SYNTHESIS OF UNSATURATED SULFUR-LINKED (1→4)-DISACCHARIDES BY SUBSTITUTION OF TOSYLOXY GROUP IN 1,6-ANHYDRO-3,4-DIDEOXY-2-*O*-TOSYL-β-D-*erythro*-HEX-3-ENOPYRANOSE WITH 1-THIOHEXOPYRANOSES

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A novel method for the synthesis of unsaturated sulfur-linked (1→4)-disaccharides is described. The starting 1,6-anhydro-3,4-dideoxy-2-*O*-tosyl-β-D-*erythro*-hex-3-enopyranose (**3**) was reacted with potassium salt of acetylated 1-thiohexopyranoses of D-*gluco*-, D-*galacto*-, and L-*galacto*-configuration to give acetylated β-glycopyranosyl-(1→4)-1,6-anhydro-2,3-dideoxy-4-thio-β-D-*erythro*-hex-2-enopyranoses **8**–**10**. Their acid methanolysis under mild conditions afforded the corresponding methyl glycosides **11**–**13**. The structure of new compounds was confirmed by ^{1}H NMR and mass spectra data.

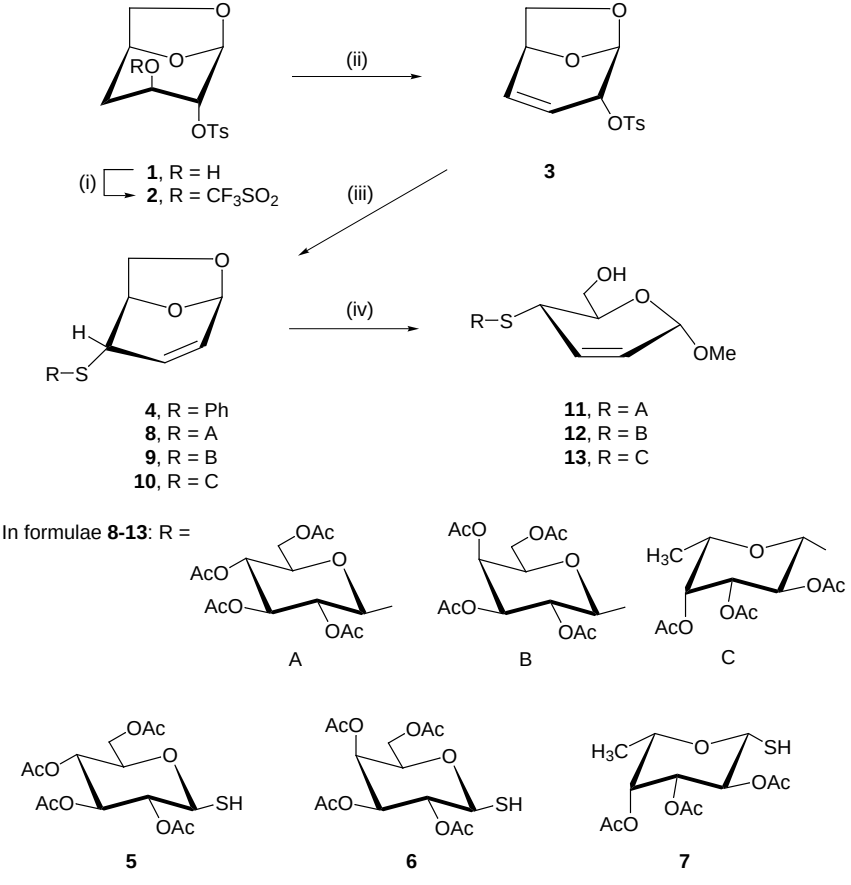
Key words: Carbohydrates; Thiosugars; Unsaturated sulfur-linked dissaccharides; 1,6-Anhydrohexopyranoses; Nucleophilic substitutions; Allylic rearrangement; ^{1}H NMR spectroscopy; Mass spectrometry.

The inhibitor activity of sulfur-linked oligosaccharides against enzyme splitting natural oligosaccharides has been continuously investigated[1]. In connection with these studies, we decided to develop a method for preparation of unsaturated thiodisaccharides (sulfur-linked (1→4)). The synthetic strategy commonly used for preparation of saturated thiodisaccharides is based either on nucleophilic substitution with 1-thioglycoses[2] of a good leaving group (*e.g.* trifluoromethanesulfonyl[3]) in a sugar molecule or on glycosylation[2b,4] of a non-anomeric thioglycose with glycosyl halogenides or other glycosyl donors[5–8]. Alternative routes towards thiooligosaccharides involve cleavage of the oxirane ring in 1,6:2,3-dianhydro-β-D-talopyranose[9] or addition to the conjugated double bond in 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose[10] (levoglucosenone).

RESULTS AND DISCUSSION

As a starting compound for syntheses (Scheme 1) of unsaturated thiodisaccharides we chose 1,6-anhydro-3,4-dideoxy-2-*O*-tosyl-β-D-*erythro*-hex-3-enopyranose (**3**), the tosyloxy group of which was previously shown[11,12] to be a good leaving group in SN2′ allylic rearrangement. Similar reactivity was observed for the corresponding chloro and bromo derivatives[12,13] of compound **3**.

Compound **3** was prepared in about 95% yield from readily accessible 1,6-anhydro-4-deoxy-2-*O*-tosyl-β-D-*xylo*-hexopyranose[14] (**1**) *via* trifluoromethanesulfonate **2** followed by elimination of trifluoromethanesulfonic



(i) $(CF_3SO_2)_2O$, pyridine;(ii) DBU; (iii) RSH, K_2CO_3/Me_2CO; (iv) pyridinium tosylate/MeOH

SCHEME 1

acid using dichloromethane solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature in a procedure without isolation of **2**. Treatment of **3** with an acetone solution of benzenethiol in the presence of potassium carbonate gave phenylthio derivative **4** in almost quantitative yield. Under similar conditions, enopyranose **3** was reacted with 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**5**) or with the corresponding acetates of 1-thio-β-D-galactopyranose **6** and 1-thio-β-L-fucopyranose **7** to give unsaturated anhydrodisaccharides **8**–**10** in about 90% yield.

As mentioned above, the tosyloxy group in compound **3** was readily replaced by sulfur nucleophiles at room temperature to give 4-substituted 4-thiolevoglucosenes **4**, **8**–**10**. This reaction involves stereoselective allylic rearrangement in keeping with previous observations when benzyl alcohol was used as a nucleophile[11a]. However, several products were isolated when sodium methoxide instead of benzyl oxide was used[11b]. The reaction of **3** with nucleophiles can theoretically yield four stereoisomers, but only one of them – the *syn*-product resulting from the allylic rearrangement – should be preferred due to favoured interaction of *syn*-oriented orbitals of the nucleophile and leaving group in the transition state[15]. In addition, steric interactions of the 1,6-anhydro bond may hinder the access of the nucleophile toward C-2 and C-4 from the *endo* side, and this effect should be more evident with bulky nucleophiles. Substitution at C-2 with retention of configuration is disfavoured by repulsive interaction between the nucleophile and the O-5 ring oxygen.

The 1,6-anhydro bond in compounds **8**–**10** was cleaved by methanolysis catalyzed with pyridinium tosylate (*cf.* ref.[16]) to give very good yields of acetylated methyl α-D-glycosides **11**–**13**. Nevertheless, small amounts of the corresponding β-glycosides were present in the reaction mixture as followed from NMR spectra of crude products.

The structure of all compounds described here was proved by NMR measurements. Expectably, the 1,6-anhydrohex-3-enose moiety adopts a $^{5}H_{O}$ conformation and the corresponding 1-thiohexopyranose moieties adopt the common $^{4}C_{1}$(D) conformations for compounds **8** and **9**, and $^{1}C_{4}$(L) conformation for compound **10**. The chemical shifts and coupling constants for H-2, H-3, and H-4 signals of compounds **4**, **8**–**10** indicate the position of the double bond between carbon atoms C-2 and C-3 of the 1,6-anhydrohexopyranose unit. The configuration at C-4 was deduced from the low value of the coupling constant *J*(H-4,H-5) = 1.3 Hz which is in agreement with the corresponding data published for l,6-anhydro-2,3,4-trideoxy-β-D-*glycero*-hex-2-enopyranose[17] and its derivatives[18]. Additionally, the proximity of H-4 to H-6 *endo* of the 1,6-anhydro group was proved by

2D-NOESY spectra of compounds **4** and **8**. The latter technique was used to establish the α-anomer configuration of methyl glycosides **11**, **12**, and **13**. Protons of the methoxy groups at C-1 interact with the proton at C-5. Optimization of the geometry of methyl glycosides **11**–**13** by the MM^+ method using program Hypercube Hyperchem™ 5.02 was in good agreement with NMR spectral data.

The described procedure for preparation of unsaturated thiodisaccharides utilizing versatile 1,6-anhydro-3,4-dideoxy-2-*O*-tosyl-β-D-*erythro*-hex-3-enopyranose (**3**) is applicable not only to various 1-thiosugars but also to other sulfur and amino nucleophiles. Hydroxymethyl group in the hex-3-enopyranose moiety of methyl glycosides **11**–**13** offers excellent possibility of additional modifications.

EXPERIMENTAL

The melting points were determined with a Boëtius micromelting-point apparatus and are uncorrected. Optical rotations were measured with a polarimeter AUTOPOL III (Rudolph Research, Flanders (NJ)) at 25 °C, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. ^1H NMR spectra were measured with Varian UNITY 400 INOVA apparatus (^1H at 400 MHz) in $CDCl_3$, chemical shifts in ppm (δ-scale) were referenced to tetramethylsilane as internal standard; coupling constants (*J*) are given in Hz. Mass spectrometry measurements were performed with a Jeol MS D 100 spectrometer (70 eV, direct inlet at 100–120 °C). Positive FAB mass spectra were measured using a ZAB-EQ spectrometer (VG Analytical, Manchester, U.K.) with BEqG geometry. Samples were dissolved in chloroform and a mixture of glycerol and thioglycerol or 3-nitrobenzyl alcohol was used as a matrix. Thin-layer chromatography (TLC) was performed on DC Alufolien plates (Merck, type 5554) coated with Kieselgel 60 F_{254}; detection with 50% sulfuric acid or 3% ethanol solution of anisaldehyde acidified with concentrated sulfuric acid, and heating. For preparative column chromatography, silica gel Kieselgel 60 (Merck, 60–230 mesh) was used. Reactions were performed in an argon atmosphere. Solutions were evaporated under diminished pressure at temperatures below 40 °C. Analytical samples were dried over phosphorus pentoxide at room temperature under diminished pressure.

1,6-Anhydro-4-deoxy-2-*O*-tosyl-3-*O*-(trifluoromethanesulfonyl)-β-D-*xylo*-hexopyranose (**2**)

Pyridine (107 μl, 1.3 mmol) was added to a solution of deoxy compound[14] **1** (100 mg, 0.33 mmol) in anhydrous dichloromethane (7.5 ml) and the solution was cooled to –16 °C. Then trifluoromethanesulfonic anhydride (65 μl, 0.4 mmol) was added dropwise under stirring and the reaction mixture was stirred at –16 °C for 1 h. After warming to room temperature, the solution was extracted with saturated aqueous solution of sodium hydrogencarbonate (5 ml) and the water layer was extracted twice with dichloromethane (2 ml). Combined organic extracts were dried and evaporated three times to dryness with toluene (2 ml) to give 140 mg (99%) of a syrup, which was crystallized from ether–light petroleum to obtain 102 mg (72%) of **2**, m.p. 87–89 °C, $[\alpha]_D$ –15 (*c* 0.25, $CHCl_3$). ^1H NMR: 1.98 dm, 1 H, $J(4\beta,4\alpha)$ = 16.1 (H-4β); 2.47 s, 3 H (CH_3); 2.57 dddd, 1 H, $J(4\alpha,4\beta)$ = 16.1, $J(4\alpha,3)$ = 5.6, $J(4\alpha,5)$ = 3.9,

J(4α,6ex) = 1.7 (H-4α); 3.76 ddd, 1 H, *J*(6ex,6en) = 7.3, *J*(5,6ex) = 5.1, *J*(6ex,4α) = 1.5 (H-6ex); 4.06 d, 1 H, *J*(6en,6ex) = 7.3 (H-6en); 4.31 q, 1 H, *J*(2,1) = 1.7, *J*(2,3) = 1.7, *J*(2,4β) = 1.7 (H-2); 4.59 bt, 1 H, *J*(5,6ex) = 4.5, *J*(5,4α) = 4.5 (H-5); 5.00 bdm, 1 H, *J*(3,4α) = 5.1 (H-3); 5.36 bs, 1 H (H-1); 7.37–7.41 m, 2 H, 7.80–7.85 m, 2 H (4 × H arom). MS (FAB), *m/z* (%): 283 ($[MH - CF_3SO_3H]^+$, 10). For $C_{14}H_{15}F_3O_8S_2$ (432.4) calculated: 38.89% C, 3.50% H, 13.18% F, 14.83 S; found: 39.12% C, 3.55% H, 13.12% F, 14.76% S.

1,6-Anhydro-3,4-dideoxy-2-*O*-tosyl-β-D-*erythro*-hex-3-enopyranose (**3**)

To a solution of deoxy compound[14] **1** (1.0 g, 3.3 mmol) in a mixture of anhydrous dichloromethane (10 ml) and pyridine (0.66 ml, 8.2 mmol) cooled to –16 °C was added dropwise trifluoromethanesulfonic anhydride (0.67 ml, 3.7 mmol) under stirring and the reaction mixture was stirred at –16 °C for 2 h. 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.64 ml, 11.0 mmol) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. Then the reaction mixture was washed with 5% aqueous HCl (20 ml), the organic layer was separated and the water solution was extracted three times with 10 ml portions of dichloromethane. The combined extracts were dried with anhydrous $MgSO_4$ and filtered through a short column of silica gel. Evaporation of the solvent gave 0.9 g (95%) crystalline compound **3** which after recrystallization from ether–light petroleum gave 0.75 g (80%), m.p. 80–81 °C (dec.), $[\alpha]_D$ –154 (*c* 0.25, $CHCl_3$); refs[11,19] m.p. 85–86 °C (dec.), $[\alpha]_D$ –161 (*c* 0.5, $CHCl_3$) and 85 °C, $[\alpha]_D$ –159 ($CHCl_3$), respectively. ^{1}H NMR: 2.46 s, 3 H (CH_3); 3.62–3.68 m, 2 H (H-6en, H-6ex); 4.39 dt, 1 H, *J*(2,3) = 3.9, *J*(2,1) = 1.5, *J*(2,4) = 1.2 (H-2); 4.74 m, 1 H (H-5); 5.50 t, 1 H, *J*(1,2) = 1.6, *J*(1,3) = 1.6 (H-1); 5.62 ddd, 1 H, *J*(2,3) = 3.9, *J*(3,4) = 9.8, *J*(1,3) = 2.0 (H-3); 6.31 ddd, 1 H, *J*(4,3) = 9.8, *J*(4,5) = 4.9, *J*(4,2) = 1.2 (H-4); 7.34–7.38 m, 2 H, 7.81–7.85 m, 2 H (4 × H arom).

1,6-Anhydro-2,3-dideoxy-4-*S*-phenyl-4-thio-β-D-*erythro*-hex-2-enopyranose (**4**)

Benzenethiol (0.71 ml, 6.9 mmol) was added dropwise to a solution of enopyranose **3** (1.3 g, 4.6 mmol) in anhydrous acetone (20 ml) containing a suspension of anhydrous K_2CO_3 (0.95 g, 6.9 mmol) at room temperature and the reaction mixture was stirred for 1 h. Then the reaction mixture was diluted with water (20 ml) and extracted three times with the total amount of 50 ml chloroform. Chloroform solution was dried ($MgSO_4$) and purified by column chromatography in dichloromethane to give 1.0 g (99%) of **4**, m.p. 52–53 °C, $[\alpha]_D$ +195 (*c* 0.25, $CHCl_3$). Literature[13] describes an alternative preparation of **4** from 1,6-anhydro-2-chloro-2-deoxy-β-D-*erythro*-hex-3-enopyranose without giving physical constants. ^{1}H NMR: 3.49 dt, 1 H, *J*(3,4) = 4.4, *J*(2,4) = 1.3, *J*(4,5) = 1.3 (H-4); 3.62 dd, 1 H, *J*(6ex,6en) = 7.8, *J*(5,6en) = 2.0 (H-6en); 3.97 dd, 1 H, *J*(6en,6ex) = 7.8, *J*(5,6ex) = 6.3 (H-6ex); 4.69 dm, 1 H, *J*(6ex,5) = 6.3 (H-5); 5.55 d, 1 H, *J*(2,1) = 3.4 (H-1); 5.85 dddd, 1 H, *J*(2,3) = 9.5, *J*(4,3) = 4.3, *J*(5,3) = 1.8, *J*(1,3) = 0.8 (H-3); 6.01 ddd, 1 H, *J*(3,2) = 9.5, *J*(1,2) = 3.3, *J*(4,2) = 1.5 (H-2). MS (EI), *m/z* (%): 220 (M^+, 49.3). For $C_{12}H_{12}O_2S_2$ (220.3) calculated: 65.43% C, 5.49% H, 14.56% S; found: 65.69% C, 5.52% H, 14.41% S.

Preparation of Anhydro Derivatives of Thiodisaccharides **8**–**10**. General Procedure

To a solution of enopyranose **3** (141 mg, 0.5 mmol) and 1-thiohexose **5** (ref.[20]), **6** (ref.[21]) or **7** (ref.[22]) (0.55 mmol) in anhydrous acetone (5 ml) finely powdered anhydrous K_2CO_3 (207 mg, 1.5 mmol) was added and the reaction mixture was stirred at room temperature for

3 h. Then the reaction mixture was poured into water (50 ml), neutralized with hydrochloric acid to pH ≈ 7, and extracted three times with 20 ml portions of dichloromethane. The combined organic extracts were dried with anhydrous $MgSO_4$, filtered and evaporated to dryness. The products were purified by column chromatography.

2,3,4,6-Tetra-O-acetyl-β-D-*glucopyranosyl-(1→4)-1,6-anhydro-2,3-dideoxy-4-thio*-β-D-*erythro-hex-2-enopyranose* (**8**). The crude product obtained from the reaction of **3** with 1-thioglucose **5** was chromatographed in a mixture of toluene–ethyl acetate (5 : 1) to obtain **8** (216 mg, 91%), m.p. 131–132 °C (methanol), $[\alpha]_D$ +103 (*c* 0.25, $CHCl_3$). ^{1}H NMR: 2.01 s, 3 H, 2.03 s, 3 H, 2.05 s, 3 H, 2.07 s, 3 H (4 × OAc); 3.20 bd, 1 H, *J*(3,4) = 4.2 (H-4); 3.62 dd, 1 H, *J*(6ex,6en) = 7.8, *J*(5,6en) = 2.0 (H-6en); 3.73 ddd, 1 H, *J*(4′,5′) = 10.0, *J*(6b′,5′) = 4.9, *J*(6a′,5′) = 2.6 (H-5′); 3.98 dd, 1 H, *J*(6en,6ex) = 7.8, *J*(5,6ex) = 6.2 (H-6ex); 4.17 dd, 1 H, *J*(6b′,6a′) = 12.3, *J*(5′,6a′) = 2.6 (H-6a′); 4.22 dd, 1 H, *J*(6a′,6b′) = 12.5, *J*(5′,6b′) = 5.0 (H-6b′); 4.63 d, 1 H, *J*(2′,l′) = 10.3 (H-1′); 4.90 dm, 1 H, *J*(6ex,5) = 6.2 (H-5); 5.05 dd, 1 H, *J*(1′,2′) = 10.4, *J*(3′,2′) = 9.2 (H-2′); 5.08 dd, 1 H, *J*(5′,4′) = 10.0, *J*(3′,4′) = 9.4 (H-4′); 5.24 t, 1 H, *J*(2′,3′) = 9.3, *J*(4′,3′) = 9.3 (H-3′); 5.50 bd, 1 H, *J*(1,2) = 3.3 (H-1); 5.64 bddd, 1 H, *J*(2,3) = 9.2, *J*(4,3) = 4.3, *J*(5,3) = 1.8 (H-3); 6.07 ddd, 1 H, *J*(3,2) = 9.5, *J*(1,2) = 3.4, *J*(4,2) = 1.7 (H-2). MS (EI), *m/z* (%): 474 (M^+, 8.1). For $C_{20}H_{26}O_{11}S$ (474.5) calculated: 50.63% C, 5.52% H, 6.76% S; found: 50.52% C, 5.58% H, 6.70% S.

2,3,4,6-Tetra-O-acetyl-β-D-*galactopyranosyl-(1→4)-1,6-anhydro-2,3-dideoxy-4-thio*-β-D-*erythro-hex-2-enopyranose* (**9**). The crude product obtained from the reaction of **3** with 1-thiogalactose **6** was chromatographed in a mixture of toluene–ethyl acetate (5 : 1) to obtain **9** (221 mg, 93%), m.p. 132–133 °C (acetone–ether–light petroleum), $[\alpha]_D$ +128 (*c* 0.25, $CHCl_3$). ^{1}H NMR: 1.99 s, 3 H, 2.03 s, 3 H, 2.06 s, 3 H, 2.16 s, 3 H (4 × OAc); 3.22 dt, 1 H, *J*(3,4) = 4.3, *J*(5,4) = 1.3, *J*(2,4) = 1.3 (H-4); 3.62 dd, 1 H, *J*(6ex,6en) = 7.8, *J*(5,6en) = 2.0 (H-6en); 3.73 td, 1 H, J_1 = 6.6, J_2 = 1.2 (H-5′); 3.99 dd, 1 H, *J*(6en,6ex) = 7.8, *J*(5,6ex) = 6.2 (H-6ex); 4.13 d, 2 H, *J* = 6.6 (H-6a′, H-6b′); 4.63 d, 1 H, *J*(2′,l′) = 10.1 (H-1′); 4.88 dm, 1 H, *J*(6ex,5) = 6.3 (H-5); 5.07 dd, 1 H, *J*(2′,3′) = 10.0, *J*(4′,3′) = 3.4 (H-3′); 5.25 t, 1 H, *J*(1′,2′) = 10.0, *J*(3′,2′) = 10.0 (H-2′); 5.44 dd, 1 H, *J*(5′,4′) = 1.2, *J*(3′,4′) = 3.4 (H-4′); 5.51 bd, 1 H, *J*(1,2) = 3.4 (H-1); 5.66 dddd, 1 H, *J*(2,3) = 9.5, *J*(4,3) = 4.3, *J*(5,3) = 1.8, *J*(1,3) = 0.6 (H-3); 6.07 ddd, 1 H, *J*(3,2) = 9.5, *J*(1,2) = 3.4, *J*(4,2) = 1.7 (H-2). MS (EI), *m/z* (%): 474 (M^+, 8.1). For $C_{20}H_{26}O_{11}S$ (474.5) calculated: 50.63% C, 5.52% H, 6.76% S; found: 50.91% C, 5.59% H, 6.70% S.

2,3,4-Tri-O-acetyl-6-deoxy-β-L-*galactopyranosyl-(1→4)-1,6-anhydro-2,3-dideoxy-4-thio*-β-D-*erythro-hex-2-enopyranose* (**10**). The crude product obtained from the reaction of **3** with 1-thiofucose **7** was chromatographed in a mixture of toluene–ethyl acetate (10 : 1) to obtain **10** (183 mg, 88%), m.p. 133–134 °C (acetone–ether–light petroleum), $[\alpha]_D$ +166 (*c* 0.25, $CHCl_3$). ^{1}H NMR: 1.20 d, 3 H, *J*(5′,6′) = 6.5 (H-6′); 1.99 s, 3 H, 2.08 s, 3 H, 2.18 s, 3 H (3 × OAc); 3.25 dt, 1 H, *J*(3,4) = 4.3, *J*(5,4) = 1.2, *J*(2,4) = 1.2 (H-4); 3.65 dd, 1 H, *J*(6ex,6en) = 7.8, *J*(5,6en) = 2.1 (H-6en); 3.80 qd, 1 H, *J*(6′,5′) = 6.5, *J*(4′,5′) = 1.1 (H-5′); 4.01 dd, 1 H, *J*(6en,6ex) = 7.9, *J*(5,6ex) = 6.2 (H-6ex); 4.78 d, 1 H, *J*(2′,l′) = 10.0 (H-1′); 4.78 m, 1 H (H-5); 5.06 dd, 1 H, *J*(2′,3′) = 10.0, *J*(4′,3′) = 3.4 (H-3′); 5.22 t, 1 H, *J*(1′,2′) = 10.0, *J*(3′,2′) = 10.0 (H-2′); 5.28 dd, 1 H, *J*(5′,4′) = 1.1, *J*(3′,4′) = 3.4 (H-4′); 5.54 bd, 1 H, *J*(1,2) = 3.4 (H-1); 5.86 dddd, 1 H, *J*(2,3) = 9.4, *J*(4,3) = 4.4, *J*(5,3) = 1.8, *J*(1,3) = 0.7 (H-3); 5.96 ddd, 1 H, *J*(3,2) = 9.5, *J*(1,2) = 3.4, *J*(4,2) = 1.5 (H-2). MS (FAB), *m/z* (%): 417 (MH^+, 2.8). For $C_{18}H_{24}O_9S$ (416.4) calculated: 51.92% C, 5.81% H, 7.70% S; found: 52.19% C, 5.88% H, 7.64% S.

Preparation of Methyl Thiodisaccharides **11**–**13**. General Procedure

1,6-Anhydrodisaccharides **8**, **9** or **10** (0.3 mmol) were dissolved in methanol (6 ml), pyridinium tosylate (8 mg, 0.03 mmol) was added and the solution was refluxed for 1 h. After evaporation of methanol, the residue was purified by column chromatography.

Methyl 2,3,4,6-tetra-O-acetyl-β-D-*glucopyranosyl-(1→4)-2,3-dideoxy-4-thio*-α-D-*erythro-hex-2-enopyranoside* (**11**). The crude product obtained by methanolysis of **8** was chromatographed in a mixture of light petroleum–ethyl acetate (1 : 1) to give **11** (139 mg, 91%), m.p. 133–135 °C, $[\alpha]_D$ +92 (*c* 0.25, $CHCl_3$). ^{1}H NMR: 2.01 s, 3 H, 2.02 s, 3 H, 2.06 s, 3 H, 2.10 s, 3 H (4 × OAc); 3.43 s, 3 H (OMe); 3.58 bdd, 1 H, *J*(5,4) = 10.4, *J*(3,4) = 1.4 (H-4); 3.71 dt, 1 H, *J*(4′,5′) = 10.1, *J*(6a′,5′) = 3.5, *J*(6b′,5′) = 3.5 (H-5′); 3.93 m, 2 H (H-6a, H-6b); 3.99 m, 1 H (H-5); 4.20 m, 2 H (H-6a′, H-6b′); 4.65 d, 1 H, *J*(2′,1′) = 10.2 (H-1′); 4.91 bs, 1 H (H-1); 5.00 t, 1 H, *J*(1′,2′) = 9.2, *J*(3′,2′) = 9.2 (H-2′); 5.07 t, 1 H, *J*(5′,4′) = 9.8, *J*(3′,4′) = 9.8 (H-4′); 5.22 t, 1 H, *J*(2′,3′) = 9.3, *J*(4′,3′) = 9.3 (H-3′); 5.89 m, 2 H (H-2, H-3). MS (FAB), *m/z* (%): 475 ([MH – MeOH]$^+$, 2.8). For $C_{21}H_{30}O_{12}S$ (506.5) calculated: 49.80% C, 5.97% H, 6.33% S; found: 49.84% C, 6.00% H, 6.27% S.

Methyl 2,3,4,6-tetra-O-acetyl-β-D-*galactopyranosyl-(1→4)-2,3-dideoxy-4-thio*-α-D-*erythro-hex-2-enopyranoside* (**12**). The crude product obtained by methanolysis of **9** was chromatographed in a mixture of light petroleum–ethyl acetate (1 : 1) to give **12** (122 mg, 80%), m.p. 135–136 °C, $[\alpha]_D$ +92 (*c* 0.25, $CHCl_3$). ^{1}H NMR: 1.99 s, 3 H, 2.06 s, 3 H, 2.08 s, 3 H, 2.16 s, 3 H (4 × OAc); 3.43 s, 3 H (OMe); 3.62 bd, 1 H, *J*(5,4) = 9.2 (H-4); 3.90–4.00 m, 4 H (H-5′, H-6a, H-6b, H-5); 4.06–4.20 m, 2 H (H-6a′, H-6b′); 4.63 d, 1 H, *J*(2′,1′) = 10.1 (H-1′); 4.90 bs, 1 H (H-1); 5.05 dd, 1 H, *J*(2′,3′) = 9.9, *J*(4′,3′) = 3.4 (H-3′); 5.22 t, 1 H, *J*(1′,2′) = 10.1, *J*(3′,2′) = 10.1 (H-2′); 5.43 bd, 1 H, *J*(3′,4′) = 3.4 (H-4′); 5.86–5.94 m, 2 H (H-2, H-3). MS (FAB), *m/z* (%): 475 ([MH – MeOH]$^+$, 3.6). For $C_{21}H_{30}O_{12}S$ (506.5) calculated: 49.80% C, 5.97% H, 6.33% S; found: 49.85% C, 6.01% H, 6.25% S.

Methyl 2,3,4-tri-O-acetyl-6-deoxy-β-L-*galactopyranosyl-(1→4)-2,3-dideoxy-4-thio*-α-D-*erythro-hex-2-enopyranoside* (**13**). The crude product obtained by methanolysis of **10** was chromatographed in a mixture of light petroleum–ethyl acetate (2 : 1) to give syrupy **13** (134 mg, 95%), $[\alpha]_D$ +82 (*c* 0.25, $CHCl_3$). ^{1}H NMR: 1.21 d, 3 H, *J*(5′,6′) = 6.4 (H-6′); 1.99 s, 3 H, 2.08 s, 3 H, 2.18 s, 3 H (3 × OAc); 3.44 s, 3 H (OMe); 3.61 dm, 1 H, *J*(5,4) = 10.4 (H-4); 3.75–3.80 m, 1 H (H-5); 3.80 qd, 1 H, *J*(6′,5′) = 6.4, *J*(4′,5′) = 1.2 (H-5′); 3.87 dd, 1 H, *J*(6a,6b) = 12.0, *J*(5,6a) = 2.8 (H-6a); 3.93 dd, 1 H, *J*(6a,6b) = 12.0, *J*(5,6b) = 4.4 (H-6b); 4.57 d, 1 H, *J*(2′,l′) = 10.1 (H-1′); 4.90 m, 1 H (H-1); 5.05 dd, 1 H, *J*(2′,3′) = 9.9, *J*(4′,3′) = 3.4 (H-3′); 5.20 t, 1 H, *J*(1′,2′) = 9.9, *J*(3′,2′) = 9.9 (H-2′); 5.26 dd, 1 H, *J*(5′,4′) = 1.2, *J*(3′,4′) = 3.4 (H-4′); 5.80 ddd, 1 H, *J*(3,2) = 10.1, *J*(1,2) = 3.1, *J*(4,2) = 2.4 (H-2); 6.10 ddd, 1 H, *J*(2,3) = 10.1, *J*(4,3) = 2.1, *J*(1,3) = 1.1 (H-3). MS (FAB), *m/z* (%): 417 ([MH – MeOH]$^+$, 2.2). For $C_{19}H_{28}O_{10}S$ (448.5) calculated: 50.88% C, 6.29% H, 7.15% S; found: 51.07% C, 6.44% H, 6.79% S.

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