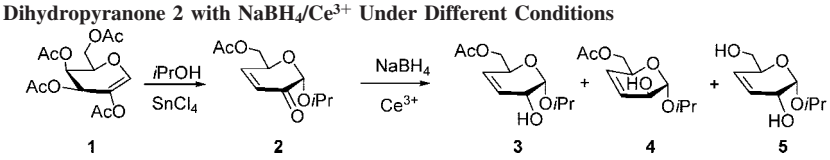
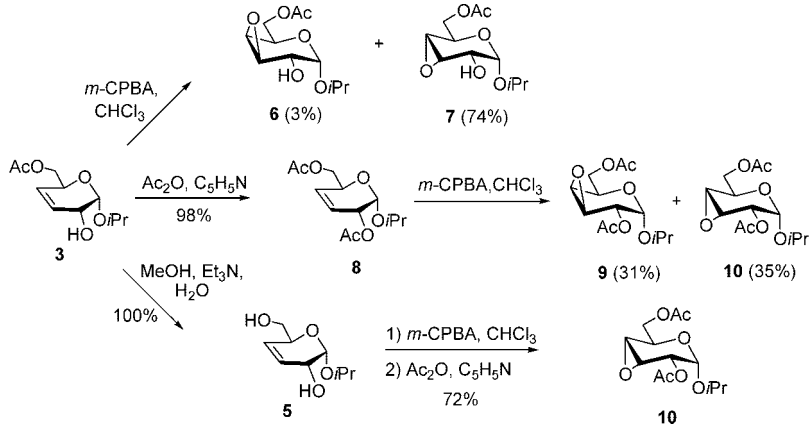
TABLE 1. Reduction of Dihydropyranone 2 with $NaBH_4/Ce^{3+}$ Under Different Conditions



entry	temp (°C)	time (min)	product distribution[a] 3	4	5
1	25	20	70	19	7
2	0	30	77	5	6
3	−18	120	83		9

[a] Yield of isolated pure compounds.

SCHEME 1



inhibitors of glycosidases.[7] Because of these biologically relevant issues, the synthesis of thiooligosaccharides is a subject of intensive current research, and many reviews on this topic have been recently published.[6,8−10]

The thioglycoside bond formation, contrary to *O*-glycoside bond formation, is usually based on S_N2 displacement of a good leaving group in a carbohydrate moiety by a sugar thiol, due to the high nucleophilicity of the thiolate anion.[8−10] Alternatively, the thioglycosidic linkage has been generated by Michael addition of 1-thioaldose derivatives to sugar enones.[11] We have employed this methodology for the synthesis of 3-deoxy-4-*S*-(1→4)-thiodisaccharides as inhibitors of β-glycoside hydrolases,[12] and for the preparation of thiodisaccharides having a thiofuranose as a nonreducing end.[13] We have also synthesized, via Michael addition, 4,6′-thioether-linked disaccharides as nonglycosidic, hydrolytically stable glycomimetics.[14] In all cases, the additions took place regioselectively at C-4 of the sugar enone to give the (1→4)-linked *S*-disaccharides. As part of our continuous interest in the synthesis and inhibitory activity of thiodisaccharides, we turned our attention to the epoxidation of 3-enopyranosides derived from sugar enones. The corresponding 3,4-anhydro sugars are expected to undergo ring-opening by a 1-thioaldose nucleophile to give (1→3)- or (1→4)-thiodisaccharides.

In the field of carbohydrates, epoxy sugars are frequently used as starting compounds in the synthesis of modified sugars[15] (halo, amino, azido, deoxy, and branched-chain derivatives). They have also been employed as reactive intermediates in the synthesis of oligosaccharides; for example, Danishefsky has succeeded in the epoxidation of glycals to give precursors of stereoregular oligosaccharides and their specifically substituted derivatives ("the glycal assembly method").[16] Lowary and coworkers described the use of 2,3-anhydro sugar thioglycosides and glycosyl sulfoxides as glycosyl donors. Upon coupling,

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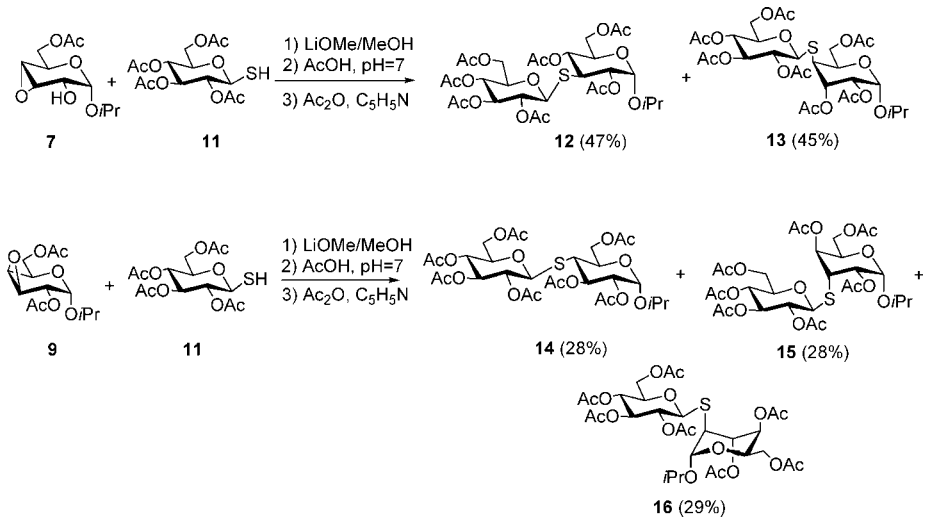
SCHEME 2



opening of the epoxide ring with lithium benzylate led to oligosaccharide containing arabinofuranosyl[17] or galactofuranosyl residues.[18] Furthermore, an example has been reported on the opening of 2,3-aziridine or 2,3-oxirane rings in sugar derivatives to give *S*-linked disaccharides with α-L-fucopyranose as a nonreducing unit.[19] Alternatively, thiodisaccharides have been prepared by 1→2 intramolecular thioglycosyl migration from 1,1′-thiolinked disaccharides,[20] or by regioselective ring-opening of 5,6-*O*-cyclic sulfate derivatives of mannofuranose by a thiosugar.[21]

All these developments prompted us to design a direct route to thiodisaccharides by ring-opening of sugar 3,4-epoxides by a nucleophilic 1-thioaldose. Therefore, we report here a convenient strategy for the synthesis of (1→3)- or (1→4)-*S*-linked disaccharides. We selected 3,4-anhydro sugars as substrates taking into account that (1→3)- and (1→4)-glycosidic linkages are common in polysaccharides of plants and fungi.[22] The precursor epoxides were prepared from a sugar enone in two highly diastereoselective steps: carbonyl reduction followed by epoxidation.

Results and Discussion

The 3,4-enopyranoside **3**, precursor of the epoxides, was obtained by Luche reduction[23] of the sugar enone **2**, prepared in one step from 2-acetoxy-3,4,6-tri-*O*-acetyl-D-galactal (**1**).[24] In the reduction, together with **3**, the epimer **4** and the diol **5** were obtained. The product distribution was highly sensitive to the temperature of the reaction (Table 1). Thus, lowering of the temperature resulted in an increment in the yield of **3**. The reduction conducted at −18 °C was highly diastereoselective, with a ratio **3**:**4** > 30:1, estimated by integration of the signals in the ^{1}H NMR spectrum of the mixture. In the reduction of **2**, the hydride approaches the carbonyl group from the less hindered β face of the molecule, opposite to the axially oriented anomeric substituent. The diol **5**, formed during the reduction by *O*-deacetylation of **3**, was quantitatively obtained by treatment of **3** with a solution of MeOH/Et_3N/H_2O.

We studied the epoxidation of hex-3-enopyranoside derivatives as a direct route to 3,4-anhydro hexoses. This constitutes an alternative procedure for the synthesis of this type of compounds, as they have been commonly prepared by means of an intramolecular displacement reaction in conveniently protected monosaccharides.[15] Thus, epoxidation of **3** with an excess of *m*-chloroperbenzoic acid (*m*-CPBA) in chloroform at 0 °C afforded diastereoselectively the 3,4-anhydro sugar **7** (Scheme 1). The β-epoxide isomer **6** was a very minor product, as indicated by the ratio **7**:**6** (>20:1), which was estimated from the NMR spectra of the mixture. The high diastereoselectivity may be attributed to the strong directing influence exerted by the allylic alcohol when peroxy acids are used (Henbest rule).[25] The *syn* delivery of the epoxide oxygen was ascribed to the coordination of the hydroxyl group with the peroxy acid. The net result of this neighboring group effect is epoxidation on the more sterically hindered α face of the molecule.

The configuration of epoxides **6** and **7** was established on the basis of NMR spectra (1D/2D). The three-membered oxirane ring fused to the pyranose severely distorted its conformation, as shown by the observed coupling constants (*J*). For example, small values (<1.0 Hz) were observed for $J_{2,3}$ in **6** and for $J_{4,5}$ in **7**, when those couplings are large (usually >9.0 Hz) in the normal $^4C_1$ conformation of the pyranose ring. The configuration of **7** was confirmed by NOE experiments, as H-4 exhibited the expected NOE contacts with H-2 and with H-6, H-6′. On the other hand, the 2,6-di-*O*-silyl derivative prepared from **6**, and later obtained by an alternative sequence (see **21**, in Scheme 3), showed a cross peak H-3, H-5 and an intense NOE contact H-4, H-5. Cross peaks were also observed for the isopropyl proton (Me_2CHO) of the anomeric substituent with H-3 and H-4 (intense). These correlations confirmed the D-*galacto* configuration for the compound.

The epoxidation of the 2,6-di-*O*-acetyl derivative **8** was also studied. The hex-3-enopyranoside **8**, prepared by conventional

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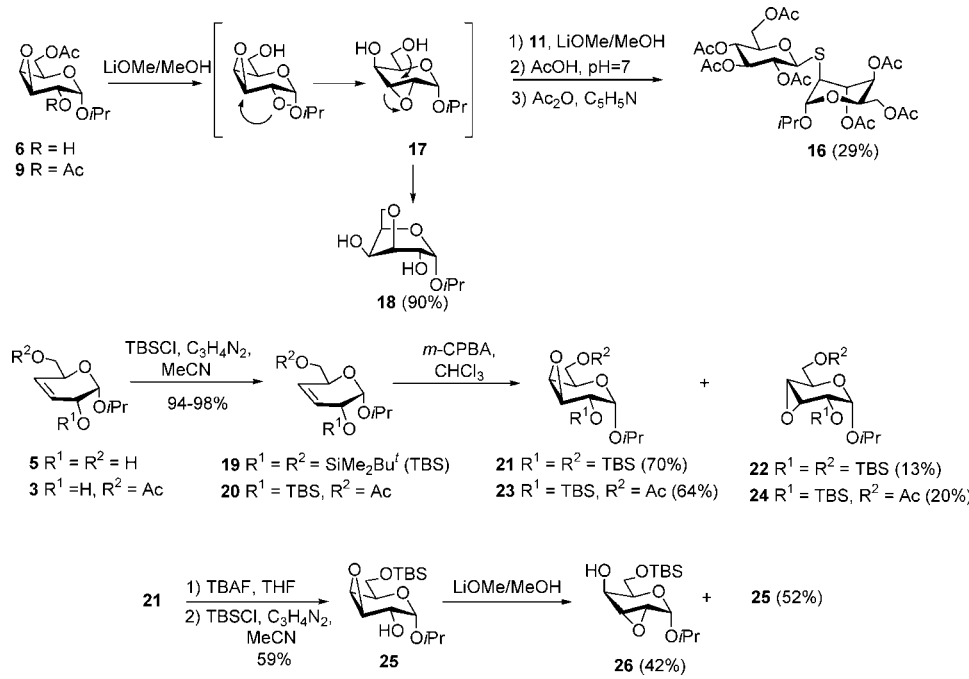
SCHEME 3



acetylation of **3**, was oxidized with *m*-CPBA at 0 °C to give a 1:1 mixture of epoxides **9** and **10**. The acetoxy group adjacent to the double bond is able to coordinate with the peroxy acid, albeit the coordinating ability is smaller than that of the hydroxyl group.[26] On the other hand, the steric hindrance of the anomeric substituent favors the attack of the peroxy acid from the β face. As a result of these two effects, no diastereoselectivity is observed in the epoxidation of **8**. In contrast, epoxidation of **5**, similar to that of **3**, was highly diastereoselective in favor of the D-*allo* epoxide **10**. This compound was the major isomer (ratio of **10**:**9** >20:1) obtained by *m*-CPBA oxidation of **5**, followed by acetylation of the mixture. This result suggests that the neighboring group effect of the allylic hydroxyl group in **5** is stronger than that of the homoallylic hydroxyl group at C-6.

The coupling reaction between the sugar epoxide **7** and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**11**), as thioglycoside donor, was studied (Scheme 2). The thiol group of **11** was activated for the nucleophilic attack to the oxirane ring by formation of the corresponding thiolate. The anomeric configuration is maintained during the reaction, because the anomerization of the glycosylthiolate is very slow.[9] Activation of **11** with NaH in DMF did not produce the expected coupling with **7**, under varied conditions. In many cases, the thiol group of **11** underwent *S*-acetylation or self-condensation to give the corresponding disulfide. Therefore, we explored the ring-opening reaction using sodium or lithium methoxide in methanol. The strongly basic medium will ensure the activation of the thiol as thiolate and the *O*-deacetylation of the protecting groups of the anhydro sugar and the 1-thioaldose. The preliminary results were encouraging as formation of thiodisaccharides was detected. The reaction conditions were optimized, with best results being obtained when the reaction was conducted for a 0.3−0.4 M solution of **7** and 10−20% molar excess of **11**, in 2 M LiOMe in MeOH, with external heating (60 °C) for 24 h. Under these conditions the overall yield for thiodisaccharides **12** and **13** was 92%, although no regioselectivity was observed. Similar yields of **12** and **13** have been obtained in the reaction of **10**, the 2-*O*-acetyl derivative of **7**, with **11**. This is an expected result as the precursor monosaccharides should undergo rapid *O*-deacetylation in the strongly alkaline reaction medium. Ring-opening reactions of oxirane derivatives by nucleophiles have been intensively studied.[15] In general, *trans*-diaxial products are obtained, in accordance with the Fürst−Plattner rule. However, diequatorial ring-opening may occur, albeit it is more hindered and energetically less favored. Many additional factors (anomeric effect, hindrance of the entering nucleophile, polar and solvent effects, neighboring group participation, etc.) often play an important role in the regioselectivity. The thiodisaccharide **13**, the 3,4-diaxial product predicted by the Fürst−Plattner rule, is produced by attack of the nucleophile to C-4 of **7**. However, the approach of **11** to C-4 is hindered by the bulky hydroxymethyl group at C-5, and the ring-opening generates a repulsive 1,3-diaxial interaction between the newly formed HO group and the anomeric substituent. In contrast, the approach of **11** to C-3, to give **12**, is sterically more favored, as the vicinal substituents of the ring at C-2 and C-4 are *anti*. Therefore, diequatorial ring-opening could take place to some extent, and accounts for the poor regioselectivity observed in the reaction of **7** with **11**. The configurations of the stereocenters generated during the thioglycosylation were readily established from NMR spectra (1D/2D). The proton linked to the sulfur-containing stereocenter resonates in a clean region of the spectrum (2.80−3.30 ppm) facilitating the determination of the coupling constants (*J*). Thus, the large values for the coupled ring protons (H-2 to H-5) indicate that all of them are axially oriented, in agreement with a 3-thio-D-*gluco* configuration for the reducing-end of **12**. Furthermore, the coupling constant value between H-1′ and H-2′ ($J_{1',2'}$ = 10.2 Hz) is indicative of the β configuration for the anomeric center bonded to sulfur (C-1′). A similar analysis of the ^{1}H NMR spectrum of **13** led to the conclusion that the reducing-end of this thiodisaccharide has 4-thio-D-*gulo* stereochemistry.

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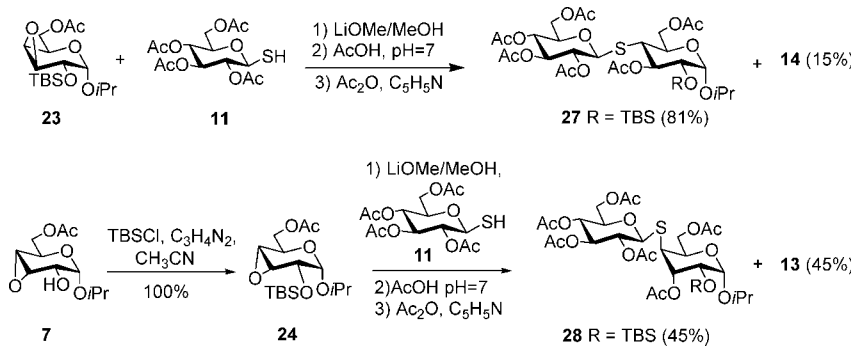
SCHEME 4



The reaction of the 3,4-anhydro-D-galactopyranoside **9** with **11** has also been conducted. In this case, together with the expected regioisomeric thiodisaccharides **14** and **15**, was isolated a byproduct identified as thiodisaccharide **16**. The stereochemistry of the reducing-end of thiodisaccharides **14**−**16** was readily established as 4-thio-D-*gluco* (**14**), 3-thio-D-*gulo* (**15**), 2-thio-D-*ido* (**16**) on the basis of NMR data, as described in detail for the analogues **12** and **13**.

The steric course of the ring-opening reaction of **9** may be explained taking into account the same effects invoked for the oxirane ring-opening of **7**. Thus, *trans*-diaxial opening of the epoxide group of **9**, by attack of the thiolate **11**, leads to the (1→3)-thiodisaccharide **15**. The approach of the nucleophile to C-3 results in a repulsive 1,3-diaxial interaction with the anomeric substituent. This interaction is absent in the diequatorial ring-opening, which takes place by approach of **11** to C-4, to give **14**. The formation of thiodisacccharide **16** may be attributed to isomerization of **9** to **17** by epoxide migration. This migration is produced by *anti* attack of the alkoxide to the vicinal oxirane ring,[15] as depicted in Scheme 3. Thus, diaxial opening of the intermediate epoxide **17**, by attack of **11** to the sterically less hindered C-2, leads to **16**. To verify the proposed 3,4→2,3 epoxide migration in compound **9**, or in its analogue **6**, they were treated with LiOMe in MeOH. The reaction yielded the 3,6-anhydro sugar **18**, instead of the expected 2,3-anhydro sugar **17**. However, the formation of **18** suggests again the participation of **17** as an intermediate, which undergoes nucleophilic attack of HO-6 to C-3. The structure of **18** was confirmed on the basis of the NMR spectra. Particularly, the ^{13}C NMR spectrum of **18** showed low field signals corresponding to C-3 and C-5, characteristic of 3,6-anhydro sugars.[27] Furthermore, this spectrum was very similar to that of the methyl glycoside analogue of **18**.[28] The formation of **18** will be prevented by protecting HO-6 in **6** or **9** by a group resistant to the alkaline conditions of epoxide migration. As the 3,4-anhydro-α-D-galacto derivatives **6** and **9** were obtained in low or moderate yield, by epoxidation of **3** or **8**, we explore first how to improve the preparation of epoxides with D-*galacto* configuration. We took into account that cyclohexenol derivatives with a bulky substituent at the allylic position underwent selective epoxidation.[29] In addition, a bulky silyl ether will also preclude the coordination of O-2 with the peroxy acid. Thus, enopyranoside **5** and its 6-*O*-acetyl derivative **3** were subjected to silylation with *tert*-butyldimethylsilyl chloride (TBSCl) to give the silyloxy derivatives **19** and **20**.

Epoxidation of the double bond of **19** with *m*-CPBA afforded a 7:1 mixture (estimated by NMR) of epoxides **21** and **22**. The configuration of **21** (3,4-anhydro-α-D-*galacto*) was confirmed chemically as this compound was also obtained by *O*-deacetylation and subsequent 2,6-di-*O*-silylation of **6** or **9**. Similar epoxidation of **20** gave a 3:1 ratio of the D-*galacto* (**23**) and D-*allo* epoxides (**24**). According to our expectations, the substitution of the allylic alcohol in **19** and **20** by the bulky silyl ether exerted stereocontrol on the epoxidation of the vicinal double bond.

With the D-*galacto* epoxides **21** and **23** in hand, we tried next to verify the proposed 3,4→2,3 epoxide migration depicted in Scheme 3. To this end, a 3,4-anhydro sugar having HO-2 free and HO-6 protected with a group potentially stable to alkali was required. Therefore, compound **21** was converted into the 6-*O*-TBS derivative **25**. This transformation was achieved in two steps: the complete *O*-desilylation of **21** with tetrabutylammonium fluoride (TBAF) followed by regioselective silylation of the primary alcohol (HO-6) with TBSCl-imidazole, to afford **25**. Upon purification by column chromatography, the 3,4-anhydro sugar **25** was treated with a LiOMe in MeOH. The reaction mixture showed by TLC that the starting **25** was partially converted into a more polar product, which was isolated and identified as the 2,3-anhydro sugar **26**, resulting from the expected migration of the oxirane ring. The structure of **26** was confirmed by NMR spectroscopy, particularly the 2D-COSY spectrum of **26** showed a cross peak between H-1 (5.17 ppm) and H-2, the proton of the epoxide system located at higher field (3.35 ppm, $J = 3.1$ Hz). This result confirms the formation of **17** as an intermediate precursor of both the thiodisaccharide **16** and the 3,6-anhydro sugar **18**. When a strong nucleophile, such as thiolate, is present in the reaction medium, the formation of the thiodisaccharide **16** prevails over the formation of the 3,6-anhydro sugar **18**.

At this point, we wanted to explore the regioselectivity for the oxirane ring-opening in the precursor sugar epoxides. On the basis of the results on epoxidation in enopyranosides, and taking into account the factors suggested for the direction of the attack of the nucleophile to the epoxide ring, we expected that introduction of a bulky substituent at the vicinal HO-2 could hinder sterically C-3 and favor the approach of the 1-thioaldose to C-4. A silyloxy group at C-2 will be particularly useful to prevent the epoxide migration in D-*galacto* derivatives. As we had already prepared the 2-*O*-silyl-3,4-epoxide **23**, the coupling of this compound with **11** was attempted (Scheme 4). The

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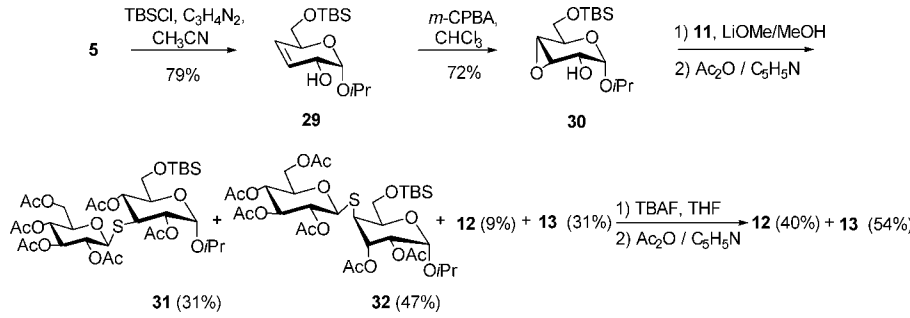
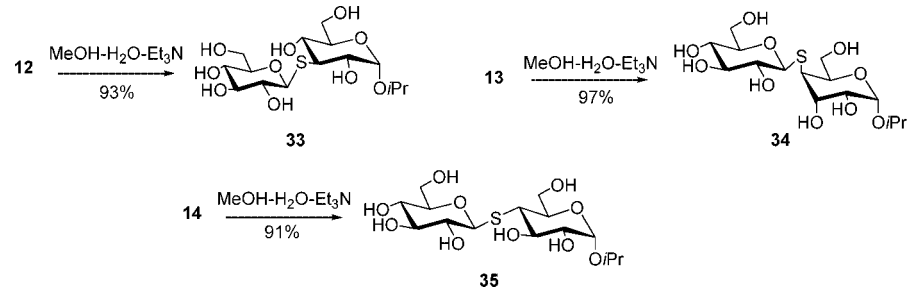
SCHEME 5



SCHEME 6



reaction, conducted under the conditions employed for the coupling of **7** or **9** with **11**, produced considerable *O*-desilylation. Therefore, more diluted solutions of LiOMe in MeOH were used; good results were obtained when a 0.8 M solution of LiOMe in MeOH was used. Under these conditions a 6:1 mixture of the 2-*O*-silyl and 2-*O*-acetyl thiodisaccharides (**27** and **14**, respectively) was obtained. However, the *O*-desilylation seems to take place once the thiodisaccharide **27** has been formed, as the accompanying product **14** possesses for the reducing end the same 4-thio-D-*gluco* configuration as **27**. According to our expectations, the opening of the oxirane ring of **23** took place with remarkable regioselectivity and excellent overall yield.

To confirm the influence of a bulky substituent at C-2 of the 3,4-anhydro sugar on the stereochemical course of the ring-opening process, the reaction between **11** and the 2-*O*-TBS derivative **24** was studied. Compound **24**, the analogue of **23** with opposite configuration for the oxirane ring, had been obtained as a minor product by oxidation of **20**, and it was alternatively prepared by silylation of **7**. The thioglycosylation of **24** with thiolate **11** was highly regioselective, similar to the analogous reaction of epoxide **23**. The hexa-*O*-acetyl-2-*O*-silyl and per-*O*-acetyl derivatives of β-D-Glc*p*-*S*-(1→4)-4-thio-α-D-Gul*p*-*O*-iPr (**28** and **13**, respectively) were isolated in 90% overall yield. These results confirmed the high stereocontrol exerted by the silyl ether at C-2, which directs the approach of the nucleophile to C-4 of α or β 3,4-epoxides.

Finally, the influence of a bulky substituent (TBS) at HO-6 on the stereochemistry of the ring-opening of the 3,4-epoxide by the sugar thiolate **11** was studied. The convenient precursor, 6-*O*-TBS-3,4-anhydro-α-D-allopyranoside (**30**), was synthesized from **5** (Scheme 5). Regioselective silylation of the primary hydroxyl group of **5** gave **29**, which was oxidized with *m*-CPBA to afford **30**. Reaction of 1-thiosugar derivative **11** with **30** led to a mixture of the 6-*O*-silyl diastereomeric products having for the reducing end the 3-thio-α-D-*gluco* and 4-thio-α-D-*gulo* configurations (**31** and **32**, respectively). These thiodisaccharides were accompanied by the corresponding per-*O*-acetylated analogues **12** and **13**, as minor products (the ratio of *gluco* (**31** + **12**) to *gulo* isomers (**32** + **13**) was 1:1.4). These four compounds could be readily isolated by column chromatography; however, to reduce the number of components, the reaction mixture was treated with TBAF in THF, followed by acetylation. This procedure led to thiodisaccharides **12** and **13** in a ratio (1:1.3) similar to that achieved from the 6-*O*-acetyl analogue **7**. This result shows that, under the conditions studied, TBS substitution at HO-6 does not have a significant influence on the regioselectivity in the 3,4-epoxide ring-opening.

Deprotection of the fully protected thiodisaccharides **12**, **13**, **14**, **27**, **28**, **31**, and **32** yielded sulfur-linked glycoside analogues of natural and unnatural disaccharides (Scheme 6). For example, *O*-deacetylation of **13** gave β-D-Glc-*S*-(1→4)-4-thio-α-D-Gul-*O*-*i*Pr, and the oxygen counterpart (β-D-Glc(1→4)Gul) has not yet been found in nature, as D-gulose is a rather unusual sugar. In contrast, the *O*-deacetylation products of **12** and **14**, the thiodisaccharides **33** and **35**, are respectively the glycoside thioanalogues of the natural disaccharides laminarabiose (Glc-β(1→3)Glc) and cellobiose (Glc-β(1→4)Glc). Laminarabiose has been obtained by hydrolysis or acetolysis of the natural polysaccharides from plant origin,[30] and is used in the agricultural field as an antiseptic.[31] Cellobiose, the basic repeating unit of cellulose, is also the constituent disaccharide of lichenan, laminaran, and other related polysaccharides. The sulfur-linked analogues of these two disaccharides have been synthesized as metabolic inhibitors. Thus, 3-thiolaminarabiose has been prepared[32] and its 1-fluoride derivative polymerized by mutated barley (1→3)-β-D-glucan endohydrolases.[33] As the enzyme degradation of cellulose is one of the most important enzyme-catalyzed reactions, derivatives of 4-thiocellobiose have been

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synthesized chemically,[34] or using engineered enzymes to catalyze the reaction of a thiosugar acceptor and an activated donor.[35] 4-Thiocellooligosaccharides have also been obtained and tested as inhibitors of cellulases.[36] Studies on the inhibition of glycosidases by thiodisaccharides **33**−**35** are in progress.

Conclusions

The epoxidation of hex-3-enopyranosides described here constitutes a rather new and highly diastereoselective route to 3,4-anhydro hexopyranoses. The allylic substituent at C-2 of 3-enopyranoside derivatives plays a critical role in the diastereoselectivity of the epoxidation. Thus, a free α-hydroxyl group at C-2 of the pyranoside directs the approach of the peroxy acid to the double bond from the more hindered face of the molecule to give the α-epoxide. In contrast, when HO-2 is protected as TBS ether, the attack of the peroxy acid takes place form the opposite *β*-face. Consequently, 3,4-anhydro sugars having opposite configuration for the oxirane ring may be diastereoselectively prepared.

We have demonstrated that sugar epoxides react with a 1-thioaldose derivative to produce the interglycosidic *S*-linkage between two pyranose units. The strategy described here is adequate for the synthesis of (1→3)- and (1→4)-thiodisaccharides, but it may be applied to the synthesis of (1→2)-thiodisaccharides, starting from the same 3,4-anhydro sugars, via epoxide migration. Due to the *trans*-opening of the oxirane ring, the sulfur atom and the newly formed vicinal hydroxyl group in the thiodisaccharides bear an *anti* relationship. Furthermore, the *S*-(1→4)-linkage could be regioselectively constructed by directing the approach of the nucleophile to the 3,4-epoxide in the ring-opening reaction. The high selectivity for C-4 attack in 2-*O*-TBS-substituted 3,4-epoxides is presumably due to steric effects, the bulky silyloxy group disfavoring attack at C-3.

The ring-opening of 3,4-anhydro sugars by a 1-thioaldose derivative was successfully applied for the synthesis of glycosides of sulfur-linked analogues of both naturally occurring and non-natural disaccharides.

Experimental Section

2-Propyl 6-*O*-Acetyl-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (3), Its α-D-*threo* Isomer (4), and 2-Propyl 3,4-Dideoxy-α-D-*erythro*-hex-3-enopyranoside (5). To a solution of 2-propyl 6-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranosid-2-ulose **2** (1.70 g, 7.46 mmol) in methanol (60 mL) was added cerium(III) chloride heptahydrate (2.78 g, 7.46 mmol). The solution was cooled to 0 °C and $NaBH_4$ (1.06 g, 28 mmol) was added. The mixture was stirred at 0 °C for 30 min, when TLC (1.5:1 EtOAc/hexane) showed a major product (R_f 0.58) and two minor components (R_f 0.45 and 0.25, respectively). The solution was neutralized with Dowex 50W (H^+) resin, filtered, and concentrated. The residue was suspended in CH_2Cl_2 and extracted with water (3 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated, and the residue was subjected to column chromatography (5:1→2.5:1 hexane/EtOAc). The first fractions of the column (R_f 0.58) afforded syrupy **3** (1.31 g, 77%); $[\alpha]_D$ +10.3 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$ + D_2O, 500 MHz) *δ* 5.79 (br d, 1H, $J_{3,4}$ = 10.5 Hz, H-4), 5.68 (dt, 1H, $J_{2,3} \approx J_{3,5}$ = 2.0 Hz, $J_{3,4}$ = 10.5 Hz, H-3), 5.10 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 4.36 (m, 1H, H-5), 4.19 (m, 1H, H-2), 4.15 (m, 2H, H-6, 6′), 4.01 (m, 1H, *J* = 6.4 Hz, Me_2CHO), 2.10 (s, 3H, CH_3CO), 1.20, 1.27 (2 d, each 3H, *J* = 6.4 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) *δ* 170.9 (CH_3CO), 129.2 (C-4), 125.7 (C-3), 95.3 (C-1), 70.9 (Me_2CHO), 66.7 (C-5), 65.6 (C-6), 63.7 (C-2), 23.3, 21.9 [$(CH_3)_2CHO$], 20.8 (CH_3CO). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.48; H, 7.66.

From further fractions of the column (R_f 0.45) was isolated syrupy **4** (86 mg, 5%); $[\alpha]_D$ +75.1 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$ + D_2O, 500 MHz) *δ* 6.60 (dddd, 1H, $J_{1,3}$ = 0.8 Hz, $J_{2,3}$ = 5.0 Hz, $J_{3,4}$ = 10.3 Hz, $J_{3,5}$ = 1.9 Hz, H-3), 5.84 (dd, 1H, $J_{3,4}$ = 10.3 Hz, $J_{4,5}$ = 1.6 Hz, H-4), 4.96 (br s, 1H, $J_{1,2}$ < 1 Hz, $J_{1,3}$ = 0.8 Hz, H-1), 4.43 (dddd, 1H, $J_{3,5}$ = 1.9 Hz, $J_{4,5}$ = 1.6 Hz, $J_{5,6}$ = 5.7 Hz, $J_{5,6'}$ = 3.9 Hz, H-5), 4.26 (dd, 1H, $J_{6,6'}$ = 11.6 Hz, $J_{5,6}$ = 5.7 Hz, H-6), 4.17 (dd, 1H, $J_{5,6'}$ = 3.9 Hz, $J_{6,6'}$ = 11.6 Hz, H-6′), 3.99 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.78 (br d, 1H, $J_{1,2}$ < 1 Hz, $J_{2,3}$ = 5.0 Hz, H-2), 2.10 (s, 3H, CH_3CO), 1.23, 1.19 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) *δ* 170.8 (CH_3CO), 128.7, 126.9 (C-3, C-4), 98.2 (C-1), 70.0 (Me_2CHO), 67.2, 65.3 (C-2, C-5), 64.3 (C-6), 23.2, 21.6 [$(CH_3)_2CHO$], 20.8 (CH_3CO). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.10; H, 8.01.

Elution with 1.5:1 hexane/EtOA afforded the product of R_f 0.25, characterized as the diol **5** (90 mg, 6%); $[\alpha]_D$ +33.8 (*c* 1.0, $CHCl_3$); lit.[37] $[\alpha]_D$ +34.6 (*c* 1.0, $CHCl_3$) and identical spectral data as the product previously reported.[37]

Reduction of **2** (0.91 g, 3.99 mmol) performed at −8 °C for 2 h led to **3** (0.76 g, 83%) and **5** (70 mg, 9%). The formation of **4** was only detected in the ^{1}H NMR spectrum of the reaction mixture (ratio **3**:**4** > 30:1).

2-Propyl 3,4-Dideoxy-α-D-*erythro*-hex-3-enopyranoside (5). Compound **3** (0.50 g, 2.17 mmol) was deacetylated with 4:1:5 MeOH/Et_3N/H_2O (4 mL) solution to give almost quantitavely **5** (0.41 g). Compound **5** showed identical properties as the product described in the previous item.

2-Propyl 6-*O*-Acetyl-3,4-*anhydro*-α-D-galactopyranoside (6) and Its α-D-Allopyranoside Isomer (7). To a stirred solution of **3** (0.34 mg, 1.48 mmol) in $CHCl_3$ (6 mL) cooled to 0 °C was slowly added technical grade (∼85%) *m*-chloroperbenzoic acid (*m*-CPBA, 0.90 g, 4.43 mmol) dissolved in $CHCl_3$ (3 mL). After stirring at 0 °C for 20 h, TLC (1:1 hexane/EtOAc) showed complete conversion of the starting material **3** into two products having R_f 0.50 and 0.39 (major). The reaction mixture was diluted with CH_2Cl_2 (15 mL) and extracted successively with cold aqueous 0.5% NaOH (2 × 30 mL), saturated solution of $NaHCO_3$ (2 × 30 mL), and brine (2 × 30 mL). The organic extract was dried ($MgSO_4$), concentrated, and subjected to column chromatography (4:1→2.5:1 hexane/EtOAc). The faster migrating minor product was recovered as a syrup that was identified as **6** (10 mg, 3%); $[\alpha]_D$ +44.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ* 4.89 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 4.28−4.30 (m, 2H, $J_{5,6} \approx J_{5,6'}$ = 6.0 Hz, H-6, H-6′), 4.23 (t, 1H, $J_{5,6} \approx J_{5,6'}$ = 6.0 Hz, H-5), 3.95 (m, 1H, *J* = 6.2 Hz, MeC*H*O), 3.81 (dd, 1H, $J_{1,2}$ = 4.8 Hz, $J_{2,3}$ < 1.0 Hz, $J_{2,OH}$ = 10.7 Hz, H-2), 3.23, 3.20 (2 d, 2H, $J_{3,4}$ = 4.1 Hz, H-3, H-4), 2.45 (d, 1H, $J_{2,OH}$ = 10.7, O*H*), 2.11 (s, 3H, CH_3CO), 1.27, 1.20 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) *δ* 170.6 (CH_3CO), 93.2 (C-1), 71.1 (Me_2CHO), 64.3, 63.8, 63.2 (C-2, C-5, C-6), 53.1, 50.0 (C-3, C-4), 23.0, 21.7 [$(CH_3)_2CHO$], 20.8 (CH_3CO). Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.99; H, 7.47.

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The second product eluted from the column was syrupy **7** (0.27 g, 74%); $[\alpha]^{25}_D$ +58.7 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.92 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 4.31 (dd, 1H, $J_{5,6}$ = 4.9 Hz, $J_{6,6'}$ = 11.1 Hz, H-6), 4.25 (dd, 1H, $J_{5,6'}$ = 5.0 Hz, $J_{6,6'}$ = 11.1 Hz, H-6′), 4.22 (dd, 1H, $J_{4,5}$ < 1.0 Hz, $J_{5,6}$ = 4.9 Hz, $J_{5,6'}$ = 5.0 Hz, H-5), 3.98 (ddd, 1H, $J_{1,2}$ = 5.5 Hz, $J_{2,3}$ = 2.3 Hz, $J_{2,OH}$ = 11.4 Hz, H-2), 3.82 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.39 (dd, 1H, $J_{2,3}$ = 2.3 Hz, $J_{3,4}$ = 4.4 Hz, H-3), 3.36 (d, 1H, $J_{3,4}$ = 4.4 Hz, H-4), 2.52 (d, 1H, $J_{2,OH}$ = 11.4 Hz, O*H*), 2.10 (s, 3H, CH_3CO), 1.24, 1.17 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.6 (CH_3CO), 95.4 (C-1), 72.3 (Me_2CHO), 65.4 (2×) (C-2, C-5), 64.2 (C-6), 55.6, 52.0 (C-3, C-4), 23.0, 21.7 [$(CH_3)_2CHO$], 20.7 (CH_3CO). Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.45; H, 7.54.

2-Propyl 2,6-Di-*O*-acetyl-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (8). Compound **3** (0.25 g, 1.09 mmol) was acetylated with acetic anhydride (1 mL) in pyridine (1 mL) at room temperature for 16 h. The residue obtained upon concentration was purified by column chromatography (9:1 hexane/EtOAc) to afford syrupy **8** (0.29 g, 98%); R_f 0.70 (1:1 EtOAc/hexane); $[\alpha]_D$ +41.2 (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.84 (dt, 1H, $J_{2,4} \approx J_{4,5}$ = 2.0 Hz, $J_{3,4}$ = 10.6 Hz, H-4), 5.75 (m, 1H, $J_{1,3}$ < 1 Hz, $J_{2,3} \approx J_{3,5}$ = 2.0 Hz, $J_{3,4}$ = 10.6 Hz, H-3), 5.33 (br d, 1H, $J_{1,2}$ = 4.3 Hz, H-1), 5.27 (dt, 1H, $J_{1,2}$ = 4.3 Hz, $J_{2,3} \approx J_{2,4} \approx J_{2,5}$ = 2.0 Hz, H-2), 4.45 (m, 1H, $J_{2,5} \approx J_{3,5} \approx J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 5.1 Hz, H-5), 4.17 (d, 2H, *J* = 5.1 Hz, H-6,6′), 3.95 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 2.11, 2.09 (2 s, each 3H, CH_3CO), 1.26, 1.15 (2 d, each 3H, *J* = 6.4 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.8, 170.4 (CH_3CO), 128.1 (C-4), 124.4 (C-3), 93.2 (C-1), 70.9 (Me_2CHO), 66.6, 66.5 (C-2, C-5), 65.4 (C-6), 23.3, 21.9 [$(CH_3)_2CHO$], 20.9, 20.8 (CH_3CO). Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.29; H, 7.16.

2-Propyl 2,6-Di-*O*-acetyl-3,4-anhydro-α-D-galactopyranoside (9) and Its α-D-Allopyranoside Isomer (10). (a) Starting from 8. The epoxidation of **8** (0.40 g, 1.47 mmol) was performed with *m*-CPBA (1.22 g, 6.01 mmol) under the same conditions described for the oxidation of **3**. After 8 h, TLC (3:1 toluene/EtOAc) revealed the formation of two products (R_f 0.38 and 0.26) in similar proportions. Separation by column chromatography (19:1→9:1 toluene/EtOAc) afforded first the less polar product, syrupy **9** (0.13 g, 31%); $[\alpha]^{25}_D$ +117.9 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.10 (dd, 1H, $J_{1,2}$ = 4.6 Hz, $J_{2,3}$ = 1.0 Hz, H-2), 4.73 (d, 1H, $J_{1,2}$ = 4.6 Hz, H-1), 4.32−4.28 (m, 3H, H-5, H-6a, H-6b), 3.86 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.30 (dd, 1H, $J_{3,4}$ = 4.0 Hz, $J_{2,3}$ = 1.0 Hz, H-3), 3.25 (d, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 2.13, 2.11 (2 s, each 3H, CH_3CO), 1.25, 1.12 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.3 MHz) δ 170.7, 169.85 (CH_3CO), 91.6 (C-1), 71.1 (Me_2CHO), 65.9, 64.0, 63.7 (C-2, C-5, C-6), 50.9, 49.6 (C-3, C-4), 23.0, 21.6 [$(CH_3)_2CHO$], 20.8, 20.6 (CH_3CO). Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 53.91; H, 6.92.

From the following fractions of the column was isolated compound **10** (0.15 g, 35%); $[\alpha]^{25}_D$ +72.2 (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.11 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1), 5.09 (dd, 1H, $J_{2,3}$ = 1.8 Hz, H-2), 4.32−4.28 (m, 3H, H-5, H-6, H-6′), 3.77 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.41 (br s, 2H, H-3,4), 2.17, 2.12 (2 s, each 3H, CH_3CO), 1.25, 1.11 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 170.6, 170.5 (CH_3CO), 93.4 (C-1), 71.7 [$(Me)_2CHO$], 68.1, 65.4 (C-2, C-5),64.1 (C-6), 55.0, 49.4 (C-3, C-4), 22.9, 21.4 [$(CH_3)_2CHO$], 20.8 (CH_3CO). Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 53.88; H, 6.89.

(b) Starting from 5. Compound **5** (50 mg, 0.27 mmol) was oxidized with *m*-CPBA as described for the epoxidation of **3**. The reaction mixture was concentrated and the residue was dissolved in 1:1 acetic anhydride−pyridine (2 mL) and stirred at room temperature for 5 h. The solvent was evaporated and the residue subjected to column chromatography to give the 3,4-anhydro sugar **10** (56 mg, 72%). This compound showed the same properties as the major isomer obtained by epoxidation of **8** (item a).

2-Propyl 2,4,6-Tri-*O*-acetyl-3-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thio-α-D-glucopyranoside (12) and 2-Propyl 2,3,6-Tri-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-thio-α-D-gulopyranoside (13). Epoxide **7** (0.15 g, 0.61 mmol) and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**11**) (0.27 mg, 0.73 mmol) were dissolved in 2 M LiOMe in MeOH (1.7 mL). The mixture was flushed with Ar and warmed to 60 °C, in a screw-cap reaction tube, for 24 h. The solution was neutralized with acetic acid and concentrated, and the residue was dissolved in pyridine (1 mL) and acetic anhydride (1 mL) and stirred at room temperature for 18 h. The residue obtained upon concentration showed by TLC (1.5:1 EtOAc/hexane) two main products (R_f 0.51 and 0.43), which were separated by column chromatography (3:1→2:1 hexane/EtOAc). The less polar product was identified as **12** (0.20 g, 47%), mp 162−163 °C; $[\alpha]^{25}_D$ +54.0 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.20 (dd, 1H, $J_{2',3'}$ = 9.1 Hz, $J_{3',4'}$ = 9.6 Hz, H-3′), 5.10 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.06 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 9.6 Hz, H-4′), 4.93 (dd, 1H, $J_{1',2'}$ = 10.2 Hz, $J_{2',3'}$ = 9.1 Hz, H-2′), 4.91 (t, 1H, $J_{3,4} = J_{4,5}$ = 10.5 Hz, H-4), 4.82 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ =11.6 Hz, H-2), 4.78 (d, 1H, $J_{1',2'}$ = 10.2 Hz, H-1′), 4.27 (dd, 1H, $J_{5',6'a}$ = 4.8 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6′a), 4.21 (dd, 1H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.12 (dd, 1H, $J_{5',6'b}$ = 2.4 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6′b), 4.08 (dd, 1H, $J_{5,6b}$ = 2.3 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 4.05 (ddd, 1H, $J_{4,5}$ = 10.5 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 2.3 Hz, H-5), 3.88 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.75 (ddd, 1H, $J_{4',5'}$ = 9.6 Hz, $J_{5',6'a}$ = 4.8 Hz, $J_{5',6'b}$ = 2.4 Hz, H-5′), 3.26 (dd, 1H, $J_{2,3}$ = 11.6 Hz, $J_{3,4}$ = 10.5 Hz, H-3), 2.13, 2.09 (×3), 2.02, 2.01, 1.99 (5 s, 21H, CH_3CO), 1.25, 1.13 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.7, 170.6, 170.2, 169.8, 169.4, 169.3 (×2), 169.1 (CH_3CO), 93.8 (C-1), 83.1 (C-1′), 75.5 (C-5′), 73.8 (C-3′), 72.4 (C-2), 71.1 (Me_2CHO), 70.3 (C-2′), 68.4 (C-5), 68.1 (C-4′), 66.7 (C-4), 62.5 (C-6), 61.8 (C-6′), 46.7 (C-3), 23.0, 21.6 [$(CH_3)_2CHO$], 20.6−20.5 (CH_3CO). Anal. Calcd for $C_{29}H_{42}O_{17}S$: C, 50.14; H, 6.09; S, 4.62. Found: C, 50.05; H, 5.94; S, 4.50.

From further fractions from the column was isolated syrupy **13** (0.19 g, 45%); $[\alpha]^{25}_D$ +31.3 (*c* 1.4, $CHCl_3$);^1H NMR ($CDCl_3$, 500 MHz) δ 5.35 (t, 1H, $J_{1,2} = J_{2,3}$ = 4.1 Hz, H-2), 5.32 (dd, 1H, $J_{2,3}$ = 4.1 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.23 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 9.3 Hz, H-3′), 5.13 (dd, 1H, $J_{3',4'}$ = 9.3 Hz, $J_{4',5'}$ = 10.0 Hz, H-4′), 5.06 (dd, 1H, $J_{1',2'}$ = 10.0 Hz, $J_{2',3'}$ = 9.3 Hz, H-2′), 5.03 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1), 4.71 (d, 1H, $J_{1',2'}$ = 10.0 Hz, H-1′), 4.65 (ddd, 1H, $J_{4,5}$ = 2.5 Hz, *J* = 4.1 Hz, *J* = 7.6 Hz, H-5), 4.22 (dd, 1H, $J_{5',6'a}$ = 4.7 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6′a), 4.20−4.14 (m, 3H, H-6a, H-6b, H-6′b), 3.87 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.73 (ddd, 1H, $J_{4',5'}$ = 10.0 Hz, $J_{5',6'a}$ = 4.7 Hz, *J* = 2.3 Hz, H-5′), 3.30 (t, 1H, $J_{3,4} = J_{4,5}$ = 2.5 Hz, H-4), 2.15, 2.09, 2.08, 2.07, 2.06, 2.02, 2.01 (7 s, each 3H, CH_3CO), 1.25, 1.13 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.6 (×3), 170.0, 169.9, 169.6, 169.3 (CH_3CO), 94.3 (C-1), 82.2 (C-1′), 76.0 (C-5′), 73.7 (C-3′), 70.7 (C-3), 70.3 (Me_2CHO), 69.5 (C-2′), 68.1 (C-4′), 65.3 (C-2), 64.9 (C-6), 63.2 (C-5), 61.7 (C-6′), 44.5 (C-4), 23.0, 21.3 [$(CH_3)_2CHO$], 21.1−20.5 (CH_3CO). Anal. Calcd for $C_{29}H_{42}O_{17}S$: C, 50.14; H, 6.09. Found: C, 49.76; H, 6.05.

Alternatively, **12** and **13** were obtained by desilylation and further acetylation of thiodisaccharides **31** and **32**.

2-Propyl 2,4,6-Tri-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-thio-α-D-glucopyranoside (14), 2-Propyl 2,4,6-Tri-*O*-acetyl-3-S-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thio-α-D-gulopyranoside (15), and 2-Propyl 2,4,6-Tri-*O*-acetyl-2-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-thio-α-D-idopyranoside (16). Epoxide **9** (0.12 g, 0.42 mmol) and the thioaldose **11** (0.19 g, 0.52 mmol) were dissolved in 2 M LiOMe in MeOH (1.50 mL) and the mixture was stirred under Ar at 65 °C for 24 h, and then neutralized, concentrated, and acetylated as described in the previous item. TLC (5:1 CH_2Cl_2/EtOAc) monitoring showed two main spots having R_f 0.54 and 0.35, respectively. Column chromatography (9:1 CH_2Cl_2/EtOAc) of the mixture afforded first the less polar product, which was identified as **14** (81 mg, 28%); $[\alpha]^{25}_D$ +44.6 (*c* 0.9, $CHCl_3$);

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.43 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 10.8 Hz, H-3), 5.23 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 9.3 Hz, H-3′), 5.16 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.07 (dd, 1H, $J_{3',4'}$ = 9.3 Hz, $J_{4',5'}$ = 10.1 Hz, H-4′), 4.93 (dd, 1H, $J_{1',2'}$ = 10.1 Hz, $J_{2',3'}$ = 9.3 Hz, H-2′), 4.78 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 4.75 (d, 1H, $J_{1',2'}$ = 10.1 Hz, H-1′), 4.50 (dd, 1H, $J_{5,6a}$ = 1.9 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.46 (dd, 1H, $J_{5,6b}$ = 4.1 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b), 4.21 (ddd, 1H, $J_{4,5}$ = 11.1 Hz, $J_{5,6a}$ = 1.9, $J_{5,6b}$ = 4.1 Hz, H-5), 4.20 (dd, 1H, $J_{5',6'a}$ = 4.3 Hz, $J_{6'a,6'b}$ = 12.2 Hz, H-6′a), 4.15 (dd, 1H, $J_{5',6'b}$ = 2.4 Hz, $J_{6'a,6'b}$ = 12.2 Hz, H-6′b), 3.86 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.69 (ddd, 1H, $J_{4',5'}$ = 10.1 Hz, $J_{5',6'a}$ = 4.3 Hz, $J_{5',6'b}$ = 2.4 Hz, H-5′), 2.92 (t, 1H, $J_{3,4}$ = 10.8 Hz, $J_{4,5}$ = 11.1 Hz, H-4), 2.10, 2.09, 2.05 (×2), 2.04, 2.03, 1.99 (6 s, 21H, CH_3CO), 1.23, 1.13 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.5 (×2), 170.3, 170.0, 169.7, 169.3 (×2) (CH_3CO), 94.2 (C-1), 82.1 (C-1′), 75.4 (C-5′), 73.7 (C-3′), 72.4 (C-2), 71.1 (Me_2CHO), 69.8 (C-2′), 68.9 (C-5), 68.0 (C-4′), 67.5 (C-3), 63.4 (C-6), 61.8 (C-6′), 46.5 (C-4), 23.1, 21.5 [$(CH_3)_2CHO$], 20.8−20.6 (CH_3CO). Anal. Calcd for $C_{29}H_{42}O_{17}S$: C, 50.14; H, 6.09. Found: C, 50.20; H, 6.23.

From further fractions of the column was isolated the component of R_f 0.35, which although chromatographically homogeneous, was in fact a 1:1 mixture of two thiodisaccharides (0.17 g, 58%). These two isomers were partially separated by column chromatography with 9:1 CH_2Cl_2/EtOAc as eluent. The first product isolated from the column was identified as **16** (85 mg, 29%), slightly unpurified with the more polar **15**. Compound **16** showed the following spectral data; $[\alpha]^{25}_D$ +24.4 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.24 (t, 1H, $J_{2,3} \approx J_{3,4}$ = 3.8 Hz, H-3), 5.23 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 9.3 Hz, H-3′), 5.10 (dd, 1H, $J_{3',4'}$ = 9.3 Hz, $J_{4',5'}$ = 10.1 Hz, H-4′), 5.06 (d, 1H, $J_{1,2}$ = 1.8, H-1), 5.01 (dd, 1H, $J_{1',2'}$ = 10.2 Hz, $J_{2',3'}$ = 9.3 Hz, H-2′), 4.86 (dd, 1H, $J_{3,4}$ = 3.8 Hz, $J_{4,5}$ = 2.4 Hz, H-4), 4.77 (d, 1H, $J_{1',2'}$ = 10.2 Hz, H-1′), 4.48 (ddd, 1H, $J_{4,5}$ = 2.4 Hz, $J_{5,6a}$ = 7.5 Hz, $J_{5,6b}$ = 5.3 Hz, H-5), 4.39 (dd, 1H, $J_{5',6'a}$ = 4.7 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6′a), 4.22 (dd, 1H, $J_{5,6a}$ = 7.5 Hz, $J_{6a,6b}$ = 11.5 Hz, H-6a), 4.17 (dd, 1H, $J_{5,6b}$ = 5.3 Hz, $J_{6a,6b}$ = 11.5 Hz, H-6b), 4.12 (dd, 1H, $J_{5',6'b}$ = 2.2 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6′b), 3.92 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.79 (ddd, 1H, $J_{4',5'}$ = 10.1 Hz, $J_{5',6'a}$ = 4.7 Hz, $J_{5',6'b}$ = 2.2 Hz, H-5′), 3.23 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.8 Hz, H-2), 2.12, 2.09 (×2), 2.08, 2.06, 2.04, 2.02 (6 s, 21H, CH_3CO), 1.24, 1.18 (2d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.6, 170.2, 170.0 (×2), 169.8, 169.4, 169.2 (CH_3CO), 98.2 (C-1), 84.5 (C-1′), 75.8 (C-5′), 74.0 (C-3′), 70.0 (Me_2CHO), 69.8 (C-2′), 68.6 (C-3), 68.0 (C-4′), 67.6 (C-4), 64.1 (C-5), 62.5 (C-6), 61.9 (C-6′), 44.3 (C-2), 23.2, 21.3 [$(CH_3)_2CHO$], 20.9, 20.7, 20.6, 20.5 (CH_3CO). Anal. Calcd for $C_{29}H_{42}O_{17}S.H_2O$: C, 48.87; H, 5.89. Found: C, 48.77; H, 5.83.

Further fractions from the column led to pure **15** (81 mg, 28%); $[\alpha]^{25}_D$ +31.3 (c 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.25 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 9.4 Hz, H-3′), 5.19 (dd, 1H, $J_{1,2}$ = 3.3 Hz, $J_{2,3}$ = 5.5 Hz, H-2), 5.10 (dd, 1H, $J_{3',4'}$ = 9.4 Hz, $J_{4',5'}$ = 10.1 Hz, H-4′), 5.03 (dd, 1H, $J_{1',2'}$ = 10.1 Hz, $J_{2',3'}$ = 9.4 Hz, H-2′), 5.01 (br dd, 1H, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 1.0 Hz, H-4), 4.96 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 4.61 (ddd, 1H, $J_{4,5}$ = 1.0 Hz, $J_{5,6a}$ = 6.3 Hz, $J_{5,6b}$ = 7.2 Hz, H-5), 4.60 (d, 1H, $J_{1',2'}$ = 10.1 Hz, H-1′), 4.26 (dd, 1H, $J_{5',6'a}$ = 4.9 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6′a), 4.18 (dd, 1H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6a), 4.15 (dd, 1H, $J_{5,6b}$ = 7.2 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6b), 4.11 (dd, 1H, $J_{5',6'b}$ = 2.2 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6′b), 3.89 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.71 (ddd, 1H, $J_{4',5'}$ = 10.1 Hz, $J_{5',6'a}$ = 4.9 Hz, $J_{5',6'b}$ = 2.2 Hz, H-5′), 3.66 (dd, 1H, $J_{2,3}$ = 5.5 Hz, $J_{3,4}$ = 3.0 Hz, H-3), 2.18, 2.10, 2.09, 2.08, 2.07, 2.03, 2.02 (7 s, each 3H, CH_3CO), 1.26, 1.15 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.6, 170.5, 170.4 (×2), 169.4, 169.0 (CH_3CO), 93.9 (C-1), 83.2 (C-1′), 76.0 (C-5′), 74.0 (C-3′), 72.8 (C-4), 70.6 (Me_2CHO), 69.6 (C-2′), 68.4 (C-4′), 66.2 (C-2), 62.9 (×2, C-5,6), 62.0 (C-6′), 42.1 (C-3), 23.0, 21.3 [$(CH_3)_2CHO$], 21.0, 20.8, 20.7, 20.6, 20.5 (CH_3CO). Anal. Calcd for $C_{29}H_{42}O_{17}S$: C, 50.14; H, 6.09. Found: C, 50.10; H, 6.01.

2-Propyl 3,6-Anhydro-α-D-galactopyranoside (18). The epoxide **9** (25 mg, 0.087 mmol) was dissolved in 0.8 M LiOMe in MeOH (0,26 mL) and stirred under Ar at 25 °C for 4 h. TLC analysis (2.5:1 EtOAc/hexane) of the reaction mixture showed complete transformation of **9** (R_f 0.52) into a product of R_f 0.23, identified as **18** (16 mg, 90%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.90 (d, 1H, $J_{1,2}$ = 2.7 Hz, H-1), 4.62 (d, 1H, $J_{4,5}$ = 1.9 Hz, H-4), 4.37 (d, 1H, $J_{2,3}$ = 5.2 Hz, H-3), 3.29 (br s, 1H, H-5), 4.08−4.07 (br s, 2H, H-6,6′), 4.03 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.87 (dd, 1H, $J_{1,2}$ = 2.7 Hz, $J_{2,3}$ = 5.2 Hz, H-2), 1.25, 1.18 (2 d, each 3H, $(CH_3)_2CHO$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 93.4 (C-1), 81.1(C-5), 77.1(C-3), 71.9 (Me_2CHO), 71.0, 70.9 (C-2,4), 69.2 (C-6), 23.3, 21.9 [$(CH_3)_2CHO$]. Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.93; H, 8.00.

2-Propyl 2,6-Di-*O*-*tert*-butyldimethylsilyl-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (19). To a solution of **5** (0.45 g, 2.39 mmol) in anhydrous acetonitrile was added *tert*-butyldimethylchlorosilane (0.90 g, 5.97 mmol) and imidazole (0.32 mg, 4.70 mmol). The reaction was stirred at room temperature for 4 h when TLC (4:1 hexane/EtOAc) revealed consumption of the starting **5** and the formation of a faster moving product (R_f 0.80). The solution was concentrated, dissolved in CH_2Cl_2, extracted with water, dried ($MgSO_4$), and concentrated. The colorless oil was purified by column chromatography (49:1 hexane/EtOAc) to afford **19** (0.94 g, 94%); $[\alpha]_D$ −13.4 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.77, 5.65 (2 d, each 1H, $J_{3,4}$ = 10.5 Hz, H-3, 4), 4.91 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.36 (m, 1H, H-5), 4.19 (m, 1H, H-2), 3.93 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.67 (dd, 1H, $J_{5,6}$ = 5.8 Hz, $J_{6,6'}$ = 10.3 Hz, H-6), 3.58 (dd, 1H, $J_{5,6'}$ = 6.0 Hz, $J_{6,6'}$ = 10.3 Hz, H-6b), 1.26, 1.18 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.90, 0.88 (2 s, each 9H, $(CH_3)_3CSiMe_2$), 0.09, 0.08, 0.05 (×2) (3 s, 12H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 127.8, 127.4 (C-3, C-4), 96.3 (C-1), 70.5 (Me_2CHO), 69.4, 65.8 (C-2, C-5), 65.7 (C-6), 25.9 [$(CH_3)_3CSiMe_2$], 23.4, 21.9 [$(CH_3)_2CHO$], 18.3 [$(CH_3)_3CSiMe_2$], −4.6, −4.7, −5.2, −5.3 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{21}H_{44}O_4Si_2$: C, 60.52; H, 10.64. Found: C, 60.23; H, 10.64.

2-Propyl 6-*O*-Acetyl-2-*O*-*tert*-butyldimethylsilyl-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (20). The allylic alcohol **3** (0.25 g, 1.09 mmol) was silylated with *tert*-butyldimethylchlorosilane (0.21 g, 1.39 mmol) and imidazole (0.75 g, 1.10 mmol) in anhydrous acetronitrile (2.1 mL). After 4 h, TLC (4:1 hexane/EtOAc) revealed formation of a faster moving product (R_f 0.64). Purification by column chromatography (49:1→9:1 hexane/EtOAc) afforded oily **20** (0.37 g, 99%); $[\alpha]_D$ −12.8 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.73, 5.66 (2 d, each 1H, $J_{3,4}$ = 10.3 Hz, H-3,4), 4.97 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1), 4.43−4.39 (m, 2H, H-2, H-5), 4.17 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 11.4 Hz, H-6), 4.14 (dd, 1H, $J_{5,6'}$ = 5.9 Hz, $J_{6,6'}$ = 11.4 Hz, H-6′), 3.96 (m, 1H, J = 6.2 Hz, $(Me)_2CHO$), 2.09 (s, 3H, CH_3CO), 1.27, 1.20 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.92 (s, 9H, $(CH_3)_3CSiMe_2$), 0.11, 0.10 (2 d, each 3H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.9 (CH_3CO), 129.4 (C-3), 125.5 (C-4), 96.3 (C-1), 70.9 (Me_2CHO), 66.9 (C-2), 65.7 (C-6), 65.4 (C-5), 25.8 [$(CH_3)_3CSiBu^t$], 23.4, 21.9 [$(CH_3)_2CHO$], 20.8 (CH_3CO), 18.2 [$(CH_3)_3CSiMe_2$], −4.6, −4.8 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{17}H_{32}O_5Si$: C, 59.27; H, 9.36. Found: C, 59.02; H, 9.54.

2-Propyl 3,4-Anhydro-2,6-di-*O*-*tert*-butyldimethylsilyl-α-D-galacto (21) and Its α-D-Allopyranoside Isomer (22). Epoxidation of compound **19** (0.92 g, 2.21 mmol) was conducted with *m*-CPBA (2.30 g, 11.30 mmol) at room temperature for 20 h, as already described. Column chromatography (99:1 hexane/EtOAc) gave the major product (R_f 0.60, 10:1 hexane/EtOAc) as an oil that was identified as **21** (0.67 g, 70%); $[\alpha]^{25}_D$ +23.3 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.67 (d, 1H, $J_{1,2}$ = 4.3 Hz, H-1), 4.10 (dd, 1H, $J_{5,6}$ = 7.5 Hz, $J_{5,6'}$ = 6.1 Hz, $J_{4,5}$ < 1.0 Hz, H-5), 3.87 (m, 1H, J = 6.2 Hz, $(Me)_2CHO$), 3.79 (d, 1H, $J_{1,2}$ = 4.3 Hz, $J_{2,3}$ < 1.0 Hz, H-2), 3.76 (dd, 1H, $J_{5,6}$ = 7.5 Hz, $J_{6,6'}$ = 9.8 Hz, H-6), 3.72 (dd, 1H, $J_{5,6'}$ = 6.1 Hz, $J_{6,6'}$ = 9.8 Hz, H-6′), 3.30 (d, 1H, $J_{3,4}$ =

4.1 Hz, H-4), 3.24 (d, 1H, $J_{3,4}$ = 4.1 Hz, H-3), 1.28, 1.17 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.92, 0.90 (2 s, each 9H, $(CH_3)_3CSiMe_2$), 0.14, 0.11, 0.09 (×2) (3 s, 12H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 94.5 (C-1), 70.7 (Me_2CHO), 66.7 (C-5), 66.4 (C-2), 62.9 (C-6), 54.6 (C-4), 50.9 (C-3), 25.8 [$(CH_3)_3CSiBu^t$], 23.1, 21.7 [$(CH_3)_2CHO$], 18.3, 18.2 [$(CH_3)_3CSiMe_2$], −4.7, −4.9, −5.4, −5.5 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{21}H_{44}O_5Si_2$: C, 58.29; H, 10.25. Found: C, 58.29; H, 10.14.

The more polar product (R_f 0.43, 10:1 hexane/EtOAc) was characterized as **22** (0.12 g, 13%); $[\alpha]^{25}_D$ +28.9 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.74 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.08 (dd, 1H, $J_{1,2}$ = 5.0 Hz, $J_{2,3}$ = 2.1 Hz, H-2), 4.07 (dd, 1H, $J_{5,6}$ = 4.8 Hz, $J_{5,6'}$ = 6.4 Hz, H-5), 3.81 (dd, 1H, $J_{5,6}$ = 4.8 Hz, $J_{6,6'}$ = 10.6 Hz, H-6), 3.76 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.71 (dd, 1H, $J_{5,6'}$ = 6.4 Hz, $J_{6,6'}$ = 10.6 Hz, H-6′), 3.40 (d, 1H, $J_{3,4}$ = 4.6 Hz, $J_{4,5}$ < 1.0 Hz, H-4), 3.24 (dd, 1H, $J_{2,3}$ = 2.1 Hz, $J_{3,4}$ = 4.6 Hz, H-3), 1.25, 1.16 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.93, 0.90 (2 s, each 9H, $(CH_3)_3CSiMe_2$), 0.14, 0.13, 0.08 (×2) (3 s, 12H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 96.5 (C-1), 71.4 (Me_2CHO), 68.2, 67.9 (C-2, C-5), 63.8 (C-6), 55.3, 52.5 (C-3, C-4), 25.9, 25.8 [$(CH_3)_3CSiMe_2$], 23.1, 21.6 [$(CH_3)_2CHO$], 18.3, 18.2 [$(CH_3)_3CSiMe_2$], −4.5, −4.6, −5.3, −5.4 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{21}H_{44}O_5Si_2$: C, 58.44; H, 10.08. Found: C, 58.29; H, 10.14.

2-Propyl 6-*O*-Acetyl-3,4-anhydro-2-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranoside (23) and Its α-D-Allopyranoside Isomer (24). The epoxidation of **20** (0.36 mg, 1.04 mmol) was conducted with *m*-CPBA (1.10 g, 5.42 mmol) under the conditions employed for the epoxidation of **19**. TLC showed the formation of two products (R_f 0.47 and 0.28, 4:1 hexane/EtOAc), which were separated by column chromatography (49:1→9:1 hexane/EtOAc). From the less polar fractions was isolated **23** (0.24 g, 64%); $[\alpha]^{25}_D$ +40.2 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.73 (d, 1H, $J_{1,2}$ = 4.3 Hz, H-1), 4.33−4.25 (m, 3H, H-5,6,6′), 3.89 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.82 (d, 1H, $J_{1,2}$ = 4.3 Hz, H-2), 3.21−3.24 (br s, 1H, H-3, H-4), 2.12 (s, 3H, CH_3CO), 1.29, 1.20 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.95 (s, 9H, $(CH_3)_3CSiMe_2$), 0.16, 0.14 (2 d, each 3H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.8 (CH_3CO), 94.6 (C-1), 71.1 (Me_2CHO), 66.1 (C-2), 64.4 (C-6), 63.8 (C-5), 54.0, 50.4 (C-3,4), 25.8 [$(CH_3)_3CSiMe_2$], 23.1, 21.8 [$(CH_3)_2CHO$], 20.8 (CH_3CO), 18.2 [$(CH_3)_3CSiMe_2$], −4.7, −4.9 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{17}H_{32}O_6Si$: C, 56.64; H, 8.95. Found: C, 56.88; H, 8.85.

From the following fractions of the column was recovered the more polar epoxide **24** (74 mg, 20%); $[\alpha]^{25}_D$ +31.1 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.77 (dd, 1H, $J_{1,2}$ = 5.0 Hz, $J_{1,3} \approx$ 1.0 Hz, H-1), 4.30−4.21 (m, 3H, H-5,6,6′), 4.10 (dd, 1H, $J_{1,2}$ = 5.0 Hz, $J_{2,3}$ = 2.1 Hz, H-2), 3.75 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.29 (d, 1H, $J_{3,4}$ = 4.5 Hz, H-4), 3.25 (m, 1H, H-3), 2.10 (s, 3H, CH_3CO), 1.24, 1.26 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.93 (s, 9H, $(CH_3)_3CSiMe_2$), 0.14, 0.12 (2 s, each 3H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.8 (CH_3CO), 96.6 (C-1), 71.9 (Me_2CHO), 67.9 (C-2), 65.3 (C-5), 64.4 (C-6), 54.9 (C-4), 52.5 (C-3), 25.8 [$(CH_3)_3CSiMe_2$], 23.1, 21.6 [$(CH_3)_2CHO$], 20.8 (CH_3CO), 18.3 [$(CH_3)_3CSiMe_2$], −4.5, −4.6 [$(CH_3)_2CSiBu^t$]. Anal. Calcd for $C_{17}H_{32}O_6Si$: C, 56.64; H, 8.95. Found: C, 56.66; H, 8.94.

Alternatively, **24** was prepared quantitavely by *tert*-butyldimethylsilylation of **6**.

2-Propyl 3,4-Anhydro-6-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranoside (25). To a solution of **21** (0.60 g, 1.38 mmol) in THF (40 mL) was added a 1 M solution of tetrabutylammonium fluoride in THF (3.2 mL) and the mixture was stirred at room temperature for 6 h, when TLC revealed complete consumption of the starting material. The mixture was concentrated and the residue was filtered through a short column of silica gel and the resulting diol (**5**, 0.26 g, 92%) was subjected to silylation under the conditions described above, using *tert*-butyldimethylchlorosilane (0.21 g, 1.40 mmol) and imidazole (0.17 g, 2.54 mmol) in acetonitrile (1.4 mL). Purification by column chromatography with 9:1 hexane/EtOAc led to the 6-*O*-silyl derivative **25** (0.26 g, 64%, R_f 0.55, 3:1 hexane/EtOAc), together with the di-*O*-silyl derivative **21** (30 mg, 6%). Compound **25** gave $[\alpha]_D$ +22.0 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.85 (d, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 4.04 (t, 1H, $J_{4,5}$ < 1.0 Hz, $J_{5,6}$ = $J_{5,6'}$ = 6.3 Hz, H-5), 3.95 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.78 (ddd, 1H, $J_{2,OH}$ = 10.8 Hz, $J_{1,2}$ = 4.4 Hz, $J_{2,3}$ = 1.1 Hz, H-2), 3.77 (dd, 1H, $J_{5,6}$ = 6.3 Hz, $J_{6,6'}$ = 9.9 Hz, H-6), 3.74 (dd, 1H, $J_{5,6'}$ = 6.3 Hz, $J_{6,6'}$ = 9.9 Hz, H-6′), 3.29 (br d, 1H, $J_{3,4}$ = 4.1 Hz, $J_{4,5}$ < 1.0 Hz, H-4), 3.24 (dd, 1H, $J_{2,3}$ = 1.1 Hz, $J_{3,4}$ = 4.1 Hz, H-3), 2.48 (d, 1H, O*H*), 1.29, 1.19 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.90 (s, 9H, $(CH_3)_3CSiMe_2$), 0.09 (s, 9H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 92.9 (C-1), 70.5 (Me_2CHO), 66.5 (C-5), 63.4 (C-2), 62.9 (C-6), 53.6 (C-3), 50.4 (C-4), 25.8 [$(CH_3)_3CSiMe_2$], 23.1, 21.6 [$(CH_3)_2CHO$], 18.3 [$(CH_3)_3CSiMe_2$], −5.4, −5.5 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49. Found: C, 56.32; H, 9.36.

2-Propyl 2,3-Anhydro-6-*O*-*tert*-butyldimethylsilyl-α-D-gulopyranoside (26). Compound **25** (30 mg, 0.09 mmol) was dissolved in 0.8 M LiOMe (0.3 mL) and the mixture was stirred under Ar at 25 °C for 4 h. TLC (3:1 hexane/EtOAc) showed partial conversion into a less polar product having R_f 0.23 (3:1 hexane/EtOAc). Purification by column chromatography (19:1→5:1 hexane/EtOAc) afforded first the starting **25** (15 mg, 52%) and then syrupy **26** (12.6 mg, 42%); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.17 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 4.16 (m, 1H, H-4), 4.00 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.85 (ddd, 1H, J = 5.3, 3.9, 1.0 Hz, H-5), 3.82 (m, 2H, H-6,6′), 3.38 (dd, 1H, $J_{2,3}$ = 3.7 Hz, $J_{3,4}$ = 2.3 Hz, H-3), 3.35 (ddd, 1H, $J_{1,2}$ = 3.1 Hz, $J_{2,3}$ = 3.7 Hz, $J_{2,4}$ = 0.5 Hz, H-2), 1.24, 1.21 (2 d, each 3H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.90 (s, 9H, $(CH_3)_3CSiMe_2$), 0.09, 0.08 (2s, each 3H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 92.1 (C-1), 69.8 (Me_2CHO), 66.6 (C-5), 65.4 (C-4), 63.8 (C-6), 52.5 (C-3), 51.8 (C-2), 25.8 [$(CH_3)_3CSiMe_2$], 23.6, 21.7 [$(CH_3)_2CHO$], 18.2 [$(CH_3)_3CSiMe_2$], −5.5 (×2) [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49. Found: C, 56.64; H, 9.61.

2-Propyl 3,6-Di-*O*-acetyl-2-*O*-*tert*-butyldimethylsilyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-thio-α-D-glucopyranoside (27) and 2-Propyl 2,3,6-Tri-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-thio-α-D-glucopyranoside (14). Oxirane **23** (0.10 g, 0.28 mmol) and the thioaldose **11** (0.11 g, 0.30 mmol) were dissolved in 0.8 M LiOMe in MeOH (0.8 mL) and the mixture was stirred under Ar at 60 °C for 24 h. The reaction mixture was processed and acetylated as described above for the analogous reaction starting from **7**. The resulting crude product showed by TLC (1:1 hexane/EtOAc) two main spots having R_f 0.61 (major) and 0.45. Purification by column chromatography (4:1→2.5:1 hexane/EtOAc) gave first the major product **27** (0.17 mg, 81%); $[\alpha]^{25}_D$ +47.5 (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5. 35 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 11.1 Hz, H-3), 5.17 (d, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 9.2 Hz, H-3′), 5.11 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.04 (dd, 1H, $J_{3',4'}$ = 9.2 Hz, $J_{4',5'}$ = 10.0 Hz, H-4′), 4.92 (dd, 1H, $J_{1',2'}$ = 10.2 Hz, $J_{2',3'}$ = 9.2 Hz, H-2′), 4.82 (d, 1H, $J_{1',2'}$ = 10.2 Hz, H-1′), 4.69 (dd, 1H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 9.7 Hz, H-2), 4.24 (dd, 1H, $J_{5',6'a}$ = 4.9 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6′a), 4.12 (dd, 1H, $J_{5,6a}$ = 2.9 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6a), 4.09 (dd, 1H, $J_{5',6'b}$ = 2.2 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6′b), 3.87 (br d, 1H, $J_{4,5}$ = 11.0 Hz, $J_{5,6a}$ = 2.9 Hz, H-5), 3.82 (m, 1H, J = 6.2 Hz, Me_2CHO), 3.80 (br d, 1H, H-6b), 3.63 (ddd, 1H, $J_{4',5'}$ = 10.0 Hz, $J_{5',6'a}$ = 4.9 Hz, H-5′), 3.03 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 11.0 Hz, H-4), 2.06, 2.04, 2.03, 2.02, 2.01, 1.98 (6 s, each 3H, CH_3CO), 1.19, 1.09 (2 d, 6H, J = 6.2 Hz, $(CH_3)_2CHO$), 0.92 (s, 9H, $(CH_3)_3SiCMe_2$), 0.09, 0.08 (2 s, each 3H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.4, 170.0, 169.4, 169.2 (×2) (CH_3CO), 94.2 (C-1), 82.8 (C-1′), 75.4 (C-5′), 74.0 (C-3′), 72.6 (C-2), 71.8(C-5), 70.5 (Me_2CHO), 70.1 (C-2′), 68.2, 68.1 (C-3,4′), 62.2 (C-6), 62.0 (C-6′), 45.9 (C-4), 26.0 [$(CH_3)_3CSiMe_2$], 23.2, 21.4 [$(CH_3)_2CHO$], 20.8−20.6 (CH_3CO), 18.4 [$(CH_3)_3CSiMe_2$], −5.0, −5.3 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{33}H_{54}O_{16}SSi$: C, 51.68; H, 7.10. Found: C, 51.38; H, 6.91.

The minor product of R_f 0.45 was also obtained as a syrup and identified as **14** (29 mg, 15%), which showed the same properties as the product obtained from the oxirane **9**.

2-Propyl 3,6-Di-*O*-acetyl-2-*O*-*tert*-butyldimethylsilyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-thio-α-D-gulopyranoside (28) and 2-Propyl 2,3,6-Tri-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-thio-α-D-gulopyranoside (13). Oxirane **24** (60 mg, 0.17 mmol) reacted with **11** (70 mg, 0.19 mmol) under the nucleophilic ring-opening conditions described for **24**. After acetylation, TLC (1:1 hexane/EtOAc) showed two products of R_f 0.65 and 0.28, respectively. Purification by column chromatography (4:1→2.5:1 hexane/EtOAc) gave first the less polar product **28** (58 mg, 45%), $[\alpha]_D$ +42.1 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.25 (t, 1H, $J_{2',3'} = J_{3',4'} = 9.3$ Hz, H-3′), 5.08 (m, 3H, H-1,2,4′), 5.00 (dd, 1H, $J_{1',2'} = 10.1$ Hz, $J_{2',3'} = 9.3$ Hz, H-2′), 4.83 (m, 1H, H-5), 4.61 (d, 1H, $J_{1',2'} = 10.1$ Hz, H-1′), 4.29 (dd, 1H, $J_{5',6'a} = 5.5$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6′a), 4.23 (dd, 1H, $J_{5,6a} = 8.7$ Hz, $J_{6a,6b} = 11.7$ Hz, H-6a), 4.20 (t, 1H, $J_{2,3} \approx J_{3,4} \approx 1.0$ Hz, H-3), 4.13 (m, 2H, H-6b,6′b), 3.76 (m, 1H, $J = 6.1$ Hz, Me_2CHO), 3.68 (ddd, 1H, $J_{4',5'} = 9.8$ Hz, $J_{5',6'a} = 5.5$ Hz, $J_{5',6'b} = 2.0$ Hz, H-5′), 3.05 (t, 1H, $J_{3,4} \approx J_{4,5} \approx 1.0$ Hz, H-4), 2.10, 2.09, 2.08, 2.06, 2.04, 2.02 (6 s, each 3H, CH_3CO), 1.21, 1.08 (2 d, each 3H, $J = 6.1$ Hz, $(CH_3)_2CHO$); 0.95 (s, 9H, $(CH_3)_3CSiMe_2$), 0.12, 0.10 (2 s, each 3H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.6, 170.2, 170.1, 169.5, 169.3 (CH_3CO), 95.3 (C-1), 82.5 (C-1′), 76.5 (C-5′), 73.8 (C-3′), 71.0 (Me_2CHO), 70.6 (C-3), 69.7 (C-2′), 68.2, 67.8 (C-2,4′), 65.2 (C-6), 63.1 (C-5), 62.1 (C-6′), 48.0 (C-4), 25.4 [$(CH_3)_3CSiMe_2$], 23.4, 21.8 [$(CH_3)_2CHO$], 20.9, 20.7, 20.66, 20.57, 20.55,20.52 (CH_3CO), 18.0 [$(CH_3)_3CSiMe_2$], −4.8, −5.0 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{33}H_{54}O_{16}SSi$: C, 51.68; H, 7.10. Found: C, 51.96; H, 7.16.

From the next fractions of the column (R_f 0.28) was recovered **13** (53 mg, 45%), which showed the same properties as described above.

2-Propyl 6-*O*-*tert*-Butyldimethylsilyl-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (29). Compound **5** (80 mg, 0.42 mmol) was silylated with TBSCl (70 mg, 0.46 mmol) under the same conditions described for the silylation of **3**. The product of intermediate mobility (R_f 0.75, 1.5:1 hexane/EtOAc) between the di-*O*-silyl derivative **19** (R_f 0.87) and **5** (R_f 0.11) was isolated by column chromatography (49:1 hexane/EtOAc) to afford **29** (100 mg, 79%); $[\alpha]_D$ −10.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.81, 5.73 (2 d, each 1H, $J_{3,4} = 10.6$ Hz, H-3, 4), 5.07 (d, 1H, $J_{1,2} = 4.3$ Hz, H-1), 4.16 (m, 2H, H-2, 5), 4.00 (m, 1H, $J = 6.2$ Hz, Me_2CHO), 3.68 (dd, 1H, $J_{5,6'} = 5.8$ Hz, $J_{6,6'} = 10.3$ Hz, H-6), 3.58 (dd, 1H, $J_{5,6'} = 6.0$ Hz, $J_{6,6'} = 10.3$ Hz, H-6′), 2.25 (d, 1H, $J_{2,OH} = 11.0$ Hz, O*H*), 1.26, 1.20 (2 d, each 3H, $J = 6.2$ Hz, $(CH_3)_2CHO$), 0.89 (s, 9H, $(CH_3)_3CSiMe_2$), 0.07 (s, 6H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 127.7, 127.6 (C-3, C-4), 95.3 (C-1), 70.6 (Me_2CHO), 69.2, 65.5 (C-2, C-5), 64.0 (C-6), 25.8 [$(CH_3)_3CSiMe_2$], 23.3, 21.9 [$(CH_3)_2CHO$], 18.3 [$(CH_3)_3CSiMe_2$], −5.3, −5.4 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.0. Found: C, 59.33; H, 9.87.

2-Propyl 3,4-Anhydro-6-*O*-*tert*-butyldimethylsilyl-α-D-allopyranoside (30). Epoxidation of **29** (80 mg, 0.26 mmol) under standard conditions led to **30** (0.06 g, 72%); R_f 0.68 (1.5:1 hexane/EtOAc); $[\alpha]_D$ +40.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.89 (d, 1H, $J_{1,2} = 5.4$ Hz, H-1), 4.02 (dd, 1H, $J_{5,6} = 4.8$ Hz, $J_{5,6'} = 6.4$, $J_{4,5} < 1.0$ Hz, H-5), 3.94 (m, 1H, H-2), 3.83 (dd, 1H, $J_{5,6} = 4.8$ Hz, $J_{6,6'} = 10.6$ Hz, H-6), 3.81 (m, 1H, $J = 6.2$ Hz, Me_2CHO), 3.72 (dd, 1H, $J_{5,6'} = 6.4$ Hz, $J_{6,6'} = 10.6$ Hz, H-6′), 3.46 (d, 1H, $J_{3,4} = 4.6$ Hz, $J_{4,5} < 1.0$ Hz, H-4), 3.37 (dd, 1H, $J_{2,3} = 2.6$ Hz, $J_{3,4} = 4.6$ Hz, H-3), 1.24, 1.17 (2 d, each 3H, $J = 6.2$ Hz, $(CH_3)_2CHO$), 0.90 (s, 9H, $(CH_3)_3CSiMe_2$), 0.09, 0.08 (s, each 3H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 95.4 (C-1), 72.0 (Me_2CHO), 67.9, 65.8 (C-2,5), 63.6 (C-6), 56.1, 52.1 (C-3,4), 25.8 [$(CH_3)_3CSiMe_2$], 23.1, 21.7 [$(CH_3)_2CHO$], 18.2 [$(CH_3)_3CSiMe_2$], −5.38, −5.42 [$(CH_3)_2SiBu^t$]. Anal. Calcd for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49. Found: C, 56.64; H, 9.58.

2-Propyl 2,4-Di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-3-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thio-α-D-glucopyranoside (31) and 2-Propyl 2,3-Di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-thio-α-D-gulopyranoside (32). Reaction of **30** (50 mg, 0.16 mmol) with **11** (70 mg, 0.19 mmol) was conducted following the same procedure previously described. After acetylation TLC (1:1 hexane/EtOAc) showed two main spots (1:1 ratio) of R_f 0.69 and 0.59, respectively. These products were separated by column chromatography (4:1→2:1 hexane/EtOAc). The first thiodisaccharide obtained was characterized as **31** (37 mg, 31%), $[\alpha]_D$ +51.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.19 (t, 1H, $J_{2',3'} = J_{3',4'} = 9.3$ Hz, H-3′), 5.07 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1), 5.05 (dd, 1H, $J_{3',4'} = 9.3$ Hz, $J_{4',5'} = 10.1$ Hz, H-4′), 4.92 (dd, 1H, $J_{1',2'} = 10.1$ Hz, $J_{2',3'} = 9.3$ Hz, H-2′), 4.82 (dd, 1H, $J_{3,4} = 11.3$ Hz, $J_{4,5} = 10.1$ Hz, H-4), 4.80 (d, 1H, $J_{1',2'} = 10.1$ Hz, H-1′), 4.78 (dd, 1H, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 11.3$ Hz, H-2), 4.25 (dd, 1H, $J_{5',6'a} = 4.9$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6′a), 4.11 (dd, 1H, $J_{5',6'b} = 2.2$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6′b), 3.90 (m, 2H, H-5,Me_2CHO), 3.73 (ddd, 1H, $J_{4',5'} = 10.1$ Hz, $J_{5',6'a} = 4.9$ Hz, $J_{5',6'b} = 2.3$ Hz, H-5′), 3.63 (m, 2H, H-6a, H-6b), 3.26 (t, 1H, $J_{2,3} = J_{3,4} = 11.3$ Hz, H-3), 2.12, 2.09, 2.07, 2.03, 2.02, 1.98 (6 s, each 3H, CH_3CO), 1.25, 1.11 (2 d, each 3H, $J = 6.2$ Hz, $(CH_3)_2CHO$), 0.89 (s, 9H, $(CH_3)_3CSiMe_2$), 0.09 (2 s, 6H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.6, 170.1, 169.8, 169.4, 169.36, 169.2 (CH_3CO), 93.2 (C-1), 83.0 (C-1′), 75.4 (C-5′), 73.9 (C-3′), 72.5 (C-2), 71.4, 70.3 (×2) (C-2′, C-5, Me_2CHO), 68.1 (C-4′), 67.2 (C-4), 62.9 (C-6), 61.9 (C-6′), 46.9 (C-3), 25.8 [$(CH_3)_3CSiMe_2$], 23.1, 21.4 [$(CH_3)_2CHO$], 20.7−20.5 ($COCH_3$), 18.3 [$(CH_3)_2CSiBu^t$], −5.4, −5.5 [$(CH_3)_2CSiBu^t$]. Anal. Calcd for $C_{33}H_{54}O_{16}SSi$: C, 51.68; H, 7.10. Found: C, 51.42; H, 6.77.

From the next fractions of the column (R_f 0.59) was isolated the major component of the mixture, identified as **32** (56 mg, 47%); $[\alpha]_D$ +19.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.37 (t, 1H, $J_{1,2} = J_{2,3} = 4.0$ Hz, H-2), 5.30 (dd, 1H, $J_{2,3} = 4.0$ Hz, $J_{3,4} = 3.4$ Hz, H-3), 5.23 (t, 1H, $J_{2',3'} = J_{3',4'} = 9.3$ Hz, H-3′), 5.13 (t, 1H, $J_{3',4'} = 9.3$ Hz, $J_{4',5'} = 10.0$ Hz, H-4′), 5.06 (d, 1H, $J_{1,2} = 4.0$ Hz, H-1), 5.04 (dd, 1H, $J_{1',2'} = 10.1$ Hz, $J_{2',3'} = 9.3$ Hz, H-2′), 4.74 (d, 1H, $J_{1',2'} = 10.1$, H-1′), 4.44 (ddd, 1H, $J_{4,5} = 2.9$ Hz, $J_{5,6a} = 7.0$ Hz, $J_{5,6b} = 4.1$ Hz, H-5), 4.23 (dd, 1H, $J_{5',6'a} = 4.5$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6′a), 4.12 (dd, 1H, $J_{5',6'b} = 2.3$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6′b), 3.92 (m, 1H, $J = 6.2$ Hz, Me_2CHO), 3.75 (dd, 1H, $J_{5,6a} = 7.0$ Hz, $J_{6a,6b} = 11.1$ Hz, H-6a), 3.72 (ddd, 1H, $J_{4',5'} = 10.0$ Hz, $J_{5',6'a} = 4.5$ Hz, $J_{5',6'b} = 2.3$ Hz, H-5′), 3.67 (dd, 1H, $J_{5,6b} = 4.1$ Hz, $J_{6a,6b} = 11.1$ Hz, H-6b), 3.32 (t, 1H, $J_{3,4} = 3.4$ Hz, $J_{4,5} = 2.9$ Hz, H-4), 2.13, 2.10, 2.07, 2.06, 2.02, 2.00 (6 s, each 3H, CH_3CO), 1.24, 1.21 (2 d, each 3H, $J = 6.2$ Hz, $(CH_3)_2CHO$), 0.89 (s, 9H, $(CH_3)_3CSiMe_2$), 0.07 (2 s, 6H, $(CH_3)_2SiBu^t$); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 170.6 (×2), 170.2, 170.1, 169.5, 169.4 (CH_3CO), 93.7 (C-1), 82.5 (C-1′), 76.0 (C-5′), 73.9 (C-3′), 70.8 (C-3), 69.8 (C-2′), 69.4 (Me_2CHO), 68.1 (C-4′), 67.0 (C-5), 65.9 (C-2), 64.3 (C-6), 61.8 (C-6′), 44.3 (C-4), 25.8 [$(CH_3)_3CSiMe_2$], 23.3, 21.2, 21.0, 20.9, 20.7, 20.6, 20.5 [$(CH_3)_2CHO$, $COCH_3$], 18.2 [$(CH_3)_2CSiBu^t$], −5.4 [$(CH_3)_2CSiBu^t$]. Anal. Calcd for $C_{33}H_{54}O_{16}SSi$: C, 51.68; H, 7.10. Found: C, 51.28; H, 6.85.

From the following fractions of the column were isolated the minor products of R_f 0.35 and 0.26 characterized as **12** (10 mg, 9%) and **13** (12 mg, 11%), respectively.

Alternatively, reaction of **30** (50 mg, 0.16 mmol) and **11** (70 mg, 0.19 mmol), under the conditions employed above, led to a crude mixture that was subjected to *O*-desilylation with 1 M TBAF in THF (0.2 mL), followed by acetylation. Purification by column chromatography (3:1→2:1 hexane/EtOAc) led to thiodisaccharides **12** (45 mg, 40%) and **13** (60 mg, 54%) as the unique isolated products.

2-Propyl 3-*S*-(β-D-Glucopyranosyl)-3-thio-α-D-glucopyranoside (33, 2-Propyl 3-Thiolaminarabioside). Compound **12** (0.15 g, 0.22 mmol) was suspended in 4:1:5 MeOH/Et_3N/H_2O (3.5 mL) and the mixture was stirred at room temperature. When TLC (1.5:1 EtOAc/hexane) showed disappearance of the starting **12** the mixture was

concentrated. The resulting residue, dissolved in water (1 mL), was eluted through a column filled with mixed bed ion-exchange resin. The deionized solution was concentrated and the product was purified by dissolution in water (1 mL) and filtration through an octadecyl C18 minicolumn. Evaporation of the solvent afforded foamy **33** (82 mg, 93%); R_f 0.55 (2.5:1:1 *n*-BuOH:EtOH:H_2O); $[\alpha]^{25}_D$ +51.3 (*c* 1.02, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ 4.94 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.63 (d, 1H $J_{1',2'}$ = 9.9 Hz, H-1′), 3.91 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.79 (dd, 1H, $J_{5',6'a}$ = 1.8 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6′a), 3.78−3.63 (m, 4H, H-5,6a,6b,6′b), 3.61 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 11.0 Hz, H-2), 3.42 (t, 1H, $J_{2',3'} = J_{2',3'}$ = 9.2 Hz, H-3′), 3.40−3.33 (m, 3H, H-4, 4′,5′), 3.25 (dd, 1H, $J_{1',2'}$ = 9.9 Hz, $J_{2',3'}$ = 9.0 Hz, H-2′), 3.04 (t, 1H, $J_{2,3} = J_{3,4}$ = 10.8 Hz, H-3), 1.16, 1.10 (2 d, 6H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR (D_2O, 125.7 MHz) δ 95.4 (C-1), 84.5 (C-1′), 79.6 (C-5′), 77.1 (C-3′), 72.5 (C-2′), 72.5 (C-5), 70.3 (Me_2CHO), 70.2 (C-2), 69.3 (C-4), 67.1 (C-4′), 60.8, 60.6 (C-6, C-6′), 51.6 (C-3), 23.0, 20.4 [$(CH_3)_2CHO$]. Anal. Calcd for $C_{15}H_{28}O_{10}S$: C, 44.99; H, 7.05; S, 8.01. Found: C, 44.94; H, 7.03; S, 8.06.

2-Propyl 4-*S*-(β-D-Glucopyranosyl)-4-thio-α-D-gulopyranoside (34). Thiodisaccharide **13** (0.15 g, 0.22 mmol) was *O*-deacetylated performed following the procedure described above for **12**. The free thiodisaccharide **34** (85 mg, 97%) was obtained as a foam, R_f 0.55 (2.5:1:1 *n*-BuOH/EtOH/H_2O); $[\alpha]^{25}_D$ +35.2 (*c* 0.9, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ 4.92 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.51 (d, 1H, $J_{1',2'}$ = 9.8 Hz, H-1′), 4.41 (m, 1H, H-5), 4.05 (t, 1H, $J_{2,3} = J_{3,4}$ = 3.4 Hz, H-3), 4.00 (t, 1H, $J_{1,2} = J_{2,3}$ = 4.0 Hz, H-2), 3.87 (m, 1H, *J* = 6.2 Hz, Me_2CHO), 3.81 (dd, 1H, $J_{5',6'a}$ = 1.5 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6′a), 3.71 (m, 2H, H-6a, H-6b), 3.61 (dd, 1H, $J_{5',6'b}$ = 1.5 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6′b), 3.39 (t, 1H, $J_{2',3'} = J_{3',4'}$ = 9.0 Hz, H-3′), 3.36 (m, 1H, H-5′), 3.31 (t, 1H, $J_{3',4'} = J_{4',5'}$ = 9.3 Hz, H-4′), 3.27 (br s, 1H, H-4), 3.21 (t, 1H, $J_{1',2'} = J_{2',3'}$ = 9.8, H-2′), 1.26, 1.20 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR (D_2O, 125.7 MHz) δ 97.2 (C-1), 85.2 (C-1′), 80.1 (C-5′), 77.4 (C-3′), 72.5 (C-2′), 72.0, 71.8 (C-3, Me_2CHO), 69.6 (C-4′), 66.0 (C-5), 64.5 (C-2), 62.3(C-6), 60.9 (C-6′), 47.1 (C-4), 23.3, 22.5 [$(CH_3)_2CHO$]. Anal. Calcd for $C_{15}H_{28}O_{10}S$: C, 44.99; H, 7.05, S, 8.01. Found: C, 44.83; H, 6.89; S, 7.82.

2-Propyl 4-*S*-(β-D-Glucopyranosyl)-4-thio-α-D-glucopyranoside (35, 2-Propyl 4-Thiocellobioside). The procedure described above for **12** and **13** was applied for the *O*-deacetylation of **14** (150 mg, 0.22 mmol). The free thiodisaccharide **35** (80 mg, 91%) was obtained as a foam, R_f 0.55 (2.5:1:1 *n*-BuOH/EtOH/H_2O); $[\alpha]^{25}_D$ +33.45 (*c* 0.95, H_2O); ^{1}H NMR (D_2O, 500 MHz) δ 5.07(d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.65 (d, 1H, $J_{1',2'}$ = 9.8 Hz, H-1′), 4.04−3.93 (m, 4H, H-5,6a,6b,Me_2CHO), 3.37 (dd, 1H, $J_{5',6'a}$ = 1.5 Hz, $J_{6'a,6'b}$ = 12.5 Hz, H-6′a), 3.79 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 10.6 Hz, H-3), 3.70 (dd, 1H, $J_{5',6'b}$ = 5.2 Hz, $J_{6'a,6'b}$ = 12.5 Hz, H-6′b), 3.58 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.50 (t, 1H, $J_{2',3'} \approx J_{3',4'}$ = 8.7 Hz, H-3′), 3.44 (m, 1H, H-5′), 3.41 (dd, 1H, $J_{3',4'}$ = 8.7 Hz, $J_{4',5'}$ = 9.7 Hz, H-4′), 3.33 (dd, 1H, $J_{1',2'}$ = 9.8 Hz, $J_{2',3'}$ = 8.7 Hz, H-2′), 2.84 (t, 1H, $J_{3,4} \approx J_{4,5}$ = 10.6 Hz, H4), 1.13, 1.08 (2 d, each 3H, *J* = 6.2 Hz, $(CH_3)_2CHO$); ^{13}C NMR (D_2O, 125.7 MHz) δ 96.3 (C-1), 83.7 (C-1′), 79.9 (C-5′), 77.0 (C-3′), 72.3, 72.2 (C-2, 2′), 72.0, 70.7 (C-5, Me_2CHO), 69.6, 69.2 (C-3, 4′), 61.3 (C-6), 60.7 (C-6′), 47.2 (C-4), 22.4, 20.5 [$(CH_3)_2CHO$]. Anal. Calcd for $C_{15}H_{28}O_{10}S$: C, 44.99; H, 7.05; S, 8.01. Found: C, 44.69; H, 7.24; S, 7.94.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **3**, **4**, **6**−**10**, **12**−**16**, and **18**−**35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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